The Interfacial Chemistry and Environmental Degradation of Adhesively Bonded Galvanised Steel

By

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Abstract

The interfacial chemistry and environmental degradation of adhesively bonded hot dipped galvanised steel (HDGS) has been investigated. The principle aim of the work has been to determine the failure mechanisms responsible for the poor durability of adhesively bonded HDGS. Surface analysis techniques have been used to characterise components of the respective adhesive systems and interrogate the surface of failed joints with a view to establishing the exact locus of failure. Durability studies have been carried out by exposing joints to 98% relative humidity at 35°C for up to 12 months. Alkali cleaned HDGS joints failed cohesively through a zinc corrosion product acting as a weak boundary layer. Joints manufactured from phosphated substrates, however, display better durability. The failed lap shear joints show areas of apparent interfacial failure limited to thin strips at the ends of the overlap, termed initiation zones. An initial study highlighted the importance of small area surface analysis, using XPS, to demonstrate that electrochemical activity was responsible for the initial bond degradation and the formation of the initiation zones at the ends of the overlap. Despite having been employed successfully in a number of adhesion studies, XPS is unable to give the molecular level of specificity that is required for the full understanding of the mechanism of such an adhesively bonded system.

ToF-SIMS has the potential to overcome the limitations of XPS and a rigorous investigation has been carried out culminating in the ToF-SIMS imaging of regions within the initiation zone. The images obtained support earlier evidence of electrochemical activity at the initiation zone showing the presence of cations (Mg\(^2^+\)), indicating cathodic behaviour played a role in the formation of the initiation zone. ToF-SIMS line scans indicate residual polymer in the initiation zone, which indicates a dual effect of electrochemical behaviour and ingress of water together being responsible for the formation of the initiation zone. This suggests weakening rather than the clear separation, prior to mechanical testing, which is observed in the case of classical cathodic delamination. ToF-SIMS images have provided analytical data that extends this model by showing corresponding cation rich and adhesive rich areas.
within the initiation zone, possibly demonstrating that the different processes dominate in different regions (a result of localised electrochemical activity), and enables cathode size to be estimated.

Small area XPS (at a spatial resolution of 20 μm) has been used to characterise areas within the initiation zone deficient in pretreatment that are similar in size to the local cathodes observed in the ToF-SIMS study. Quantified XPS line scans identified areas of high carbon content, once again inferring that water ingress plays a part in the failure mechanism. SEM also identified areas denuded of the phosphate pretreatment that are a result of exposure to a hostile environment, as a uniform pretreatment exists prior to bonding. Dissolution of phosphate crystals may have occurred within the alkaline environment produced by the cathodic half reaction. Mechanical data obtained throughout the durability study has reinforced the importance of the initiation zone with its size being directly related to joint performance (load to failure).

Electrochemical activity has been found to be responsible for initial bond degradation. By using an established model, it is proposed that cathodic activity is a result of local corrosion cells set up at the substrate/adhesive interface.
I am particularly grateful to Professor John Watts for his continual support, encouragement and excellent supervision throughout this study. I must also acknowledge Corus (formally British Steel plc.) for sponsoring the project, in particular Anthony Cronin, Dr. Tim English, Dr. Brian Jones, Dr. John Ling, Alan Seeds, Dr. Byron Williams and Ray Williams for their industrial support and guidance. Many thanks also go to Professor James Castle for his help concerning electrochemical modelling used in this project.

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<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AIE</td>
<td>Argon ion etched</td>
</tr>
<tr>
<td>CAE</td>
<td>Constant analyser energy</td>
</tr>
<tr>
<td>CHA</td>
<td>Concentric hemispherical analyser</td>
</tr>
<tr>
<td>CPS</td>
<td>Counts per second</td>
</tr>
<tr>
<td>CRS</td>
<td>Cold rolled steel</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DCS</td>
<td>Defined collection system</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl ether of bisphenol-A</td>
</tr>
<tr>
<td>DSS</td>
<td>Defined source system</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FAB</td>
<td>Fast atom beam</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite element analysis,</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half-maximum</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Glancing Incidence X-ray Diffraction</td>
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<tr>
<td>HDGS</td>
<td>Hot Dipped Galvanised steel</td>
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<tr>
<td>HSA</td>
<td>Hemispherical analyser</td>
</tr>
<tr>
<td>IEPS</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>LMIS</td>
<td>Liquid metal ion source</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrolidone</td>
</tr>
<tr>
<td>PCAs</td>
<td>Polycyclic aromatics</td>
</tr>
<tr>
<td>PD</td>
<td>Potential difference</td>
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<tr>
<td>PDMS</td>
<td>Poly(dimethyl siloxane),</td>
</tr>
<tr>
<td>PEEK</td>
<td>Poly (ether ether ketone)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly (ethylene terephthalate)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (methyl methacrylate)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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</tr>
<tr>
<td>PS</td>
<td>Poly (styrene)</td>
</tr>
<tr>
<td>PSEI</td>
<td>Particle surface electronic interactions</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly (tetra fluoro ethylene)</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly (vinyl chloride)</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>RH</td>
<td>Relative humidity</td>
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<tr>
<td>SAXPS</td>
<td>Small area XPS</td>
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<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
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<tr>
<td>TDCB</td>
<td>Tapered double cantilever beam</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of flight</td>
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<tr>
<td>ToF-SIMS</td>
<td>Time of flight secondary ion mass spectrometry</td>
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<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>WBL</td>
<td>Weak boundary layer</td>
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<td>XPS</td>
<td>X-ray photo electron spectroscopy</td>
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Chapter One

Introduction

Structural adhesives are successfully used, in the automotive industry, for non-structural parts (for example bonnet and boot reinforcing sections and skin attachment), but adhesive bonding has yet to be used for joining the monocoque structure of a steel high volume production automobile, [1]. Current bodyshell design and construction, particularly for high volume production, is based primarily on the spot welded assembly of sheet steel components and highly automated processes are employed to manufacture large numbers of bodysshells to high standards. Automotive engineers are beginning to recognise that adhesive bonding offers a wider range of applications and one of these possible growth areas is metal to metal bonding for load bearing sections. Adhesives offer the designer a freedom of choice in joint design, for example allowing one-sided fixing and the complex section designs seen in the modern lightweight car, without the constraints imposed by the need for two-sided access needed for spot welding [2, 3]. With adequate preparation a strong non-visible joint can be fabricated which is stiffer than a welded or riveted joint in a similar structure. Improved strength and stiffness available on bonded structures may be used to reduce vehicle weight and hence fuel consumption. Other advantages include reduced corrosion and improved noise, vibration and harshness characteristics and improved energy absorption during impact loading [4].

Modern lightweight bodysshells make many demands on joining techniques. During their lives they must endure normal static loads which hold components together as well as varying degrees of impact loads experienced in service ranging from the slamming of doors to the large impact forces generated in vehicle collisions which
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Introduction

may involve high speeds. There are other considerations to be taken into account such as fatigue loading generated by road, powertrain, chassis forces and temperature cycles. These static impact and fatigue performance requirements need to be maintained under a variety of hostile conditions; for example temperatures can range from -30°F up to +100°F. Durability is the major factor in the use of adhesive bonding and the poor durability of adhesively bonded galvanised steel is one of the key issues considered in this project. The durability of adhesive joints has tended to be tested under accelerated ageing within the automotive industry and relative humidity chambers have been used in this study. Whilst it is easy to be critical of the results of all accelerated tests, they are able to give the industry some sort of reasonable guideline which can be used to partly bridge the confidence gap of using a new technology. Indeed, without such tests experimental periods of up to 15 years would be required to determine the performance of adhesives.

At present the automotive industry is concentrating on reducing weight without compromising performance, affordability, safety, durability and cost, another benefit would be reduced fuel consumption. These aims have led to design changes, allowing a reduction in thickness and the steady growth of materials such as galvanised steels.

Adhesively bonded galvanised steel flanges have the potential to overcome such shortcomings with no weight penalty. It is hoped that, elucidating the mechanism of failure, the findings of this work may be of help on the wider scale in industry and perhaps lead to the greater acceptance by design engineers of automotive applications.

The principal aim of this work is to further the understanding of the failure mechanisms that are responsible for the poor durability of adhesively bonded hot-dipped galvanised steel (HDGS). This will be undertaken by carrying out a durability study on a variety of joints, considering differing pretreatments exposed to a hostile environment. The forces of adhesion act over very short distances, approximately 5 Å and so surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) are ideally suited to provide better understanding of a joint system. Such techniques allow characterisation of joint
components, substrate to polymer bond interaction and determination of exact locus of failure.

Both XPS and SIMS have been used in novel but complementary ways throughout this study. The molecular specificity of ToF-SIMS has been exploited to characterise adhesives and also identify residual polymer of failed adhesives, whilst small area XPS, has interrogated specific regions, yielding quantifiable data. By defining the exact locus of failure and determining the surface chemistry of interfaces it is anticipated that a comprehensive model for the mechanism of failure for the respective adhesive systems may be proposed.

This study has the following objectives;

1) To characterise the surface chemistry of HDGS and investigate the effect of aluminium on acid-base interaction sites.

2) To carry out preliminary work in the development of an environmentally friendly pretreatment; the rare earth metal yttrium. Deposition characteristics are investigated along with a durability study.

3) Determine the failure mechanism for adhesively bonded HDGS. This includes the development of ToF-SIMS analysis for analysis of failed joints along with the use of small area XPS and will consider the effect of environmental degradation on both adhesive and pretreatment.

4) To compare mechanical data with surface analytical data and determine if the features observed by XPS and SIMS are significant in overall joint performance.
2.1. Introduction

Man has been using natural adhesives, as part of a joining process, for thousands of years. As early as 3000 BC layers of papyrus were stuck together using flour paste [5]. The ancient Egyptians used adhesives to veneer the treasures of Tutankhamun and there is evidence from their coffins that they used gum Arabic and some natural resins as glues. The Romans used egg white to apply gold leaf to ornaments. Mammalian collagen was used to make various protein glues (skin and bone) along with hide gelatine, blood, milk derivatives (casein and albumin). Vegetables containing starch and dextrins also formed the basis for many early adhesives. Even as late as the first decade of the twentieth century biplanes were predominately fabricated using adhesive bonding with adhesives based on casein. Indeed only in the last sixty years has synthetic adhesive chemistry been able to make significant progress to reach the status that it holds in industry today.

A major problem with natural adhesives was the extremely poor “in service” durability that they exhibited and the advent of synthetic adhesives in the 1930's and 40's allowed adhesive bonding to be used in more demanding applications. Adhesives based on synthetic polymers offered a greater amount of versatility, allowing properties such as flow characteristics and cure time to be controlled depending on their particular application. An early success of synthetic adhesives was the Second
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Adhesive Bonding: Adhesion, Pretreatment and Failure Mechanisms

World War “Mosquito” aircraft which relied mainly on urea-formaldehyde resin adhesive to bond together its wooden structure.

Kinloch defines an adhesive as "a material which when applied to surfaces of materials can join them together and resist separation" and uses the term adhesion to describe the attraction between two substances [6]. It is important to make the distinction between adhesion and bond strength, for example low bond strength may not necessarily be a result of poor adhesion. Adhesion ("intermolecular attraction") refers to the thermodynamic work of adhesion which, will be discussed later, and can be related to certain chemical parameters. The bond strength of a joint is related to the failure mechanism, which is very rarely, in the dry state, a result of poor adhesion between the adhesive and adherend (substrate). More often failure occurs because of a cohesive failure through the polymer adhesive or the adherend itself, for example through a thick oxide layer. Naturally poor adhesion can result in low bond strength, for example it is imperative that for good adhesion and joint strength adequate surface preparation is undertaken or failure may occur at low bond strengths. The correct adhesive system must also be used, that is to say that certain adherends are not compatible with particular adhesives and that all components of the adhesive bond, including the environment, must be chosen carefully to give a sound adhesive system.

Whilst scientific and technological advances have widened the use of adhesive bonding, its rapid growth in industry during the latter half of the twentieth century is due to the numerous advantages of adhesives over other joining techniques, which include [6]:

1. The ability to join dissimilar materials, such as metals, composites and wood. This also leads to a greater amount of design flexibility.
2. An improved stress distribution resulting in a better fatigue life, for example adhesives are the ideal joining technique for helicopter blades, which undergo high fatigue stresses.
3. It is convenient and cost effective.
4. Improved joint appearance. An adhesive bond can be blemish free, aesthetically pleasing and easy to conceal, (provided spew fillets are removed).

5
5. An improvement in corrosion resistance. There is no heat-affected zone as there is with welding and due to the organic nature of polymer adhesives if dissimilar metals are joined there will be minimum risk from electrolytic corrosion.

6. The ability to join thin sheet material efficiently.

Notwithstanding these advantages there are inevitably some disadvantages to adhesive bonding;

1. One of the key issues with adhesive bonding is durability and often a pretreatment is required to achieve an acceptable service life.

2. As adhesives are generally based on polymers the upper service temperature is often limited.

3. The strength and toughness of polymer adhesives is low compared to that of metal and so for bonding of thick metal substrates, unless a large overlap area is used which in general is undesirable, adhesive bonding is not well a suited technique.

4. There are limited non-destructive testing methods compared to other joining techniques.

Despite these disadvantages the adhesives industry continues to grow and much of the diversity in adhesives and adhesive bonding that has developed over past half century or so has been a result of a substantial amount of scientific research allowing strong, stiff but lightweight components to be manufactured. These advances now see adhesives used in the home, office, industry and even medicine, where the versatility of adhesives is highlighted by applications ranging from the ubiquitous surgical tape to the bonding of implant components to human tissue [7].
2.2. Interfacial Contact

2.2.1. Introduction

For a polymer adhesive to meet the requirements of the above definition there are certain basic properties the polymer must possess. It must wet the surface, for this to occur it must be a liquid (i.e. have a low viscosity), spread and make a contact angle approaching zero. This is the stage where it is important that intimate interfacial contact between the adhesive and the substrate is established. Next the adhesive must harden to a cohesively strong solid, this allows the joint to bear loads and occurs as a result of chemical reaction, loss of solvent or water or by cooling, the exception to this is pressure sensitive adhesives such as “sellotape”. The desired result is an adhesive bond with strong and stable intrinsic adhesion forces across the adhesive/substrate interface. In order to predict the propensity for intimate contact, wetting equilibria of the adhesive system must be taken into account, an indication of the kinetics of wetting may also be made. Thermodynamic considerations can be used to predict the work of adhesion for a system using the surface free energies of the adhesive, substrate and adhesive/substrate interfaces. The condition of a substrate surface plays a role in the wetting process; “clean” metals have very high surface free energies and so will be completely wetted by low surface energy polymer adhesives or coatings. On exposure to the atmosphere, however, a whole host of contamination can be found on the metal surface dramatically reducing its surface free energy, which is manifested in a higher contact angle with a wetting liquid. A hierarchy of contamination layers will quickly form on the surface, each reducing the surface free energy of the metal substrate, from oxides to hydrocarbon. Surface free energies of some of the potential contamination layers are shown in Table 2.1.
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<table>
<thead>
<tr>
<th>Substance / contamination</th>
<th>$\gamma$ / mJ m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>10-50</td>
</tr>
<tr>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>Oxide</td>
<td>200-500</td>
</tr>
<tr>
<td>“Clean” Metals</td>
<td>1000-5000</td>
</tr>
</tbody>
</table>

Table 2.1. The hierarchy of surface free energies that contaminate surfaces on exposure to hostile environments.

2.2.2. Wetting Equilibria

Wetting characteristics of a surface are directly related to the surface free energy (mJ/m$^2$). Plastics, rubbers and polymer matrix fibre composites are examples of materials with low surface free energies, typically under 50 mJ/m$^2$ and therefore, often require surface treatment prior to coating or adhesive bonding. Most metals, their oxides and ceramics have high surface free energies, typically greater than 500 mJ/m$^2$, and as such are wetted readily giving a high level of intimate contact with the adhesive.

The surface free energy of a solid can be determined readily from measurements of the contact angle formed between a liquid droplet on a substrate at equilibrium. This is possible as all liquids display surface tension, (which is equivalent to the surface free energy), and is a direct measure of intermolecular forces, between the bulk material and the surface layer. The contact angle is defined as the angle produced between the liquid/vapour interface when a tangent is drawn from point where all three phases meet (i.e. solid/liquid/vapour) known as the triple point, Figure 2.1. For the system to be at equilibrium the triple point must be stationary, the contact angle is then related to the surface free energies of the three interfaces by the Young Equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$  \hspace{1cm} (2.1)
where $\gamma_{sl} =$ surface free energy of the solid/liquid interface

$\gamma_{lv} =$ surface free energy of the liquid/vapour interface

and $\gamma_{sv} =$ surface free energy of the solid/vapour interface

Figure 2.1. A schematic of a liquid drop resting at equilibrium on a solid surface, showing the surface tension forces that can be resolved to form the Young equation.

The term $\gamma_{sv}$ represents the surface free energy of the solid covered by a monolayer of the vapour and is generally considerably lower than the surface free energy of the solid in a vacuum, $\gamma_s$. This occurs as result of vapour absorbing onto the surface, thus reducing the surface energy. This difference in surface free energies is termed the spreading pressure ($\pi$);

$$\pi = (\gamma_s - \gamma_{sv}) \tag{2.2}$$

Where $\pi =$ spreading pressure

$\gamma_s =$ surface free energy of the solid in a vacuum

and $\gamma_{sv} =$ surface free energy of the solid/vapour interface

The ideal scenario for adhesion is observed when $\theta = 0$ and is termed spreading (i.e. spontaneous wetting), rearranging Equation 2.1 for $\theta = 0$ then $\gamma_{sv} - \gamma_{sl}$ must be equal to $\gamma_{lv}$ so the criterion for spreading may be written as;
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\[ \gamma_{sv} \geq \gamma_{st} + \gamma_{lv} \]  2.3

For \( \theta \) between 90° and 0° wetting of a surface may take place although not over the entire surface, i.e. non-spreading, without help such as the application of pressure. There are of course occasions where non-wetting occurs. Figure 2.2 shows the various degrees of wetting as well as highlighting the importance of spontaneous spreading in an adhesive system.

![Figure 2.2. A schematic of (a) wetting (b) spreading and (c) non wetting scenario.](image)

There are several methods that exist for the measurement of contact angles, which vary from simply measuring the gradient of a sessile drop on a flat surface to more complicated methods such as the Willhelmy plate technique, enabling the contact angle of fibres to be measured. Wetting plays a principal role in adhesion and must be obtained for adhesion to occur, various methods are available to evaluate contact angle measurement and have been reviewed in the literature [8].

2.2.3. Thermodynamic Considerations

Surface free energies are used to describe the thermodynamic stability of a joint; to predict the likelihood of two materials becoming spontaneously separated, by calculating the work of adhesion, \( W_A \). The work of adhesion may be defined as the free energy change required to separate two phases, A and B, cleanly along the interface. A negative value of \( W_A \) indicates that an adhesive system is energetically unstable and that separation will occur spontaneously, whilst a positive value shows that the bond will be thermodynamically stable. If the surface free energies (\( \gamma_A \) and
γ\textsubscript{AB} and interfacial free energies (γ\textsubscript{AB}) are known, the thermodynamic work of adhesion required to separate a unit area of a solid and liquid phase can be calculated using the Dupré equation:

\[ W_A = \gamma_A + \gamma_B - \gamma_{AB} \]  \hspace{1cm} (2.4)

The term γ\textsubscript{AB} needs to be calculated in order to predict W\textsubscript{A} and this was originally achieved by analogy with the Berthelot relationship for gases, which assumed that the relationship for the attractive constants between like molecules A\textsubscript{aa} and A\textsubscript{bb} and unlike molecules A\textsubscript{ab} may be expressed as:

\[ \frac{A_{ab}}{(A_{aa}A_{bb})^{1/2}} = 1 \]  \hspace{1cm} (2.5)

Thus the interfacial free energy, γ\textsubscript{AB}, may be expressed in terms of the two component phases as:

\[ \gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_A \gamma_B)^{1/2} \]  \hspace{1cm} (2.6)

This approach does not take into account the different types of forces available for interaction at the interface, although usually surface free energy can be represented quite satisfactorily by dispersion (γ\textsuperscript{d}) and polar components (γ\textsuperscript{p}) in the following manner:

\[ \gamma_A = \gamma_A^d + \gamma_A^p \]  \hspace{1cm} (2.7)

Using this assumption Fowkes rewrote Equation 2.6 and so for two phases, with surface free energy values containing both dispersion and polar forces the interfacial free energy change may be calculated as:

\[ \gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_A \gamma_B^d)^{1/2} - 2(\gamma_A \gamma_B^p)^{1/2} \]  \hspace{1cm} (2.8)
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Having determined the expression for the interfacial free energy, $\gamma_{AB}$, the work of adhesion may now be calculated by substituting $\gamma_{AB}$ into the Dupre equation.

$$W_A = -2(\gamma_A d \gamma_B d)^{1/2} + 2(\gamma_A p \gamma_B p)^{1/2}$$  \hspace{1cm} 2.9

This approach can be used to consider the thermodynamic stability of an adhesive system under dry conditions and encouragingly a positive value of $W_A$ often results, however, as will be discussed later in this chapter, one of the critical issues with adhesive bonding is its performance under aggressive conditions. Water is one of the most deleterious and unfortunately most common environments that an adhesive bond encounters. In the presence of a third phase, such as water, Equation 2.4 may be modified allowing the thermodynamic stability of an adhesive system in a liquid environment ($W_{AL}$) to be assessed.

$$W_{AL} = \gamma_{AL} + \gamma_{BL} - \gamma_{AB}$$  \hspace{1cm} 2.10

Using the concept introduced above (i.e. taking into account dispersion and polar contributions) an expression for $W_{AL}$ for an adhesive system in the presence of a third phase may be written as:

$$W_{AL} = 2[\gamma_{LV} - (\gamma_A d \gamma_{LV} d)^{1/2} - \gamma_A p \gamma_{LV} p)^{1/2} - (\gamma_B d \gamma_{LV} d)^{1/2} - \gamma_B p \gamma_{LV} p)^{1/2} - (\gamma_A d \gamma_B d)^{1/2} - \gamma_A p \gamma_B p)^{1/2}]$$  \hspace{1cm} 2.11

The two expressions for the $W_A$ can provide important information as they predict the change in the thermodynamic behaviour of a bond on changing from a dry to a wet environment. For example a positive dry value changing to a negative value in a wet environment would infer that a stable joint, that may fail cohesively, when exposed to dry conditions, will experience a deterioration in joint strength with its locus of failure becoming interfacial under wet conditions. In the case of a wet environment negative values are often observed, however it should be remembered that the work of adhesion is a thermodynamic calculation and only relates to joint stability, not life time. Indeed
a negative value for $W_A$ may be calculated but the system may operate for a considerable time before failure.

2.3. Mechanisms of Adhesion

2.3.1. Introduction

The importance of achieving intimate molecular contact as well as the need to establish forces of intrinsic adhesion across the adhesive/substrate interface has been emphasised. These adhesion forces must be sufficiently stable and strong to ensure a good service life for the adhesive joint. The methods by which these forces act across an interface are referred to as the mechanisms of adhesion, however, over the years no individual "mechanism" has been universally accepted and various mechanisms have been postulated for particular applications and reviewed at reasonable length in the literature. Four of the main mechanisms of adhesion are:

(a) Mechanical interlocking.
(b) Diffusion theory.
(c) Electronic theory.
(d) Adsorption theory.

2.3.2. Mechanical Interlocking

This theory, essentially, proposes that mechanical keying, or interlocking, of the adhesive into irregularities of the substrate causes adhesion of the two phases, i.e. adhesion occurs with no chemical interaction between the adhesive and substrate. One of the few genuine examples of mechanical interlocking is the often referred to mercury amalgam in a tooth filling. The dentist undercuts the tooth in an "ink bottle" style and applies pressure, pushing the amalgam into the cavity, no interaction between liquid and solid is observed and the amalgam is held in place by the geometry of the cavity alone.
Much work has been reported on the phenomenon of mechanical interlocking, leading to improved adhesion due to a roughening of surface topography. Whist it is now understood that an adherend should be roughened prior to adhesion, for example grit blasting, it is rare that any subsequent improvement in adhesion is related to mechanical interlocking but, more likely the removal of a WBL or increased surface area, allowing more chemical interaction between the respective surfaces.

2.3.3. Diffusion Theory

Voyutskii [9] developed the diffusion theory considering the autohesion of polymers, the term autohesion refers to the intrinsic adhesion of polymers to themselves. It is proposed that autohesion occurs as result of diffusion between two interacting materials resulting in adhesion. In order for autohesion to take place it is essential that the respective surfaces have sufficient coalescence, contact alone is not sufficient, a gradual restoration of a high molecular structure in the zone of contact is vital, it is the diffusion of macromolecules that gives the bond its strength. Voyutskii carried out a series of time and temperature dependent experiments to confirm his diffusion theory showing an increase in joint strength for respective time and temperature increases expected for a diffusion process. The interdiffusion of the two polymers requires a degree of chain mobility and mutual solubility of one within the other, with mutual solubility being reached if the two polymers posses similar solubility parameters. The solubility parameter, $\delta$, may be defined as the square root of cohesive energy density and is considered to be a reliable way to predict whether polymers are compatible. Other factors that play role in the diffusion theory are the size and shape of molecules, diffusion is also made easier the lower the viscosity of the polymer. Voyutskii reported that the more flexible, and the fewer side branches the greater the possibility for diffusion and so increased propensity for autohesion.

Where solubility parameters of amorphous polymers are similar autohesion may well be observed, however, this is not a common situation. This theory is not applicable for adhesion between organic and inorganic material, for example onto metallic substrates. There may even be problems where both components are polymers with
similar solubility parameters, if one of the polymers is crystalline in nature, the diffusion mechanism breaks down as the crystalline polymer will not be soluble.

2.3.4. The Electronic Theory

If an adhesive and substrate have different electronic band structure, electron transfer may occur to balance the fermi levels, resulting in the formation of a double layer of electrical charge at the interface. Electrostatic forces are responsible for the adhesion and if such an interface is created this is the basis of the electronic theory of adhesion.

On consideration of the physics of separation, Deraguin reported that sparks are seen and a cracking noise heard on the removal of electronic tape from a substrate [10]. Before Deraguin's work, surface tension had explained adhesion phenomena. Deraguin, however, discovered, using peel tests, that the force required for actual separation of films was several orders of magnitude higher than those predicted by surface free energy effects alone. The disclosure of a double layer effect at an interface suggests that the interfacial region of a joint behaves as a parallel plate capacitor, with a positive charge one side of the boundary and a negative charge the other, leading to a potential difference (PD) set up across the boundary. Separation of the boundary occurs when the PD between the two phases increases proportionally as the distance, \( h \), increases, Figure 2.3. This PD is limited only by electric discharge in the gap (which depends on the surrounding gas pressure) and adhesion is due to the attractive forces across the electrical double layer. These forces may be represented by work required to separate the respective phases \( (A_e) \) and can be calculated using:

\[
A_e = \frac{h_e \varepsilon_d}{8\pi} (dV_c/dh_e)
\]

Where \( V_c \) is the discharge potential at the discharge gap, \( h_e \) and \( \varepsilon_d \) is the dielectric constant.
As with the other mechanisms discussed the electronic theory of adhesion has been demonstrated in certain specialised circumstances. One major flaw of the theory is the assumption of failure to be at the adhesive/substrate interface which, in practice, is rarely observed and it appears that in general there are few examples of the electronic double layer being the prime reason for adhesion.

2.3.5. The Adsorption Theory

With sufficient intimate molecular contact, materials may adhere as a result of the intermolecular forces, which are established between atoms and molecules in the adhesive and substrate. There are a number of bond types that may occur and broadly be grouped into different categories, Table 2.2. Chemical interaction, which may be exemplified by primary bonds, have high bond energies and are formed due to adhesive molecules chemically reacting with the substrate thus forming chemical bonds across the interface (chemisorption), chemical interaction is also possible with acid base interactions. Physical interactions (secondary forces) are assumed to be weaker with a maximum bond energy of approximately 80 kJmol⁻¹, Van der Waals forces (including dipole interactions and dispersion/London forces). A final category of the bonds responsible for the forces of adhesion are donor-acceptor bonds, with acid-base interactions the most widely applicable example, for example hydrogen bonds.
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<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Energy (kJ mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Bonds</td>
<td></td>
</tr>
<tr>
<td>Ionic</td>
<td>600-1100</td>
</tr>
<tr>
<td>Covalent</td>
<td>60-700</td>
</tr>
<tr>
<td>Metallic</td>
<td>110-350</td>
</tr>
<tr>
<td>Donor-Acceptor Bonds</td>
<td></td>
</tr>
<tr>
<td>Brönsted acid base interactions (i.e. upto a primary ionic bond)</td>
<td>Up to 1000</td>
</tr>
<tr>
<td>Lewis acid-base interactions</td>
<td>Up to 80</td>
</tr>
<tr>
<td>Hydrogen Bonds</td>
<td></td>
</tr>
<tr>
<td>Including fluorine</td>
<td>Up to 40</td>
</tr>
<tr>
<td>Excluding fluorine</td>
<td>10-25</td>
</tr>
<tr>
<td>Secondary Bonds</td>
<td></td>
</tr>
<tr>
<td>Van der Waals Bonds</td>
<td></td>
</tr>
<tr>
<td>Permanent dipole-dipole interactions</td>
<td>4-20</td>
</tr>
<tr>
<td>Dipole-induced dipole interactions</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Dispersion (London Forces)</td>
<td>0.08-40</td>
</tr>
</tbody>
</table>

Table 2.2. Bond types and typical bond energies [6].

2.3.5.1. Secondary and Primary Bonds

All materials exhibit secondary forces, in particular dispersion interactions, and these are frequently the forces responsible for adhesion between dissimilar materials. Experimental work has shown that secondary forces are sufficient to account for measured joint strengths. Huntsberger [11] has shown that dispersion forces alone, at a separation of 1 nm, can result in a tensile strength of 100 MPa. In reality much lower values occur due to the presence of air voids and defects acting as stress concentrations. In most cases adhesion can be ascribed to secondary forces, if this is the case quantitative assessment of interfacial bonds is possible by estimating the interfacial free energy and then calculating the work of adhesion, \( W_{A} \), as described in section 2.2.2, provided the surface free energies of the individual components are known.
Whilst, in the majority of cases secondary bonding has been responsible for intrinsic adhesion, it has become clear, more recently, that specific interactions such as donor-acceptor acid-base forces and primary bonds may exist across an interface. One example of where primary bonds may be found to play a role in adhesion is in the formation of an **interphase**. An interphase may be considered as a region of changing composition and properties between the adhesive and the substrate forming a three dimensional region rather than a two dimensional interface. For example Watts, using XPS, observed that a chemical reaction between mild steel (substrate) and polybutadiene (organic phase) occurs forming an interphase [12]. Silane adhesion promoters are another example of primary bonding in adhesion. Silane molecules adsorb onto the substrate surface forming primary bonds, the organofunctional groups react with the adhesive and thus a network structure is formed [13, 14].

### 2.3.5.2. Donor-acceptor Interactions

Most polymers have functionalised sites that are electron donor (Lewis base) or electron acceptors (Lewis acid) that provide enhanced specific intermolecular interactions, with adhering substrates, known as acid-base interactions [15]. Hydrogen bonds are typically acid-base bonds with oxygen acting as the Lewis base and hydrogen the Lewis acid, Figure 2.4.

![Figure 2.4. Schematic of a hydrogen bond](image)

Bolger [16] in 1967 made the important assertion that the only forces to consider in addition to dispersion forces were acid-base interactions, i.e. hydrogen bonds. Bolger was able to derive an expression which allowed the relative probability of acid-base interactions to be calculated, involving the arithmetic difference between the
isoelectric point (IEPS) of the surface and pKa of the polar groups in the organic phase.

At normal bonding temperatures the outermost surface of a metal oxide is hydrated giving a large number of hydroxyl groups. The identity of the metal atom (M) influences the activity of the surface hydroxyl groups (-OH), i.e. the acidity or basicity of the hydroxyl groups. These surfaces adsorb water molecules via hydrogen bonding, this allows the surface to act as a Brönsted acid (proton donor) or Brönsted base (proton acceptor) [16]:

\[
\begin{align*}
-\text{MOH} & \quad \text{OH}_2 \quad \text{MOH}^+ \quad \text{H}_2\text{O} \quad \text{MO} \quad \text{HOH} \\
\end{align*}
\]

As the pH in the aqueous phase is altered by the addition of water (electrolyte) the surface acquires a charge:

\[
\begin{align*}
\text{H}^+ & \quad \text{OH}^- \\
-\text{MOH}_2 & \quad \text{OH}_2 \quad -\text{MOH}^+ \quad \text{H}_2\text{O} \quad -\text{MO} \quad \text{HOH} \\
\end{align*}
\]

This surface charge can be calculated from zeta potential measurements as function of pH using suspensions of powdered oxide in water. At a given pH the number of positive charges will equal the number of negative charges and the zeta potential will equal zero, (the pH value will vary for different metal oxides). The IEPS is the pH of the solution when the zeta potential equals zero and depends on the valence state and radius of the cation. High pH indicates a basic surface and low values represent acidic surfaces.

Considering Bolger's interaction parameter:

- \( \Delta_A \) - surface interaction with an organic acid.
- \( \Delta_B \) - surface interaction with an organic base.

and Bolger's equation:

\[
\begin{align*}
\Delta_A &= \text{IEPS} - \frac{pK_A}{A} \\
\Delta_B &= pK_A/(B) - \text{IEPS}
\end{align*}
\]
Large positive values for $\Delta_A$ and $\Delta_B$ imply that stronger ionic forces dominate over weaker dipole interactions (a shift to the right in Figure 2.5). At large negative values, acid-base interactions are negligible and interfacial forces are essentially van der Waals. At $\Delta = 0$ acid-base interactions are of a similar magnitude to van der Waals forces, the ideal situation. On occasion where large positive values of $\Delta$ exist the acid-base contributions may well be strong enough to induce chemical attack or corrosion.

Figure 2.5. Acid base contributions as predicted by $\Delta_A$ and $\Delta_B$ from Equations 2.15 and 2.16.

Bolger's approach, whilst useful in the specific case of adhesion between polymers and oxide surfaces, is limited to Brønsted acid-base interactions and a more general treatment should be based on electron donor-acceptor (Lewis acid/base) interactions. Drago developed a four parameter equation considering electrostatic and covalent interactions in the acid-base bond:

$$\Delta H = E_A E_B + C_A C_B$$  \hspace{1cm} 2.17

Where $E_A$- propensity of acidic component to form ionic bonds
$E_B$- propensity of basic component to form ionic bonds
$C_A$- propensity of acidic component to form covalent bonds
$C_B$- propensity of basic component to form covalent bonds
Acids with a large $E_A$ will react strongly with bases with large $E_B$ values. The main criticism of this four-parameter approach is that configurational entropy is not taken into account. Drago originally carried out his work with small gas molecules [17]. Polymer molecules can be large and therefore will undergo a large entropy change in order for the rearrangement of the viscous polymer to take place and allow adhesion to the metal oxide.

Acid-base interactions are very important in the adhesion of polymers to substrates for protection against interfacial incursion by water. Determination of the acidic and basic strength of the functional sites of adhesive and adherends allows a quantitative measure of the acid-base, polar, interactions between respective materials. Today there are many laboratory techniques used to determine Drago's $E$ and $C$ constants in order to calculate the enthalpy of interaction [18].

2.3.6. Concluding Remarks

Some of the fundamental aspects of adhesion have been considered thus far. As yet, no comment has been made concerning durability, however, reasonable durability cannot exist if initial intrinsic adhesion is poor. It is important to be aware of some of the critical conditions required for obtaining interfacial contact, for example that the thermodynamic requirements for wetting are met.

Initial intimate contact is only the first stage towards a stable joint and once the possibility of strong intermolecular contact has been established the generation of adhesive forces across the interfaces is required. The nature of four types of adhesion forces have been discussed and whilst special applications or situations may have their own particular "mechanism" of adhesion in most cases the principal mechanism is the adsorption theory, relying on intermolecular forces across the bonding interfaces.

Having established a strong and apparently stable level of adhesion the susceptibility of an adhesive bond to environmental degradation is a primary concern to the adhesives industry and particularly where galvanised steel is the substrate. A thermodynamic approach may predict that water induced failure can lead to an
interfacial failure, however, there are other driving forces, with more rapid kinetics of failure, that can result in a true interfacial failure. One such mechanism is cathodic delamination/disbondment, which may be particularly prevalent where there is the possibility for electrochemical activity. The next section looks at some of the more severe effects of environmental exposure to adhesive bonds and organic coatings, considering the degradation that occurs at the adhesive/substrate interface.

2.4. Cathodic Delamination

2.4.1. Introduction

The advantages and requirements of intrinsic adhesion have been reviewed above, however, this project is essentially concerned with the mechanism of bond degradation and the majority of research throughout this project will concentrate on failure mechanisms at the adhesive/substrate interface. Common degradation mechanisms of an organic coating include cracking or crazing at low or high temperatures, bond breakage within the polymer matrix as a result of hydrolysis or oxidation and these processes can, for the most part, also occur within adhesive bonding. Many coated metals are subject to defects, such as scratches or holidays in the coating, resulting in the exposure of unprotected metal, which will corrode generating electrons as a result of the anodic dissolution of the metal, for example steel. These electrons are then consumed at adjacent sites in which water and oxygen are cathodically reduced to hydroxyl ions. Often in these cases lifting of the coating is observed around the defect. This undesirable situation is known as cathodic delamination and arises due to the separation of anodic and cathodic half reactions in the vicinity of the defect. The cathodic reaction, or more strictly the products of the cathodic reaction, adversely affects the bond between the coating and the substrate and the coating separates from the metal [19].

Cathodic delamination or disbondment is defined as the detachment of strongly adhering organic coatings or adhesives under the influence of a cathodic potential resulting from an impressed current or galvanic conduction effects and has long been recognised as a problem on electrochemically active surfaces [20,
The potential may occur from the application of an impressed current, a sacrificial anode or generated locally, as in the area surrounding an active anode. The key reaction of the mechanism is the cathodic reduction of oxygen to yield aggressive hydroxyl ions and thus an increase in local pH values, Equation 2.18.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \quad 2.18 \]

The cathodic reaction, which occurs at the delaminating front, generates hydroxyl ions, which are the major destructive influence on the polymer/substrate bond. Considering the generation of hydroxyl ions in the cathodic half reaction, it is not surprising that studies have indicated that the pH under the organic coating is high where cathodic delamination is observed [20].

Evans [22] first described cathodic delamination in 1929 as the "alkaline peeling of the coat" and it is now generally accepted most failures in a coating show that a proportion of the failed zone is associated with a localised cathodic potential. A series of electrochemical reactions are set up when a small defect occurs in a paint film. At the defect gross corrosion will take place via the anodic reaction (i.e. in the case of steel, rust) which will be balanced by a cathodic reaction taking place close to the defect, under the paint film, resulting in the reduction of water and oxygen to generate hydroxyl ions, Figure 2.6. Equation 2.18 infers that the availability of water and oxygen is paramount and as most paint films are permeable this does not seem an unreasonable assumption. The build up of hydroxyl ions under the film leads to an increase in pH and allows disbondment to occur, leaving more exposed metal to become anodic, and rusting to spread.

![Figure 2.6. The corrosion transport process associated with disbondment.](image)

Until the early 1970s only the anodic reaction responsible for gross corrosion/rusting was considered critically important with little or no attention paid to regions of
cathodic influence. The attitude towards cathodic activity around defects changed once there was the realisation that cathodic regions showed accelerated adhesion failure of coatings. This lead to concern within the oil and gas industries, that used a combination of impressed current cathodic protection and high performance organic coatings to ensure corrosion-free operation of pipelines. Under ideal conditions this method of protection would be satisfactory but problems occur at holidays within the coating where rapid delamination may take place as a result of the applied cathodic potential. With cathodic disbondment now a recognised problem standardised tests were developed in the UK [23] and USA [24].

As discussed earlier there are different mechanisms of adhesion between adhesive and adherend, which may be grouped into four main categories; (a) mechanical interlocking (b) interdiffusion at the interface, (c) electronic interaction at the interface and (d) by adsorption of components of the polymer to the oxide or metallic surface. Free energy change calculations predict that often water alone is sufficient to break bonds from all four categories. Cathodic disbondment, however, is able to break down primary bonds and other specific secondary interactions formed in category (d), such as acid-base bonds and it is this fact that makes cathodic activity so damaging to coating or adhesive systems.

2.4.2. Mechanisms of Cathodic Delamination

Watts reviewed the interfacial chemistry of cathodic delamination with a view to obtaining a more complete understanding of the mechanism [25]. Watts also tried to establish rate-controlling steps and relate them to type of coating, substrate and mode of failure. The advent of surface analysis has proved invaluable in characterising cathodically disbonded/delaminated surfaces, being able to analyse thin surface layers of corrosion product and characteristic polymers. XPS and SIMS have been able to identify characteristic signatures of electrochemical behaviour by detecting very thin overlayers, chemical modification and the segregation of specific ions or molecules to the failure interface.
The mechanisms of cathodic delamination can be classified depending on failure type. These groups have one feature in common: cathodically generated alkali leading to high pH at an interface, which is responsible for failure, the three mechanisms are described below;

**Oxide reduction** —dissolution of the substrate oxide to which the polymer adheres leaving a void at the interface and hence blistering. Ritter [26] examined this mechanism using ellipsometric studies and subcoating pH measurements to determine the spatial development of cathodic areas under the coating. The technique involves the passage of elliptically polarised light through a transparent coating and reflection from the substrate surface. A pH probe was used to monitor, simultaneously, the environment at the coating/substrate interface. Changes in the phase and amplitude of the reflected light are measured and indicate alterations in surface roughness and thickness of the surface oxide film. Ritter found that air and thermally formed oxide films could be dissolved under high alkaline conditions (i.e. in strong NaOH solutions, at cathodic potentials; supporting evidence that oxide dissolution was a mechanism of cathodic delamination). An indication of the specific conditions required for oxide dissolution may be inferred by considering a respective metal’s Pourbaix diagram. The iron Pourbaix diagram is shown in Figure 2.7 and indicates that for dissolution of iron “oxides” high pH and very noble potentials are required.

![Figure 2.7. Simplified Iron Pourbaix diagram showing zones of corrosion, immunity and passivity.](image)
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Failure of the polymer. – Here, the polymer is attacked close to, but not at the interface. This leaves a thin polymer layer (approximately 2 nm) on the failure surface that can only be identified by sensitive surface analysis techniques. It has been proposed that a failure mechanism of this nature requires permeation of hydroxyl ions and their metal counter ions together with water molecules. Hammond et al [27] used XPS to determine the composition of failure surfaces generated by corrosion-induced de-adhesion of organic coatings on bare steel. Examination of the high-resolution spectra suggested that at least some of the products formed were a result of polymer degradation by cathodically produced hydroxyl ions and confirmed failure of the polymer coating near the interface. For example, in the case of an epoxy-ester resin, carboxylate residues characteristic of ester saponification were observed on both failure interfaces. These observations were considered to be a result of alkaline hydrolysis of the polymer. For this mechanism to be the result of cathodic activity cations, associated with hydroxyl ions, would always be identified at the failed interface, however Castle and Watts have found this not to be the case [28]. Whilst acknowledging that failure can occur close to the polymer metal interface, leaving a residual organic phase, they deduced that electrolyte aggregation (water) was responsible for failure. Such a “cohesive” type of failure is capable of recovering up to 80 % of its original bond strength on drying out, cathodic activity would induce permanent damage to a coating, and so this failure was termed coating degradation and subsequently a “wet adhesion” failure. Residual adhesive remaining on an interface in a failure of this nature only exists at a thickness of approximately 2 nm and consequently can only be identified by surface analysis techniques.

Interfacial failure – This is the classical form of alkaline-induced failure originally described by Evans and discussed in more detail by Koeler who claimed to have observed a true “clean” polymer/substrate interfacial failure [29]. A true interfacial failure is generally the result of electrochemical activity and is characteristically very clean. The identification of such a failure, therefore, can only be detected using surface analysis techniques as it is the composition of the outermost surface layers that characterise the failure type. Koeler studied cathodic disbondment of the oleoresinous coated steel by immersion in an aerated Na₂B₄O₇ solution (ammonium hydroxide was also used) polarised at -0.5 V. Blistering appeared and he used scotch tape on half the affected area in order to highlight the delaminated regions. Koeler
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described this as a true interfacial failure claiming that not a high enough pH had been reached to cause oxide dissolution or disruptive attack of the coating. The other half of the sample Koeler allowed to dry, the blisters disappeared and apparently re-adhered like a traditional “wet adhesion failure”. This latter observation calls into question the earlier delamination observations, the use of XPS on the delaminated areas would have helped to determine if the observed features were a result of true interfacial failure and highlights the importance of surface analysis to the adhesion community.

It is apparent, from the findings of the above work that slight changes in the locus of failure imply different failure mechanisms. The spectroscopic signal from surface analysis techniques is capable of differentiating between such changes and therefore determining mechanisms of failure. This project is concerned with the characterisation of failed interfaces and in turn establishing failure mechanisms of adhesive bonds and surface analysis (namely XPS and SIMS) potentially could play a significant role in an attempt to achieve the overall aims of the project.

Each of the above mechanisms may dominate under different circumstances depending on the coating or adhesive system. One of the first organic systems to be studied in detail was polybutadiene [30]. Polybutadiene on steel is complex system with of all three failure mechanisms existing. This situation arises due to the presence of an interphase layer zone of iron carboxylate between the coating and steel substrate. Under UK test specifications with a panel exposed to a 0.5 M NaCl solution at a potential of –1500 mV Watts has reported an affected area represented by a blistered central region and a weakly adhering outer zone. XPS analysis at the edge of the blistered region was able to identify that oxide reduction had occurred. The spectrum contained metallic components that were absent in the centre of the region, indicating that the oxide thickness had substantially been reduced and then regrown Figure 2.8.
Figure 2.8. Iron 2p3/2 spectra from a blistered disbondment zone (a) reduced thickness of oxide at the crevice tip; outer region and (b) regrown oxide located at the centre of the blistered region [25].

Watts concluded that oxide dissolution was brought about by pH excursions at the crevice tip. The survey spectrum from the blistered region shows a very low C 1s intensity (a small amount present as a result of atmospheric contamination) indicating a clean "true interfacial" failure. This was due to lateral diffusion of hydroxyl ions from the exposed metal interface driving the crevice forward. The survey spectrum acquired from the weakened outer area revealed much larger quantities of carbon, with this failure zone being characteristic of the interphase region and diagnosed as coating hydrolysis, resulting from the downward diffusion of water molecules through the polymer film and is characteristic of the wet adhesion type failure discussed earlier, Figure 2.9.
Figure 2.9. XPS survey spectra of the metal surface following cathodic delamination of polybutadiene from mild steel, (a) from a blistered zone, showing interfacial failure (b) metal with a thin polymeric overlayer as a result of hydrolysis [25].

From the brief discussion provided above it is clear how the different mechanisms may compete in one system. In the polybutadiene system, however, the most importance may be attached to the zone of interfacial failure in the central, blistered, region, the reduction of oxide mechanism only can only take place in this instance once the interfacial failure has exposed the steel substrate.

Thicker coatings of the type used for line pipes in the oil and gas industries are much more resistant to cathodic disbondment. In general cohesive failures are observed, however, as surface roughness increases, a topic that will discussed later, a mixed mode of failure is observed [31]. A characteristic feature of the failure is the large amount of oxide reduction that occurs just in front of the interfacial region. By once again following the UK specification test, in which a 6 mm diameter hole is drilled
through the coating, a characteristic silver coloured halo of reduced oxide is observed around the defect on exposure to a cathodic potential (the normal oxide colour being golden). Unlike the polybutadiene model, where reduction of the oxide occurred as a consequence of a true interfacial cathodic delamination, the oxide reduction acts as a precursor to the interfacial delamination, opening up a crevice for hydroxyl ion to attack the polymer/substrate interface and allow a delamination front to grow.

Of the three mechanisms discussed it is clear that the under-film alkalinity produced by the cathodic half reaction plays a key role in the case of oxide reduction and interfacial failure. The misconceptions of early work concerning hydrolysis of the polymer have subsequently been shown not to be a result of cathodic activity but coating damage as a result of water aggregation. It will be seen later in this chapter that the composition of the diffusing electrolyte will affect the rate of coating degradation but does not actually alter the mechanism of failure.

Cathodic activity has been found to be responsible for failure of thick and thin coatings, and subsequent work has identified similar mechanisms responsible for failure of adhesive joints, [32, 33]. Davis investigated the mode of failure for a series of bonded iron substrates exposed to a hostile environment. After 7500 hours Davis observed a visually metal failure surface around the outside of the failed overlaps. This region appeared to be composed of a dull outer ring and a bright inner ring Figure 2.10 (b). Surface analysis showed electrochemical activity to be responsible for the failure region and the identification of relevant marker ions finding cathodic activity responsible for driving the failure region forward. As with Watts' coatings work, cathodic activity had initiated failure at the adhesive/substrate interface, exposing substrate material to anodic activity and allowing the regrowth of oxide and the formation of the dull region in Figure 2.10.
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Figure 2.10. Schematic diagram describing the failure of adhesively bonded mild steel; (a) demonstrating cathodic activity driving the crack tip forward and (b) the dull and bright regions (signifying cathodic and anodic activity respectively) visible on a failed lap joint overlap.

2.4.3. The Role of Water

In principle the cathodic half reaction, Equation 2.18, could occur in a non-aqueous environment, with enough water being present in the polymer film. All reported investigations, however, have been conducted where water has been present as a liquid phase and so water has played the role of reactant and supporting electrolyte. Water as a reactant can arrive at the interface through numerous routes via molecular
diffusion or as a liquid phase either through pores or nucleation from molecular dispersion. It is desirable for paint films to be impervious to water and oxygen, preventing either reactants from the cathodic half equation reaching the metal interface, although in practice, this is never the case. Indeed generally, paint films are so permeable to water and oxygen that the coatings struggle to effect the cathodic reaction. Coatings with high ionic resistance, however, will impede the movement of ions and thereby reduce the corrosion current to a small value. The effective resistance of organic coatings may be influenced in three ways: (a) electrolytes underneath the film coating of the substrate, (b) ionogenic (ion producing material present in the coating) groups in the film, for example carboxyl groups attached to polymer chains may contain a negative charge and, therefore, be regarded as very large anions, [34] (c) water and electrolytes in the surrounding environment.

Mayne and Mills’ investigated the transport of water through organic coatings [35]. They examined the effect of solutions of potassium chloride on the electrolytic resistance of organic films. Potassium chloride was chosen to provide good conductivity and unpigmented films were used in order to eliminate the complexities of polymer/pigment interaction. The films’ resistance was found to vary in two ways. Either the resistance increased with increased concentration of electrolyte (inverse or I type behaviour) or, conversely resistance decreased with increased concentration (direct or D type). Mayne determined that for I films the changes in resistance were dependent upon the availability of water in the solution and so was associated with the osmotic behaviour of the film. D type films, in contrast, followed the resistance of the solution in which they were immersed and this was thought to be due to the presence of pore like features filled with solution, therefore offering a direct route to the polymer/metal interface. Another major and perhaps more telling difference between the transport paths was microhardness values. The D type areas were shown to be significantly softer than the I type areas and that the distribution of hardness was related to film resistivity. This led to the conclusions that the organic films studied had a very heterogeneous structure possibly brought about by differences in crosslink density. The softer D type area could play a significant role in the cathodic delamination process of coatings or adhesive bonds by offering a direct route to one or some of the reactants to an interface, where failure could potentially occur.
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Castle considered the role of liquid water in a recent review of cathodic disbondment [20] and proposed that the presence of water as a condensed phase is required for the pH of electrolyte to rise to high enough level to satisfy the various debonding mechanisms. The requirement for water to be present in the condensed phase is because the activity of water dissolved in the polymer will be under the influence of substituent groups and is therefore much lower than unity. If the activity of water falls below unity the electrochemical potential at which hydroxyl ions are produced is shifted and it becomes harder to reach the conditions necessary for cathodic delamination. Water diffuses through the free volume of the polymer in its molecular form. For liquid water to exist nucleation of the molecular phase must take place, this is not easy within polymers unless a non-organic additive is present, for example a dust particle. On nucleation, water condenses to the liquid phase thus assuming an activity of unity and allowing cathodic disbondment to occur, provided all other requirements are met, at the substrate interface.

2.4.4. The Role of Cations

Water is just one of the ingredients for cathodic disbonding/delamination, others include cathodic potential, oxygen and cations. Cations are vital to the process as they balance the negatively charged hydroxide on the product side of the cathodic half reaction. Indeed, often cations can be used as markers for cathodic activity on a substrate surface, defining areas where cathodic activity has occurred. Castle and Epler [36], using XPS, showed that brass in a magnesium chloride solution, when held at a cathodic potential would eventually be covered in a magnesium hydroxide compound whilst when held at anodic potentials an increase in chloride ions was observed, Figure 2.11. Castle and Epler’s work exemplified the case for cations being used as markers for cathodic activity and also highlights their charge balancing role in the overall process of cathodic disbonding.
Different test solutions have indicated that the rate of coating failure is critically dependent on the solution composition [37]. Work by Skar [38] showed that the disbonding of a film was higher in caesium chloride than in sodium chloride solution. Skar suggested that this phenomenon was a result of cation size, with the ratio of charge to ionic radius determining the size of the solvated ion. Sodium ions are bigger than caesium ions when solvated and disbonding rate was shown to be highest for the smaller solvated ion as it was more mobile and would form the more stable hydroxide. Watts [37] also showed that delamination rate was dependent on the size of cation in solution. Watts concluded that diffusion of solvated ions through the film might allow an aggregation of cations and hence water molecules at the interface leading to rapid failure. In the case of larger divalent ions Watts found that their concentration was greatly reduced at the failure interface, compared to that of alkali metals, suggesting that the solvated ions were trapped in the polymer film, thus reducing diffusion of water to the interface and resulting in a slower failure rate. These examples are also in agreement with work by Leidheiser confirming that the tendency for disbonding ranks in the same order as the conductance of the ion in aqueous solution and inversely with the size of the hydration sheath [39].
One of the early questions concerning the cathodic delamination of coatings was whether downward diffusion through the bulk of the polymer or lateral diffusion along the interface from an exposed edge or defect was the rate-controlling step leading to failure. Part of the confusion was inherently brought about by the design of the majority of delamination tests, where a defect is machined into the test plate using a twist drill at 160°, removing the coating to create a flat based coating and thus automatically introducing the lateral diffusion path into the test as well the pre-existing route through the polymer. Having reviewed the literature, it now seems clear that where a lateral diffusion path is available, failure is much faster. Indeed, unless D type regions or pores are present within adhesive diffusion of water may only lead to coating degradation.

2.4.5. Concluding Remarks

This project is concerned with the poor durability of adhesively bonded galvanised steel. The phenomenon of cathodic delamination or disbondment has been reviewed and shown to have severe irreversible effects on adhesive/substrate interfaces on exposure to hostile environments. Failure is associated with localised cathodic activity as a result of an applied potential or the need to balance anodic activity, for example a defect in a coating. The cathodic reduction of water and oxygen produces aggressive hydroxyl ions, which cause a rise in underfilm pH, and allows delamination of the organic phase to occur. The reactants of water and oxygen are a necessity and unfortunately permeable to most organic phases, making the failure mechanism so destructive to many adhesive and coating systems.

Much of the fundamental research relating to cathodic delamination has been carried out using mild steel and so in the context of this project the next section reviews work carried out on the performance and failure mechanisms of adhesively bonded galvanised steel.
2.5. Durability of Adhesively Bonded HDGS

The performance of adhesives, sealants and coatings are frequently limited by the poor response of the metal/polymer interface to aggressive environments. One of the principle steps in being able to improve the durability of an adhesively bonded system is to understand the mechanism of failure by defining the exact locus of failure. Surface analysis techniques, such as XPS and SIMS, have been used for a number of years in adhesive bonding studies [40, 41, 42]. The ability to detect very low levels of adhesive, associated with a thin organic overlayer, has enabled precise failure mechanisms to be determined, for example deciphering between a “true” interfacial and visually interfacial failure, which can actually be a thin cohesive failure close to the substrate. As already mentioned, water ingress in adhesive bonds is known to reduce bond performance greatly and has been highlighted as playing a major role in failure of environmentally exposed adhesive joints. There are ways to improve durability such as modifying the adhesive and substrate with inhibitors or pretreatments. These changes, however, can only be made as long the cause of initial poor durability is understood.

In the automotive industry zinc coated steels are being introduced in greater quantities to improve the corrosion protection of vehicle body shell structure [43]. The aim is to reduce weight with no sacrifice to performance, affordability, safety and cost. These aims have led to design changes, allowing a reduction in thickness and steady growth of materials such as galvanised steels.

When bonded galvanised steel joints are exposed to corrosive environments, such as a salt spray test, bond durability is primarily governed by interfacial corrosion between the adhesive and substrate, zinc will cathodically protect the exposed iron at the free cut edge of the substrate. Immediate thoughts of improving durability would take into account thickness and composition of the zinc coating. According to van Ooij the corrosion products zinc hydroxy-chloride (4Zn(OH)$_2$.ZnCl$_2$) and zinc hydroxy-carbonate form beneath the paint of an automotive cathode electrocoat applied on galvanised steel after a cyclic corrosion test [44]. Van Ooij proposed that the basic properties of the corrosion products caused poor adhesion of the paint (epoxy-
urethane) due to the loss of their acid/base interaction. Under similar test conditions Foister [45] also reported gross corrosion of the zinc, with the same corrosion product, to be responsible for joint failure. The effect of substrate morphology and oxide layer chemistry on bond strength and durability for a series of galvanised steels was also investigated. Significant differences in surface morphology between electroplated (rough) and hot dipped (smooth) galvanised steel were observed. Unsurprisingly the type of process chosen also had a profound effect on the surface chemistry with uniform zinc surface for the electroplated surface and substantial amount of additives being present in the hot dipped coatings, such as Al, Si and Pb. Whilst realising that it was difficult to separate effects attributable to surfaces roughness from those due solely to surface chemistry, Foister concluded, having made empirical observations, that bond strengths and durabilities increase as surface roughness increases, and that bonded surfaces which are uniform in zinc (electroplated) are less susceptible to environmental corrosion than those hot dipped surfaces characterised by chemical heterogeneity. These conclusions are not that surprising, as one would expect rough surfaces to help intrinsic adhesion and that chemical heterogeneity may aid the formation of local galvanic cells in a damp environment. Maeda et al has also studied the effects of surface composition on the durability of adhesively bonded HDGS [46]. They revealed that surface aluminium in combination with lead, which had segregated to the substrate surface via grain boundaries, decreased aged lap shear joint strength.

Early work in this area at Ford Laboratories, Dearborn, USA, looked at how the choice of adhesive could play a role in the performance of adhesively bonded HDGS and could be responsible, in part, for poor durability [47]. In an initial paper Holubka et al [47] studied the effect of adhesive composition on bond durability on a series of substrates including electrogalvanised steel. The joints were also subjected to different ageing techniques, relative humidity and cyclic loading. Holubka found that the locus of failure after corrosion exposure was mainly cohesive for crosslinked epoxy and acrylic adhesives and almost entirely visually interfacial for urethane and poly (vinyl chloride) (PVC) based adhesives. Under cyclic loading the PVC based adhesives also gave by far the poorest performance. These joints showed a rapid drop in bond strength and the next series of papers from Ford investigated their failure mechanisms.
Holubka’s work also studied the performance of cold rolled steel (CRS) as a substrate, which interestingly had shown rapid and catastrophic reductions in bond strength, as was the case with the galvanised steel. In both cases visual interfacial failures were observed, however, high resolution XPS spectra from the CRS, supported by quantitative analyses, suggested that failure did not occur at, but near, the adhesive/substrate interface, inferring the “wet adhesion” failure identified previously by Watts and others [25]. The galvanised steel substrate, in contrast, showed zinc on both failure surfaces along with substantially less carbon on the metal side compared to that of the CRS substrate. These results indicated that the locus of failure was much closer to the zinc substrate than in the case of the CRS joints. High resolution XPS from the adhesive interface showed that the corrosion product was essentially in the form of zinc chloride probably resulting from the dehydrochlorination of PVC during cure. The degradation was associated with the substrate interface, as ionic chloride was not observed in the bulk adhesive. These results suggest that the dehydrochlorination process is some way dependent on the substrate to which the adhesive is applied and that the surface mediated degradation of PVC may occur on reactive metallic substrates, resulting in an interfacial layer of degraded products. Commercial adhesives based on PVC typically incorporate a variety of additives, such as resin modifiers, to improve bond performance.

Holubka in his original paper also reported on the effect of epoxy resin and a crosslinking dicyandiamide added to a PVC formulation with CRS and galvanised steel. DeVries et al followed this up with an examination of the failed interfaces in order to determine the any difference in mechanism of failure [48]. Improved bond strengths were attained despite the fact that both substrates, once more, failed interfacially. XPS results on the CRS sample, however, detected no iron on either interfacial surface, suggesting that the failure had left a substantial polymer residue on the metal substrate indicating that failure was actually cohesive. With the galvanised steel joint zinc was observed on both failure surfaces, the failure was much closer to the substrate. The chlorine concentration at the interface was about half of that in the bulk adhesive, inferring the dechlorination had taken place, however, there was also a tendency for the resin/crosslinker system to segregate to the interface region. In comparison with the unmodified system, DeVries concludes that the addition of the
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epoxy/dicyadiamide modifier substantially lessened the extent of thermal degradation and was responsible for the improvement in bond strength.

Dickie continued Ford Laboratory's investigation by carrying out a set of experiments to ascertain whether the failure mechanisms of joints is effected when an external mechanical load is applied [49, 32]. The substrates were bonded in the "as received" condition and the unloaded joints were subjected to a corrosion test cycle of 15 min immersion in an aqueous solution of 5% NaCl, 75 minute ambient temperature dry off and 22.5 hour of static humidity exposure at 85 % relative humidity at 50°C. A mixed mode failure was observed, with regions of interfacial and cohesive failure. The cohesive regions were easily identified, as spectra from the respective regions were characteristic of the bulk polymer. The visually interfacial regions, which started from either end of the overlap, showed high levels of zinc and chlorine on both substrate and adhesive surfaces suggesting that the locus of the interfacial failure was within a layer of corrosion products formed between the adherend and the adhesive. The anodic dissolution of the substrate was considered to be the dominating process responsible for the formation of the weak corrosion layer. Joints were also subjected to cyclic corrosion exposure under a static mechanical load. Specimens were aged under similar conditions as before but tested under an imposed static load, mounted in a spring–loaded fixture calibrated to provide the desired load. Whilst the absence of an applied load did not result in spontaneous rupture within the time scale of the experiments, loading the joints led to an acceleration of the failure process and also spontaneous rupture. All specimens showed partly cohesive and interfacial failure, but unlike the unloaded joints, where the interfacial area was distributed around the whole edge of the overlap, the interfacial area on the loaded samples was restricted to either end of the overlap, with virtually no ingress along the sides of the overlap, (Figure 2.12).

The locus of failure and mechanism of the corrosion processes responsible for spontaneous rupture were studied using imaging XPS, intended to allow the interfacial chemistry to be resolved spatially over the entire failure surface (at a analysis area of 0.4 mm x 0.8 mm). As discussed earlier, on the unstressed specimens, subjected to cyclic corrosion, zinc and a substantial amount of chlorine was observed over the whole interfacial area (with the notable absence of sodium) confirming that the corrosion process was dominated by anodic dissolution of the
substrate. For specimens exposed under load cathodic sodium was present throughout the interfacial failure regions as well as at rather high concentration in localised areas. Dickie also makes the point that chlorine was also present throughout these failure regions. Importantly there are local areas of high chlorine concentration that are complementary to local maxima in the sodium maps. There were some coincident areas of sodium and chlorine and this suggests that some contamination of the failure interfaces by the electrolyte had occurred after rupture. This highlights one of the shortcomings of Dickie’s practice of carrying out surface analysis on spontaneously ruptured joints, as the opportunity to examine an “as failed” surface is lost and would be a highly undesirable situation in the context of the present study.

Figure 2.12. Schematic representation of the corrosion distribution for specimens subjected to corrosion exposure (a) without load (b) with load [32].

Whilst ingress of electrolyte had clearly occurred there was still evidence for the formation of local anodic and cathodic regions within the interfacial area, with high chlorine areas evidence of anodic dissolution and other areas rich in sodium corresponding with areas of carbonate or bicarbonate as defining markers for cathodic
activity. In this case Dickie supposes that the carbonate or bicarbonate trace is the result of high local pH from a local cathodic site [44] although in the past carbonate formation has been attributed to the formation of zinc hydroxycarbonate by the reaction of water and carbon dioxide with zinc oxide [27].

Dickie likens the formation of cathodes and anodes to the phenomenon known as crevice corrosion. Crevice corrosion involves the development of small interfacial volumes of stagnant electrolyte, a differential aeration cell is established with the metal inside the cell becoming anodic with oxygen concentration being reduced and the metal outside the crevice becoming cathodic. Ionic transport balances the charge and maintains current flow. Within the crevice, the hydrolysis of metal chloride acidifies the electrolyte and accelerates the dissolution of metal. Whilst Dickie’s proposal of a crevice corrosion type mechanism, being responsible for the presence of cathodes in the interfacial areas is plausible, at no point does he discuss the effect of the large iron cathode on the edge of the exposed cut edge of the galvanised steel substrate. This is almost certainly responsible for the anodic dissolution of the zinc in the unstressed samples as a result of the zinc fulfilling its cathodic protection duties. The presence of an exposed iron cathode at the free cut edge has many complicated implications for the electrochemical activity of an adhesively bonded galvanised steel joint and will be discussed later in the thesis.

Dickie’s work has introduced yet another factor that can affect the failure mechanisms of a galvanised steel lap joint. The application of an external mechanical load reveals the presence of local cathodes and anodes set up on the substrate surface resulting in a spontaneous failure. Care must be taken, however, when relying on images to give chemical information about the surfaces. It is vital that a threshold or detection limit is carefully established in order to determine the level of sensitivity being dealt with and this is not mentioned in Dickie’s paper. Conclusions drawn from Dickie’s work are that the formation of cathodes is made possible by the continual opening of a bond line allowing access of electrolyte and oxygen, vital ingredients for the cathodic half equation. Rapid failure may well be brought about due to the formation of cathodes, which increase the rate of anodic dissolution due to the reduction of resistance between the cell sites. Increased diffusion rates with applied stress could also play a
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role, especially in the early stages of exposure before the formation of internal cathodic sites.

In a series of papers by Jethwa and Kinloch on the “Fatigue and Durability of Adhesive Joints” they collaborated with both Dickie and Watts concentrating on failure mechanisms [50]. Durability is known to be the principal issue when considering adhesive bonding, however, for adhesive bonding to be considered as an alternative structural joining technique improvement in its fatigue behaviour must also be understood as structural components undergo dynamically applied loads throughout their life time. Jethwa exposed electro-galvanised TDCB specimens in dry and wet environments to cyclic fatigue tests and then used surface analysis techniques, principally XPS, to determine the loci and mechanisms of failure. Under almost dry conditions failure, predictably occurred cohesively through the adhesive, however, under the more aggressive wet conditions zinc was found on both sides of the failure surface by surface analysis and visible by the presence of a white deposit, the corrosion product known as white rust (ZnO). XPS revealed that the level of carbon on the metal side of the joint was particularly low which is consistent with a voluminous corrosion product, i.e. a high surface area. Jethwa concluded that failure was driven by anodic behaviour, indeed a significant concentration of chlorine was identified on the failure surfaces, a marker for anodic behaviour. Anodic activity at the crack tip, lead to the production of a weak voluminous corrosion product allowing the crack to propagate close to the adhesive/zinc oxide interface but through the white rust.

This section has highlighted the poor durability of adhesively bonded galvanised steel in a hostile environment. In all cases electrochemical activity has played a role in the failure mechanisms, with anodic dissolution being the principle cause of joint failure. The relevance of the project to the automotive industry has also been highlighted, with extremely poor durability performance of adhesively bonded HDGS naturally not acceptable in an industry where a product is expected to last between 10 and 15 years. The severe anodic undercutting of the zinc coating, however, is not unexpected and the zinc is designed to act as a sacrificial anode to protect any exposed iron, this is discussed in detail later in the thesis. One way that the zinc coating may be protected would be to employ a pretreatment and so also improve the durability of
adhesive bonds. This project looks at the use of galvanised steel with a pretreatment, in particular phosphating, and the next section considers some of the benefits that pretreatments can offer adhesive bonding.

2.6. Surface Pretreatments

2.6.1. Introduction

The need for wetting and good interfacial contact is essential for intrinsic adhesion, as discussed in section 2.2. Substrates with low surface energies, such as polymers do not display good wetting characteristics and so joint performance is greatly reduced. In these cases it is often necessary to increase the surface free energy by pretreating the substrate using techniques such as chemical or plasma etching and corona discharge. Increasing the surface free energy of substrates (i.e. to make the substrate more active and receptive to adhesion) is the principal aim of pretreatments and this can be achieved in various ways.

The removal of any weak boundary layer (WBL) from a substrate prior to bonding is vital and if not removed may act as a locus of failure leading to a relatively low joint strength. As discussed earlier commercial materials are usually not very clean, covered with a protective layer of grease, oil mill scale and corrosion products. A clean metal surface with high surface free energy is able to adsorb strongly attaching contamination from the atmosphere. Weak boundary layers can even form after bonding has taken place with segregation of adhesive components diffusing to an interface possibly providing a weak locus of failure [51]. Another way in which the degree of intimate contact may be maximised is by modifying the surface chemistry. The introduction of surface groups may increase surface free energy by introducing polar groups, allowing the possibility of acid-base interactions. For example polymers such as polyethylene do not have surface groups that contribute to a high surface energy but can have them readily introduced by flame or corona discharge treatment. As already mentioned there are not many examples where mechanical interlocking can claim to be the primary mechanism of adhesion, however, changing the surface
roughness may lead to enhanced joint strength by offering more sites for intrinsic adhesion.

The effect of such treatments may be to increase the strength of the dry joint but usually, more importantly, to improve durability on exposure to hostile environment. Adhesive joints in the automotive industry have to sustain their strength and stiffness throughout the lifetime of a car under a wide range of environmental conditions. The durability of adhesive joints in such conditions depends greatly upon the physical and chemical interactions between the adhesive and the substrate. It is these interactions that can be altered, engineered and enhanced by the use of a surface pretreatment.

The application of chemical conversion coatings to metal surfaces prior to painting is a well-established technique to provide good paint adhesion and corrosion resistance. Both phosphating and chromating are commonly used as a pretreatment of zinc coated materials.

2.6.2. Phosphating

2.6.2.1. Development of Phosphating

It is generally accepted that the performance of an adhesive system can be improved through the use of an appropriate pretreatment [52]. By changing the nature of the substrate surface (e.g. chemistry or morphology) it is possible to reduce the rate of corrosion and bring a metallic surface to a condition which will favour the acceptance of a continuous and adherent protective organic coating, this is often achieved in practice by the application of a conversion coating. Phosphating is the most widely used form of metal pretreatment, has been used for over 100 years and if deposited under proper conditions, gives the substrate better corrosion resistance and improves adhesion of coatings [53,54].

The evolution of the modern phosphate process finds its roots at the beginning of the twentieth century from the early patent of Thomas Watts Coslett of Birmingham, UK [55]. This 1906 patent, which considered the use of phosphoric acid with iron filings
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now, seems far removed from the present day treatment as it was slow, not continuous and carried out at high temperature. Acceleration of the process was reported by Bullock and Calcott in 1909 [56], they used an electric current with the item to be phosphated being made the cathode. The application of approximately 2 V reduced the treatment time for a Coslett-type bath from 2.5 hours to half an hour. The same year Coslett also reported the effect of an applied current but also introduced the idea of using a zinc phosphate bath prepared by dissolving zinc or zinc phosphate in phosphoric acid. If the period before the First World War saw the basic process established the inter-war period saw the establishment of the phosphating industry on a large scale. Maintaining the balanced ratio between free and combined phosphoric acid was a problem that was overcome by Allen [57] who used crystals of manganese dihydrogen phosphate during phosphating in a process known as “Parkerizing” named after the brothers who founded the Parker Rust Proof Co. in America. The problem was that coating formation took one hour, thus limiting the process to batch production.

By now improved adhesion performance and the resultant durability of paint applied to phosphated steel was recognised and began commercial use in the early 1930's. A major step forward came in 1929 when small amounts of copper salts were found to reduce coating times to as little as 10 minutes, consequently and perhaps more significantly this allowed phosphating to be used a continuous process. The discovery that the addition of oxidising agents, such as nitrates lead to even shorter processing times 2-5 minutes, resulting in increased production with less equipment and floor space required. Faster coating formation was observed as addition of the oxidising agents prevents the formation of hydrogen on the metal surface. All this progress allowed industrial exploitation of the phosphating process to take place. Spraying the phosphate coating onto an object, instead of immersing, was introduced in the mid 1930's, once again reducing the production time to sixty to ninety seconds at lower temperature and solution concentration. Shorter processing time also lowered costs requiring less floor space and as a continuous process solution could be used that drained off an object was collected and resprayed. Spraying offered several other advantages, which will be covered in the next section, but include the coating of larger objects, such as automobile bodies, and a fine grain crystal structure suitable for painting. Since the early years of phosphate development little has fundamentally
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changed, improvements have included the lowering of temperature, controlling of coating weight (using refining agents) and the development of high speed processes for use in continuous strip lines, with processing times as low as five seconds. The above section has briefly discussed some of the history and developments in phosphating and some of the theoretical considerations of those developments will now be considered.

2.6.2.2. Chemical Considerations of the Phosphating Process

The phosphating process, in general, can be thought of as acid attack/dissolution with subsequent crystal growth of a precipitated salt on a metal surface. Orthophosphoric acid, \( \text{H}_3\text{PO}_4 \), is tribasic and so possesses three replaceable hydrogen atoms, allowing a series of salts shown below:

\[
\begin{align*}
\text{M}_2\text{HPO}_4 & \quad \text{M}_2\text{PO}_4 & \quad \text{MPO}_4 \\
\text{Primary} & \quad \text{Secondary} & \quad \text{Tertiary}
\end{align*}
\]

Where M is a univalent metal.

The formation of crystalline phosphate coatings on metal surfaces depends on the solubility characteristics of the phosphates. Whilst the mechanism involved in the formation of phosphate coatings is quite complex for most solutions it depends on the following equilibrium.

\[
\begin{align*}
\text{Primary phosphate} \quad & \Leftrightarrow \quad \text{Tertiary phosphate} \\
\text{Soluble} \quad & \Leftrightarrow \quad \text{insoluble}
\end{align*}
\]

Phosphating is performed with acid aqueous solutions, the coating formed is chemically bound to the surface and is known to act as a conversion coating. A variety of reactions may occur, however, the formation of the coating may be represented by the following equations:
Equation 2.19 describes the acid attack on the metal substrate while Equation 2.20 considers the formation of insoluble tertiary phosphates, which form the coating. So, an increase in pH at local cathodes, induced by anodic dissolution of the zinc will result in the equilibrium of Equation 2.20 shifting to the right leading to the precipitation of Zn$_3$(PO$_4$)$_2$ in the form of the tetrahydrate Zn$_3$(PO$_4$)$_2$.4H$_2$O, hopeite crystals.

Due to the consumption of phosphoric acid in Equation 2.20 there always needs to be a certain amount of free phosphoric acid present in the primary phosphate solution to repress hydrolysis and keep the bath stable. Too much free phosphoric acid, however, may lead to more substrate dissolution than is necessary.

The build up of "sludge" (insoluble waste products) is an inherent problem with the use of phosphating baths and is brought about as not all zinc can necessarily be incorporated into the coating. As a consequence sludge modifiers are often used to prevent the formation of scale on heat exchangers, tank walls and other surfaces inside the phosphating bath. The problem maybe amplified if cold rolled steel is the substrate, as additional sludge is generated when the excess Fe$^{2+}$ ions are removed from the phosphate solution by oxidising accelerators, which are discussed in the next section. In the presence of an iron substrate zinc iron phosphate, Zn$_2$Fe(PO$_4$)$_2$.4H$_2$O (phosphophyllite), may also contribute to the coating and Cheever has shown that the relative amounts and properties of hopeite and phosphophyllite are influenced by the degree of agitation of the bath [58].

2.6.2.3. Accelerators

Phosphating is essentially, an electrochemical phenomena in which dissolution of the metal occurs at the micro-anodes and evolution of hydrogen, followed by hydrolysis and precipitation of insoluble phosphates take place at micro-cathodes as shown in
Figure 2.13. As mentioned in section 2.6.2.1, in practice the phosphating reaction can be slow. Technology in the 1930's introduced accelerators allowing processing time to be reduced from hours to minutes and ultimately seconds. Accelerators increase the rate at which zinc phosphate coatings are formed and can be used in three ways.

1. The addition of soluble (less basic) metal salts
2. The addition of oxidising agents
3. Physical means

The formation of phosphate coatings occurs at the local cathodes on metallic surfaces while metal dissolves at the local anodes. The coating rate will depend on the ratio of the local anodes to cathodes, which in turn depend on a number of variables such as type of metal, grain boundaries, inclusions and machining of the metal. The addition of small amounts of soluble metal salts less basic than the metal being treated, such as copper, greatly increases the speed of the reaction. These accelerating metal salts plate out during the acid attack resulting in additional cathodic sites and allowing crystal growth to initiate. Care must be taken, however, not to use too much copper to avoid the deposition of a coat of metallic copper instead of the desired phosphate coating.

By far the most important class of accelerators are the oxidising agents which includes nitrates, nitrites, chlorates, peroxides or organonitrites. They react with...
hydrogen formed at the surface of the substrate and prevent polarisation of the metal surface by the accumulation of hydrogen gas at the solution/metal interface. Furthermore, in the case of an iron substrate, these accelerators can also keep the solution iron free by oxidising the iron, thus preventing the build up of Fe$^{2+}$ ions and the deposition of an iron phosphate coating at the expense of the desired zinc phosphate coating. By reacting with hydrogen, oxidising agents can also minimise hydrogen embrittlement of an iron substrate.

The rate at which a phosphate coating is deposited can also be affected by physical means, that is to say by the actual method of application. Phosphate coatings can be applied using spray or immersion techniques. The relevant method of application is naturally driven by the requirements of a particular industry with each method having its individual advantages relating to capital, investment, energy consumption, maintenance and system performance. Spray phosphating onto a metal surface results in shorter coating times or a lower application temperature to be used for a given application time, requires less floor space and typically costs less than immersion equipment. Spraying has the advantage that fresh solution is always presented to the metal surface, the solution adjacent to the metal surface never becomes depleted in coat forming ions, which can occur in an immersion system. Spray coating appears to be well suited to mass production, however, high energy and maintenance costs as well as coating imperfections, due to drips and misaligned nozzles are some of the disadvantages of choosing a spraying technique over an immersion bath. Another disadvantage of the spay coating system is that, whilst ideal for strip products, not all areas of an object can necessarily be covered, for example with car body in white areas between inner and outer doors that are shielded from the spray. In these cases immersion systems should be employed, the inaccessible areas are reached as the entire body is submerged. Most immersion systems will contain some sort of agitation system this allows fresh solution to be supplied to the metal surface and also helps to avoid uneven step marks caused by uneven motion of the conveyor as the object enters the phosphating solution. Air pockets can occasionally develop around sections of an immersed body, which can impede the flow of solution and limit the formation of a coating. The problem of air pockets can generally be overcome by adequate entry and exit angles and also gentle oscillation of the object. During the immersion of cold rolled steel there can sometimes be a problem with ferrous ions
produced on acid treatment and present in solution, becoming incorporated into the phosphate crystals. This is not a problem with spray coating as fresh solution is always supplied to the substrate surface. This difference in composition is reflected in the morphology of the crystals. The morphology of some coatings formed by immersion is nodular and contains a relatively high percentage of phosphophyllite (Zn$_2$Fe(PO$_4$)$_2$.4H$_2$O) [59]. Spray coatings, in contrast, are typically platelets and needle like in appearance and composed primarily of hopeite Zn$_3$(PO$_4$)$_2$.4H$_2$O. The advantage of the phosphophyllite (incorporation of iron into the crystal structure) over the hopeite crystal is its greater stability under alkaline conditions. This could indicate a greater resistance to cathodic attack of an adhesive bond. The phosphating system used in this study was applied by spaying, however, whilst an immersed coating was not investigated it is unlikely that the morphology of the two systems would differ greatly, as zinc phosphate on a zinc substrate will yield almost 100% hopeite regardless of the application technique.

2.6.2.4. Phosphating of HDGS for Adhesive Bonding

Phosphating has traditionally been used in the metal treatment industry for consumer goods and automotive application to provide improved corrosion resistance and a larger interfacial area for bonding, it can also be used as an effective pretreatment for the adhesive coating of HDGS [60]. This is surprising; zinc phosphate pretreatments consist of acicular crystals that grow from the basal plane of a substrate and are thought to be mechanically weak, Figure 2.14. Paint coatings are never subjected to any structural load and so the integral strength of the crystals at the basal plane is never tested; it is their corrosion resistance that is important. In adhesive bonding, however, mechanical loading is ever present and indeed in dry joints failure often occurs at the substrate basal plane with the phosphate crystals acting as a WBL. Despite this inherent problem, on ageing under hostile conditions, the corrosion inhibiting nature of phosphating yields much improved results over unpretreated HDGS, which exhibits very poor performance [60, 61, 62].
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Figure 2.14. (a) Schematic of a side view of acicular phosphate crystals, (b) micrograph of zinc phosphate crystals

It is well known that phosphating is seriously affected by surface carbon contamination, surface dissolution of the metal is inhibited resulting in poor adhesion performance [63]. The condition of the substrate prior to phosphating is vital and with HDGS substrates this can depend on the condition of the galvanising bath as well as the amount of carbon contamination present. The response of zinc alloy coated steels to phosphating can vary depending on the manufacturing method used. Electrogalvanised steel, for example, is formed by electrolytically depositing zinc from acidic electrolytes. This gives a very pure zinc surface, which reacts readily with phosphating chemicals. HDGS in contrast is manufactured using a molten bath with various additives to improve the quality of the zinc layer. In order to understand the phosphatability of HDGS it is useful to touch upon and appreciate some of the variables that exist in the galvanising process that in turn play a role in the surface chemistry of HDGS.

Hot dipped substrates are reported to be chemically heterogeneous with segregation of elements such as Al, Pb, Si, and Cd to the surface of the zinc deposit. The surface enrichment of these elements results from their extremely low solid solubility in the zinc matrix. As the solidification front moves from the steel/zinc interface to the surface, the modifying elements become concentrated and finally aggregate in the zinc surface layer. The galvanised steel system studied in this project only seems to include aluminium as an additive. Aluminium is an essential element in the galvanising process as it prevents the growth of a brittle zinc/iron intermetallic compound at the steel/coating interface, which can, naturally lead to poor adhesive bond performance. Aluminium generally segregates to the surface at grain boundaries.
(Figure 2.15) and the surface characterisation of hot dipped galvanised steel is discussed in more detail in Chapter 4.

Figure 2.15. Auger map illustrating the spatial distribution of Al-O at the zinc (red) grain boundaries [64]

As well as carbon, it has been reported that surface aluminium can also reduce phosphatability of HDGS, as a result of the fact that both these elements inhibit the dissolution of zinc. The build up of aluminium ions poison the phosphating bath and inhibit the formation of a phosphate coating. One way to combat this problem is to add a fluoride modifier, which will complex with the aluminium thus removing aluminium from the bath in its free state, Equation 2.21.

\[ \text{Al}^{3+} + 6\text{F}^- \Rightarrow (\text{AlF}_6)^{3-} \quad 2.21 \]

An alternative method of eliminating the deleterious effects of aluminium from the surface is to employ an aggressive alkaline cleaning procedure (pH > 12), this step, in general, is primarily used as degreasing stage and so also removes carbon contamination. The effect of alkali cleaning on the removal of aluminium has been investigated in this project and is discussed in more detail in Chapter 4 along with the effect of aluminium on the acid base properties and phosphatability of HDGS.

One potential problem that can occur with a defect in a paint film or at the edge of an adhesive joint overlap is associated with alkaline build up from the cathodic half
reaction to produce aggressive hydroxyl ions and in turn lead to disbonding or delamination. When paint systems are applied over phosphate conversion coatings disbonding has been attributed to the degradation of the phosphate crystals where the hydroxide, produced via the cathodic reaction, chemically dissolves the zinc phosphate [52, 63, 65]. Wiggle studied the electrochemical reactions involved in the corrosion process and investigated their individual and combined effects on the adhesion failure at a scribe line of phosphated panels in order to determine which reactions and mechanisms were most important [52]. An external potential was applied to achieve the desired conditions. As expected the zinc phosphate conversion coating retarded the lateral undercutting of the paint coating, due to the anodic dissolution reaction. With the cathodically polarised samples failure occurred at the metal/paint interface, no visible corrosion or anodic etching had occurred and pH sensitive paper revealed a highly alkaline condition. Wiggle concluded that the hydroxide ion played a predominant role with a phosphated substrate system and that both corrosion reactions had to be considered when designing for corrosion protection and prevention.

Roberts studied alkaline dissolution of phosphate coating on steel by immersion testing in NaOH solutions. Alkali attack of the phosphate pretreatment was measured using EDX and quantitative chemical analysis to examine the residue remaining on the panels, Figure 2.16. Both techniques show that phosphorous is removed more rapidly from the coating than zinc, indeed in the case of EDX it was clear that even once all the phosphorous has been removed zinc still remains on the substrate. Roberts indicated that phosphate degradation involved selective removal of the phosphate tetrahedral complexes within the crystals and that the structure becomes rich in zinc or hydrated zinc oxide. A very strong dependence on the rate of removal of the phosphate coating upon pH was shown to exist, Figure 2.17. On looking at the morphology of phosphate coatings Roberts observed fine cracks in the original crystals. Their origin is unclear but may be a result of internal growth stresses, due to impingement of growing crystal or even mechanical damage incurred during processing, for example on rolling. Cheever and Wojtkowiak describe these features as "slit-like capillaries" and suggest that these capillary features provide excellent wetting properties allowing a polymer or primer to flow over a larger surface area and penetrate into the crystals [66]. Whilst Cheever suggested cracks in the crystals aid
adhesion Roberts infers that these cracks may act as key sights for alkali attack to initiate as edges are more susceptible to attack than planar surfaces.

Figure 2.16. EDX and Chemical analysis of % Zn and % P remaining in phosphate coating after exposure to pH 12.5 NaOH [65].

Figure 2.17. Rate of phosphate degradation as a function of pH [65].

In order to reduce the effect of alkali degradation of phosphate coatings acid solutions of hexavalent chromium compounds are often used as a post treatment rinse. One of the reasons for improvement in corrosion resistance is that it is able to neutralise areas of high alkalinity. Whilst coverage of phosphate crystals often appears to be uniform, fissures may actually exist between crystals (porosity has not been discussed in detail
but will be briefly mentioned in the next section) and a chrome rinse is able to fill and passivate these pores.

2.6.2.5. Quality Control

Over the past one hundred years the phosphating processes has been developed to the stage that it is now used in large-scale production within industry. There are many chemical factors that influence the phosphating process and the resultant coatings. Coating modifiers, accelerators, sludge modifiers, application techniques and post treatments all play a role in the coatings performance. Porosity, which has not been discussed, always exists to some extent, even in a coating regarded as complete. Many authors have tried to develop tests for porosity, Zurilla and Hospadaruk developed an electrochemical polarisation test to measure relative porosity values rapidly and directly on zinc phosphated steel [63]. They based their measurements on the principle that for a porous phosphate coating, oxygen would be reduced on cathodically active surfaces (uncoated steel) but not on inactive surfaces (phosphated areas) and that the magnitude of the current would be a relative measure of coating porosity. Coating thickness or weight, as it is usually referred to as, is another variable that can effect the performance of adhesive bonds. Coating weight can be determined using specular reflectance infrared absorbance (SRIRA), which is a non-destructive technique first reported by Cheever in 1978 [67]. Before this the determination of coating weight was carried out using destructive tests involving weighing a standard test panel before and after stripping in an aggressive solution which attacks the phosphate coating but not the substrate. Coating weight control is a factor that requires constant care and is dependent on three variables, time, temperature and concentration. Of these, concentration is preferred as it can be controlled with relative ease by the addition of modifiers and accelerators. Temperature due to energy consumption should always be kept as low as possible and coating weight control by changing the process time can sometimes lead to incomplete coverage. Another factor that may effect the performance of phosphate coatings is their thermal stability. Phosphate coatings formed in aqueous solutions are normally hydrated, for example hopeite ($\text{Zn}_3(\text{PO}_4)_2\cdot4\text{H}_2\text{O}$). Pure hopeite losses two molecules of water of
crystallisation between 70-140°C and can undergo considerable weight loss and change in appearance (from grey to brown) as temperature increases.

Current zinc phosphating technology is automated, minimising both process and quality variations whilst producing phosphate crystals with improved performance. Phosphating is now a well established pretreatment for the coating industry offering a large rough area for adhesion as well improved corrosion performance. The pretreatment also seems to give encouraging durability results for adhesive bonds suggesting that its corrosion resistance more than compensates for any mechanical weakness at the basal plane due to its deposition characteristics.

2.7. Concluding Remarks

One of the most important requirements of an adhesive joint is the retention of strength during its service life. Durability is a key issue in the widening use of adhesive bonding technology and is problem that has been reported at length in the literature [32, 44, 45, 49]. The primary objective of this study is to determine the failure mechanisms responsible for the poor durability performance of adhesively bonded HDGS. It is hoped that this review has introduced some of the topics and subject areas that are relevant to the findings reported in this thesis. This chapter has considered some of the more fundamental aspects of adhesion, highlighting and stressing the importance the need for clean interfaces prior to adhesion and intimate contact. Some of the key factors that may effect the durability performance of an adhesive bond have been discussed with particular attention paid to cathodic delamination, in which the production of aggressive hydroxyl ions have deleterious effects on the adhesive/substrate interface. Previous studies of the adhesive bonding of galvanised steel have been reviewed, which has been invaluable to this study and applied to the findings of this project.

One of the common themes to the review of the failure mechanisms and durability studies was the use of surface analysis to determine surface chemistry. Adhesion is primarily concerned with bringing surfaces in contact and durability studies with analysis of failed interfaces. Surface analysis techniques, such as XPS and SIMS,
have the potential to play a major role in this project and it is hoped in Chapter 3 their aptitude and relevance to this project will be demonstrated. Surface analysis is a powerful tool to the adhesion scientist, capable of analysing the outermost atomic layers of a surface and so, in the case of adhesion, study failure surfaces with a view to determining loci and mechanisms of failure.
3.1. Introduction

The definition of the exact locus of failure and subsequent understanding of failure mechanisms is important when considering bond failure. It is the chemistry at the interface that determines the adhesion of the system, which in turn has an effect on the performance of the system in an aggressive environment. The term adhesion is used to describe the attraction between two surfaces and it is generally accepted that interaction occurs between the outermost layers of the respective substrates. Modern surface analysis techniques, capable of a depth resolution of 1 – 5 nm, therefore, are powerful tools for the adhesion scientist. Surface analysis provides a major contribution to adhesion science; characterising substrates prior to joint fabrication, investigation of the substrate to polymer bond and determination of the locus of failure.

There are many techniques available to the adhesion scientist, however, the most widely employed techniques in the adhesion community are x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). These two techniques complement each other, with both offering surface specific analytical information. XPS offers quantitative, elemental and chemical state information ideal for the study of inorganics, however, despite being employed successfully in a number of adhesion studies [40, 41, 42] it inherently lacks the specificity to provide
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the molecular information that is essential for the full understanding of the adhesive and interfacial chemistry. In contrast ToF-SIMS demonstrates the potential to fulfil this requirement with high spatial resolution by the use of a focused ion beam and a high degree of molecular sensitivity. The technique is eminently suited to study such effects as segregation of low molecular weight components to the surface and the orientation of polymer molecules against the substrate [68].

Whilst experimental work has been carried out in other areas, with SEM and mechanical testing being two examples, it is XPS and ToF-SIMS surface analysis techniques that will be used extensively throughout this study. In this chapter, therefore, XPS and ToF-SIMS are reviewed in some detail. Particular attention has been given to the study of polymers by ToF-SIMS and with the advent of the launch of a new small area XPS instrument, the VG Scientific Sigma Probe, installed at the University of Surrey towards the end of the project, time is spent discussing how small area XPS can be beneficial in diagnosing the loci and mechanisms of failure.

3.2. X-ray Photoelectron Spectroscopy

3.2.1. Introduction

The surface sensitivity and quantitative chemical analysis capabilities of XPS have made it one of today’s most widely used surface analysis techniques. XPS is now well established for its qualitative and quantitative surface chemical information derived from core level spectra, with the ability to detect, non-destructively, all elements, except hydrogen and helium. In addition molecular orbital information is attainable from high resolution studies of the valance band (0-30 eV binding energy). XPS utilises the photoelectric effect, which was originally observed by Hertz in 1887, explained by Einstein at the turn of the twentieth century and exploited for surface analysis by Seigbahn in the 1950’s.

In this section consideration is given to the basic principles of X-ray induced photoemission, the various levels of information that may be extracted from an XPS spectrum and the manner in which such data should be interpreted. For a more
detailed discussion of the process and technique there are a number advanced texts available in the literature [69, 70, 71].

3.2.2. Basic Principle of XPS

XPS involves the irradiation of a sample with low energy X-ray photons, normally AlKα or MgKα in an ultra high vacuum (UHV) system. The photons, which have fixed energy, hv, interact with the outermost layers of the specimen resulting in excitation and ejection of core electrons, Figure 3.1. The kinetic energy (Ek) of the photo-emitted electrons are measured experimentally by the spectrometer, however, the detected photoelectrons are generally expressed in terms of characteristic binding energy (Eb), which is a function of the energy level and chemical state of the parent element. The binding energy is related to the kinetic energy by the following equation:

\[ E_B = h\nu - E_k - W \]  

Where W = is the work function of the spectrometer.

- \( h \) = Planck’s constant
- \( \nu \) = frequency of light

![Figure 3.1. Schematic of the XPS process.](image)
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The term $E_b$ may be defined as the energy required to remove an electron to infinity with zero kinetic energy. This definition makes it clear that only electrons bound with less energy than the source may be ejected. Consider the survey spectrum of a clean gold surface in Figure 3.2, the photo electron spectrum demonstrates the electronic structure as all electrons with a binding energy less than 1253 eV (the excitation energy of Mg Kα radiation) are emitted, Au 3d$^{5/2}$ electrons, for example, have a binding energy of 2206 eV.

![Figure 3.2. Survey spectrum of gold using Mg Kα radiation [72].](image)

The photoelectron spectrum is in reality a montage of four distinct parts, the photoelectron peaks created by direct excitation of electrons from core orbitals, already discussed, but also an energy loss background structure associated with each of these peaks, valence band structure and Auger electron peaks.

In Auger electron spectroscopy (AES) specimens are irradiated with electrons and core electrons are ejected similar to XPS. Once an atom is ionised it must return to its ground state, following the creation of a hole in the core level the atom relaxes by filling the hole with an electron from an outer level. The energy difference of these two levels ($E_K - E_L$) becomes available as excess kinetic energy and in order to conform with the principle of the conservation of energy, this excess energy is used to either emit a X-ray photon, known as X-ray Fluorescence, or ejection of another electron from an outer level, this is known as an Auger electron, Figure 3.3. The only requirement for the ejection of an electron is the formation of a core level hole and...
whilst in AES, this is usually achieved with an electron beam any primary incident beam capable of core level ionisation can give rise to Auger transitions, hence Auger peaks are observed in XPS spectra. Unlike XPS, however, emitted Auger electrons do not necessarily have a well defined binding energy and chemical state information may only be achieved where all electrons involved in excitation are emitted from core level orbitals.

Figure 3.3. Schematic diagram of the process of Auger emission in a solid.

X-rays can readily travel through solids electrons, however, exhibit significantly less ability to do so and so only tend to escape from approximately the outer 10 nm of a surface. Some of these electrons escape with no energy loss (elastically scattered) and are responsible for the characteristic peaks in the spectrum. Those electrons that escape from a surface and have undergone inelastic scattering (i.e. suffer loss of energy) make up the background, particularly at the high binding energy (i.e. low kinetic) end of the spectrum.

All three distinct components of a photoelectron spectrum can be used on their own or in combination to give a variety of information about a sample. The photoelectron peaks usually display smaller widths than the Auger peaks and are considered to be of much more value in the identification of chemical state. Photoelectron peaks can be used, analytically in conjunction with Auger peaks in order to distinguish between different chemical species and states using the Auger parameter ($\alpha$). In order to provide any useful analytical information the accurate definition of peak position is important, sometimes however, this may not be completely accurate for reasons such
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as spectrometer calibration or sample charging (which will be discussed later). The
use of the Auger parameter is an elegant way of overcoming such effects, it takes into
account the chemical shift on both the Auger and photoelectron lines as it is
dependent on the separation of the two lines and can be expressed as follows:

\[ \alpha = E_B + E_K - \hbar \nu \] 3.2

The background shape of a photoelectron spectrum can also yield important
information concerning the state of the sample surface. With “clean” samples the
background after a peak will be horizontal or even have a slightly negative slope. In
case of a thin overlayer, however, electrons leaving the buried phase will suffer a
slight reduction in their kinetic energy thus contributing to the background on the high
binding energy side of a peak. This causes the slope of the background to become
positive and is known as a positive post peak slope. Castle et al have devised a kappa
(\( \kappa \)) function in which the background is used to describe chemical state and is shown
to be particularly useful for the transition elements [73].

3.2.3. Depth of Analysis and Related Phenomena

It has already been mentioned that the X-rays used as an excitation source in XPS are
capable of penetrating deep into a sample. The depth of analysis of the characteristic
photoelectrons, however is governed by the escape depth, which is proportional to,
amongst other parameters, their kinetic energy. If the depth of analysis varies with
the kinetic energy of the electrons under consideration it will also vary with energy of
the incident beam, therefore, Al K\( \alpha \) radiation (1486 eV) is less surface specific than
Mg K\( \alpha \) radiation (1253 eV) as the kinetic energy of the escaping electrons will be
greater. The depth of analysis can be directly derived from the inelastic mean free
path (\( \lambda \)) of the electron and varies as a function of \( E_K^{0.5} \) [71]. \( \lambda \) may be defined as the
average distance (in nm) that an electron with a given energy travels between
successive inelastic collisions. The intensity of electrons (I) emitted from a depth (d)
is given by the Beer-Lambert relationship:

\[ I = I_0 \exp (-d/\lambda \sin \theta) \] 3.3

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Where $I_0 =$ The intensity from an infinitely thick clean substrate

$\theta =$ The electron take off angle relative to the sample surface.

If we consider the Beer Lambert relation it is clear that the variation of electron intensity increases exponentially with depth into the surface as shown in Figure 3.4.

Figure 3.4. Electron emission as a function of depth, the horizontal dashed line indicates a distance from the surface of the inelastic mean free path ($\lambda$). [70]

The XPS analysis depth is generally taken as $3\lambda$, however, analysis is heavily biased towards the surface layers with an analysis probability volume which is analogous to an exponential decay cone. Indeed if a 90° take off angle is considered, 65 % of the total signal originates from the outer $1\lambda$ of the specimen, 85% from $2\lambda$ and 95 % from $3\lambda$. So for normal emission virtually all signal is from a depth of $3\lambda$ and with $\lambda$ being in the range of 1.5 - 3 nm the surface sensitivity of XPS can be estimated.

The vertical depth of analysis for XPS has been estimated at $3\lambda \sin \theta$, i.e. the depth of analysis is dependent on the take off angle. By changing the take off angle the analysis depth must also change. If the sample is tilted so that the take off angle is 15° then instead of most of the signal coming from a depth of $3\lambda$, as it had for normal emission, it now comes from a depth of $3\lambda \sin 15$ or $0.8\lambda$, Figure 3.5. This is known as
angle resolved XPS and by quantifying spectra acquired from a range of different take off angles and modelling results using a forward transform process it is possible to postulate a non-destructive compositional depth profile. It is possible to estimate overlayer thickness using the Beer Lambert equation with two take off angles thus creating a set of simultaneous equations.

\[ \begin{align*}
\theta = 15^\circ & \quad d = 0.8 \lambda \\
\theta = 35^\circ & \quad d = 1.7 \lambda \\
\theta = 90^\circ & \quad d = 3 \lambda
\end{align*} \]

where \( \lambda \) is the electron inelastic mean free path

Figure 3.5. Angular resolved XPS: the variation of analysis depth with take off angle. [70]

The use of angular resolved XPS can also characterise the nature of an overlayer by differentiating between an island like and homogeneous overlayer. The Beer Lambert equation may be rewritten to consider the intensity of electrons emitted from an overlayer, for example an oxide, to give:

\[ I = I_o[1 - \exp(-d/\lambda \sin \theta)] \]

For a uniform surface a plot of overlayer intensity divided by substrate intensity (\( I_A/I_B \)) against take off angle (\( \theta \)) will result in an exponential decrease of intensity ratios with take off angle. For an island distribution however, the quantity \( I_A/I_B \) would show no angular dependence, Figure 3.6.
So far the idea of depth profiling has been discussed in terms of a non-destructive technique, a methodology created by manipulating the Beer Lambert equation, thus restricting the depth of analysis to $3\lambda$ and essentially still analysing the outermost layer of an as received sample. Alternatively, depth profiling may be carried out by removal of material from the sample surface, in situ, by erosion with inert gas ions. The use of non-destructive angular dependent methods becomes increasingly uncertain as a function of depth and removal of material by ion bombardment allows compositional changes to be monitored more deeply into a sample, approximately 1 \( \mu \)m. Ion bombardment is usually carried out sequentially, with an analysis carried out between each etch step allowing an elemental profile verses time to be built up. It is not always easy to relate time to depth and so generally sputter rate is related to an international standard (Ta$_2$O$_5$/Ta). Great care should be taken when ion etching to ensure that any ion induced chemical reactions that occur during depth profiling are not identified and attributed to pre-existent chemistry of the specimen. Primary ions may become implanted into a sample and appear in subsequent spectra. When looking at chemically heterogeneous surfaces preferential sputtering of an element
may become a problem effectively reducing the concentration of that element at the surface and effecting quantification results. These problems can be overcome by careful laboratory procedure and sputter depth profiling is the most common method used to give compositional depth profiles. Generally up to 1 µm is removed, after which ex-situ methods may be used, such as polishing and taper sectioning. Ion guns are also often used as an insitu cleaning step or even as primary ion beams for analysis, for example in SIMS.

3.2.4. Quantitative Analysis

The previous sections has, in part, dealt with qualitative analysis considering simple characteristics such as identification of elements present and features like background and chemical state information. In the introduction, however, it was stated that one of the strengths of XPS is its ability to provide quantitative information. Quantitative analysis of a surface composition by XPS may be based on first principles or an empirical relationship together with published, or in house, sensitivity factors.

Quantification of peak intensities is usually performed using integrated peak areas. Consequently, there is often the need for background subtraction and this can be done in a variety of ways. For example, the subtraction of a linear background, which is subjective and dependent on the operator choosing consistent energy windows or the more popular Shirley S-shaped background where the background intensity increases in proportion to the integral of the peak lying above it, making it less susceptible to inconsistencies by the operator. Tougaard has recently developed another background that operates over a narrow energy window and reveals a large fraction of the “real” peak area usually ignored by other methods [74].

As mentioned above the quantification of peak intensities can be carried out by calculating integrated peaks areas. From first principles the intensity of a photoelectron peaks is a complex function and has been reviewed in detail by Seah [69]. A simplified integral is given in Equation 3.5 although the complex nature of the calculation is still evident. If an incident X-ray photon of energy hv ionises core
level X of element A in a solid, the photoelectron intensity detected by the spectrometer is:

\[
I_A = I_0 p \sigma(h\nu,E_X) G(E_X) D(E_X) \int_0^\infty N_A(z) \exp\{-z/\lambda_m(E_X) \cos \alpha\} dz
\]

3.5

Where: \(I_0\) is the X-ray flux illuminating the sample, \(p\) is a roughness factor (which affects X-ray illumination and photoelectron ejection through shadowing effects), \(\sigma(h\nu,E_X)\) is the photoionisation cross-section for ionisation of X by photon \(h\nu\), \(G(E_X)\) is the spectrometer étendue (the product of the transmission efficiency and the area from which the electron are emitted) at kinetic energy \(E_X\), \(D(E_X)\) is the detector efficiency at energy \(E_X\), \(N_A(z)\) is the distribution of atoms A with depth \(z\), \(\lambda_m(E_X)\) is the inelastic mean free path of electrons \(E_X\) in matrix M (containing atoms A) and \(\alpha\) is the angle of emission to the surface normal.

Equation 3.5 may be simplified further if it is assumed that the composition of the analysed volume is homogeneous:

\[
I_A(X) = I_0 \sigma N_A \lambda_m K
\]

3.6

Where \(K\) is a term that covers instrumental factors such as the analyser transmission function and detector efficiency.

The simplified equation highlights the factors that affect the measured peak intensity. The photoionisation cross-section, \(\sigma\), is the transition probability per unit time for excitation of a single photoelectron and depends on the photon energy, \(h\nu\), atomic number and core level.

The above equations may be used for quantification from first principles but more usually experimentally determined sensitivity factors \((F)\) will be employed. Wagner has provided one of the most widely used tables of sensitivity factors in which all intensities are considered relative to fluorine \((F_F = 1.0)\). Wagner's data was obtained
from freshly powdered stoichiometric compounds, of which the majority contained fluorine allowing direct reference to $I_F$. Wagner's sensitivity factors have been used throughout this study for quantification.

Sensitivity factors include the terms $\sigma$, $\lambda$, and $K$ and also assumes that the X-ray flux is constant. Atomic percent of the area is determined by dividing the peak area by the sensitivity factor and then dividing by a sum of all normalised intensities:

$$[A] \text{ atomic } \% = \left\{ \frac{(I_A/F_A)}{(\Sigma I/F)} \right\} \times 100 \quad 3.7$$

Sensitivity factors are applicable only to a given instrument type and excitation source, although more often than not a complete set are found within the manufacturers data system. Once again, surface composition is assumed to be uniform, this is rarely the case and so in segregation or monolayer studies it would be advisable to acquire spectra from different take off angles, in general however, the use of sensitivity factors has been found to be reliable.

3.2.5. Instrumentation

3.2.5.1. Introduction

The design and construction of an electron spectrometer is very complex and consists of many components, all of which are essential for the acquisition of acceptable and reliable spectra. Firstly the sample to be analysed must be inserted into the analysis chamber and placed in the optimum analysis position by the use of a suitable sample manipulation mechanism. An X-ray source is required for the excitation of photoelectrons with an electron energy analyser and detector subsequently necessary. The whole XPS process is carried out within a vacuum chamber, which must be maintained under ultra high vacuum conditions. Combined, all of these components make up the spectrometer or surface analysis instrument. These days a data system is considered an integral part of the system and may be used to manipulate acquired data in many different ways.
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3.2.5.2. Ultra High Vacuum Requirements

The principal analytical techniques used in this study, namely XPS and SIMS, must be operated under UHV conditions (between $10^{-8}$ and $10^{-10}$ mbar, the reasons and conditions for this will be briefly discussed, although for an in depth discussion on the attainment of UHV the reader is referred to Chambres’ review of “Basic Vacuum Technology” [75].

The primary reason for analysis to be carried out under UHV conditions is inherently linked to the surface sensitivity of the techniques and the natural drive for reduction in surface free energy. As mentioned in Chapter 2 a surface will always try to reduce its surface free energy, often by building up a hierarchy of contamination layers. Even at $10^{-6}$ mbar a monolayer of gas may be absorbed after 1 s. Considering the fact that a detection limit of XPS is approximately 1% monolayer after a typical acquisition time of around 900 s [76] it is clear that UHV is needed to obtain a spectrum of an unmodified surface. A second reason for analysis to be carried out under UHV conditions is that low energy electrons are easily scattered by contamination molecules within the chamber. In order to maintain a satisfactory signal to noise ratio the level of residual gasses must be kept to a minimum.

Attainment of UHV is not just a matter of using the correct combination of pumps, of which there are many, but also careful consideration material selection, assembly and maintenance. There are two key requirements for the fabrication of UHV vessel (a) it must be constructed from materials that do not out-gas significantly and (b) it does not permit gas to enter from the outside due to diffusion or inappropriate seals. Other materials requirements include availability, machineability and resistance to elevated temperatures.

Austenitic stainless steel is often the material of choice, it has a low vapour pressure from ambient temperature up to 600 K and is non magnetic so able to screen electrons from any possible magnetic field effects. Out gassing effects may be reduced further by giving the surface a fine polish, reducing surface area and allowing a thin tenacious chrome rich oxide to build up. Baking the entire vacuum system (400 – 600
K) will remove adsorbed gasses from the chamber walls and so reduce the amount of outgassing when run at room temperature. Choice of material for other sections of the chamber must also be made carefully for example ductile copper gaskets are used to fit flanges together. Each of the flanges has a circular knife-edge, tapered towards the external diameter, machined within a recess that bites into the copper gasket.

In order to reduce the number density of gas particles, and therefore the pressure, in a vessel, gas particles must be removed. This in essence is the purpose of the vacuum pump. Fundamentally they can be put into two categories:

Transfer or compression pumps –which removes gas particle from the system and transfers them to the outside.

Entrapment pumps – which trap molecules in various ways such as condensation or chemically binding the species being pumped to a chamber wall.

Four pumps have been used to attain UHV on surface analysis systems, sputter ion and sublimation pumps are both examples of entrapment pumps which are employed on the ToF-SIMS and the ESCALAB MK II systems and are generally used as ancillary pumps with the diffusion pumps, which are the work horses of the system pumping large volumes of gasses at high speeds and area able to reduce vaccua from $10^{-2}$ to $10^{-10}$. A schematic of a diffusion pump is shown in Figure 3.7. Pump fluid, usually with a low vapour pressure oil such as a polyphenyl ether, is heated at the base of the pump. Vapour rises up the chimney and emerges at supersonic speeds; the high-speed jets give random incoming gas molecules momentum in the direction of the outlet, where they are removed by a mechanical pump (this is often a rotary pump which is also used to pump a fast entry lock chamber).

An obvious concern with the use of a diffusion pump is contamination of a chamber via backstreaming of oil. This over come by the use of a baffle arrangement using a liquid nitrogen cold trap, the cold trap also allows high speed pumping of water vapour. More recently turbo molecular pumps, once considered unreliable have become increasingly popular and this type is used to pump the entry lock on the VG
Scientific Sigma Probe used in this project. Turbo molecular pumps are also transfer pumps and work as result of gas particles receiving an impulse in the required direction of flow, through impact with the rapidly moving surfaces of a series of rotor blades constructed in the form of a turbine. The gas to be pumped arrives at the top of the pump where the blades are large and is transferred to the lower "compression stages" where the blades have a shorter radial spin, from here it is removed by a backing pump, usually a rotary pump.

Figure 3.7. Schematic diagram showing the mode of operation of a diffusion pump.
1 Heater, 2 Boiler, 3 Pumping body, 4 Cooling coil, 5. High vacuum flange connection, 6 Gas particles, 7 Vapour jet, 8 Backing vacuum connection port, A-D Nozzles [77].

3.2.5.3. X-ray Sources

There are two limiting factors that govern the anode material used as an XPS X-ray source. The natural line width should be less than or equal to 1.0 eV in order to provide an energy resolution of approximately 1.0 eV that is generally required by
XPS. The characteristic photon energy must also be high enough to excite photoelectrons with a useful cross-section over a sufficient energy range allowing all elements of the periodic table to be analysed, except hydrogen and helium.

Considering the first of these two points, Table 3.1 shows the possible materials that would give an acceptable amount of energy resolution, all other candidate materials have a unmonochromised X-ray line widths of greater than 1.0 eV. Taking into account the second limiting factor shortens this list yet further. The relationship governing the interaction of an X-ray photon with a core level was described in Equation 3.1, from this it is clear that both Y M\(_2\) and Zr M\(_2\) have line energies which are too low for analytical use, despite having line widths that meet the \(< 1.0\) eV criteria. Silicon, seemingly meeting all the requirements, is a semiconductor and so has poor heat conduction properties, it is also not easy to fabricate the anode from silicon. Thus universally anodes are made from magnesium and aluminium.

<table>
<thead>
<tr>
<th>Line</th>
<th>Energy, eV</th>
<th>Width, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y M(_2)</td>
<td>132.3</td>
<td>0.47</td>
</tr>
<tr>
<td>Zr M(_2)</td>
<td>151.4</td>
<td>0.77</td>
</tr>
<tr>
<td>Mg K(_\alpha)</td>
<td>1253.6</td>
<td>0.70</td>
</tr>
<tr>
<td>Al K(_\alpha)</td>
<td>1486.6</td>
<td>0.85</td>
</tr>
<tr>
<td>Si K(_\alpha)</td>
<td>1739.5</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3.1. Energies and widths of characteristic soft X-rays that could potentially fulfil the energy resolution required for XPS.

X-rays are generated in a material by bombardment with electrons of sufficient energy. X-ray photoemission starts at the ionisation threshold of the core level involved and increases significantly with increasing electron energy. In general the electron energy should be at least one order of magnitude greater than that of the threshold, indeed most electron spectrometers provide electron accelerating potentials up to 15 kV. Films of aluminium and magnesium may be deposited onto one copper anode with two angled faces, creating a twin anode as shown by the set up in Figure 3.8. Film thickness is about 10 \(\mu\)m and chosen so that Cu L\(_\alpha\) radiation is avoided.
with no significant penalty to heat transfer. Each anode has a filament with an accelerating potential of up to 15 kV applied to the anode. To ensure that electrons from a particular filament only hit its respective anode shields are placed accordingly, Figure 3.8. Finally on their way to the sample the soft X-rays generated pass through an aperture covered with a thin aluminium foil window, which is used to prevent contamination from the source and also electrons affecting the analysis.

![Diagram of a twin anode X-ray source](image-url)

Figure 3.8. Schematic diagram of a twin anode X-ray source [78].

A problem with twin anode unmonochromised sources is that soft X-ray emission does not consist of a single characteristic X-ray line. Most of the energy goes into the principal characteristic line, which for aluminium and magnesium is the Kα_{1,2} but other satellites exist, for example the Kα_{3,4} and the Kβ, which are capable of generating features in the photoelectron spectrum. Another feature is that these lines sit on a continuous background known as Bremsstrahlung radiation, which also contributes to background generated in the final spectrum. Alternatively the use of a monochromated source can be employed to generate spectra without satellite peaks and Bremsstrahlung radiation. Monochromators are also used as a means of focussing X-ray beams for small area analysis, which has played a crucial role in this study. Monochromated sources, therefore will be discussed in the small area XPS section, 3.2.6.
XPS spectra may be plotted as intensity verses kinetic energy and is achieved by the use of an electrostatic electron energy analyser, which measures the distribution of energy of the electrons, emitted from the sample in a serial manner. Over the years there have been various analysers tried but in general the concentric hemispherical analyser (CHA or HSA) is used in XPS. The other popular electron analyser in use today is cylindrical mirror analyser which is considered to offer a higher degree of sensitivity and so more suited for use in AES, where as the CHA offers the level of spectral resolution required for XPS. Spectral or energy resolution may be defined in two ways: absolute resolution, the full width at half-maximum (FWHM) $\Delta E$ or the base width $\Delta E_b$, where ideally $\Delta E_b = 2\Delta E$ or relative resolution (R), which depends on the kinetic energy ($E_0$) of the particular peak (i.e. peak position), and is defined as $R = \Delta E/E_0$.

XPS relies upon identification of features such as chemical state across a large energy range, it therefore requires, the same absolute resolution across the spectrum. This is difficult to achieve without making the analyser very large and so emitted photoelectrons are not analysed at their original energy but retarded before they enter the analyser. The CHA is combined with an electron pre-retardation stage and is generally run in the constant analyser energy (CAE) mode. Electrons are retarded without altering their absolute energy spread and with CAE mode electrons are retarded to the same energy. A constant voltage is applied across the hemispheres only allowing electrons of certain energy to pass into the analyser. The lower this constant voltage or pass energy the better the resolution and common values chosen are from 150 and 100 eV for survey spectra to 50, 20 or even 10 eV for high resolution spectra. Spectra are acquired by ramping the retarding field (pre-retardation) potential resulting in a different range of electron energies passing into the analyser for detection. A schematic of the CHA is shown in Figure 3.9, it is made up of two concentric hemispheres with radii $R_1$ and $R_2$ with a mean equipotential surface between the hemispheres of radius $R_o$. A potential difference is applied across the hemispheres such that the outer ($V_2$) is more negative than the inner ($V_1$).
Electrons emitted from the sample are focused to the entrance slit of the analyser via the use of a transfer lens assembly, the entrance and exit slits of the analyser are both centred on R₀.

Figure 3.9. Cross-sectional view of a hemispherical electron energy analyser [79].

The detector is placed at the exit slit (position F in Figure 3.9), the simplest system is a single channeltron, although three six or more tend to be used on modern instruments. A channeltron is a coiled tube of glass coated on the inside with tin oxide and when a potential of 3-4 kV is applied a single electron will produce a cascade effect which gives high electron gain prior to signal amplification.

3.2.6. Small Area XPS

3.2.6.1. Introduction

Historically XPS has been considered a large area technique with relatively poor spatial resolution compared to AES and SIMS. Essentially it is an area integrating form of analysis giving a representative analysis over areas from 10 – 100 mm². Over the past 15 years, however, there has been a move for XPS to offer a higher degree of spatial resolution. This could help the adhesion scientist a great deal in diagnosing failure mechanisms from specific areas of a fracture surface without interference from other areas of the failure. There is now a large range of methods available for
improving spatial resolution, from selected area analysis to imaging and all manufacturers offer some form of small area analysis in the range of 15 – 100 μm. The real issue is the sensitivity of XPS at these very small analysis sizes. Small Area XPS (SAXPS) may sub-divided into two categories the defined source system (DSS), where the area of illumination of the specimen is reduced and the defined collection system (DCS), involving the collection of electrons from a selected area defined by the electron optics of the analyser of the irradiated specimen in normal XPS. Various ways in which these systems are achieved will be discussed briefly with particular attention paid to the microfocusing monochromator employed by the Sigma Probe, more in depth discussions can be found in the literature [80, 81].

3.2.6.2. Defined Collection System

There are various methods of collecting from a selected analysis area, one such way of achieving this is via electron optical means. Collimation of the photoelectrons was carried out by Keast and Downing [82]. Here, the size of the X-ray beam is the same as for conventional XPS, however, an earthed tube is placed between the specimen and the source slit. This acts as a collimator, which together with a tilted electron shield restricts electrons entering the analyser to those originating from a selected area from the specimen. The spatial resolution attained is equal to the internal diameter of the collimator with 700μm a quoted value. In theory reducing the diameter of the tube could attain improved spatial resolution, however, much of the electron flux is lost as a result of scattering and absorption within the tube. Keast and Downing reported acceptable count rates although it should be noted that they were analysing gold which has photoelectron lines of a high cross section and a much lower sensitivity and could be expected from materials of a lower yield such as polymers.

The use of a high magnification lens preceding the analyser provides an alternative method of selecting an area by electron optical means. If a lens of relatively high magnification is placed in front of the analyser, maximising the number of photoelectrons detected from an irradiated spot, then the aperture to the analyser ratio will determine the size of the sample observed. The analysis area may be defined as the aperture area to lens magnification ratio, for example for aperture size d and lens
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magnification x6 a spot size of d/6 will be analysed from the sample. Using such lenses it is possible to obtain a spatial resolution of the order of 100 μm.

3.2.6.3. Defined Source System

As with DSS a range of techniques are available to produce a small area of X-ray illumination on a sample. Once again collimation, this time of the source, may be achieved by placing one or two apertures between the sample and source. Focussing of the X-ray source is possible by carefully designed zone plates that can act in a similar manner to a lens. These two methods, as with many proposed small area techniques however, suffer from poor efficiency seriously reducing the number of X-rays reaching the specimen and are therefore impractical with conventional sources.

One of the fundamental problems with attaining small area XPS is the inability to focus the excitation beam (X-rays) by the use of electrostatic or electromagnetic lenses unlike charged particle techniques such as SIMS and AES, which use primary ion and electron beams respectively. Various methods of selected area analysis methodologies have been discussed but unless they are capable of matching small area analysis with detection of a reasonable electron flux to give an efficient signal to noise ratio they are not suitable. The V.G. Scientific Sigma Probe launched in 1998, tackles these problems with use of a micro-focussing monochromator and a transfer lens with a wide acceptance angle, an approach first used by the SSI instruments of the 1980’s. Localisation of the X-ray beam by crystal optics (the use of a monochromator) has become very popular as a DSS and as will be seen in the next section offers improved spectral resolution.

3.2.6.4. Monochromated XPS

Conventional sources such as Al Kα and Mg Kα X-rays lines consist of unresolved doublets (Kα₁ and Kα₂) as well as satellites and the Bremsstrahlung continuum, this was discussed in section 3.2.5.2. The need for higher spectral resolution has led to the development of monochromated X-ray sources, which enable the characteristic line width to be significantly reduced (below 0.5 eV), usually from the Kα₁,₂ doublet.
This removes satellites and also the Bremsstrahlung radiation from the spectrum reducing background significantly. Monochromation depends upon the dispersion of X-ray energies by diffraction at a crystal according to the Bragg relation:

$$n\lambda = 2dsin\theta$$

Where $n = $ Order of diffraction  
$\lambda = $ X-ray wavelength  
$d = $ Crystal spacing  
$\theta = $ Bragg angle

The crystal material universally used in XPS, for monochromation, is quartz (orientation 1010) as it offers practical advantages being able to withstand bake out temperatures and relatively easy to manipulate as, if sufficiently thin, it can be bent elastically. A schematic of the monochromator set up is shown in Figure 3.10.

Figure 3.10. A schematic diagram showing the design requirements for an X-ray monochromator on a photoelectron spectrometer [78].
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The three key elements, the X-ray source, quartz crystal and sample are all placed in their respective positions on a Rowland sphere. X-rays emitted from the source are dispersed through the crystal by diffraction (satisfying the Bragg conditions) and refocused to a point on the sphere, which is coincident with the sample. It is this refocussing phenomenon that enables monochromation to provide small area XPS as spot size can now be reduced by using a finely focussed electron beam to excite the X-ray at the anode. Naturally by reducing the line width of the X-ray beam the photon flux available on the sample is greatly reduced compared to conventional XPS, this can result in longer acquisition times being required for spectra of acceptable quality to be achieved. Obviously this is undesirable, however, the X-ray flux can be increased either by increasing the incident electron beam current or by employing a more efficient collection system, i.e. using a wider acceptance angle.

3.2.7. The VG Scientific Sigma Probe XPS System

3.2.7.1. System Overview

The need for improved spatial resolution at high sensitivity has seen the development of the VG Scientific Sigma probe, launched in 1998, Figure 3.11. Using a microfocused monochromatic Al Kα X-ray source the spectrometer has an ultimate spatial resolution of better than 15 µm.

Figure 3.11. The VG Scientific Sigma Probe.
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Experimental Techniques

An optimisation of the of input and transfer lens, termed the *Radian lens*, captures the maximum possible number of photoelectrons from the sample and transfers them to the analyser with minimum loss. This is achieved by positioning the lens very close to the sample stage and also collecting electrons emitted from the surface over a cone of up to ±30°; the lens has a wide acceptance angle, Figure 3.12. When mounted horizontally the lens axis is at 37° to the sample and the optical conditions ensure that, despite the analysis of small area, sensitivity is improved and acquisition time reduced compared with other methods of small area XPS.

Figure 3.12. The sample stage of the VG Scientific Sigma Probe (a) showing wide angled lens close to the sample stage and (b) demonstrating the clipping procedure capable of mounting different types of samples.

The sample stage is 70 mm x 70 mm and capable of multi-sample or large sample handling, a complete 4 inch wafer can be introduced into the analysis chamber. The sample stage is motorised on all five axes and can be programmed, controlled by a VG Scientific Eclipse data system to allow unattended operation, the saving of analysis positions also comes in particularly usefully when wishing to return to areas for further analysis. Although the benefits of positioning the lens close to the sample appears obvious great care must be taken to avoid damage to the lens when focusing a sample, this could lead to misalignment of the analyser and poor counting statistics despite the analysis position being apparently setup correctly.

Another feature of the Radian Lens is that it may be operated in an angle sensitive mode. A small range of electron emergence angles can be selected either from near normal or from grazing emergence, in this way angle dependant information can be measured, a non-destructive form of depth profiling without tilting the sample.
Usually angle resolved XPS requires the sample to be tilted and thus alter the analysis position and shape slightly, which when dealing with small area analysis can have a major effect on the spectra acquired.

One of the novel features of the Sigma Probe is the use of a zoom microscope with a CCD TV camera which allows the sample to be viewed in detail in the analysis position. This can be of great significance to the adhesion scientist, identifying features on a failed interface that hitherto were unnoticed. For small area analysis to be effective knowledge of a precise analysis position is vital, this is achieved on the Sigma Probe by the use of the zoom microscope, a circular graticule, and probe light which illuminates the focal point of the monochromated source, Figure 3.13. The probe light follows the path of the X-ray beam on to the sample identifying the exact analysis position and so when used with the graticule position and size of analysis area is known.

Figure 3.13. Schematic diagram of the X-ray monochromator showing the electron beam (red) focused on the aluminium anode. The resulting X-rays (purple) are then focused by the quartz crystal onto the sample. A probe light (yellow) is reflected from the anode and the crystal, highlighting the analysed area.
3.2.7.2. Charge Compensation on the Sigma Probe

The control and understanding of surface potential is a crucial step in the successful analysis of any surface by XPS, particularly those surfaces of non-conductors. The ability to compensate the surface charging and accurately calibrate the binding energy scale, particularly with electrically inhomogeneous samples, has been a cause of continuous concern during the evolution of XPS. Metson has recently reviewed some of the issues concerning charge compensation in XPS analysis [83].

Throughout this project failed interfaces and components from adhesive systems have been analysed. This has invariably led to the analysis of insulating materials either in the form of bulk adhesive or a section of cohesive failure though polymer adhesive. The Sigma Probe offers many benefits to the operator and in general is a very user-friendly machine, however its charge compensating capability, employing an electron flood gun, is not always simple to use for a relative new comer to the machine. The flood gun is used to neutralise charge build up on the surface of insulating samples. When a sample is irradiated with X-rays, photoelectrons are emitted from the sample surface. In the case of conducting samples, these electrons are immediately replaced by electrons conducted through the bulk of the sample, such that there is a continuous flow of electrons conducted from the sample holder, through the sample and into the vacuum. If the sample is an insulator, electrons emitted from the surface cannot be replaced from the bulk and consequently a charge will build up on the sample surface. The surface charge will alter the energies of the emitted electrons such that they are no longer representative of the composition of the sample.

The Sigma Probe flood gun provides a diffuse beam of low energy electrons eliminating stray charges on any insulating surfaces outside the analysis area. In the case of small area analysis, however the process becomes slightly more complicated as ideally the X-ray beam should be positioned in the centre of the charge compensating electron beam. By shifting the electron compensating beam in the X and Y direction along with adjusting the focus the skilled operator is able to determine the best possible conditions for spectrum acquisition.
In a recent study a strong chemical interaction between toughening particles (PEEK) and an epoxy based matrix was found to exist on the fracture surface of carbon fibre/epoxy composite [84]. Interestingly in the high resolution C1s spectrum differential charging was observed with the non-conducting matrix material charging and the electrically-conducting graphite components not charging with a C1s line at approximately 285 eV, Figure 3.14. In this situation charge compensation is made more difficult as the charging matrix component not only has to compensated for but also matched with the conducting fibre component, Figure 3.15. By comparing Figures 3.14 and 3.15 it can be seen that correct charge compensation also leads to a reduced FWHM of the peak an a more intense signal, with approximately 7500 counts per second (cps) registered for the charged compensated spectra compared to a total intensity of approximately 5500 cps for the charging specimen.

![Figure 3.14. High resolution C 1s spectrum from CFRP, with no charge compensation, showing differential charging as a result of two phases at the surface (a) the insulating matrix (b) the conducting fibre.](image)
Figure 3.15. High resolution C 1s spectrum of charge compensated CFRP with differential charging effects removed.

3.2.8. Concluding Remarks

XPS has proven itself to be a reliable method for surface analysis over the past thirty years, and quantification routines are well established and usually available in data analysis software that accompanies the instrument hardware. The basic principles of XPS have been reviewed with particular methodologies of spectral acquisition and interpretation considered. The advantage of XPS lie within the techniques simplicity, flexibility and high information content and as such is the most popular surface analysis method at present. Other qualities of XPS that have been exploited through this project include the routine use of quantification, conventional XPS (large area analysis) and the use of a microfocusing monochromator to achieve the desired spectral resolution.

There are certain limitations to XPS, for example the lack of molecular sensitivity when analysing polymers, however when used in conjunction with other complimentary surface analysis techniques, SIMS in the context of this study, XPS is able play a pivotal role in expanding the understanding of the chemistry of surfaces.
3.3. Time of Flight Secondary Ion Mass Spectrometry

3.3.1. Introduction

The surface and interfacial chemistry of adhesives and organic coatings can have a major effect on the properties and performance of adhesive bonds. Interfacial stability in an aggressive environment is a major factor in determining the long-term durability of adhesive joints. No one technique provides the total information required about a surface and whilst XPS offers elemental and chemical state information and despite being employed successfully in many adhesion studies [32, 44, 49] it inherently lacks the specificity to provide the molecular information that is essential for the full understanding of the adhesive and interfacial chemistry. In contrast ToF-SIMS demonstrates the potential to fulfil this requirement with high spatial resolution through the use of a focused ion beam and a high degree of molecular sensitivity. The technique is eminently suited to study such effects as segregation of low molecular weight components to the surface and the orientation of polymer molecules against the substrate [68]. The secondary ion spectra may exhibit arrays of signals that are highly characteristic of the parent molecules and may be considered to be of possible value in studies of adhesives and interface chemistry.

It is apparent, therefore, that ToF-SIMS analysis is able to make an important contribution in determining joint durability, reasons for joint failure (e.g. explaining the formation of notch like initiation zones observed in this project), and role of joint components during the ageing process. The aim of the following review is to aid the reader in understanding the SIMS phenomena, care and caution linked with analysis of polymers (adhesives) and the role that ToF-SIMS can play in determining failure mechanisms in an adhesive joint.

3.3.2. The SIMS Phenomenon

The bombardment of a material surface with a beam of energetic ions and the subsequent mass analysis of the sputtered ions and ion clusters is the basic principle of SIMS. SIMS analysis has three modes of operation, the first being the dynamic mode,
in which a high flux of primary ions is directed at the material surface giving a very high yield of secondary ions. The beam sputters away the surface layers and the surface changes during the analysis. Clearly this is a destructive technique and whilst plotting intensity of mass fragments against a function of time allows depth profiles to be built up, the analysis is not representative of the surface and relies on particle removal or destruction of the surface. Static SIMS involves the bombardment of a sample with a low density flux of positive ions (or neutral atoms) and the mass analysis of the positive and negative secondary ions characterise an unmodified surface. SIMS may also be used in the imaging mode attaining a possible spatial resolution of < 1 μm.

There are two processes involved in the SIMS phenomenon: the emission of the particle, or sputtering and particle ionisation. Neither of these two processes are understood fully and there is a good deal of controversy as to whether they occur simultaneously or consecutively.

3.3.2.1. Sputtering

The process by which a high energy particle impacts on a solid surface giving rise to the emission of low energy secondary ions is known as sputtering [85]. The mechanisms are far from understood and either physical or chemical effects can dominate the interactions of the ion beam with the surface. With physical sputtering, the ion beam incident on the material sets up a collision cascade in the surface layers of the solid with energy transferred from the ions to the atoms of the target. If more energy is transferred on collision than the binding energy of the target atom a recoil may be observed, if a surface atom receives more energy from a collision than it's binding energy then sputtering of this surface atom will be observed. Collision cascades as a result of subsurface recoils may also reach surface atoms and, therefore, cause sputtering, Figure 3.16.
Three different situations may occur for physical sputtering;

(a) single knock on regime - a direct or almost direct impact process between incident particle and sputtered particle. Energy transfer is enough to generate primary recoils but no more. If these primary recoils are able to give enough energy to the sample surface atoms then sputtering will occur.

(b) linear cascade regime - knock on collisions are started between atoms in the near surface region. Recoils from ion/target collisions have sufficient energy to generate further recoils which may lead to sputtering. Some energy will be dissipated into the bulk by displacement cascades.

(c) spike regime - these seem to occur at higher primary beam densities and result in a high density of recoils and therefore number of moving particles within a certain volume of the target material.

![Schematic of sputtering by elastic collisions](image)

Figure 3.16. Schematic of sputtering by elastic collisions: (a) single knock on regime, (b) linear cascade regime and (c) spike regime [79].

Low energy ion beams lead to a collision effect that fall within the single knock-on regime and higher energies follow the line cascade regime unless heavy ions are involved which may stop and give a spike. Sputtering caused by electronic excitation is yet another possibility and may well be relevant to insulating materials when trying to explain the sputtering phenomenon. Here, one may observe the excitation energy of the excited electrons states being transformed to atomic motion and hence sputtering.
3.3.2.2. Ionisation

3.3.2.2.1. Introduction

A minor proportion (10 %) of the particles released from the surface are ionised and
known as secondary ions, SIMS is concerned with the analysis of these secondary
ions. Ionisation occurs at or close to emission of the specimen matrix particles. The
yield of secondary ions consequently relies heavily on the electrical state of the surface
of the material being analysed. A number of ionisation processes have been proposed.
This project is primarily involved with organic samples (polymer adhesive), so
covalent "molecular" bonding must be taken into account and consideration that
ionisation may take place not only at emission, but also by subsequent fragmentation
of vibrationally excited molecules. The models for ionisation discussed, therefore, are
for the generation of secondary ions from molecular solids.

3.3.2.2.2. Nascent Ion Molecule Model

This model for secondary ion emission was originally designed to explain secondary
ion emission from oxides by Gerhard and Plog and has now been used to interpret the
secondary ion generation from polymers [86, 87]. They suggest that the rapid
electronic transition rates, which occur in the surface, will neutralise any ions before
they can escape. The model supposes that neutral molecules leave the surface (called
"nascent" ion molecules), these molecules have the ability of becoming ions outside
the surface potential barrier and that dissociation must take place at a distance from the
surface where the electronic influence of the surface will be extraordinarily small or
the ions would return to a decharged state, Figure 3.17.
Figure 3.17. The basic process occurring during the emission of clusters and ions according to the nascent ion molecule model [87].

Secondary ion generation is a result of sputtered neutral molecules as a consequence of energy transfer from the collision cascade in the solid, which in turn gives rise to collision energy transfer between the atoms of the depositing molecule allowing dissociation of the molecule into ions at a specified distance from the surface. The model contains three steps of mass transfer;

(a) Energy transfer in the collision cascade of a matrix inhomogeneous in mass. This allows non-symmetrical collisions to occur thus ensuring production of neutral sputtered particles.

(b) Collision energy transfer between atoms of the nascent ion molecule leaving the surface. The energy in its centre-of-mass system dictates the energy available for the dissociative ion formation. This energy depends on the mass ratio of the colliding particles.

(c) Charge exchange during dynamical dissociation of the ionic bond atoms of the nascent ion molecules. Its efficiency depends on the escape velocity of the molecule's particles with respect to each other and on the escape velocity of the nascent ion molecule from the surface.
3.3.2.2.3. Desorption Ionisation

Cooks and Busch proposed a model that introduces a concept of desorption occurring in order for ionisation to take place although it is emphasised that the two processes occur separately [88]. It introduces the concept that the initial excitation process is due to energy transfer brought about by a vibrational/thermal motion as far as the molecules are concerned. The model allows for a wide variety of emissions to occur. Preformed species (existing as ions within the material prior to bombardment - no ionisation step is required) may desorb directly and unimolecular dissociation of these species may occur to produce further fragment ions. Neutral molecules may also desorb and interact with the surface or free electrons (generated by the impact process) to form ions. Cationization of neutral ions may also occur in the selvedge region (a region immediately above the sample where electronic/chemical interactions may occur). The desorption ionisation model suggests that desorption is followed by two chemical reactions taking place in two distinct regions;

(a) In the selvedge, fast ion/molecule reactions or electron ionisation.
(b) In free space, unimolecular dissociations governed by the internal energy of the parent ion.

There is no net creation of ions during the desorption process. The particle is either emitted as an ion or, if desorbed, as a neutral molecule which may react with a desorbed ion or an electron. For any of these scenarios a mass spectrum may be achieved without any ion creation process.

In summary, energy is deposited at the surface and converted from its original form into vibrational energy. Chemical rather than physical factors primarily dictate the nature of the spectra and ion yields. Both association and dissociation reactions occur, the former in selvedge and the latter mainly in the free vacuum. This model seems suitable for the application of static SIMS and so analysis of organic material, as low mass fragmentation is related to a high ion yield. It seems unreasonable, however, to think that the primary beam does not produce more ions other than preformed,
especially when considering the primary bombardment introduces charge to the surface in the form of an ion beam.

3.3.3. Instrumentation

3.3.3.1. Ion Sources

The production of a stable ion beam is essential if an acceptable SIMS spectrum is to be attained. Three features that are desirable from an ion gun in the study of particular features of an adhesively bonded joint are, a small spot resolution, an inert bombarding ion (preventing chemical reaction with the surface, although because of poor spatial resolution, this makes the production of small area analysis implausible and so a liquid metal ion source tends to be used) and finally a relatively large bombarding particle, which increases sputtering efficiency. The parameters, given a high quality ion optical column for transporting and focussing the beam, that determine the final current and spot size include brightness, extractable current and energy spread. There are a variety of ion gun sources used in SIMS which can be chosen depending on the requirements of a particular gun, three of the most popular ion sources are discussed concentrating on liquid metal ion sources, the ion gun used by the instruments in this study.

The simplest and most basic ion source is the electron impact ioniser, which is very popular with quadrupole analysers. A beam of electrons accelerated from a hot filament is allowed to collide with a gas, causing a fraction of the gas atoms to be ionised and extracted using a high potential field. The gas enters the chamber through the axis of the hot filament with the chamber negatively charged to draw electrons from the filament sides and so ionise the maximum fraction of the gas atoms. The beam current may be increased simply by increasing the gas pressure. These sources usually operate using inert gases with a variable energy of 0.1-5 keV allowing a range of spot sizes down to 50 μm.

Liquid metal ion sources (LMIS) are capable of producing a very narrow defined ion beam with a minimum spot size of 50 nm. Here, liquid metal, from a heated
reservoir, is drawn over a fine tungsten tip with a radius of approximately 1 μm. Metals with melting points close to room temperature are often chosen and generally indium or gallium is used. A high negative voltage is applied to extraction electrodes in front of the tip producing a high field strength around the tip. Opposing electrostatic and surface tension forces acting on the liquid metal cause it to be drawn into a cone shape (the Taylor cone) with a very fine curvature of radius, with a diameter as low as 4 nm and the ions are extracted by field emission. This produces a source with a very high brightness that can be focussed to very small diameters. The energy spread however can be fairly large (up to 35 eV) and so optimum performance for high spatial resolution is achieved using the lowest possible ion current and a high extraction potential.

One drawback with a LMIS is that it can be prone to contamination and so should only be run under UHV conditions in order to avoid oxidation of the liquid metal and “spikes” on the tip. This can result in deviation of the beam during analysis and so affect the spectral resolution. By increasing the emission current it is possible to cause a “flashover” of the tip and so discharge the spike. Caution must also be taken not to allow the tip to dry out, which can also result from oxidation, this requires physical re-wetting of the tip and hence breaking of the vacuum, causing unnecessary down time. LMIS are ideally suited as pulsed sources and are widely used for high resolution ToF-SIMS, including imaging, although pulsing the beam will reduce spatial resolution compared to a continuous beam.

3.3.3.2. Wein Filter

Gallium has two isotopes $^{60}$Ga and $^{71}$Ga, the primary ion beam may also contain cluster ions such as Ga$^{3+}$. These unwanted ions have a deleterious affect on spectral resolution and so a Wein filter is employed between the ion gun and the specimen, Figure 3.18. A Wein filter acts as a mass separator allowing only ions of one m/z into the aperture of the analysis chamber using magnetic and electrostatic forces. These forces are chosen such that the desired ions follow a trajectory slightly different to the axis of the filter and ion gun, hence removing neutral species, as well as unwanted
ions, since they will be unaffected by any field and continue in the direction they entered the filter.

![Schematic diagram of a Wein filter](image)

Figure 3.18. Schematic diagram of a Wein filter.

### 3.3.3.3. Mass Analysers

The three different modes of SIMS have contrasting requirements as far as their analysers are concerned, dynamic SIMS relies on a high degree of sensitivity with the preservation of surface structure not being important, whereas for static SIMS it is necessary to collect as much information per unit damage as possible and with imaging SIMS spatial resolution is of key importance. Three commonly used analysers are the quadrupole, magnetic sector and time of flight instruments.

The **quadrupole analyser** consists of a combination of direct current (DC) and radio frequency (RF) applied to four parallel rods, Figure 3.19. Opposite rods have the same potential applied to them, with a constant DC and oscillating RF component and for each pair of rods the sign of this potential is opposite. The rapid switching of the fields sends most ions into unstable oscillations of increasing amplitude until they strike the rods, however, ions of a certain m/z follow a stable trajectory and are able to reach the detector. Whilst quadrupole systems are relatively cheap and UHV compatible they struggle to detect high mass ions (m/z = 1000) and suffer from low transmission. It is a scanning instrument so that it only allows sequential transmission of ions, all other ions being discarded.
Historically magnetic sector analysers have been used for dynamic SIMS offering high transmission, spectral resolution and high mass detection. Here, ions are accelerated from the sample into a curved magnetic field. Masses are separated by the behaviour in the magnetic field (B) with the radius of curvature (R) being directly related to particle velocity (v) Equation 3.9.

\[ R = \frac{mv^2}{zVB} \]  \hspace{1cm} 3.9

Only ions with a specific velocity and charge emerge through the exit slit for any given magnetic field; a spectrum could be generated by varying either B or v. As with the quadrupole, collection of data is sequential and so information loss remains high.

The time of flight analysers identify ions of varying mass by detecting the time it takes an ion to travel a fixed distance having been accelerated by an extraction voltage, generally around 5 kV. The primary ion beam is pulsed by a fast blanking plates (pulsed by deflecting across an aperture) and so produces a “packet” of secondary ions, which are then accelerated by a fixed potential. The applied voltage imparts virtually the same kinetic energy to all the sputtered particles before they enter the field free drift tube. Consideration of Equation 3.10 shows that ions will have different drift velocities because they all have the same kinetic energy but
different masses. Mass separation occurs as the ions or fragments drift along the tube with ions of lowest mass arriving first and the heavier ions and larger fragments last.

\[ E_K = \frac{1}{2} m v^2 \]  

3.10

For a linear drift tube of flight path \( L \);

\[ t - t_0 = L(\frac{m}{2E_K})^{\frac{1}{2}} \]  

3.11

Where \( t_0 \) is the start time and \( t \) the arrival time of the singly charged secondary ion with mass \( m \). Between pulses (and "packets" of emitted ions) the sample bias drops to zero ensuring a finite time between pulses and that heavy ions/fragment at the end of one pulse are not caught up by light ions from the next pulse. Computers are able to take into account this "dead time" and relate each repeated pulse to a mass spectrum. A pulsing beam offers further advantages; the possibility to reduce charging effects by flooding a sample with low energy electrons between pulses (low energy electrons would not have any effect on a surface constantly at a high potential). ToF analysers, also, provide parallel acquisition detecting all ions/fragments at the same time (thus reducing analysis time, which can be critical when analysing damage sensitive samples). In this study a VG Ionex type 23 system was used with pulse widths between 10 and 50 ns. Sputtered particles are extracted using a bias of ± 5 kV.

One possible problem with the time of flight analyser is that the kinetic energy spread results with ions of the same mass entering the flight tube with slightly different velocities, naturally this has a deleterious affect on the mass resolution. Energy compensation is required, therefore, and in the two machines used in this study it is provided by Poschenrieder and reflectron analysers. The Poschenrieder analyser imposes toroidal electrostatic field produced by electrostatic sectors and subjects ions to an electromagnetic field causing them to travel in an arc, Figure 3.20. If the two ions of the same mass entering the drift tube with different velocities are now considered, the ion with the greater velocity will travel on an outer part of the arc,
travelling a greater distance and ensuring that ions of the same mass arrive at the detector at the same time.

The more popular reflectron analyser is capable of better mass resolution using an electrostatic ion mirror, with ions travelling down a flight tube reflecting off the compensating ion mirror and travelling back down a parallel field free drift tube to a detector, Figure 3.21. The ion mirror consists of a series of precisely spaced rings, each acting as an electrostatic lens with a gradually increasing retarding field. The faster moving ion (more energetic) this time penetrates deeper into the electric field of the ion mirror with the slower ion taking a shorter route. When tuned correctly complete energy compensation is achieved by the mirror and so all ions of the same mass will arrive at the detector at the same time.

Figure 3.20. Schematic of a Poschenrieder ToF-SIMS mass analyser.
3.3.3.4. Detection Limits and Detectors

The level of sensitivity of a SIMS instrument is superior to almost all other techniques as parts per million are detected routinely in dynamic SIMS and under certain circumstances parts per billion have been detected, e.g. boron in silicon [78]. As with XPS, however, the sensitivity for detection varies with element and also the sign of charge on the ion, yields can vary by as much as five orders of magnitude. This has the possible effect of observing an intense peak for an ion that whilst not present on the surface in a large amount has a high yield, whereas small peaks may be observed for an ion with a low SIMS sensitivity despite being in abundance at the sample surface.

The VG Ionex type 23 system employs a detection system based on a dual channel plate stacked in series, with a channel plate consisting of an array of channel multipliers a few tens of microns in diameter fused into a thin disc. The channel plates rely on the conversion of mass impact to the release of electrons with a charge gain of $10^6$ electrons ion$^{-1}$. Electrons are accelerated towards a phosphor screen resulting in visible scintillation. The signal produced by the channel plates are sorted by the data system and amplified with a resolution of 1 ns so that they are added into

Figure 3.21. Schematic of an electrostatic ion mirror used in a Reflectron ToF-SIMS instrument.
the appropriate spectral (mass) channels. The detection efficiency is greater the higher the velocity of the ion and so for ions of extremely high mass a post accelerating potential can be applied. One precaution that can be taken to increase the life time of a detector is veto the first 5-10 mass units, these contain the ions with the greatest velocity but contribute little to any surface information.

3.3.4. Imaging SIMS

The combination of a Poschenrieder or reflectron mass analyser with a LMIS enables surface analysis with high spatial resolution to be carried out. There is the potential to digitally raster the beam across the surface with a chosen number of pixels (for example 128 x 128) to produce an image. The advantage of the ToF analyser is that the whole spectrum is collected at each pixel, allowing several masses or groups of masses to be collected at the same time, i.e. one scan over an area can produce multiple images due to parallel acquisition.

In this study adhesively failed lap shear joints have been imaged in order to determine the role of the adhesive in bond durability. One precaution that must be taken when carrying out imaging SIMS of an organic system is that a low primary ion dose is used to avoid any significant damage to the surface. In imaging SIMS it is often difficult to obtain a sufficient secondary ion yield without going over the static “limit” of $10^{13}$ ions cm$^{-2}$ per analysis. This is much easier to achieve with a ToF compared to a quadrupole analyser. Low ion beam currents are essential for imaging as this actually helps improve lateral resolution. In Chapter 6 an imaging methodology is developed for the analysis of an adhesively bonded joint indicating the various steps that must be taken before imaging can be carried out with confidence, for example establishment of the static “limit” for the adhesive system. The acquisition of good quality spectra is essential before any imaging can be carried out and under no circumstances should imaging replace the use of spectra, a spectrum will nearly always contain more chemical information than an image. Once spectra have been acquired and key ions/fragments identified, images can provide important spatially resolved chemical data.
3.3.5. Problems Associated with Acquisition of Secondary Ion Mass Spectra from Organic Materials

3.3.5.1. Introduction

The analysis of organic material has been traditionally difficult to analyse, they are chemically complex, usually electronically insulating and in the case of SIMS sensitive to particle bombardment. Until the late 1980's the surface analysis of polymeric materials relied heavily on XPS and despite the elemental and chemical state information offered by the technique it has several limitations concerned with the analysis of organic material. The principal problem with the technique concerns polymer characterisation, chemical shifts of important core levels (e.g. Cls) only have a small dynamic range leading to ambiguity of spectra interpretation and until recently spatial resolution has been poor (150 μm at best). SIMS, on the other hand, offers both the potential for polymer surface characterisation via fingerprint mass spectra and for analysis at high spatial resolution (1 μm). In order to realise this potential there are some limitations of the SIMS technique that must be overcome. The sample is susceptible to a high rate of beam damage and there is also a need for charge neutralisation which may lead to uncertainties in the surface potential, these features impose rather stringent experimental restrictions on the analytical set up of the machine.

3.3.5.2. Sample Charging

When an insulating sample is bombarded by a positive ion beam the surface potential rises due to the input of positive charge and the emission of secondary electrons. The surface potential can rise rapidly (by hundreds of electronvolts) giving rise to the possibility of the kinetic energy of the emitted ions rising well above the acceptance window of the analyser. This results in the loss of the SIMS spectrum. A solution to this problem is to irradiate the sample with a beam of relatively low energy electrons. In principle this allows the surface to return to a neutral state as the electrons are attracted to regions of positive charge. This situation seems to be satisfactory for positive static SIMS analysis. Brown and Vickerman noticed that whilst positive
SIMS spectra gave structural polymer information, no complementary negative spectra was being acquired [89]. These authors suggested that negative spectra, were in fact, in a better position to yield structural information about the polymer as they do not suffer from the intense C\textsubscript{x}H\textsubscript{y} fragments (whilst structurally important, almost always represent side chain groups) that dominate positive spectra. If a surface is positively charged, a potential barrier exists which negative ions must overcome before being emitted from the surface, so only higher energy negative ions would be detected (i.e. elemental secondary ion rather than multi-atom cluster ions). In order to release the full energy distribution of negative ions from the surface it is therefore reasonable to expect that a neutral or slightly negative surface should exist. One draw back of electron bombardment is sample degradation and electron stimulated ion emission, these issues were addressed by Hunt et al who stressed the importance of the use of low energy electrons for charge neutralisation [90].

The use of an atom beam also alleviates the problem of charge build-up of a sample surface. The atom beam is generated by charge exchanging ions, for example argon ions are passed through an argon gas chamber some of the ions gain an electron from the gas phase thus becoming atoms, despite loosing their charge enough velocity and direction is maintained to form a fast atom beam, FAB [91]. The unaffected ions are easily deflected away and have no interaction with the sample surface. In this situation any tendency of the surface to build up positive charge by loss of secondary electrons will be counteracted by a proportion of those electrons returning to the surface. This self-compensating mechanism prevents, in most cases, the surface potential from passing outside the energy window for positive ions. Clearly, even under atom bombardment, negative ion collection still requires the surface potential to be brought negative. Some electron input is required, although considerably less than with ion bombardment. These approaches allow polymers to be studied without special sample preparation.
3.3.5.3. The Importance of Static Conditions for SIMS Analysis of Polymers

It has already been mentioned that organic material is sensitive to particle bombardment and that the use of electron flood guns for charge compensation may cause "damage" and electron stimulated ion desorption to the sample surface. Damage to the surface from either of these factors can change the spectral interpretation of a particular system. In order for surface analysis information to be of value to the study of a polymer (or adhesive) the sputtered species must be characteristic of the unmodified or virgin polymer. Analysis, therefore, must take place within the "static" regime, i.e. spectra must be acquired during the accumulation of a total primary ion dose which is significantly less than the primary ion dose required to cause "damage" to the surface.

Briggs and Hearn realised that the form and rate of sample damage during ion bombardment is a major issue in the development of SIMS as an analytical technique applied to polymers [92]. They carried out a series of measurements on thin films of PMMA poly (methyl methacrylate) and noticed that a dramatic reduction in structural peaks was observed on pre-irradiated samples \(6 \times 10^{13} \text{ ions cm}^{-2}\). These spectral changes as a function of dose could be monitored in two ways:

(a) running static SIMS spectra sequentially, predosing at a higher current density.
(b) following the intensity of a chosen peak with time (dose) at a fixed current density.

Interpretation of the results led to the damage of PMMA being categorised into four stages; (1) at low dose primary ion impact sites are well separated, the secondary ion yield is constant or may increase (if emission is aided by previous chain scission) (2) Major fragments representing the polymer then decline in intensity as "damage" structures increase pendant groups are preferentially lost and the polymer may become cyclic. (3) ultimately aromatic units are formed (4) as the composition becomes more cross-linked and carbon rich the overall secondary ion yield decreases. The detailed
changes in spectra were also studied as a function of primary ion mass and energy and as expected total ion yield increased with particle mass (Xe>Ar). This work established that a total dose of $10^{13}$ primary ions cm$^{-2}$ was the maximum permissible before new spectral features become evident due to bombardment. Briggs and Hearn also studied poly (tetra fluoro ethylene)PVC and poly (styrene)PS, they noticed that the different polymers behaved differently under the ion beam. Damage for PVC was easy to detect with the polymer yielding a similar damage spectra to PMMA after approximately half the ion dose, (i.e. cyclic ions present). PS, on the other hand showed much less damage even after a dose of $10^{14}$ ions cm$^{-2}$. From these findings Briggs and Hearn indicated that the presence of polycyclic aromatics (PCAs) was a sign of damage to a polymer. They justified the lack of apparent damage to PS by the fact that aromatic molecules were present in the undamaged spectra. The use of an aromatic structure as a sign of damage highlights the difference of analysis between XPS and SIMS as XPS examines chemistry at the surface where as SIMS analyses fragments of rearranged fragments that have left the surface. Previous XPS studies, by Briggs, had shown that the characteristic C1s shake up satellite ($\pi-\pi^*$) from PS is destroyed by approximately $10^{14}$ ions cm$^{-2}$ [93]. In a later study by Leggett and Vickerman cyclic ions were observed even at low primary dose rates on PVC and PMMA spectra [94]. This posed the question of whether PCAs are signs of damage or, in fact, just normal emission/rearrangement fragment patterns that can be expected in mass spectrometry. PCA groups may be formed as pendant groups are lost and rearrangement of fragments occurs and may demonstrate a propensity to form due to their high stability. This highlights the essence of the SSIMS process in that it not only analyses fragments characteristic of the surface but also rearranged fragments which could, mistakenly be thought of as signs of damage. It is important, therefore, to monitor the surface damage by the decrease in characteristic ions with respect to ion dose, not by the presence of rearranged fragments.

Leggett and Vickerman made a comparative study for PTFE and PET comparing argon and xenon particles both in the charged and uncharged state to evaluate the differences in the damage rates observed [94]. Under ion bombardment there is a dramatic fall in the intensities of all the significant secondary ions (even within the so called "static" limit). Under atom bombardment, however, there is little loss of
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intensity by the static limit. The normalised intensity variation demonstrates that the order of damage rates are

\[ \text{Ar} < \text{Xe} < \text{Ar}^+ < \text{Xe}^+ \]

In general decay rates were much faster for bombardment with charged particles indicating that electronic interactions between the surface and the bombarding particle were an important contribution to damage. It is generally believed that incident ions are neutralised prior to impact with a solid. Increased damage rates under ion beam bombardment must therefore be due to particle surface electronic interactions (PSEIs). This allows transfer of electrons from the solid to the approaching ion via a resonant or Auger process thus charging the surface region to an excited state. If these exited states are antibonding we may observe bond dissociation.

The important advances in being aware of and overcoming the limitations of SIMS, discussed above have allowed the technique to become an important tool in the surface analysis of polymers. The majority of this work was carried out on a quadrupole mass analyser. Whilst a great deal of useful information has been acquired about polymer surface chemistry using this analyser it has a low transmission device (increasing the chance of damage at higher magnifications) and is a scanning instrument which only allows sequential transmission of ions (all other ions are discarded). The development of ToF-SIMS with higher transmission allows high spatial resolution analysis and imaging. The process utilises a pulsed beam so whilst this restricts the primary source to an ion beam, not atomic, spectral acquisition is possible with a dose of $10^9$-$10^{12}$ ions cm$^{-2}$/analysis. The pulsed ion beam also enables all ions to be analysed in one parallel acquisition mode so no secondary ions are discarded. The more complex the organic materials being studied the greater the mass range required and the possibility of mass spectral overlap can become a serious problem for interpretation. Once again the ToF-SIMS analyser out performs the quadrupole by currently providing a mass resolution of 5000-10000 and in theory having a limitless mass range (whilst a quadrupole analyser is limited to a mass range of about 1000 amu).
3.3.6. The Characterisation of Polymer Surfaces for Use in Adhesion Studies

In recent years SSIMS has been demonstrated to be a useful tool for the detailed characterisation of organic surfaces. The technique is especially powerful for the study of interactions at polymer-metal interfaces, with ToF-SIMS being highly suited to study such effects as segregation of low molecular weight components to the substrate surface and orientation of polymer molecules against the substrate. It is now well understood that the surface and interfacial chemistry of adhesives and organic coatings can have a major effect on the properties and performance of adhesive bonds and coatings. The importance of the characterisation of interfaces lies in the fact that the chemistry at the interface determines the adhesion of the system which in turn has an effect on the performance of the system in an aggressive environment. It should be noted that material diffusing to the interface may improve adhesion by acting as a coupling agent or, equally inhibiting normal interactions across the interface resulting in poor adhesion. As seen from the earlier part of the review different systems will require different analytical conditions for optimum SIMS analysis.

Analysis of each component, especially the polymer adhesive, is an essential first step in the detailed study of both general adhesive chemistry and the factors that effect the composition of the adhesive at the interface. Several handbooks with collections of standard spectra of low molecular-weight or polymeric organic materials have now been published [95]. Treverton et al [96] set out characterise some of the common constituents present in epoxy adhesive formulations. They discussed how the fingerprinting ability of SIMS made it possible to allow curing chemistry and structural changes of an adhesive at an interface to be monitored (i.e. curing may provide a reduction in secondary ion yield and new peaks from the cross-linked polymer may be observed in the spectra). The work identified the bisphenol-A ion at m/z 135 in the positive spectra and also negative ion peaks deriving from the bisphenol-A ion. Treverton concluded by stating that characteristic secondary ion spectra recorded for two materials (Epikote 828 and dicyandiamide) exhibited a number of identifiable and uniquely diagnostic signals, which should be of use in the study of surface and interface chemistry. Treverton and his co-workers continued their
work of the characterisation of important constituents that could form the foundation of further investigations on the surface and interfacial chemistry of adhesives and coating [97]. This time they used silver cationisation to assist in the analysis of oligomeric distribution. A number of Epikote systems were analysed and once again characteristic epoxy and bisphenol-A ions were detected (in the positive spectra $m/z$ 57, 191, 252 and 269 were assigned to epoxy fragments and $m/z$ 135 and 213 were given to the bisphenol-A fragment, Figure 3.22 shows a fragment diagram and typical spectra. Treverton was now convinced that ToF-SIMS offered the potential for understanding full adhesive chemistry and that quantitative relationships could be made between certain fragments by using the relative intensities of the characteristic components comprising of the oligomer chains. For example it was shown that the bisphenol-A component is relatively unaffected by crosslinking and so may be seen in fully crosslinked systems and possibly play a role on the interface chemistry of adhesive structures.

Van Ooij and Sabata characterised polymer surfaces and polymer-metal interfaces by ToF-SIMS [98]. Their analysis of the paint-metal interfaces allowed conclusions to be drawn about the cure state of the paint and preferential segregation of low-molecular paint constituents to the metal surface to be made. Another conclusion from the study included determination of the cleanliness of the failure; a clean metal surface was identified by the high intensity of the chromium peak. The effect of cure temperature could also be monitored by characteristic peaks in the spectra which define the amount of crosslinking or non crosslinking. Davis and Watts have employed ToF-SIMS also to analyse the interfacial chemistry of an adhesive joint [33]. ToF-SIMS was used to determine the exact nature of adhesive failure, once again providing further details on organic material remaining on the metal side of an aged failed joint exploiting the technique's excellent sensitivity allowing very low levels of contaminant species to be determined. They carried out linescans across the width of a single lap joint overlap enabling surface chemistry across the entire failure region to be examined. Plots of peak intensity versus position were made. As a result of the confidence in the sensitivity of SIMS the workers were able to confirm that true interfacial failure was being observed with no signs of epoxy present at the metal interface. Findings of cations at the crack tip of failure front led to the conclusion that the interfacial failure observed was brought about by electrochemical activity.
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Figure 3.22. Positive SIMS spectrum of Epikote 828 resin, showing the Fragment diagram for the peaks observed in the spectrum [97].

Oligomer (m/z = 340)

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{O} & - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{CH}_2\text{CHCH}_2 \rightarrow \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
m/z = 269
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CHCH}_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
m/z = 191
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{C}_6\text{H}_4 - \text{OH} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
m/z = 135
\]

\[
\begin{align*}
\text{CH}_2 & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_2\text{CHCH}_2
\end{align*}
\]

\[
m/z = 57
\]
3.3.7. Concluding Remarks

Static SIMS is developing into one of the most significant techniques for characterising the surface chemistry of complex materials. As mentioned in the introduction, however, no one technique provides the total information required about a surface and XPS has also been used throughout this study. The subtleties governing ion fragmentation lead to the technique detecting even slight chemical changes in surface structure. If a fragmentation pattern of a molecule is known, the appearance of a set of peaks often leads to an unmistakable characterisation of the sample surface, even at low concentrations.

Like XPS, SIMS has many assets to offer the adhesion scientist; characterisation of polymeric material, deposition characteristics of an organic coating and determination of loci of failure. In this project the molecular sensitivity and spatial resolution of imaging SIMS have been exploited in a new methodology, which hopefully, has not only facilitated this research but will also aid further work in this subject area.
Chapter Four

Surface Characterisation of Hot Dipped Galvanised Steel

4.1. Introduction

For an adhesive bond to form the organic phase must wet the substrate and establish intimate interfacial contact with the substrate, as discussed in Chapter 2. If the surface is not clean, for example covered with hydrocarbon contamination, wetting will be inhibited and a cleaning procedure is often required [6]. The interface characteristics of “clean” substrates can also have adverse effects on establishing strong and stable adhesive forces. For example, a heterogeneous interface may offer preferential sites for adhesion thus leaving weaker poorly adhered areas. In order to understand the failure mechanisms of an adhesive system the individual components of that system must be fully characterised.

Hot dip galvanising baths contain many additives [99], which if present on the surface of the final substrate may affect the adhesive properties and consequently failure mechanisms of adhesive bonds [45]. In this chapter the surface of as received HDGS is characterised, and the effect of alkali cleaning on the substrate surface also investigated using XPS. The acid-base properties of the resultant substrates will be compared using the thin film approach of Leadley and Watts [100].
4.2. The Production of HDGS

Hot dip galvanising is the most common of the zinc coating processes with two million tons of zinc used to coat approximately 40 million tons of steel and cast iron a year [101]. Different coating processes are used for different products; for fabricated work, batch immersion is used, however for sheet steel, a continuous immersion technique is employed, a typical Sendzimir type galvanising line for sheet material is shown in Figure 4.1. A Sendzimir cold rolling mill features several roll arrangements and is designed such that each work roll is supported throughout its entire length by a series of intermediate rolls. The modern continuous hot dip process can be divided into three main stages, cleaning of the rolled strip, annealing and finally passing it through a molten zinc bath to coat. Hot dip coatings are produced on steel objects by passing the properly prepared base metal through a bath of molten coating metal. The cleaning and annealing processes can be carried out simultaneously by preheating in an oxidising atmosphere to burn off oils and grease. In addition, successful hot dipping requires the surface of the molten bath to be kept clean, particularly on entrance to the bath, since oxide films of the coating metal at this point will be picked up by the surface of the base metal entering the bath and will interfere with the wetting of the latter by the molten coating metal. The strip then enters a high temperature oven (900-1000°C) in a reducing atmosphere (hydrogen and nitrogen) resulting in metallic iron allowing the regrowth of a “pure” oxide in the cooling stage (step 7) which is preferred for bonding. Next the strip travels through a bath of molten zinc at approximately 450°C. Coating thickness and weight may be controlled by gas jets in a gas wiping method. The appearance of hot dipped coatings can often be “spangled”, this is as a result of the differing crystal orientation of the zinc grains.
Above its melting point, zinc readily forms intermetallic compounds with iron. These alloys form at the interface between the base iron and the coating zinc and ultimately constitute an appreciable portion of the finished coating [102]. After solidification, the coating consists of an outer layer approaching the metal of the coating bath in composition and several inner layers, termed the *alloy layer*, consisting of intermetallic phases of iron and zinc, which are successively richer in iron with depth, Figure 4.2.

Figure 4.1. General view of a Sendzimir type hot dip galvanising line [99].

Figure 4.2. Micrograph showing the nature of the alloy layer, consisting of Zn-Fe intermetallics that contribute to the coating layer of HDGS, magnification x1000 [102].
While electrogalvanising gives primarily zinc oxide plus unavoidable carbon contamination, hot dipped coatings may often be chemically heterogeneous as the zinc bath contains other elements such as aluminium, lead or antimony which moderate alloying reactions, retard the formation of particles in the bath and improve bath fluidity. Silicon and phosphorous can give increased zinc-iron alloying and so thicker coatings. Magnesium is often added to improve corrosion resistance and antimony can be deliberately added to lead-free baths in order to produce a normal spangled sheet, without this addition a lead-free bath produces fine grained zinc coatings. A large area XPS survey spectrum acquired from the as received HDGS used throughout this study is shown in Figure 4.3. The anticipated Zn 2p peaks are present as well as the ubiquitous carbon and oxygen peaks. Closer inspection of the lower binding energy end of the survey spectrum reveals a strong presence of aluminium, Figure 4.3 (b). Indeed quantification of the data reveals that aluminium represents approximately 13 atomic % of the surface concentration compared to just 6 atomic % zinc.

Aluminium is an essential addition to the zinc molten bath in order to suppress the growth of a brittle Zn/Fe intermetallic compound (the alloy layer) at the steel coating interface, which causes poor formability (adhesion of zinc) of the coated sheet, Figure 4.4. Chlorine is also present in the spectrum and was often present on the as received substrate surface, however, this is considered to be present as a result of contamination as opposed to related to the galvanising process.

An interesting feature of the spectrum in Figure 4.3, is the sloping background observed after the O1s peak. This sharp rise in background is due to the presence of zinc LMM Auger peaks, at 585 and 662 eV, these zinc auger peaks have a low photoelectron cross section and whilst not observed as intense peaks they are noticed as points where the spectrum background increases. The as received substrate was covered in a visible layer of oily grease and despite being wiped vigorously with acetone prior to entering the spectrometer it is quite possible that a thin layer of hydrocarbon contamination remained on the surface for analysis. In Figure 4.9 a spectrum of alkali cleaned HDGS indicates a much smaller C 1s contribution, which is also reflected by the more pronounced zinc Auger signals followed by a flatter or even downward sloping background, suggesting a "clean" interface. Industry often
employs an alkali cleaning solution to remove deleterious contaminants such as hydrocarbons it has also been reported that an additional benefit of using such an aggressive cleaner is that the thin layer of surface segregated aluminium is removed leaving a virtually homogeneous zinc surface \[103\].

![XPS survey spectrum of as received HDGS: (a) 0-1200 eV (b) 0-180 eV.](image)

Figure 4.3. XPS survey spectrum of as received HDGS: (a) 0-1200 eV (b) 0-180 eV.
The surface segregation of aluminium is due to its extremely low solid solubility in a zinc matrix. As the solidification reaction proceeds at the steel/zinc interface the solidification front moves towards the surface side of the coating and so an element such as aluminium, with a low solid solubility in the solid zinc will concentrate in the residual solution and finally precipitate in the surface layer of the zinc coating [102]. A natural path for the segregation of the aluminium is along the grain boundaries of the zinc coating, this would result in a heterogeneous interface; not a desirable situation for a durable adhesive bond. In order to characterise the degree of distribution between zinc and aluminium at the surface of HDGS used in this study scanning Auger microscopy was carried out.

Before mapping could be carried out spectra were acquired enabling the correct energy ranges to be selected for mapping. Figure 4.5 clearly shows segregation of Aluminium at the grain boundaries with zinc concentrated within the middle of the grains. An SEM acquired of the corresponding area, prior to analysis, defines the grains, highlighting the relevance of grain boundaries to the segregation of the aluminium, Figure 4.6.
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Figure 4.5. Scanning Auger microscopy images showing the heterogeneous nature of the surface of HDGS (a) zinc (b) aluminium.

Figure 4.6. SEM micrograph showing the region from which the Auger images of Figure 4.5 were acquired.

Imaging XPS also revealed zinc rich areas on the surface of as received HDGS, Figure 4.7. Imaging XPS was carried out using a VG Scientific ESCALAB 220iXL; the excitation source used was monochromated Al Kα radiation. Small area XPS at a spot size of 50 μm was carried out from areas of high and low concentrations of zinc as shown in Figure 4.7. XPS spectra of the low binding energy region (0-120 eV) from the respective areas are shown in Figure 4.8 and the most noticeable difference between the two spectra is the smaller Al 2p peak from the apparent zinc rich region.
Figure 4.7. XPS images acquired from the surface of as received HDGS (A) zinc image showing the areas that small area XPS spectra were acquired from and (B) an aluminium image.

Figure 4.8. Low binding energy spectra of as received HDGS taken from the areas identified in Figure 4.9; (a) high zinc concentration and (b) low zinc concentration.
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Quantification using the Al 2p and Zn 3p peaks without including other elements (i.e. carbon and oxygen) will not indicate concentrations (atomic %) of the components but does allow the ratios of the respective elements in the relative areas to be determined, Table 4.1.

<table>
<thead>
<tr>
<th>Region</th>
<th>Relative Concentration (atomic %)</th>
<th>Zn:Al Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Zn 73.74</td>
<td>Al 26.26</td>
</tr>
<tr>
<td>(b)</td>
<td>Zn 26.43</td>
<td>Al 73.57</td>
</tr>
</tbody>
</table>

Table 4.1. The relative concentrations of zinc and aluminium on as received HDGS from (a) a high zinc area and (b) a low zinc area.

By using the Zn 3p peak rather than the Zn 2p, which is conventionally used because of its large photoelectron cross-section (Zn2p 3/2 = 3.4 compared with 0.2 for Zn3p), the depth of analysis for each element is almost identical. Zn 2p electrons have a considerably higher binding energy (1023 eV) compared with Zn 3p electrons (90 eV) and so provide an analysis characteristic of the outermost surface; the inelastic mean free path (\(\lambda\)) for Zn 3p is approximately twice that of Zn 2p3/2. The quantification results of Table 4.1 show a change in the zinc aluminium ratio of almost an order of magnitude between the high and low zinc regions and serves as further evidence of the heterogeneous nature of as received HDGS.

4.3. Alkali Cleaning of HDGS

The purpose of the cleaning step in the pretreatment is to remove oils, fats, metal particles and other impurities from the surface. The hydroxide ions in the cleaner saponify fatty compounds and form water-soluble soap. Surfactants in the cleaner help to remove oil from the surface. Owing to its alkalinity, the cleaner also attacks the metal surface causing dissolution of the oxide layer and of the metal under hydrogen evolution. The attack on the surface by the hydroxide ions can be described by the following reaction:
Hörnstum has reported that alkali cleaning not only reduces the aluminium level but also has a slight polishing effect on the HDGS surface, he also carried out chemical analysis on the cleaning solution and, not surprisingly, found a build up of zinc and aluminium in the bath [103].

In this study all as received HDGS was alkali cleaned before any experimental work was carried out. A commercial alkali cleaner, Novamax 187 U, was used in a 3% solution at 60°C to clean the as received HDGS. Panels were dipped for 30 s periods until the surface wetted readily during a rinsing step under running water, this was determined using the water break test. A spectrum characteristic of as received HDGS treated with an alkali cleaning solution is shown in Figure 4.9. The cleaning solution, composed of sodium hydroxide, showed no signs of leaving any contamination on the sample with a very low concentration of carbon detected. A negative post peak slope of the background is observed, which, as discussed earlier, is in contrast to the spectrum acquired from the as received substrate. A trace of calcium has been detected with its origin presumed to be from the water during the rinsing stage. The spectrum shown in Figure 4.9 also indicates that all surface aluminium has been removed. The removal of aluminium is highly desirable; the possibility of electrochemical activity at the interface is reduced as a substrate becomes more homogeneous.
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Figure 4.9. XPS survey spectra of alkali cleaned HDGS.

The water break test is used in industry as a means of inspecting the condition and suitability of a substrate for adhesion. In short, the wetting characteristics of a surface are monitored and essentially the test result is dependent on the judgement of the researcher, with a wetting surface defined as one that remains covered by a film of water on withdrawal from a rinsing bath. Unlike contact angle measurements no values are recorded and so the subjective nature of the test makes it susceptible to inconsistencies. The test is, however, relatively fast and does allow large areas of surface material to be inspected simultaneously. Whilst, for the most part, total dip time of 1.5 minutes (3 dips) was adequate for cleaning there were occasions when a longer dip time was required. This was simply due to varying amount of hydrocarbon contamination on the surface, however these different treatment times would also affect the degree of aluminium removal, with shorter treatment times leaving more aluminium on the substrate surface. This is demonstrated in Figure 4.10 where spectra acquired on as received HDGS is compared to two alkali cleaned samples. Both the alkali cleaned samples passed the water break test however, different concentrations of aluminium were left on the surface, 8.4 atomic % aluminium compared with complete removal after 1 and 2 minute dip times respectively. This is hardly surprising as the water break test will only be sensitive to low surface energy contamination, however both ZnO and Al₂O₃ are high-energy surfaces.
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Figure 4.10. 0-200 eV survey spectra comparing as received HDGS with two different alkali treated HDGS both of which passed the water break test, (a) As received HDGS (b) 1 minute alkali cleaned HDGS (c) 2 minute alkali cleaned HDGS.

To study the effect of alkali cleaning an investigation was carried out to determine the consistency of the removal of aluminium and also the validity of using the water break test as a method for checking the state of alkali cleaned HDGS. XPS spectra were acquired from HDGS specimens treated with Novamax 187 U for a number of different dip times (from one to five 30s dips). Three specimens were analysed for each dip time and the results plotted as concentration of aluminium against cleaning/dip time, Figure 4.11.

During the alkali cleaning, samples passed the water break test after 2 dips (60 s) on every occasion. This can be related to the significant reduction in the concentration of adventitious carbon after 60 s of cleaning. This is reflected in a slight diminution in concentration of aluminium, however, the removal of aluminium is not complete until 150 s dip time. The reduction in the surface concentration of aluminium does not occur in consistent manner. This most likely reflects variations in the level of aluminium and/or hydrocarbon contamination in the as received sheet, however, aluminium records a negligible value after 150 s treatment time. To examine this relationship samples should have been analysed between each cleaning dip, the results do indicate, however, that the water break test is not suitable to monitor whether a homogeneous surface, preferred for adhesive bonding, has been produced. Analysis
of the samples did indicate, however, that 150 s was adequate to remove aluminium from the surface.

![Graph showing variation aluminium concentration on the surface of HDGS against cleaning time.](image)

Figure 4.11. Graph showing variation aluminium concentration on the surface of HDGS against cleaning time.

This brief study has shown the water break test not to be a suitable method of surface characterisation of HDGS for adhesive bonding. Whilst an alkali cleaning procedure may reduce the levels of hydrocarbon contamination to acceptably low levels and indeed pass the water break test, this in no way guarantees the production of a homogeneous zinc surface suitable for adhesive bonding. However, whist this study has indicated that aluminium may exist on a surface that has passed the water break test at no time throughout the durability study was aluminium identified on any of the failure interfaces analysed. This inferred that the alkali cleaning carried out to prepare
substrates for adhesive bonding had completely removed aluminium from the bonding interfaces and that aluminium played no part in the failure mechanisms observed.

In the pretreatment of strip products the alkali cleaning stage is carried out as part of the continuous process. As the main objective is to remove hydrocarbon contamination, the cleaning step is incorporated using a spraying technique for a period of time in the order of seconds rather than minutes. The degree of removal of aluminium is never monitored, and so whilst the interfaces studied in this project have largely concerned homogeneous zinc substrates, it is important to be aware not only that aluminium may be present on a HDGS interface but also the consequences of that aluminium on the durability performance of adhesively bonded galvanised steel.

4.4. The Effect of the Concentration of Aluminium on the Acid-Base Interaction Sites on HDGS

4.4.1. Introduction

One of the most important characteristics of a substrate that may affect subsequent adhesion of a polymer is its acid-base properties. One of the most important properties of polymers which has enabled them to be widely used in adhesion and coating applications, is their ability to be readily adsorbed onto solid surfaces. In the adhesion of polymers to inorganic substrates various chemical or conformation changes may occur in the interphase region, by understanding these changes/interactions it may be possible to alter the chemistry of the substrate to provide the desired properties. Over the past five years the University of Surrey has investigated the use of XPS as a tool in assessing the proportion of acid-base sites available at a substrate surface. Beamson and co analysed a series of thin PMMA films, of differing thickness, spin cast onto silicon wafer [104]. By studying the C1s spectrum they noticed that whilst the thicker films yielded spectra identical to those taken from bulk PMMA there was a binding energy shift of 0.1 eV higher for the carboxyl carbon component in the thinnest film. This small increase in the binding energy shift of the carboxyl group was attributed to interaction between the PMMA and the substrate. Despite the fact that no mention of acid-base interactions were
made, Beamson’s findings were in fact in agreement with observations reported by Zazzerra whom, using internal reflection IR spectroscopy, reported that carboxyl groups of PMMA are hydrogen bonded to silanol sites on a silicon substrate [105]. Hydrogen bonding is a classic example of an acid-base interaction. The acidity of the silanol groups at the silicon surface causes an increase in the electropositivity of the carboxyl carbon due to electron withdrawal from the carboxyl oxygen, this results in the binding energy shift of the carboxyl components observed in Beamson’s C1s spectra. Although not realised at the time this was an indication that the acid-base interaction between a polymer and its and inorganic substrate could be assessed using XPS. Simulation work determining the interaction between PMMA and aluminium has shown that close to the interface the polymer chains lie relatively flat, parallel to the aluminium [106], the differences in binding energy for carbon components also appear to confirm that there is an interphase between the bulk PMMA and its substrate.

4.4.2. Specific Interactions between Carboxyl Probe Molecules and Inorganic Substrates

Realising the potential of analysing ultra thin films for evaluation of acid-base interactions, Leadley and Watts investigated the interaction of PMMA with a series of oxidised substrates [100]. Peak fitting the C1s spectrum and considering binding energy shifts of the carboxyl components they were able to identify three separate interactions occurring at the PMMA/substrate interface:

- **Acidic sites**- attributed to hydrogen bonding.
- **Weak basic sites**- interaction with carboxylate anions formed as a result of hydrolysis.
- **Strong basic sites**- as a result of nucleophilic attack of the acyl carboxyl carbon from strong basic sites on certain substrates.

The mechanisms of these interactions are explained in more detail in Table 4.2.
Table 4.2. Proposed acid base interactions of PAA.

Leadley and Watts followed up their PMMA investigation by using PAA (poly acrylic acid) as the probing molecule, a simpler molecule which had the advantage of adsorbing onto an oxide surface as a very thin film (8-12 Å) and so aid the identification of specific interactions. One concern over the use of PAA as the probe...
molecule was its susceptibility to damage from the X-ray beam and photo-electrons excited from the metallic substrate. In the current work the acid-base properties of the of HDGS have been investigated using monochromatic Al Kα XPS. Thin films of PAA have been used to probe the surface of HDGS to determine the effect of differing concentrations of aluminium on the acid-base properties of HDGS. Spectroscopy considerations and sample preparation has been discussed and followed by an assessment of the resultant spectra with a view to characterising the substrate.

4.4.3. Experimental

4.4.3.1. Spectroscopy

Leadley and Watts reported that thin films of PAA are subject to sample degradation when exposed to monochromated Al Kα X-rays, which result in changes in the observed C1s spectrum [107]. They noticed that the size of the C3-O peak, characteristic of hydroxyl and ether groups and identified at a binding energy shift of 1.7 eV in high resolution C1s spectra (as illustrated later), varied for different substrates. The size of the C3-O peak was monitored as function of X-ray exposure and indeed shown to give an indication of sample degradation. Leadley proposed that the observed damage was a result of cross inking caused by the coupling of X-ray induced radicals. These radicals may be formed through the cleavage of an α-hydrogen atom or C-H cleavage adjacent to the ester linkage. A schematic of Leadley’s proposed mechanism for cross-linking in thin PAA films exposed to an X-ray source is shown in Figure 4.12.
Figure 4.12. Proposed mechanism for cross-linking in thin PAA films exposed to X-ray radiation [107].

By using the VG Scientific Sigma Probe XPS machine, using a microfocusing monochromatic Al Kα X-ray source and with an efficient collection system reasonably short acquisition times were achieved, generating spectra that could be peak fitted. The analyser was operated in the fixed analysis transmission mode with a pass energy of 100 eV for survey spectra and 20 eV for core level high resolution scans.

### 4.4.3.2. Sample Preparation

The substrates used in this study were 1mm diameter discs punched out of strip HDGS. Panels of HDGS were subjected to different times of alkali cleaning, the conditions were given earlier, resulting in different concentrations of atomic percent aluminium present at the HDGS interface. Five different HDGS samples were analysed, as received, three alkali cleaned and an argon ion etched sample. Each of the samples were analysed by XPS and the data quantified to determine the concentration of aluminium, Table 4.3. A zinc foil disc was also prepared. Thin polymer films were prepared by casting onto the substrate from a 0.01% w/w PAA ([MW = 450000] Aldridge Chemical Company) solution in methanol.
Table 4.3. Samples with different surface concentrations of aluminium, coated with PAA in the acid-base interaction site study.

### 4.4.4. The Analysis of Thin PAA Films on HDGS with Different Concentrations of Aluminium at the Interface

A series of HDGS samples, with varying surface concentrations of aluminium have been coated with thin films of PAA and analysed using XPS, with particular attention paid to the high resolution C 1$s$ spectrum, allowing specific acid-base interactions between the polymer and HDGS substrate to be characterised. Figure 4.13 shows the XPS survey spectrum of PAA cast on to as received HDGS, characteristic substrate peaks are clearly visible and so the carbon peak may be considered to be predominantly indicative of PAA at the polymer substrate interface.

![XPS survey spectrum of a thin film of PAA on a HDGS substrate](image)

Figure 4.13. The XPS survey spectrum of a thin film of PAA on a HDGS substrate.
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The peak-fitting regime used to interrogate the C1s narrow spectra employed the same methodology as that followed by Leadley and Watts. As a starting point each narrow scan was originally fitted with the three peak fitting scheme characteristic of bulk PAA as determined by Beamson and Briggs [108] and shown in Figure 4.14.

![Figure 4.14](image_url)

Figure 4.14. High resolution C 1s spectrum of bulk PAA characterised using a three peak fit regime, (1) aliphatic carbon, (2) beta-shifted carbon (C₂-C=O) and (3) carboxylic acid (C₄OOH) [108].

In order to achieve a good peak fitting regime Leadley added a series of peaks each identifying a specific interaction or damage effect, with the aim of attaining better agreement with the experimental data. Initially a fourth peak was added at a binding energy shift of 1.7 eV (C₃-O) and was indicative of either hydroxyl or ether components as a result of previously discussed degradation to the thin film. With four peaks fitted Leadley noted that the full width half maximum (FWHM) of the carboxylic acid contribution (C₄OOH) was unacceptably broad, compared to the beta-shifted carbon peak (C₂-C=O). The C₄OOH peak also displayed a binding energy shift in the range of 3.8 – 4.1 eV, lower than the shift of 4.2 eV experienced from bulk PAA. A fifth peak at a shift of 3.3 – 3.5 eV was added, indicative of carboxylate species (C₃a) and weak basic sites. On aluminium substrates it was reported that the five peak fitting strategy did not accurately represent the experimental results with asymmetry on the high binding energy side of the carboxyl component and so a sixth peak was employed. This sixth peak was fitted at a binding energy shift of 4.9 – 5.0 eV (C₄b), approximately 0.8 eV higher than that of the characteristic carboxyl component and is considered to represent strong basic sites as a result of nucleophilic
attack of the acyl carboxyl carbon from the oxidised substrate. The six peak strategy was also required for copper and nickel substrates. In the case of silicon oxide, however, the five peak regime was satisfactory, however the C<sub>4</sub>OOH component of the C 1s spectrum had a high binding energy shift of 4.3 eV, 0.1 eV greater than that observed in thicker films. This was considered to be indicative of hydrogen bonding and so representative of acidic sites on the surface.

The high resolution C 1s spectra generated from the respective coated HDGS substrates, in this project, were peak fitted following Leadley’s methodology. As with Leadley’s work, extra peaks were required, in addition to the peaks present from bulk PAA, to achieve good agreement with experimental data and in all cases the six peak fit regime was necessary. The peak at a binding energy shift of 1.7 eV (C<sub>3</sub>-O) indicative of damage was always required although kept to acceptably low level.

For each sample the carboxyl component contained three peaks only two of which were indicative of interaction between the PAA and substrate, the C<sub>3a</sub> (weak base) and C<sub>4a</sub> (strong base), the main C<sub>4</sub>OOH component is representative of the bulk PAA only and not characteristic of any interaction. Whilst both zinc and aluminium are both amphoteric, diagnosis of acid-base sites using the thin film technique has only identified basic sites including strong basic sites. The percentage of each components interaction, C<sub>3a</sub> (weak base) and C<sub>4a</sub> (strong base), was calculated without taking into account the C<sub>4</sub>OOH component, this was to ensure that any possible variation in thickness of polymer film did not effect the relative intensities of the interacting components. The calculations were made using the peak areas. Three of the fitted spectra are shown in Figure 4.15 and visually there is a noticeable difference between the proportion of strong and weak basic sites as the percentage of aluminium increases.
Figure 4.15. A comparison of the C1s spectra of thin film of PAA on: (a) as received HDGS 13 atomic % Al (b) alkali cleaned HDGS; 5 atomic % Al (c) alkali cleaned HDGS; 0 atomic % Al. C3a = weak base interaction, C4a = strong base interaction, (C3-O) = damage to PAA and C4OOH = carboxyl group indicating no interaction.
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<table>
<thead>
<tr>
<th>Sample Number</th>
<th>1 as received HDGS</th>
<th>2 Akali cleaned</th>
<th>3 Alkali cleaned</th>
<th>4 Alkali cleaned</th>
<th>5 Zinc Foil</th>
<th>6 ion etched</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of aluminium / atomic %</td>
<td>13</td>
<td>10</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 4.16. Graph showing the relative percentage of strong and weak basic sites on HDGS as a function of concentration of aluminium.

The graph plotted in Figure 4.16 shows how the relative percentages for weak and strong basic sites vary with a change in the surface concentration of aluminium in HDGS. As the concentration of aluminium decreases so does the percentage of the strong basic interaction sites. This trend seems to suggest that the presence of aluminium plays a significant role on acid-base properties of HDGS, resulting in an increase in the number of strongly basic sites. It should be noted, however, that even with zero percent aluminium (after adequate alkali cleaning) strong basic sites do exist (44%) although weak basic sites dominate (56%).

4.5. Effect on Aluminium on the phosphating of HDGS

This project is predominantly concerned with the failure mechanism of adhesively bonded HDGS, treated with a phosphate conversion coating, and so with the heterogeneous nature of the HDGS in this project realised the effect of aluminium on
phosphating was investigated. The phosphating process, described in Chapter 2, actually involves metal dissolution and so if alkali cleaning had left a small amount of aluminium on the surface it may be removed on phosphating, however the coating rate is known to depend on many variables including type of metal and grain boundaries. So, whilst remaining aluminium may be removed during the acid attack it has been reported aluminium actually inhibits the metal dissolution and formation of the phosphate coating.

The same panels that were used to produce the samples for the acid-base investigation were phosphated (Table 4.3). XRD and SEM analysis was carried out on samples of differing aluminium concentration. A standard Philips diffractometer with a thin film analyser was used to perform glancing incidence X-ray diffraction (GIXRD) on three phosphated panels, as received HDGS, 13% aluminium on HDGS and aluminium sheet. Scans were collected for each panel analysed over a range of $10^\circ < 2\theta < 60^\circ$ with $\theta$ fixed at $0.2^\circ$ incidence angle using copper radiation. All results obtained indicate that the phosphate exits in the form of hopeite, $\text{Zn}_3(\text{PO}_4)_4\cdot 4\text{H}_2\text{O}$.

SEM analysis was carried out using a Hitachi S-3200N in the full vacuum mode, samples were gold coated and a primary beam potential of 20 KV was used. As with the GIXRD little difference was observed between the crystal formation of the as received and alkali cleaned HDGS with a surface aluminium concentrations of 13 and zero atomic percent respectively. Figure 4.17 (e) shows that phosphating of the aluminium sheet was not uniform. This looks as if it was connected to the scratched condition of the interface that presumably existed prior to phosphating and may not be related to the actual phosphating procedure. Closer inspection of the phosphated aluminium, Figure 4.17 (f), reveals quite a different morphology than the crystals on the phosphated zinc, with a much larger plate like structure. The presence of aluminium on the as received HDGS does not seem to have had a significant effect on phosphate formation with the SEMs in Figures 4.17 (c) and (d) both showing the acicular structure that is characteristic of hopeite crystals.
4.6. Pretreatments Used in this Study

Four pretreatments have been considered within this project, three of them are commercially available and are therefore surrounded by the usual constraints pertaining to commercial confidentiality. The fourth is the subject of development within this project and is fully described in Chapter 5. The alkali cleaning has been used on its own to provide a clean and homogeneous zinc surface. The efficiency of
the process has been discussed earlier in this chapter and if used correctly complete removal of surface segregated aluminium is possible.

The alkali cleaning stage has been used as a precursor to all the other pretreatment systems employed in this project. As with adhesion the presentation of a chemically homogeneous surface to a potential pretreatment is highly desirable. Phosphating has been used in conjunction with a dry in place chromate treatment. The performance of this substrate system has been the main focus of durability studies carried out in this project. Chromating is a widespread method providing a coating based on hexavalent chromium and trivalent chromium. The dry-in-place chromate treatment is applied by immersion of an object in an acidic hexavalent chromium solution. Acid attack involving slight dissolution of the substrate is required for deposition and the hexavalent chromium is reduced to trivalent chromium, which forms $\text{Cr(OH)}_3$ passivation films. Comparative durability studies were carried out with a mixed oxide chrome rinse pretreatment. A strip of HDGS is alkali cleaned, rinsed and immersed in the pretreatment bath at 60°C. The mixed oxide pretreatment comprises of Co, Ni and Fe and acts as an adhesion promoter and a barrier to hostile environments. The deposition process occurs by alkali etching of the surface. The HDGS strip passes through the pretreatment at a speed of 100 ft / min resulting in a treatment time of approximately 15s. After another rinse stage the strip passes through a chrome rinse stage once again employed for corrosion inhibition. The pretreatments introduced above are not environmentally friendly; phosphating can generate toxic waste and it is becoming increasingly likely that environmental legislation will severely restrict the use of hexavalent chromium in the not too distant future.

The requirement for the development of environmentally friendly pretreatments is reflected in this project by an initial investigation into the use of yttrium on HDGS. Deposition of yttrium onto HDGS takes place as a result of aqueous corrosion and any waste products generated are not hazardous to the environment. In the next chapter optimum conditions for deposition of yttrium on alkali cleaned HDGS are determined and the durability of yttrium pretreated joints are investigated.
4.7. Concluding Remarks

There are many additives that can be used in the hot dip galvanising of steel, which have the potential to alter the surface properties and thus affect adhesion characteristics. The surface of the HDGS used in this study has been characterised by surface analysis techniques. On the as received substrate zinc and aluminium were detected, with aluminium actually present at the surface in greater concentration than zinc. Aluminium was expected, added to prevent the growth of a brittle Fe-Zn intermetallic, and Auger microscopy has shown that it is concentrated at the grain boundaries. The aluminium surface contamination of HDGS has, in the past been correlated with poor adhesion performance [109] and the poor durability of galvanised steel in wet weather [46]; often a pretreatment procedure such as alkali cleaning is sufficient to remove surface segregated aluminium. It has been shown however, that the alkali cleaning procedure used in this study was not consistent, and that the water break test, employed by British Steel Strip products, is not a suitable method of surface characterisation (it is not capable of indicating the removal of aluminium). Cleaning times will be dependent on factors such as the degree of hydrocarbon contamination and concentration of surface aluminium and so will vary, although a cleaning time of 150 s was found to remove aluminium on every occasion.

The affect of aluminium on the acid-base properties of HDGS were investigated by using thin films of PAA to chemically probe the surface. Aluminium and zinc are generally considered to be amphoteric, however only basic sites available for interaction with PAA have been identified. The proportions of strong to weak basic sites were, however, related to the concentration of aluminium, as the concentration of aluminium increases so do the number of strong basic interaction sites. Despite these observations the presence of aluminium was found to have no effect on the crystal structure or morphology of phosphate crystal on HDGS, it’s possible that the acid attack nature of the procedure actually aids the removal of any excess aluminium. Whilst it has been reported that aluminium can play a deleterious role in the durability of adhesively bonded HDGS and shown here that it does dictate, to a certain extent the adhesion characteristics, no aluminium was identified on fracture surfaces throughout the durability studies. This infers that the alkali cleaning stage completely
removed all surface contaminating aluminium or that aluminium plays no role in subsequent failure mechanisms allowing surfaces of the HDGS substrates to be considered as zinc.

<table>
<thead>
<tr>
<th>Substrate\pretreatment systems used in the study</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.4. The pretreatment and substrates used in this study.
Chapter Five

The Development of a Novel Environmentally Friendly Pretreatment: The Deposition of Yttrium on HDGS

5.1. Introduction

In Chapter 4 the importance of the efficacy of the alkali cleaning stage of the HDGS substrate was discussed. If the optimum conditions are not employed a heterogeneous surface (i.e. composed of zinc and aluminium rich areas) will result, with its attendant implications on polymer adhesion. Often, acceptable long-term bonding requires modification of the surface with metal pretreatments being essential to provide durable performance, acting as both an adhesion promoter for the organic phase and additional corrosion resistance [110].

Some of the most widely used pretreatments utilise hexavalent chromium (Cr$^{6+}$) compounds applied as conversion coatings or rinse treatments. While such processes may increase the corrosion resistance of metal surfaces, they have a very serious drawback. Chromium associated with both chromium treatments and water rinses cannot be removed cost effectively, exposing toxic Cr$^{6+}$ to the environment and consequently creating a serious pollution problem [111]. Phosphate conversion coatings (sometimes in conjunction with a chrome containing post rinse) have traditionally been used in the coating industry, however, a potential disadvantage for their use in adhesive bonding has been that their thickness can typically be in the order of micrometers deposited as a porous layer of acicular crystals [112]. When one
considers that adhesion is generally concerned with the outer most atomic layers of an interface this thickness is relatively large and can, potentially offer an additional fracture path for failed adhesive bonds via a weak boundary layer, particularly at the basal plane as referred to in Chapter 2. Over the past decade alternative pretreatments using rare earth metals, such as yttrium, often in conjunction with silane coupling agents have been investigated and shown that an increase in bond strengths for dry and water immersed lap joints are attainable [110]. Work by Cayless has shown, for mild steel substrates, that as well as being environmentally friendly such rare earth metal treatments can produce a much thinner layer than conventional pretreatments, the order of nanometers have been quoted [112], potentially making them well suited for adhesive bonding.

Davis continued Cayless’ work establishing an understanding of the local electrochemical processes that leads to the deposition of cationic yttrium on heterogeneous surfaces, such as mild steel, which contain defects like inclusions [113]. The work carried out by both Cayless and Davis concentrated on steel, however, Cayless has suggested that rare earth pretreatments may be applicable to other metal substrates such as aluminium and zinc. In this chapter the use of an yttrium pretreatment system for adhesively bonded HDGS has been investigated. Quantified XPS data and scanning Auger microscopy have been used to ascertain the optimum deposition conditions and uptake characteristics from solutions of yttrium nitrate. Substrates pretreated in this way are then used to fabricate adhesive bonds and exposed to environmental degradation. Failure mechanisms of the aged joints have been subsequently investigated in order to determine the suitability of yttrium as a pretreatment for HDGS.

5.2. The Driving Force for the Deposition of Yttrium

Aqueous corrosion processes are often the result of local electrochemical cells being set up on a substrate surface. Small local anodic and cathodic sites may exist due to heterogeneity’s or impurities of a surface, such corrosion cells may only generate low corrosion currents and so usually result in general attack of the entire metallic substrate. Care must be taken, however, where permanent small anodes exist on a
surface, for example inclusions in iron, which may act as precursors to pitting, can lead to far more serious and detrimental corrosion as implied by the catchment area principle. The rate of corrosion is dependent upon the total anodic current and its intensity is proportional to the anodic current density. The total anodic reaction equals the total cathodic reaction since electrons cannot be stored. The potentially dangerous combination of electrode areas is, therefore, a large cathode and a small anode. This is the catchment area principle and conversely a far safer situation exists where a large anode and a small cathode are present.

Figure 5.1. Pourbaix diagram for yttrium showing that yttrium oxide is unstable in an aqueous environment and will be hydrated to its hydroxide spontaneously [114].

Cathodic deposition of yttrium is known to occur as a result of localised pH excursions during cathodic reactions, this is due to an increase in concentration of hydroxyl ions, a product of the cathodic reaction [114]. A Pourbaix diagram summarises the thermodynamic data, plotting electrode potential against pH and thus defining regions in which various ions and products are stable. Although they are theoretical, concern pure metals and do not take kinetics into consideration, Pourbaix diagrams do give an indication of the corrosion behaviour of a metal in water and so can often be used to define electrodeposition conditions. Studying the Pourbaix diagram for yttrium, shown in Figure 5.1, it can be seen that yttrium is generally
unstable in the presence of aqueous solutions of any pH with a very low equilibrium potential, -2.5 V \[114\]. It is also noticeable that, depending on concentration, yttrium is stable as a hydroxide above a pH of 6.5 as yttrium oxide is spontaneously converted to its hydroxide in the presence of water.

Cayless has shown that yttrium can be deposited onto steel surfaces from a dilute solution of aqueous yttrium nitrate, however, no explanation for the exact mechanism of deposition was given. Davis continued the work by investigating the nature of deposition in an attempt to confirm that the uptake of yttrium is corrosion driven and not just an example of physisorption \[113\]. Three surfaces of varying reactivity were exposed to yttrium nitrate solution with the concentration of yttrium monitored using XPS. Davis reported that the deposition of yttrium depended on the reactivity of the substrate and so was indeed electrochemically driven, Table 5.1.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Concentration of yttrium (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>12.0</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>2.2</td>
</tr>
<tr>
<td>Glass</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 5.1. The effect of substrate reactivity on yttrium deposition \[113\].

After each pretreatment Davis rinsed his samples in water in an attempt to remove any physically absorbed yttrium, this technique was shown to be adequate as analysis of the glass sample revealed zero uptake of yttrium.

Having confirmed the role of electrochemistry associated with the uptake of yttrium Davis went on to show coverage of yttrium was not uniform using XPS, imaging Auger and SIMS. Cathodic areas immediately adjacent to local anodes indicated back deposition of iron oxides on top of the yttrium, this resulted in non-uniform coverage. In terms of a pretreatment for adhesive bonding this potentially causes problems, possibly offering preferential sites for bond degradation.
For the purposes of this study optimum conditions for the deposition of yttrium on HDGS had to be determined. This involved establishing the kinetic and concentration parameters for the uptake experiments. The coverage of the modified oxide layer was also investigated using AES.

5.3. Experimental

10 mm diameter discs were punched out of alkali cleaned HDGS, details of the alkali cleaning procedure were described in the previous chapter. Yttrium was deposited by dipping the HDGS discs into solutions of yttrium nitrate at the chosen concentration for a fixed amount of time with deposition being allowed to take place at the free corrosion potential. As already mentioned a wash treatment after dipping is required to remove any physisorbed yttrium species and discs were rinsed for 30s in milli-Q water after exposure to the yttrium nitrate solutions and dried using a metalographic dryer to avoid water stains. These uptake experiments were in keeping with the early work of Cayless and the subsequent work of Davis [112, 113].

The yttrium nitrate (Y(NO₃)₃) solutions were made using milli-Q water to reduce contamination and adjusted to pH 7 by adding dropwise quantities of NaOH. Adjustments were made to solution pH prior to dipping as initial pH values of the solution varied considerably with concentration, Figure 5.2. The optimum deposition conditions were determined by carrying out a series of experiments to establish kinetics of uptake and concentration effects of the dipping solutions, the results of these experiments are discussed the next section.
Standard XPS analysis was carried out to determine the uptake of yttrium using the VG Scientific ESCALAB Mk II. Aluminium Kα radiation was used with resultant spectra quantified using Wagner sensitivity factors to determine surface composition. Auger images and spectra were acquired to analyse coverage of the yttrium pretreatments with a VG Scientific MA500 scanning Auger microscope. Point analysis and maps were obtained with a beam of 12 kV at 10 nA with the maps acquired at x 250 magnification and a (P-B)/B algorithm used to correct for topography. EDX was also acquired, allowing surface and bulk information to be collected simultaneously and some comment to be made on thickness of the yttrium layer.

5.4. Deposition Characteristics of Yttrium on HDGS

5.4.1. Characterisation of an yttrium pretreatment on HDGS

For optimum deposition conditions to be realised a series of uptake experiments were carried out, as briefly mentioned in the previous section. The aim of these experiments was to establish the kinetics of deposition, by fixing the concentration of the pretreatment solution and varying dip time, and the concentration at which the most yttrium was deposited, by this time fixing dip time and varying concentration of
the respective solutions. This was intended to produce uptake curves, similar to adsorption isotherms, from which optimum deposition conditions could be determined. Surface composition was determined by quantifying large area XPS spectra. A typical survey spectrum of HDGS treated with yttrium nitrate is shown in Figure 5.3. Yttrium peaks are clearly visible, for example the 3d electrons at 161 eV, indicating that some uptake has occurred. Zinc substrate peaks are also present, suggesting that yttrium is either deposited in a very thin layer allowing characteristic zinc electrons to be excited with no significant energy loss or that yttrium coverage is not uniform leaving bare patches of zinc to be detected. Surface concentration of carbon is low, at approximately 35 atomic %, indicating the cleanliness of the process; Davis attributed this to the use milli-Q water and found much larger carbon peaks as a result of contamination were obtained with "normal" laboratory water [115]

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Zn</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (Atomic %)</td>
<td>35.7</td>
<td>51.7</td>
<td>4.5</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Figure 5.3. A large area XPS survey spectrum of HDGS showing characteristic yttrium peaks found when HDGS is placed in a Y(NO₃)₃ solution.

Examination of the core level spectra in Figure 5.4 (c) shows the 5/2 and 3/2 components of 3d yttrium doublet clearly at around 161 eV. Information concerning the nature of deposited yttrium can also be gained by studying the background, for example analysing the post peak slope (PPS) of the spectrum. After the yttrium 3p
doublet at 301 eV and 313 eV a negative PPS is observed implying that yttrium is present as a surface phase, this is further supported as the background through the zinc LMM Auger peaks has a positive slope suggesting that the zinc maybe buried. Caution must be taken with the later observation, however, as no noticeable increase in background is noticed after the zinc 2p doublet. The high resolution oxygen 1s, Figure 5.4 (b) on the other hand appears as a symmetrical peak with no shape indicating the existence of one component. By charge referencing the C-C component of the carbon peak to 285 eV (a shift of -2.61 eV) the adjusted oxygen 1s line falls at 531.8 eV, the position for a hydroxide component an oxide component would be expected at a lower value around 529.5 eV [108]. According to the Pourbaix diagram yttrium was expected to deposit as a hydroxide and this seems to be confirmed by the core level spectra. Considering the C 1s core level spectrum there is a noticeable component at a binding energy shift of approximately 4.2 eV from the main C-C peak and may well be indicative of a carbonate, Figure 5.4 (a). The yttrium pretreatment solution may be susceptible to the absorption of carbon dioxide from the atmosphere resulting in the formation of a carbonate corrosion product. The carbonate component of the O 1s line is coincident with the hydroxide component and thus explains the lack of observed shape in Figure, 5.4 (c).
Figure 5.4. High resolution XPS spectra from yttrium treated HDGS; (a) C 1s, (b) O 1s, (c) Y 3d and Zn 2p.
5.4.2. Determining Optimum Deposition Conditions

In order to establish the kinetics of uptake an initial solution concentration had to be chosen. Davis’ work, using iron as the substrate, had deposited yttrium at a concentration of $10^{-4}$ M and so this concentration was used to determine the optimum time for an yttrium deposit on HDGS. With an iron substrate the kinetics of deposition are rapid with values of 1 atomic percent deposited after just half a second and a plateau of 12 atomic percent reached after only 30 s. Initially, following Davis’ protocol short treatment times were used, however very low yields of yttrium were detected, for example only 0.4 atomic percent after 30 s. Consequently, much longer dip times than those required for iron were used and the results for 4, 6, 8 and 10 minutes are plotted in Figure 5.5. Even after 10 minutes a plateau for the uptake of yttrium had not necessarily been reached and so additional experiments for 15 and 30 minutes were necessary to confirm that an adsorption plateau had been reached after 10 minutes of treatment time.

![Graph showing the uptake of yttrium](image)

Figure 5.5. Graph showing the uptake of yttrium (deposited from an yttrium nitrate solution of fixed concentration) on cleaned HDGS against treatment time.

Davis determined that the deposition of yttrium on iron was driven by electrochemical reactions, with defects at the substrate surface, such as inclusions acting as anodes allowing the surrounding surfaces to behave cathodically and yttrium to deposit. The surface of HDGS does not display inclusions that can act as precursors...
to local anodic activity, which may explain the longer treatment times required to reach the maximum uptake of yttrium. Whilst the kinetics of deposition for HDGS are much slower than reported for iron a plateau for yttrium uptake is reached after 10 minutes and this treatment time was used to determine the optimum concentration for the rare earth pretreatment i.e. the experiments were repeated this time varying concentration with a fixed treatment time.

![Graph showing the uptake of yttrium on cleaned HDGS against concentration of yttrium nitrate pretreatment solution.](image)

Figure 5.6. Graph showing the uptake of yttrium (deposited after a fixed treatment time of 10 minutes) on cleaned HDGS against concentration of yttrium nitrate pretreatment solution.

A plot of yttrium uptake against concentration of the pretreatment solution shows that concentration plays a strong role in the deposition characteristics, Figure 5.6. Unlike the time dependent data a plateau does not appear to be realised with maximum uptake (9.2 atomic percent) achieved at a concentration of $10^{-2}$ M, surprisingly this was followed by a reduction in the uptake of yttrium to approximately 8 atomic percent from a $10^{-1}$ M solution. Due to time constraints it was not possible to investigate this phenomenon further, however, Davis’ work discussed the possibility of back deposited substrate material over already pretreated areas, this could possible explain a drop off in detected yttrium at the higher concentration of treatment solutions. Although for this to be the case a reduction in yttrium uptake would also be expected in the time dependent graph. Considering the results shown in Figures 5.5 and 5.6 the optimum conditions for the uptake of yttrium have been taken as 10 minutes treatment time in $10^{-2}$ M solution of yttrium nitrate. With the optimum conditions of the
5.4.3. Yttrium Coverage on HDGS

The mechanism for the uptake of rare earth metal ions is known to be electrochemically driven, relying on the existence of local anodes and cathodes. In the case of iron the presence of inclusions, whilst aiding the deposition process, is responsible for a non-uniform coating, the yttrium not covering anodic sites. To investigate the coverage of yttrium on HDGS, Auger imaging was employed; energy dispersive X-ray analysis (EDX) with an analysis depth in the order of one micrometer as opposed to the nanometers offered by AES, was simultaneously carried out. A series of point analyses were initially carried out to establish relevant regions of interest to image i.e. characteristic yttrium and zinc regions. The spectrum in Figure 5.7 shows a typical spectrum acquired from yttrium treated HDGS, with carbon at 263 eV. Oxygen is found at 503 eV, the characteristic peak for imaging yttrium is at 1730 eV (Y LMM) at the particular point of analysis the zinc contribution is very low indicated by the Zn LMM peak at 990eV.

![Auger spectrum of yttrium deposited on HDGS showing the characteristic LMM peaks used for scanning auger microscopy.](image)
Chapter Five: The Development of a Novel Environmentally Friendly Pretreatment: The Deposition of Yttrium on HDGS

Imaging at a magnification of x 250, giving a 160 x 160 μm field of view, identified a patchy yttrium coating, Figure 5.8. The yttrium and zinc maps, Figure 5.8 (a) and (c) respectively, are complementary showing yttrium rich areas where concentration of zinc is low and intense zinc regions in areas of depleted yttrium. The oxygen image corresponds with the yttrium image with apparent oxygen free areas filled by the intense zinc regions, the intensity and size of the zinc regions may well be defining local anodes that may ultimately be responsible for yttrium deposition. An EDX spectrum taken from the same area shows an intense yttrium peak indicating that a relatively thick layer of yttrium had been deposited, Figure 5.9. One of the original intentions of using a rare earth metal pretreatment, however, is to provide a thin film coating in the order of nanometers. It is unlikely that oxygen free areas exist, however, one of the disadvantages of imaging is that a threshold concentration must be detected in order to register signal in a pixel. A low surface concentration of an element may not reach the lowest threshold and so appear not to exist on a resultant pixel of an image. The zinc rich areas of Figure 5.8 may well identify anodic areas which during the deposition process, will exist as clean zinc. On withdrawal from the yttrium nitrate solution the clean zinc rich areas will oxidise spontaneously, due to the thermodynamic driving force to reduce the surface free energy. The fresh zinc oxide, however, may only exist as a thin layer and the required threshold for the imaging of oxygen may not be met thus giving the impression that denuded areas of oxygen exist and are coincident with zinc rich areas as in Figure 5.8.

Figure 5.8. Auger images demonstrating the deposition characteristic of yttrium on HDGS.
The EDX spectrum of Figure 5.9 infers that, in the case of yttrium on HDGS, a thick coating is formed. The situation could potentially be detrimental for adhesive bonding, for example depending on the cohesive strength of the pretreatment, it may act as a weak boundary layer. The effect, if any of a relatively thick, heterogeneous coating would be examined throughout the durability study which set out to determine whether an yttrium treated HDGS provides resistance to bond degradation in a hostile environment.

5.5. The Failure Mechanisms of Adhesively Bonded Yttrium Treated HDGS

The HDGS substrate used was 1.2 mm thick, alkali cleaned, using Novamax 187 U and pretreated in a $10^{-2}$ M yttrium nitrate solution for 10 minutes, as described in the previous section. Single lap shear specimens were fabricated from 110 mm by 20 mm coupons with an overlap of 10 mm. A polybutadiene sealant adhesive (Evode M33) was used and glue line thickness set at 250 µm using glass ballotini during fabrication. M33 was an adhesive of known formulation and is discussed more detail in Chapter 7 (where the formulation is shown in Table 7.1) [116]. The joints were aged for 8 months at 35 °C in 95% relative humidity and then mechanically tested using a 1195 Instron machine with a 5 kN load cell at a cross head speed of 5 mm
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The Development of a Novel Environmentally Friendly Pretreatment: The Deposition of Yttrium on HDGS

Analysis of the failed joints was carried out using a VG Scientific ESCALAB Mk II spectrometer in the constant analyser energy (CAE) mode with Al Kα X-ray radiation.

The durability study of the yttrium pretreated HDGS was run in parallel with unpretreated (control) and phosphated HDGS joints. Durability results from these systems may be mentioned briefly although the majority of discussion will concentrate on the yttrium system, the failure mechanisms of the control and phosphate systems are reported at length in Chapters 6 and 7. The photograph in Figure 5.10 displays the visual failure characteristics of a dry adhesive bond and it appears to fail interfacially across the entire overlap area between the substrate and the adhesive. An interfacial failure for a dry joint generally reflects extremely poor bond performance and does not bode well for bond durability. The other substrate systems failed cohesively through the adhesive in the dry state (not exposed to accelerated ageing).

Figure 5.10. Photograph showing the failed interfaces of an exposed (dry) yttrium treated HDGS adhesive bond.

The visual failure characteristics of the subsequently aged joints are virtually identical to that of dry joint and it seems reasonable to assume that the mechanisms of failure for the system is related to the pretreatment. It is very rare for a genuine interfacial failure to occur and with the knowledge that thickness of the yttrium coating may be in the order of micrometers failure through the coating is a plausible explanation. The sizes of the (visually) metal and polymer areas of the failed interfaces were

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sufficiently large for standard area XPS to be carried out. Survey spectra acquired from the dry joint and a 7 month aged joint are shown in Figures 5.11 and 5.12 respectively.

Figure 5.11. Survey spectra acquired from the failure surfaces of yttrium pretreated HDGS dry joint (a) adhesive side (b) metal side.
Figure 5.12. Survey spectra acquired from the failure surfaces of yttrium pretreated HDGS aged for 7 months at relative humidity (a) adhesive side (b) metal side.

Figure 5.11 (a) describes the failure path from the dry joint, the polymer side shows a spectrum characteristic of the polymer with a very intense C 1s peak (93 atomic %) and calcium and sulphur peaks known to be from the adhesive. The most noticeable difference between the failed interfaces is the presence of yttrium on the metal side, Figure 5.11 (b), indicating failure between the yttrium coating and polymer adhesive. There is an indication of adhesive present on the metal side, Ca2p and S 2p, however yttrium coverage is known to be patchy and traces of adhesive may exist on the metal side as a result of adhesion within areas devoid of pretreatment. The C 1s line is lower than for the polymer side of the joint (58 atomic %) and is accompanied with a more intense oxygen peak, more indication that the failure interface is dominated by
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metallic areas. Spectra from the seven month sample, Figure 5.12 (a) and (b), provide a similar locus of failure with an interfacial failure being observed at the yttrium/adhesive interface. The other two substrate systems (alkali cleaned and phosphated) both fail cohesively through the adhesive, for the most part, however in the case of an yttrium pretreatment an interfacial locus of failure is observed. The seeming lack of low level residual adhesion between yttrium pretreatment and adhesive has a severe effect on the overall joint strength/performance. This is reflected in the mechanical data shown in Figure 5.13, which compares the yttrium treated HDGS to the unpretreated HDGS, which, as already mentioned will be discussed in more detail later in the thesis.

![Graph comparing durability performance of control joints and yttrium pretreated joints](image)

Figure 5.13. Graph comparing the durability performance of control joints and yttrium pretreated joints.

5.6. Concluding Remarks

The use of yttrium as a rare earth metal pretreatment system for adhesively bonded galvanised steel has been investigated. The nature of the deposit and conditions for maximum deposition of yttrium on HDGS has been determined. By analysing high resolution XPS spectra it has been found that yttrium decorates the galvanised steel substrate as a hydroxide and this result is constant with the yttrium Pourbaix diagram. The deposition of yttrium is known to be electrochemically driven and so the rate of
uptake will depend on the substrate and its condition. The kinetics for deposition on HDGS are much slower than those reported by Davis for iron, with a plateau only being reached after 10 minutes as opposed to 30 s at concentration of approximately 8 not 12 atomic percent. The concentration that yielded the largest surface concentration of yttrium was $10^{-2}$ M, increasing the concentration to $10^{-1}$ M actually saw a reduction in the amount of yttrium deposited onto HDGS.

Coating coverage was examined using Auger microscopy and was found to be heterogeneous with very intense zinc spot in areas devoid of yttrium, possibly identifying anodic sites. The deeper analysis technique of EDX shows a strong yttrium peak suggesting that yttrium is present at a thickness in the order of micrometers not nanometers as implied in the literature. The deposition of yttrium as a thick layer calls into the question the maximum uptake conditions being considered as the "optimum" conditions for yttrium on HDGS. The distinction between maximum uptake (surface concentration) and coverage should be considered and if "optimum" conditions are thought to be maximum coverage (possibly resulting in a thinner yttrium layer) shorter treatment times may be adequate.

Despite forming a thick coating a durability study carried out on yttrium treated HDGS bonds has shown that failure does not occur through the coating but at the coating/adhesive interface. In terms of future use of yttrium as a pretreatment this is not promising, although there are possibilities; an alternative adhesive may yield improved durability performance and there has been evidence that yttrium coupled with a silane adhesion promoter gives encouraging results [110, 113]. In the context of this project an yttrium pretreatment was developed and shown to give poor durability results with the mechanisms of failure defined. The next two chapters concentrate on the performance of a more traditional pretreatment, phosphating. As with the yttrium system a durability study has been carried out with surface analysis used to determine the failure mechanisms, however unlike the yttrium samples standard area XPS was not sufficient to give a complete picture and complementary surface analysis techniques have been used in novel and challenging ways to help understand the adhesive bond systems under examination.
Chapter Six

The Forensic Analysis of Failed Joints by ToF-SIMS

6.1. Introduction

As discussed in Chapter 2, one of the most important requirements of an adhesive joint is the retention of strength during its service life. Durability is a key issue in the widening use of adhesive bonding technology and is a problem that has been discussed by many authors. Dickie and co-workers have studied, in detail, the degradation of HDGS establishing that electrochemical activity was responsible for regions of interfacial failure [32, 49]. Electrochemical activity at an interfacial site in an iron substrate system has also been reported with cathodic delamination found responsible for a true interfacial failure [33].

This chapter predominantly reports a surface analysis investigation carried out by ToF-SIMS. The study was instigated by preliminary XPS analysis of the failure surfaces of aged, adhesively bonded, HDGS fabricated using a structural epoxy in a lap joint configuration. Pretreated HDGS joints show areas of apparent interfacial failure, however, these regions are limited to thin strips at the ends of the overlap and for the purposes of this study have been termed initiation zones. These initiation zones seem to be a result of environmental exposure and appear to act as initiation sites for crack propagation on mechanical testing, acting as "notch like" features. A diagnostic methodology for ToF-SIMS imaging within these initiation zones has
been developed with a view to establishing the role of electrochemical activity in the initial degradation of HDGS joints. Imaging ToF-SIMS, if used in the correct manner, may aid the diagnosis of failure, by providing a two-dimensional chemical visualisation of the failure. The current study highlights the ability of ToF-SIMS to not only provide mass-selected images of diagnostic electrochemical ions but also to map characteristic molecules and mass fragments from the adhesive and sets out to establish a protocol for ToF-SIMS imaging, for the analysis of the failure surface of adhesively bonded lap joints of a HDGS/epoxy system.

6.2. Experimental Details

6.2.1. Materials
Single lap shear specimens were fabricated from 110 mm by 20 mm coupons with an overlap of 10 mm. Two HDGS substrate systems were employed; alkali cleaned HDGS, as the control system, and a substrate treated with a phosphate conversion coating followed by a chrome rinse. A commercial epoxy adhesive (3M 7823) was used and glue line thickness set at 250 μm using glass ballotini. Whilst the exact formulation of the adhesive is not revealed by the manufacturer, the safety data sheet indicates the adhesive is epoxy based (Diglycidyl ether of Bisphenol-A, DGEBA) with fillers, amorphous silica and strontium chromate presumably as a corrosion inhibitor, more detail is given in Table 6.1. The joints were aged for 12 months at 35°C in a 95 % relative humidity chamber and then mechanically tested using a 1195 Instron machine with a 5 kN load cell at a cross head speed of 5 mm min⁻¹.
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### Component of adhesive Composition (%)

<table>
<thead>
<tr>
<th>Component of adhesive</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epichlorohydrin-bisphenol A (Base resin)</td>
<td>40-45</td>
</tr>
<tr>
<td>Resin Fillers</td>
<td>20-25</td>
</tr>
<tr>
<td>Methacrylate-butadiene-styrene Resin</td>
<td>9-11</td>
</tr>
<tr>
<td>Aliphatic glycidal ether</td>
<td>5-10</td>
</tr>
<tr>
<td>Epoxy resin-ester adduct (plasticiser)</td>
<td>1-10</td>
</tr>
<tr>
<td>Amorphoussilica (filler)</td>
<td>2-5</td>
</tr>
<tr>
<td>Strontium chromate (VI) (corrosion inhibitor)</td>
<td>2-3</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>1-2</td>
</tr>
<tr>
<td>3-(4-Chlorophenyl)-1,1-dimethylurea</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Table 6.1. Composition of the 3M commercial epoxy as given by the safety data sheet.

6.2.2. The Lap Shear Joint Configuration

The principal emphasis of this work is very much towards determining the failure mechanisms of adhesively bonded HDGS by the use of surface analysis. The lap joint configuration was chosen with this in mind, as it provides an excellent “as failed” surface, which is crucial for surface analysis. Other joint configurations such as double cantilever beams allow the failed surface to be exposed during ageing, thus contaminating the surfaces of the failed interfaces and hindering the search for the loci and mechanisms for failure. The joint is easy to make and the results are sensitive to both adhesive quality and adherend surface preparation. Lap shear joints, of similar adhesive systems as those employed in this work, were also on test in a parallel study at Welsh Technology Centre, British Steel, and so durability data generated throughout the course of the project could potentially be compared with other adhesive systems.

Lap joints, in which two sheets are joined together with an overlay, are the most commonly used configuration for durability studies, however their stress distribution
can be highly complex with the adhesive layer exposed to different stress concentrations within the overlap. The purpose of an adhesive joint is to efficiently transfer load from one adherend to another. This results in regions of stress concentration due to mismatches in material properties and changes in geometry across the joint. The fundamental complication with the lap joint design is that on mechanical testing, in wedge grips, the joint itself undergoes many different loading conditions, for example shear and tension.

Over the years numerous authors have contributed to the discussion on the overall stress analysis of a lap shear joint [117, 118]. Most of this work has been based on the early findings of Volkerson who first considered/allowed adherends to deform elastically, resulting in shear stress concentrations at the ends of the overlaps [119, 120]. Since this early work many other factors have been found to affect stress distribution in a lap joint, such as the directions of the applied force, plastic deformation of the adhesive and the presence of spew fillets [121, 122]. Nowadays detailed stress analyses are possible due to the development of finite element analysis, (FEA), techniques and significant advances in computer software. These techniques mathematically model stress analysis problems and, in theory, are capable of determining the stress in a body of almost any geometry. The choice of lap joint was made with the primary desire to yield useful surface analysis data and not to study fracture mechanics, although mechanical data has proved to be advantageous and complementary to certain conclusions reached by characteristic surface data and so beneficial to the overall study.

6.2.3. Surface Analysis

Standard and small area XPS and ToF-SIMS were used to study the failure surfaces of the lap shear joints. Standard area XPS analysis (5 x 2 mm diameter analysis area) was performed using a VG Scientific ESCALAB MkII using conventional Al Kα radiation whilst small area XPS (250 μm) was carried out using the VG ESCALAB 220iXL, the excitation source used was monochromatic Al Kα radiation. ToF-SIMS was carried out using a VG Scientific Type 23 instrument equipped with a 2 stage reflectron mass spectrometer and a 30 kV pulsed gallium liquid metal ion source. The
The VGX 7000 software which runs on a DEC PDP11/73 computer under a micro RSX operating system. ToF-SIMS line scans were constructed from spectra acquired across the initiation zone of the respective failed surfaces. All the SIMS data was normalised by dividing the intensity of the ion of interest by that of the total ion yield in the mass range m/z = 5 - 400. After carefully establishing the static limit for the adhesive system, mass selected images were collected to determine if certain ions were concentrated in particular areas, to allow their role in the failure mechanism to be determined.

6.3. Visual Assessment of Failed Surfaces

The visual characteristics of the failure surfaces after five months ageing for both substrate systems are shown in Figure 6.1. Visual examination of the failed joints immediately identifies differences in the failure mechanisms of the substrate systems.

![Figure 6.1. Photographs of failed HDGS adhesive bonds, (a) alkali cleaned HDGS and (b) phosphated HDGS.](image)

The control joint appears to have failed almost completely interfacially between the polymer and substrate, visually showing a metal and polymer side. Closer inspection of the failed interfaces, however, reveals white residue on both failure surfaces, this is characteristic of the zinc corrosion product and is often referred to as “white rust”. The phosphated sample on the other hand has failed cohesively through the polymer
adhesive. The failure characteristics of a phosphated joint aged for 10 months are also shown in Figure 6.2 with a schematic indicating the areas analysed given in Figure 6.3. It can be seen that the fracture path passes apparently at random through the overlap, with different routes being taken by the crack. With the joint shown in Figure 6.2 fracture has passed from close proximity of one substrate, to the other approximately half way along the overlap. Despite the differences in appearance of the failed phosphated joints they all displayed characteristic strips of visually interfacial failure at the ends of the overlap which have been described as the “initiation zone”.

By studying the formation of this so-called "initiation zone" it is hoped that an understanding of the initial bond degradation may be reached, consequently surface analysis was concentrated in this region during the study. A HDGS system may have the potential for extensive electrochemical activity to occur, with exposed iron acting as a cathode and protective zinc the anode, the penetration of the visually interfacial failure, however, is not as great as that observed in the case of classical cathodic delamination observed with pure iron substrates [33]. An initial assessment of the visual characteristics of the failed joints indicates that environmental degradation plays a role in the loss of bond performance as the size of the initiation zone is considerably larger in the 10 month joint.
Selected area XPS carried out in initiation zones and adjacent areas (A,B,C and D)  

SIMS lines scan – point analysis across initiation zone from X to Y  

Initiation zones  

A  

B  

C  

D  

Visually metal  

Visually adhesive  

Figure 6.3. A schematic representation of the failure of a lap shear joint, showing the positions of selected area XPS and ToF-SIMS line scan.

6.4. Standard and Small Area XPS

Standard area XPS spectra acquired from the failed interfaces of the control joint shown above are presented in Figure 6.4. The spectra are remarkably similar; the spectra of the metal side displaying an intense Zn 2p 3/2 peak at around 1021 eV with the adhesive side also showing strong characteristics of a zinc spectrum. With the presence of zinc on both sides of the failed surfaces it seems reasonable to conclude that failure has occurred through a zinc corrosion product which has acted as a weak boundary layer. This is to be expected as zinc will act as a sacrificial anode cathodically protecting any exposed iron, unfortunately this results in bond degradation with anodic dissolution of zinc producing a weak corrosion product.
These findings are in agreement with the results of various workers such as Dickie, Foister and van Ooij whose work was reviewed in Chapter 2.

The formation of, and subsequent failure through, a layer of zinc corrosion product has severe consequences on the performance of adhesively bonded alkali cleaned HDGS. As will be seen in Chapter 8 a reduction in performance of retained bond strength, one indication of durability, occurs after 7 months with joints actually falling apart on loading into the Instron machine after just 9 months.

Figure 6.4. Standard Area XPS survey spectra acquired from the failure surfaces of a 5 month RH aged lap joint, with both sides dominated by zinc corrosion product, (Thicker line = polymer side, thinner line = metal side).

Thus the failure mode of the control joints is straightforward, and the remainder of the chapter will concentrate on the analysis of joints prepared from conversion coated HDGS, i.e. the system known to provide good durability. XPS survey spectra were recorded from the locations identified in Figure 6.3 and are shown in Figure 6.5.

Table 6.2 indicates the quantified XPS results from areas of interest on the failed interfaces, identified in Figure 6.3. The spectra for the two initiation zones, A and C from Figures 6.3 and 6.5, show carbon at 47.5 % for the metal side and 66.2% for the
polymer side. More notably there were cations (Mg$^{2+}$ and Ca$^{2+}$) and anions (Cl$^-$) present in the initiation zones but not in areas adjacent to them. The presence of these cations was always associated with the low assay of carbon, indicative of the "metal" failure surface. This indicates that they are not markers for the adhesive, although they may have leached from the adhesive during the exposure to high levels of humidity and subsequently deposited on areas of cathodic activity. If they were merely indicative of a failure within the adhesive such ions would always be observed when the bulk of the adhesive is examined, but this is not the case. A more plausible source of the magnesium ions is the glass ballotini used to control glue line thickness. An XPS spectrum of this material is shown in Figure 6.6 along with the chemical analysis including some 4.2 atomic % magnesium. The role of ballotini in the overall mechanism of failure is discussed in more detail in Chapters 8 and 9.

![Figure 6.5](Image)

Figure 6.5. Selected area XPS analysis (250 μm diameter spot size) taken from the areas defined in Figure 6.3, with respective XPS quantification data presented in Table 6.2. (A) metal initiation zone, (B) visually polymer area adjacent to metal initiation zone, (C) polymer initiation zone and (D) visually metal area adjacent to polymer initiation zone.
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<table>
<thead>
<tr>
<th>Element</th>
<th>Metal initiation zone (A)</th>
<th>Adjacent polymer zone (B)</th>
<th>Polymer initiation zone (C)</th>
<th>Adjacent metal zone (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>47.5</td>
<td>69.9</td>
<td>66.2</td>
<td>55.6</td>
</tr>
<tr>
<td>O</td>
<td>33.3</td>
<td>23.2</td>
<td>22.3</td>
<td>33.0</td>
</tr>
<tr>
<td>Zn</td>
<td>5.1</td>
<td>1.9</td>
<td>1.5</td>
<td>4.1</td>
</tr>
<tr>
<td>N</td>
<td>4.5</td>
<td>3.0</td>
<td>8.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Si</td>
<td>2.1</td>
<td>--</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>P</td>
<td>6.2</td>
<td>2.03</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cl</td>
<td>1.2</td>
<td>--</td>
<td>1.1</td>
<td>--</td>
</tr>
<tr>
<td>Ca</td>
<td>Trace</td>
<td>--</td>
<td>Trace</td>
<td>--</td>
</tr>
<tr>
<td>Mg</td>
<td>Trace</td>
<td>--</td>
<td>Trace</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 6.2. Quantification of selected area XPS analysis taken from the areas shown in Figure 6.3.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Mg</th>
<th>Na</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (atomic %)</td>
<td>6.1</td>
<td>62.1</td>
<td>22.2</td>
<td>4.2</td>
<td>4.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Figure 6.6. Small area XPS survey spectrum (50 μm spot size) of argon ion etched ballotini.

The XPS analysis indicates that electrochemical activity has occurred within the initiation zone with evidence of cathodic and anodic sites existing at the interface. The carbon level, however, is higher than one would expect for pure cathodic delamination. This suggests that the development of the initiation zone was the
product of a conjoint effect of aggressive hydroxyl ions and water ingress. This may explain the high carbon concentration and possibly indicates a weakening of the interfacial bond and not actual separation prior to mechanical testing. Small area XPS analysis of the initiation zones was able to demonstrate that electrochemical activity is responsible for initial bond degradation. A reasonably high concentration of carbon was also detected, however, due to the lack of molecular specificity in XPS this may indicate either significant hydrocarbon contamination or the presence of residual polymer on the initiation zone interface. If an organic phase is present the area integrating nature of XPS is also unable to establish whether the remaining adhesive is localised (existing as an island like formation) or as an overlayer. ToF-SIMS, in principle has the potential to overcome these limitations of XPS and provide surface information concerning the presence of the organic phase at the initiation zone.

6.5. ToF-SIMS Analysis of Adhesive and Failure Surfaces

6.5.1. Introduction

In order to achieve the intended objectives of this chapter, the use of mass selected ToF-SIMS images as a diagnostic tool for the analysis of adhesive joint failure surfaces, a series of preliminary experiments were undertaken to ensure that all the potential limitations encountered in the static SIMS of a complex polymer system were considered and, if possible, circumvented. A series of thin film analyses were carried out to identify the characteristic peaks of the virgin adhesive. This was followed by a damage study to determine the static limit for the polymer system under consideration; acquiring mass selected images within the static limit ensures analysis of the unmodified specimen and that images are truly representative of the failed polymer surface. Point analyses were used to construct line scans across the initiation zone and to establish a protocol for the removal of surface topography in the presentation of mass selected data. Once these objectives had been met ToF-SIMS images could be acquired from the initiation zone of an aged lap shear joint.

6.5.2. Characterisation of the Adhesive

This was achieved by first studying the uncured adhesive. A controlled volume of a 1% w/w solution of the adhesive in acetone was dropped onto aluminium foil and the solvent allowed to evaporate. This yielded a thin polymer film that was not susceptible to electrostatic charging during analysis.
Figure 6.7. Positive ToF-SIMS spectrum of a 1 % (w/w) solution of Adhesive in acetone, characterising the adhesive and showing peaks at m/z 269, 252 and 191.

The resultant positive SIMS spectra are presented in Figure 6.7. and the expected ions from epoxy groups (at m/z = 191, 252, and 269) and bisphenol groups (m/z = 135 and 213) are seen, the relevant fragment patterns are shown in Table 6.3 and are in good agreement with the observations made in previous work on commercial materials of this type [96].
Table 6.3. Typical characteristic positive fragment ions of the epoxy type adhesive.

Whilst these ions are characteristic of the uncured adhesive, they may not be characteristic of the cured adhesive that will be present at the locus of failure of an adhesive joint. A comparison of the adhesive in its uncured and cured state was made by preparing specimens in which thin layers of polymer were smeared onto aluminium substrates, one was then heated at 180°C for 30 minutes in air to simulate cure. Spectra from the uncured sample showed traces of a siloxane present (probably poly(dimethyl siloxane), PDMS) with peaks at $m/z = 73$ and 147, whilst for the cured material these peaks were dominant in the spectrum, as shown in Figure 6.8.
Figure 6.8. Positive ToF-SIMS spectrum of the cured adhesive; dominated by characteristic PDMA peaks.

This observation prompted the question of whether the new peaks at $m/z = 73$ and $147$ were present as a result of polymerisation of siloxanes in the formulation as adhesion promoters or due to PDMS, to which SIMS is particularly sensitive and often appears in spectra of contaminated samples. In an effort to rule out contamination during cure the experiment was repeated using an exceptionally clean oven. Similar spectra were found for the two different curing environments, indicating that the source of the siloxane was from within the adhesive itself.

PDMS is widely used as a mould release agent and so on curing would have a propensity to segregate to a surface in an attempt to reduce the surface free energy of the system. If this is the case with our adhesive system we may not actually encounter the $m/z = 73$ and $147$ peaks at the concentration observed in the spectra of Figure 6.8 in the final analysis of the fractured lap shear joint. It was decided, therefore, to produce a simulated fracture surface to analyse the bulk polymer/adhesive. This was done by applying a thick smear of the adhesive onto a
metallic sample backing plate, usually used for mounting specimens. A circular cover plate was placed over the adhesive forcing a bulb of adhesive to rise, through the aperture in the plate. The adhesive was cured and a simulated fracture created by slicing through the base of the adhesive bulb, as indicated schematically in Figure 6.9. Analysis of the simulated fracture surface showed a dramatic reduction in the intensity of the PDMS peaks relative to ions assigned to bisphenol A and other characteristic adhesive components (e.g. $m/z = 91$ and 77) as shown in Figure 6.10. Comparison of the simulated fracture data with spectra from a cohesive fracture surface of a dry joint showed good agreement, confirming that peaks observed at $m/z = 73$ and 147 did not play a major role in the characterisation of an adhesive fracture surface. With the adhesive fully characterised with fingerprint spectra having been obtained, the next step was to determine the static SIMS limit for this material.

![Figure 6.9](image.png)

**Figure 6.9.** A schematic representation showing the steps involved in fabricating a simulated fracture surface, (a) smear excess of adhesive onto the metal backing plate, (b) place cover plate over the top forcing a bulb of adhesive to rise and (c) after curing, slice.
Figure 6.10. Positive ToF-SIMS spectrum of simulated fracture surface, showing the removal of siloxane peaks.

6.5.3. Establishment of the Static Limit for ToF-SIMS Analysis of the Adhesive

Secondary ion mass spectrometry, by nature, is a destructive technique, employing an ion beam that ablates the sample surface. For any ToF-SIMS study of a polymer, therefore, a static limit for the system must be established in order to ensure analysis of the unmodified polymer. Consecutive analyses were carried out at one magnification, thus incrementally increasing the ion dose for each analysis. This procedure was repeated in different areas at different magnifications. This enables a static limit (i.e. the critical primary ion dose) to be presented in the form of plots of relative counts verses selected masses (at a constant magnification), or a plot of relative counts verses magnification (for selected masses).

Primary ion current can be measured by monitoring the primary ion beam in the continuous or pulsed mode. ToF-SIMS analysis utilises a pulsed primary ion beam, however, it is more practical to measure the primary ion current in the continuous mode. Assuming a square wave relationship between pulsed primary ion current and the continuous mode, as given in Equation 6.1, the total primary ion dose can be calculated if the continuous primary ion current has been measured:
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\[ I_{\text{pulsed}} \cdot t_{\text{pulsed}} = I_{\text{cont}} \cdot t_{\text{pulsed}} \cdot R_p \]

Where:
- \( I_{\text{pulsed}} \) = time average primary ion beam current in pulsed mode
- \( I_{\text{cont}} \) = primary ion beam current in continuous mode (nA)
- \( t_{\text{pulsed}} \) = primary ion beam pulsed length
- \( R_p \) = pulsed frequency

With the initial analysis complete the total primary ion dose rates for the possible experimental variations were calculated using Equation 6.2 given below:

Total Primary ion dose = \( N_p \cdot P \cdot I_{\text{cont}} \cdot t_{\text{pulsed}} \cdot 6.250 \cdot A \)

Where:
- \( A \) = Analysis area (cm\(^2\))
- \( N \) = Number of frames
- \( P \) = Pulses per pixel (256 x 256 pixels per frame)
- \( I_{\text{cont}} \) = Continuous primary beam current (nA)
- \( t_p \) = Primary-ion pulse length -- (50 ns)

\[ (1 \text{ amp} = 6.25 \times 10^{18} \text{ ions s}^{-1}) \]

In the case of the analytical conditions used in the current work the following values were employed, directly selectable from acquisition software: \( N = 50 \), \( P = 32767 \) and \( t_p = 50 \text{ ns} \), with \( A \) and \( I_{\text{cont}} \) determined as described below.

The primary ion current was measured using a Faraday cup positioned in the path of the beam and a Keithley model 485 autoranging picoammeter. Faraday cups comprise of a normal analysis stub with a hole (with an aspect ratio of 0.4) in the middle thus suppressing any secondary ion emission allowing maximum values of beam current to be measured. The analysis area was interpolated from previous unpublished work from this laboratory, in which the rastered analysis areas for different beam energies were determined by carrying out imaging SIMS on a precision ruled Si wafer, which was etched at different beam energies and four selected magnifications Figure 6.11 [123].
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Figure 6.11. Etch areas on a precision ruled Si wafer at 22 keV beam energy: x2000, x1000, and x500 magnification [123].

With the data required for total primary ion dose per analysis collated, graphs showing relative peak intensity versus total ion doses were plotted, Figures 6.12 and 6.13. All peak intensities were normalised to total ions, \( m/z = 5 - 400 \). An alternative route to normalisation was carried out using the \( m/z = 27 \) ion, representative of \( C_2H_3^+ \). This produced good results, indeed the profiles were the same shape as those presented below, but because of the possible presence of \(^{27}\text{Al}^+\) in the spectrum (perhaps from an aluminosilicate filler in the adhesive, or residual aluminium on the HDGS surface) the normalisation scheme using the total ion intensity was preferred.

![Graph showing relative peak intensities (normalised to total ions) versus total ion dose at x500 magnification.](image)

Figure 6.12. Graph showing relative peak intensities (normalised to total ions) versus total ion dose at x500 magnification.
Figure 6.13. (a) Graph showing relative peak intensity (normalised to total ions) versus total ion dose at x1000 magnification. Note the rapid decrease of intensity of medium mass peaks at m/z = 67 and 91, matched with the increase at m/z = 88. (b) Graph showing relative peak intensity (normalised to total ions) versus total ion dose at x 1000 magnification (medium to higher mass).

Characteristic masses selected for monitoring damage were as follows; aromatics m/z = 67, 91, 115, 128, other fingerprinting organic masses included m/z = 105, 135 and 141, finally ^{88}\text{Sr}^{+} to represent an inorganic component of the adhesive. Table 6.4.
Table 6.4. Characteristic positive fragments/ions used in the damage study.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragment/ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>91</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>115</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>128</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>105</td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>141</td>
<td><img src="image" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 6.12, shows data from the damage study carried out x500 magnification and apart from an initial increase in all masses, which may be considered to be a result of removal of general hydrocarbon contaminant from the surface, no decrease in the intensity of any of the peaks is noted. This suggests that the "static" limit for the polymer system has not been reached at ion dose of $2 \times 10^{13}$ ions cm$^{-2}$. With magnification increased to x1000, Figures 6.13a and 6.13b, a continuous decrease in the lower mass aromatics (m/z = 67 and 91) after the first exposure is observed, this is accompanied by a complementary increase of the inorganic mass 88. Such a result is surprising, as it is normally the larger organic ions that are more sensitive to damage. In this instance the emergence of the Sr$^{+}$ is associated the loss in intensity of m/z = 67 and 91. Inorganic components, such as fillers or pigments, are always covered by a thin layer of organic in a properly prepared adhesive or paint. The smaller low mass organic molecules, therefore, may be more susceptible to damage than the high mass organic fragments. Also, as these organic ions reduce in intensity, a matching rise in
intensity would be expected from the inorganic. Taking these considerations into account and examining the data shown in Figure 6.13, it appears that there are two "static" limits for the system, one for the lower mass organics \((2 \times 10^{13} \text{ ionic cm}^{-2})\) and one for the higher mass organics (approximately \(4 \times 10^{13} \text{ ions cm}^{-2}\)). Despite the apparent ambiguity of the definition of static conditions for the adhesive system, both values given are within the general static limit of \(10^{13} \text{ ions cm}^{-2}\), as defined by Briggs [12], and imaging should be achieved successfully within the set of experimental constraints to allow imaging of a damage free surface.

6.5.4. Line Scan Across an Initiation Zone: The Topography Issue

A ToF-SIMS line scan was carried out across the initiation zone of an aged joint, Figure 6.3 shows the areas analysed. Peaks of interest were chosen to conduct a profile of peak intensity verses position. For example, the \(^{24}\text{Mg}^+\) ion increases dramatically in intensity at the crack tip of the initiation zone. The original profile of ion intensity versus relative position displays how the line scan was dominated by topography Figure 6.14 (a). Normalising intensities to total ions, however, has made it possible to resolve topographical issues and see how relative intensities of selected masses vary across the initiation zone. Here, the molecular specificity of SIMS is apparent, with definite traces of characteristic polymer identified for the first time on the initiation zone. A perennial problem for SIMS is that its ion yield is sensitive to topography. If changes in surface topography are not taken into account, acquired data is not dominated by elemental effects but by topographic effects. Whilst there is no standard method of dealing with topographic issues normalising to total ions seems reliable and has also been used elsewhere [124].

The importance of the line scan becomes apparent when analysing the normalised intensities, Figure 6.14 (b), and it is easy to see distinctive surface characteristics associated with different areas across the initiation zone and the thick polymer section. The linescan, therefore, identifies ions and fragments that would be relevant in subsequent imaging. The linescan also offers a one dimensional view of the electrochemical activity in the initiation zone and visual assessment of the spectra indicates that there may be a concentration of cations at the crack tip. This is confirmed when looking at normalised line scans of \(m/z = 24\) and the characteristic epoxy mass \(m/z = 135\). The inclusion of the \(^{88}\text{Sr}^+\) ion (indicative of the strontium chromate pigment) is shown to vary in concentration with the epoxy fragment at \(m/z = 135\) rather than the \(^{24}\text{Mg}^+\) ion, confirming its role as an adhesive marker.
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Figure 6.14. Positive ToF-SIMS line scan across the initiation zone as described in Figure 6.3: (a) Selected masses demonstrating dominance of topography, (b) Normalised line scans of m/z 24 (Mg⁺) and m/z 135 (C₉H₁₁O⁺) – markers for cation and adhesive respectively – both normalised to total ion counts.
6.5.5. ToF-SIMS Imaging of a Single Lap Joint Initiation Zone

Peaks of interest for mapping of the initiation zone are as follows:

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}\text{Ca}^+$ and $^{24}\text{Mg}^+$</td>
<td>Cationic markers for electrochemical activity</td>
</tr>
<tr>
<td>$^{88}\text{Sr}^+$</td>
<td>Inorganic component of adhesive</td>
</tr>
<tr>
<td>$m/z = 77$ and $91$, $105$ and $115$</td>
<td>Organic markers</td>
</tr>
<tr>
<td>$^{52}\text{Cr}^+$ and $^{64}\text{Zn}^+$</td>
<td>Substrate</td>
</tr>
</tbody>
</table>

The images obtained display well defined cationic rich zones (Figure 6.15), possibly suggesting that local cathodic cells are set up in within the initiation zone. The images characteristic of adhesive peaks ($m/z = 77$ and $91$ and $m/z = 88$) also show the traces of polymer within the initiation zone to be "patchy", Figure 6.16, indicating that water ingress may weaken areas within the adhesive and so lead to very thin cohesive failure through the polymer within the initiation zone. The obvious question of whether the cationic Mg$^{2+}$ patches coincided with the adhesive patches resolved by overlaying the two sets of complementary images. Figure 6.17 confirms that there are areas within the initiation zone that are cation rich and adhesive deficient and conversely adhesively rich areas that are deficient in cations.

Figure 6.15. Positive ToF-SIMS image highlighting cation rich areas, possibly indicating that local cathodic cells are set up within the initiation zone, (Image shows, left to right, top to bottom, total counts, $m/z = 40$, 52 and 24).
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Figure 6.16. ToF-SIMS image showing that characteristic polymer ions, also, form in concentrated regions within the initiation zone. This may give evidence to the ingress of water playing a role in initial bond degradation as well as electrochemical activity, (Image shows, left to right, top to bottom, total counts, m/z = 88, 77 + 91, and 60 + 43).

(a)

(b)

Figure 6.17. Positive ToF-SIMS images showing that cation rich areas within the initiation zone do not coincide with polymer adhesive rich areas, (a) m/z = 88 on 24; (b) m/z = 77 + 91 on 24.
The data acquired in this manner might be improved by the use of an appropriate algorithm to correct for sample topography. The data of Figure 6.13 shows that this can readily be achieved by the use of the total ion yield, or indeed, a suitable non-specific ion such as $^{27}\text{C}_2\text{H}_3^+$. 

### 6.6. Failure Mechanism: The Role of Electrochemical Activity

As mentioned in the introduction cathodic behaviour has been found to be responsible for initial degradation in other lap shear systems, whilst described in Chapter 2 a brief reprise of the effect of cathodic activity at an interface will be given here. Cathodic activity has been defined by the presence of cations at the interface. The idea of cathodic and anodic markers identifying electrochemical activity was first introduced by Castle and Epler in the mid 1970's [36]. Cathodic delamination can be defined as the detachment of strongly adhering organic coatings under the influence of a cathodic potential and has been recognised as a problem for electrochemically active surfaces since 1936.

Consider a metal discontinuously covered with an organic coating. The resulting system is vulnerable to cathodic delamination when subsequently exposed to a hostile atmosphere. The coated metal may behave as a cathode and the exposed metal as an anode. The ensuing electrochemical reaction produces cathodic products (specifically hydroxyl ions) under the coating, which may have deleterious effects on the bonding of the metal to the coating and so cause the coating to "delaminate". Cathodic reactions in the presence of oxygen involve an increase in pH, either by the consumption of hydrogen ions, or the reduction of oxygen and water to produce hydroxyl ions.

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \Rightarrow 4\text{OH}^- \quad 6.3$$

The above explanation is widely accepted and has been discussed extensively by Watts in previous communications, but is it applicable to a HDGS substrate? A freshly cut edge of HDGS is a natural galvanic cell with the anodic zinc coating corroding preferentially to protected the cathodic iron;

$$\text{Zn} \Rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad 6.4$$

As a result, the cathodic reaction will take place generating hydroxyl ions due to the reduction of water and oxygen via the consumption of electrons. As already
discussed, under the correct conditions a defect in a coating will become anodic allowing cathodic activity to generate aggressive hydroxyl ions under the polymer film causing delamination at the coating/substrate interface. Consequently more substrate is exposed, becomes anodic and a cathodic delamination front moves forwards. For this mechanism to be applicable to an adhesively bonded HDGS system the cathodic activity would occur as a result of anodic behaviour from the exposed zinc (along the sides of the cut substrate) and a delaminating front leaving an entirely interfacial zone would be expected, as with previous work on mild steel [33]. The SIMS images, however, have indicated that localised cathodic cells are set up within the initiation zone. The complementary XPS and SIMS data have identified electrochemical activity as being responsible for the formation of the initiation zone. The origin of this electrochemical activity is considered from a theoretical standpoint in Chapter 8 and related to the observed analytical data.

The images obtained support earlier evidence of electrochemical activity at the initiation zone shown by the presence of cations (Mg$^{2+}$), indicating the role of cathodic behaviour in the formation of the initiation zone. It should be noted that this concentration of cations is "patchy" and not, as suggested by the line scan data concentrated at the crack tip. A major advantage of the imaging technique is that it describes the two dimensional distribution of species and so allows an estimation of the size of the cathodic cells, which appears of the order of 100 micrometers across. The sensitivity of SIMS is demonstrated by the clear polymer images obtained. These patches of polymer within the initiation zone, along with the corresponding images, suggest that a conjoint effect seems to be responsible for the formation of the initiation zone, this was implied earlier by the preliminary XPS study. The traces of polymer seem to indicate that water ingress plays a role along with cathodic behaviour, creating the cathodic weakening effect, proposed earlier, rather than the classical cathodic delamination model [33]. This model is further supported by the earlier small area XPS data which showed 47% C 1s at the initiation zone, a level not high enough for a cohesive polymer surface, but too high for a pure interfacial (cathodic delamination) failure surface.

By the use of ToF-SIMS imaging it was possible to take the work a step further by analysing a large area relatively quickly, demonstrating that there seems to be corresponding cation and polymer rich areas within the initiation zone. This is the principal advantage of the imaging technique, provided preliminary work has been carried out with spectra of the polymer understood, a sample with a known zone of
interest can be analysed quickly yielding spatial information on a two dimensional plane.

6.7. Concluding Remarks

A thin strip of interfacial failure has been identified at the ends of overlaps on a hot dipped galvanised/epoxy lap shear system, which has been termed the “initiation zone”. Small area XPS established electrochemical activity within the initiation zone. Following this preliminary result, a method has been developed for imaging the initiation zone of an adhesive joint successfully by ToF-SIMS, with images obtained supporting earlier evidence of cathodic behaviour playing a role in the formation of the initiation zone emphasised by the presence of cations (Mg$^{2+}$).

The molecular sensitivity has proved to invaluable as it allows the identification of characteristic adhesive ions within the initiation zone. Whilst initial XPS data suggested that residual adhesive may exist in the initiation zone, ToF-SIMS, using linescans and imaging, has been able to show that there are regions within the initiation zone that fail cohesively through the adhesive. A specific interaction takes place between a polymer and a substrate on adhesion. This results in a well ordered organic layer, with reduced free volume next to the substrate interface. Diffusing water molecules are unable to penetrate the well ordered layer and aggregate close to but not at the substrate interface. On mechanical testing the aggregated water acts as a weak boundary layer, thus leaving approximately 2 nm of polymer on the substrate and yielding a “wet adhesion” failure that can only be detected by surface analysis. The SIMS imaging identifies corresponding cation rich and adhesive rich areas within the initiation zone, showing local cathodic cells of approximately 100μm across, demonstrating that the different processes dominate in different regions.

With cathodic activity also identified a possible dual effect of electrochemical behaviour and ingress of water may be responsible for the formation of the initiation zone, suggesting “cathodic weakening” rather than delamination prior to mechanical testing, as described in the published model of cathodic delamination [33]. The use of SIMS in this work has allowed the role of the polymer adhesive in the formation of the initiation zone to be monitored and has been instrumental in confirming the ideas proposed by the initial XPS analysis. The molecular sensitivity has not only identified residual adhesive within the initiation zone but also that the organic phase exists as patches interspersed with local cathodic cells. In the next chapter the affect of cathodic activity on the phosphate pretreatment is considered using small area XPS at a spatial resolution of 20 μm. XPS is well suited to analysis of phosphate
pretreatments. The P2p peak can display a large chemical shift allowing an indication of the distribution of the surface phases to be made and any possible degradation to the phosphate pretreatment identified.
Chapter Seven

A Small Area XPS Investigation into the Effect of Environmental Degradation of a Phosphate Pretreatment.

7.1. Introduction

It is generally accepted that the performance of an adhesive system can be improved through the use of a pretreatment [110]. By changing the nature of the substrate surface (e.g. chemistry or morphology) it is possible to reduce the rate of corrosion and bring a metallic surface to a condition which will favour the acceptance of a continuous and adherent protective organic coating, this is often achieved in practice by the application of a conversion coating. Phosphating is the most widely used form of metal pretreatment, has been used for over 100 years and if deposited under proper conditions, gives the substrate better corrosion resistance and adhesion of coatings [53, 54]. Phosphating has traditionally been used in the paint industry for consumer goods and automotive applications to provide improved corrosion resistance and a larger interfacial area for bonding, and whilst a somewhat controversial choice for reasons that will be explained later, it can also be used as an effective pretreatment for the adhesive bonding of HDGS [60].

In the previous chapter a ToF-SIMS investigation of adhesively bonded HDGS, identified areas of apparent interfacial failure limited to thin strips at the end of the lap shear joint overlap termed “initiation” zones. ToF-SIMS images from these regions
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identified definite local cathodic cells (approximately 100 μm in size) and also complementary polymer rich areas suggesting a cathodic "weakening" effect, due to water ingress and cathodic activity, rather than classical cathodic delamination. The response of adhesively bonded HDGS to load and environment was studied by Dickie et al [32, 49] who reported electrochemical activity as an important precursor to interfacial failure. Similar conclusions were reached for mild steel [33], which confirmed that true interfacial failure was a result of cathodic delamination. The establishment of electrochemical activity within the initiation zone was critical in defining the mechanism of failure for the joint system. The role of electrochemical activity and its effect on the substrate is one of the aspects considered in this chapter.

This chapter reports the changes that occur in the pretreatment layer within an initiation zone of a lap shear joint adhesively bonded HDGS on exposure to a humid environment. These observations are interpreted in terms of the degradation of the pretreatment layer and are considered in the light of currently accepted failure mechanisms when the joint is exposed to an aqueous aggressive environment.

Small area XPS (at a spatial resolution of 20 μm diameter spot size) and SEM, have been used to characterise areas within the initiation zone of aged joints as well analysing the substrate prior to bonding allowing the effect of any electrochemical activity to determined. As discussed at the end of the Chapter 6 XPS is well suited to monitoring the potential degradation of a phosphate layer, with certain advantages over SIMS. Its ability to provide information on the hierarchy and distribution of surface phases makes it conducive to the study of conversion coatings.

7.2. Experimental Details

As with the SIMS investigation the substrate used in the study was 1.2 mm thick HDGS that had been pretreated with a phosphate conversion coating followed by a chrome rinse. Single lap shear specimens were fabricated from 110 mm by 20 mm coupons with an overlap of 10 mm. A polybutadiene sealant adhesive (Evode M33) was used and glue line thickness set at 250 μm using glass ballotini during fabrication. The joints were aged for 12 months at 35 °C in 95% relative humidity
and then mechanically tested using a 1195 Instron machine with a 5 kN load cell at a cross head speed of 5 mm min\(^{-1}\).

The interpretation of analysis from the failure surfaces of adhesive joints is made more straightforward if the adhesive formulation has been disclosed by the manufacturer. After considerable communication with Evode the polybutadiene based sealant type adhesive, Elastosol M33, was provided along with the manufacturers' formulation, which is given in Table 7.1. Lubrook has reported on the behaviour of metal substrates with rubber based adhesives, which cure via a vulcanisation process [125]. Whilst this adhesive was reported as giving reasonable results with iron substrates, poor performance was observed with zinc substrates and so the use of such an adhesive in this project could possibly show the benefits of a pretreatment.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene</td>
<td>40.68</td>
</tr>
<tr>
<td>Sulphur</td>
<td>5.14</td>
</tr>
<tr>
<td>Black pigment</td>
<td>0.48</td>
</tr>
<tr>
<td>MBTS (Dibenzothiazyl disulphate)</td>
<td>7.40</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>4.50</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>8.04</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>33.76</td>
</tr>
</tbody>
</table>

Table 7.1. Composition of the sealant type adhesive, Elastosol M33.

XPS analysis was performed with a V.G. Scientific Sigma Probe using a microfocused monochromatic AlK\(\alpha\) X-ray source. For insulating samples a flood gun supplying electrons of 6 eV energy, was used for the management of surface charge. The spectrometer was controlled by a V.G. Scientific Eclipse data system, which was also used for subsequent data processing. SEM analysis was carried out using a Hitachi S-3200N in the full vacuum mode, samples were gold coated and a primary beam potential of 20kV was used.
7.3. Visual Assessment of the Failure Surfaces

The visual characteristics of the failure surfaces and areas analysed are shown as a schematic in Figure 7.1.

Figure 7.1. A schematic of the visual failure characteristics of a typical joint discussed in the study: (a) a side elevation of the fracture path and (b) a plan of failed overlap interfaces identifying the metal initiation zone, ballotini “pits” and areas from which the XPS spectra shown in Figures 7.5, 7.8 and 7.10 were acquired.
The adhesive exhibits a cohesive failure throughout most of the overlap, with large amounts of polymer on both failure surfaces. There are, however, strips of interfacial failure at the ends of the joint overlaps akin to the initiation zones observed on joint systems fabricated with the structural epoxy adhesive. The load to failure, 0.65 kN, was characteristically low for a sealant adhesively bonded joint resulting in no plastic deformation of the substrate, with stronger structural adhesives plastically deformed hinges are often observed adjacent to the overlap area.

7.4. Characterisation of the Phosphated Substrate

One of the principal aims of this study was to investigate the effect of any possible electrochemical activity on the substrate within the initiation zone. Initial characterisation of the as received phosphated substrate was carried out by an SEM investigation. Pretreatment coverage was found to be uniform, demonstrated by Figure 7.2 which, whilst only showing a small area, is a typical representation of the surface and sufficiently characterises the phosphate coverage, showing no denuded areas. Closer inspection of the crystals themselves, Figure 7.3, indicates that there are defects in the individual crystals. Transverse cracks seem to have been introduced into the crystals, more than likely at some point during the deposition process or subsequent processes of the treated strip, for example rolling.

Figure 7.2. SEM of as received phosphate crystals on HDGS; showing uniform coverage of pretreatment.
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Figure 7.3. SEM of as received phosphate crystals on HDGS; showing “micro” cracks through individual crystals.

A large area XPS survey spectrum taken from a section of the unbonded substrate material allows characteristic peaks to be identified, Figure 7.4. Well defined P2p and P2s transitions, at 133eV and 190eV respectively, can be seen and are indicative of the phosphate pretreatment, silicon peaks are present and may well have originated from the phosphating bath, as silicates may be present as surfactant additives. Evidence of the chrome rinse is apparent with the Cr2p doublet discernible despite the fact that it coincident with some of the zinc Auger peaks which effectively means that the detection limit for Cr in this system is poorer than normally encountered in XPS. This problem can easily be overcome when using a twin anode source as switching from Al Kα to Mg Kα radiation shifts the Auger peaks by 233 eV on a binding energy scale whilst the photoelectron peaks are unmoved, however, as this work was carried out using a monochromated source, this practice could not be used. The zinc peaks observed are characteristic of the phosphate crystals and not the HDGS substrate. SEM analysis has shown pretreatment coverage to be uniform and the levels of concentration of Cr and Si (characteristic pretreatment components) detected indicate that the spectrum is characteristic of the pretreatment only. The quantitative surface chemical analysis by XPS is presented in Table 7.2.
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<table>
<thead>
<tr>
<th>Spectra</th>
<th>Element / atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>As received phosphated HDGS</td>
<td>38.4</td>
</tr>
<tr>
<td>Cohesively failed polymer</td>
<td>70.9</td>
</tr>
<tr>
<td>Ballotini “pit”</td>
<td>88.8</td>
</tr>
<tr>
<td>Initiation zone bright area</td>
<td>17.7</td>
</tr>
<tr>
<td>Initiation zone dark area</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Table 7.2. Quantitative surface analysis of the spectra shown in Figures 7.4, 7.5, 7.8 and 7.10.

Figure 7.4. Large Area XPS (400 μm diameter spot size) from unbonded phosphate HDGS substrate, (a) Standard survey spectrum 0-1200 eV (b) Enlarged section of survey spectrum 0-200eV.
7.5. XPS and SEM Analysis of the Failure Interfaces

Large area XPS analysis (400 μm diameter spot size) carried out on the middle of joint overlaps confirms the visual observations, i.e. the cohesive nature of failure for the majority of the overlap, Figure 7.5 shows a typical spectrum from the middle of the overlap and is characteristic of the adhesive only. The sulphur is present as a cross-linking agent and calcium is added as a filler in the form of calcium carbonate. Quantification of the spectrum shows both sulphur and calcium to exist at approximately 4%. The absence of characteristic pretreatment peaks (P and Cr) suggest that the zinc peaks (1.2%) are not indicative of the substrate but are actually characteristic of the adhesive, included in the formulation as zinc oxide acting as an inhibitor.

![Graph](image)

Figure 7.5 Large Area XPS (400μm diameter spot size) taken from an area of cohesive failure of bulk M33 adhesive, (a) standard survey spectrum 0-1200 eV (b) enlarged section of survey spectrum 0-200 eV.
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A SEM image of the overlap, Figure 7.6, clearly shows the visually interfacial initiation zone discussed above, but also distinct holes in the adjacent polymer that have been left by the ballotini, which are ejected on mechanical testing of the joints. SEM of these ballotini “pits” appear to have identified phosphate crystals from the pretreatment, this calls into question the integrity of bond between polymer and the substrate at these points, Figure 7.7. As the characteristic phosphate morphology is seen at the base of the “pit” this would seem to indicate that there was no adhesive between substrate and ballotini thus reducing the effective load bearing capacity of the adhesive joint.

![Figure 7.6. SEM of an aged joint overlap showing an initiation zone and holes left by ballotini that removed on mechanical testing.](image)

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Figure 7.7. SEM from the base of a ballotini pit showing the apparent presence of phosphate crystals.

An XPS survey spectrum, at 50 μm diameter spot size, taken from the bottom of a “pit”, Figure 7.8, did not reveal the presence of any phosphorus, characteristic of the phosphate pretreatment. Only carbon, oxygen and sulphur peaks characteristic of the polymer were detected indicating that the presence of ballotini does not compromise the bond between substrate and adhesive. It should be noted, however, that there are differences between the two characteristic polymer spectra shown in Figures 7.5 and 7.8, with a noticeable reduction of oxygen and lack of calcium present in the spectrum acquired from the ballotini pit area.

Figure 7.8. Small Area XPS (50μm diameter spot size) spectrum from the base of a ballotini pit, characteristic of polymer with no sign of substrate marker peaks.
The difference in the spectra of Figures 7.5 and 7.8 is not unexpected and indeed typifies previous results in which the polymer adjacent to a solid surface is devoid of all inorganic material, as a result of the effective dispersion of pigments and extenders in the resin. This is observed by surface analysis whenever failure occurs between an inorganic phase be it substrate or particulate matter. This is exemplified by the analysis from the base of the ballotini pits, the cohesive failure of the adhesive, on the other hand, exposes inorganic additions to the adhesive, such as the calcium carbonate and other minor constituents.

As already mentioned small areas XPS was carried out using the VG Scientific Sigma Probe, the use of a zoom microscope was also employed allowing a detailed investigation of the initiation zones revealing discrete features of failure surfaces. An optical image of an aged joint indicated the existence of dark and bright patches, approximately 100 μm in size within the initiation zone as shown in Figure 7.9.

![Figure 7.9. Optical microscope image taken on the Sigma Probe of an initiation zone within a joint, exposing the light and dark areas that exists. During mechanical testing the load was applied in a direction, which is consistent with a horizontal orientation in this micrograph.](image)

Small area XPS at 20 μm resolution was used in these areas to ensure that analysis was confined to the bright and dark areas, thus allowing the difference in composition between the respective areas to be interpreted. The bright area gives a spectrum indicating a very clean (polymer free) zinc surface with a high zinc (30.2 atomic %) and low carbon (17.7 atomic %) concentration, suggesting identification of the HDGS
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substrate, Figure 7.10 (a). The high amount of zinc present would suggest that the HDGS substrate was being detected as 30 atomic % is far higher than was found on the pretreated substrate material. The spectrum from the dark areas of the initiation zone (Figure 7.10 b) yields a slightly higher carbon 1s intensity (44.8 atomic %). This is probably low enough to still indicate an adhesive free area, however, inorganic components of the adhesive (Sulphur compounds used as cross linking agents) together with the slightly increased C1s line indicate that a trace of polymer may be left behind at the interface on failure. The presence of phosphorous peaks (P2p and P2s) in the spectrum from the dark region are the most significant difference between the two spectra shown in Figure 7.10.

Figure 7.10. Spectra from (a) bright area in initiation zone showing clean zinc surface and (b) dark areas with P2s and P2p peaks indicative of pretreatment; both these zones are within the initiation zone.

As already mentioned phosphorous peaks are indicative of the phosphate pretreatment and their absence from the bright area spectrum may well be the result of dissolution of the pretreatment layer resulting in a very clean spectrum of the galvanised steel substrate, which would account for the low carbon assay reported above.
Analysis of the bright and dark areas was followed by a series of point analyses, with a 50 μm diameter spot size spaced equidistant across the initiation zone and identified as points 1-6 in Figure 7.11. The subsequent XPS data was quantified and plotted against relative position across the initiation zone allowing the intensities of the relevant elements to be determined, as shown in the line scan of Figure 7.12. On inspection of the carbon concentration line it appears that only Points 5 and 6 are at a level which is low enough to be representative of a clean metal surface, indicating an interfacial failure. Whilst Points 3 and 4 are visually interfacial metal they possess a level of carbon between 70 and 80 atomic %. This is high and indicates the presence of a thin polymer overlayer, which is consistent with the work carried out in the previous SIMS study, where water ingress was determined to play a role in the formation of the initiation zone, leading to a cohesive failure. The low carbon areas are matched with increases in oxygen and zinc, inferring that an interfacial failure initiation zone of approximately 100 μm exists. The 100 μm clean zinc region also coincides with a significant increase in the amount of calcium present, which could be used as a marker for cathodic activity and is once again in agreement with previous chapter. In Point 3 of the line scan the only trace of phosphate pretreatment is
observed, this reinforces the idea of patchiness of the phosphate layer within the initiation zone.

Figure 7.12. Quantified data from point analysis across the initiation zone used to construct a line scan.

A SEM inspection of the initiation zone, Figure 7.13, confirms that there are areas devoid of phosphate crystals within an initiation zone of the aged joint. Bare patches of phosphate pretreatment could be present as a result of damage after mechanical testing, with crystals fracturing at the basal plane, however, if this were the case the phosphate basal plane would still be detected by XPS even though the acicular crystals would have been removed. The denuded areas of phosphate pretreatment may well be the result of attack from aggressive hydroxyl ions, the product of
cathodic activity. This has previously been discussed by Wiggle et al [65] who, on investigating corrosion at scratches in paint films, reported that hydroxide produced by the cathodic corrosion reaction chemically dissolves the zinc phosphate producing adhesion failure. Roberts et al [52] reported that there is very strong dependence of the rate of removal of the phosphate coating with pH and has shown direct evidence that zinc phosphate degradation occurs by alkali attack. Further evidence that may support the argument for cathodic activity, not only being responsible for the formation of initiation zones, but also the subsequent dissolution of phosphate conversion coating in adhesive bonds, is that all interfacial failure has occurred within a narrow region around the edges of the failed interfaces. Corrosion that is dominated by the cathodic reaction is limited to areas where there is an abundant supply of oxygen. This is more likely to occur at the edge of the overlap where the diffusion path for oxygen and water within the polymer is at its shortest.

![Figure 7.13. SEM showing denuded phosphate regions with a metal initiation zone.](image)

Whilst it has been shown that dissolution of phosphate crystals within the initiation zone occur on exposure to a hostile environment (it is known that a uniform coating exists prior to bonding) it was felt necessary to examine the coating after curing but before exposure to accelerated ageing to determine if any substantial changes to the conversion coating occur as a result of thermal treatment. A phosphated substrate covered by adhesive (approximately 250 \( \mu \text{m} \) thick) was exposed to typical cure conditions, 180°\( \text{C} \) for 30 minutes, experienced by the phosphate pretreatment. After
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cure the polymer was stripped using N-methyl pyrrolidone (NMP), by immersing the adhesive covered substrate in NMP at 60°C [126], within minutes the polymer had delaminated without any apparent change or damage to the phosphate crystal morphology. SEM analysis of the heat treated substrate revealed large cracks which had propagated throughout the pretreatment and around the individual crystals of the phosphate layer, Figure 7.14. The most likely explanation for the formation of the larger cracks is due to the probable mismatch in the coefficient of expansion between the substrate and pretreatment. Zinc has a higher coefficient of expansion than phosphate crystals hence, on exposure to high temperature will expand by a greater amount introducing tension into the phosphate layer resulting in cracking at the surface. It is not clear if the cracks would propagate through the individual crystal if the defects observed in Figure 7.3 were not present in the as received substrate.

![Figure 7.14. SEM showing “macro” cracks through the phosphate layer after experiencing adhesive curing conditions of 180°C for 30 minutes.](image)

Despite significant cracking in the phosphate layer there is no evidence to suggest that the denuded features observed in the initiation zone of the exposed joint were present prior to accelerated ageing. Indeed it is possible that both the "micro" and "macro" cracks reported from the SEM investigation could actually act as capillary like features and assist the transport of the hydroxyl ions through the crystals to the metal substrate, where the cathodic reaction would occur because of the ready supply of electrons, actually aiding the kinetics of phosphate dissolution [66]. Areas of denuded phosphated crystals appear to be the result of cathodic activity and supports the
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observations reported in Chapter 6. Despite the use of an alternative adhesive, XPS has observed traces of polymer evident in the initiation zone further supporting the importance of cathodic activity in the failure mechanism.

7.6. Concluding Remarks

The failure mechanism of an aged phosphated HDGS sealant adhesive lap joint system has been investigated using XPS. As expected for the sealant adhesive the majority of the joint overlap has failed cohesively. The present study indicates that failure for the polybutadiene sealant adhesive occurs in broadly the same manner as that observed for the epoxy structural adhesive. The use of XPS has extended the model proposed in Chapter 6 as the work has also identified traces of polymer within the initiation zone accompanied with denuded phosphate patches. Using the optical microscope it proved possible to select typical areas within the 400 μm field of view to characterise areas within the initiation zone deficient in pretreatment that are similar in size to the local cathodes observed in the ToF-SIMS study. Such areas were analysed by XPS using a 20 μm diameter spot. The XPS work offers complementary data to the ToF-SIMS images and shows the effect of cathodic activity on the phosphate pretreatment. The production of aggressive hydroxyl ions, via the cathodic corrosion reaction, has resulted in the dissolution of phosphate crystals within the pretreatment. Small area XPS identified areas with and without phosphate pretreatment and the quantified XPS linescan data shows areas of high carbon content supporting the ToF-SIMS data, implying the presence of the polymer adhesive within the initiation zone. This would suggest that failure was not only a result of cathodic behaviour but water ingress also, resulting in a weakening rather than the separation prior to mechanical testing that had been observed in previous work [33]. A SEM investigation of the phosphated substrate showed that denuded phosphate areas were a result of the exposure to relative humidity as uniform phosphate crystal coverage exists prior to bonding, although micro cracks were observed at higher magnification. The crystal coverage remains uniform after curing despite the formation of “macro” cracks running through and around crystals due to the mismatch in the coefficient of expansion between the pretreatment layer and the zinc substrate. Neither of these types of cracks appears to be related to, or responsible for, the phosphate free areas.
There are two important developments that spring from the work in this chapter and are of particular importance to the adhesion scientist. Firstly the spatial resolution of the XPS data generated has been vital to the study. In the earlier work a 250 μm diameter spot size was used and as recently as five years ago may have been considered small area analysis, however in the context of this work a 250 μm spot size may only be considered as selected area XPS. XPS is an area integrating technique and spot sizes much smaller than 250 μm were required to analyse the features observed in this study. The development of the Sigma Probe small area XPS system allowed a spatial resolution of 20 μm to be realised and the respective failure surface to be interrogated in great detail. The use of the zoom microscope camera is beneficial when analysing such small areas and also allows samples to be comprehensively scanned, detecting analytically important areas. These developments are not just of importance the adhesion scientist, permitting specific areas of failed interfaces to be analysed, but also to other specialised research areas like the pharmaceutical and semiconductor industries [127].

As well as the progress in analytical spectroscopy, the other significant step taken forward as a result of the data generated in this chapter is that a similar mechanism of failure has been proposed to that in Chapter 6 despite the use of a different adhesive. In the past the durability performance of yttrium pretreated substrates have been found to be dependent on adhesive type [128], this is not totally unexpected as the individual components are known to play role in failure behaviour of adhesive bonds. Here, this does not appear to be the case with cathodic activity and water ingress both combining to form a cathodic "weakening" effect. In Chapter 8 simple electrochemical modelling and mechanical data will be discussed in an attempt to determine the origin of the cathodic activity and the rate determining step for the initial bond degradation that ultimately leads to the formation of the initiation zone.
Chapter Eight

The Source of Cathodic Activity and its Role in the Formation of the Initiation Zone

8.1. Introduction

In an attempt to diagnose the mechanism of failure for adhesively bonded galvanised steel considerable importance has been attached to defining the locus of failure within the initiation zone, first discussed in Chapter 6. Extensive surface analysis, carried out within this region, has conclusively identified two distinct failure regions (for phosphated HDGS) (a) an interfacial failure path and (b) a cohesive failure of the adhesive very close to the substrate/polymer interface, which has been described as a wet adhesion type of failure. Imaging SIMS identified both of these loci of failure with magnesium rich areas identifying regions of cathodic behaviour, responsible for interfacial failure. The presence of aggressive cathodic activity was confirmed using small area XPS, where dissolution of phosphate crystals was recognised as the result of attack by hydroxyl ions. The wet adhesion type failure appears to be due to ingress of water aggregating close to but not at the adhesive/substrate interface resulting in a cohesive failure within the organic phase.

The proposed failure path, whilst supported by surface analytical data, contains two elements that are significantly different to models previously proposed for mild steel lap joints [33]:

(a) The cathodic activity appears patchy and does not seem to form a delamination front that moves forward homogeneously from the edge of
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the overlap, rather local cathodic cells (approximately 100 µm in size) form at preferential sites.

(b) The exposed (cut) edge of galvanised steel contains an anode (zinc) and a relatively large cathode (iron) which may have a propensity to consume all electrons from any resultant electrochemical activity.

A natural progression from these observations is to consider whether the lack of a uniform delamination front is the result of the relatively large iron cathode exposed at the cut edge of the joint. Davis studied the failure mechanisms of mild steel lap joints and concluded that cathodic activity was responsible for initial degradation around the perimeter of the overlap. Surface analysis showed that cathodic activity was concentrated at the “crevice tip” and had been responsible for driving the crack forward with separation occurring before mechanical testing, i.e. a uniform form front of “true” interfacial failure had moved forward from the edges of the overlap. The accepted origin of the cathodic delamination behaviour is analogous to a holiday or scratch in the coating of steel, as discussed in Chapter 2. At the exposed edge of the joint gross corrosion (anodic activity) will occur, this must be balanced by a cathodic reaction. This cathodic activity reduces oxygen and water to generate aggressive hydroxyl ions which will accumulate at the tip of a constantly extending crevice and will then drive a delamination front forward. Galvanised steel lap joints, unlike mild steel, offer the possibility of additional electrochemical activity across the exposed edge of the coupon, with the zinc coating acting as an anode and cathodically protecting iron. This provides two possible paths for electrochemical activity; (a) the exposed iron and zinc and (b) exposed and covered zinc. Whilst this project is concerned with durability an understanding of the role and purpose of the zinc coating is necessary in order to understand the origin of any possible electrochemical activity that may effect the durability of adhesively bonded HDGS.

8.2. Zinc as a Sacrificial Anode

Iron, which is used in a wide range of applications as the major constituent of mild and low alloy steels, is generally unstable and tends to react with its environment relatively quickly. Depending on various conditions rust, the corrosion product of
iron, can have a much larger volume than the steel from which it has formed, naturally having deleterious affects on the adhesion of the organic phase. Fundamentally corrosion is an electrochemical process, zinc coated ferrous alloys offer improved corrosion resistance, have developed rapidly and are the biggest single use of zinc. As long as the coating is continuous and impervious corrosion behaviour will be similar to that of solid zinc, however, should the coating become perforated or discontinuous, for example the cut edge of HDGS, a galvanic cell may be formed in the presence of a hostile atmosphere. Galvanic corrosion occurs when two different metals are electrically coupled when exposed to an electrolyte. Zinc, which is more active than iron, will corrode (it becomes the anode) whilst the iron becomes the protected cathode. For a corrosion current to flow a potential difference (PD) must exist between the relevant metals; for zinc (0.76 V) and iron (0.44 V) the PD is 0.32V allowing electrons to flow through the cell, this current is a measure of the galvanic corrosion. The PD given above was calculated using the standard electrode potential given. The standard electrode potential of a metal is defined as the potential difference between the respective metal's standard half cell and a standard hydrogen electrode; where the standard half cell of a metal is a pure metal electrode (M) immersed in a 1 molar solution of its ions (M\(^{2+}\)) at a pressure of 1 atm and a temperature of 25°C.

This effective means of corrosion prevention is known as **cathodic protection** and simply involves supplying the metal protected with electrons thus preventing dissolution. With an exposed edge of HDGS the zinc, acting as a **sacrificial anode**, oxidises loosing electrons which are consumed at the cathodic iron resulting in following corrosion half equations.

\[
\begin{align*}
\text{Anode: dissolution of zinc} \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \\
\text{Cathode: consumption of electrons} \\
O_2 + 2H_2O + 4e^- & = 4OH^- 
\end{align*}
\]
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An alternative method of cathodic protection uses an impressed current from an external power source to artificially provide a source of electrons for the metal being protected to consume.

Under special circumstances cases of potential reversal have been reported, with zinc becoming cathodic to steel, generally at elevated temperatures (between 60 and 90°C), where both zinc and steel have become passivated spontaneously with the steel passivating more slowly resulting in a temporary polarisation reversal [129]. Temperature did not exceed 40°C throughout any of the ageing studies in this work and it seems reasonable to assume that a large driving force for electrochemical action between zinc and iron at coupon edges existed. Indeed, surface analysis results, from the alkali cleaned substrate system, presented in Chapters 6 indicate that gross anodic dissolution of zinc, resulting in a voluminous weak corrosion product layer, offered a failure path on mechanical testing. Pretreated joints, however, seem to have inhibited anodic activity with cathodic activity being partly responsible for failure under the polymer adhesive at the overlap edge. The next section discusses the potential distribution at the cut edge of HDGS and attempts to estimate the currents in involved between different sets of possible electrochemical cells, with a view to determining the origin of cathodic activity under the adhesive.

8.3. Electrochemical Activity Around the Cut Edge of Galvanised Steel

At the start of this chapter it was proposed that one of the possible mechanisms for cathodic activity was analogous to cathodic delamination under a defect in a coating, leading to true interfacial failure at the coating /substrate interface. In order for this to occur, electrons, produced by the exposed anodic zinc, must be consumed by the adhesively covered zinc at the overlap edge, despite the possibility of a large driving force for a flow of electrons from the exposed zinc to the exposed iron.

By estimating the potential distribution around the cut edge of adhesively bonded HDGS the likelihood of a corrosion cell existing between the exposed and covered zinc may be predicted. The potential distribution around a long narrow scratch has
been modelled by Mellville [130, 131]. A schematic of the scratch is given in Figure 8.1, and considers an infinite plate in the x-y plane at z = 0 with a narrow scratch of infinite length and width $2\ell$ covering the region $-\ell < x < +\ell$.

![Diagram of scratch model](image)

Figure 8.1. Schematic representation of a scratch used by Melville to model potential distribution.

Melville emphasises that his model can be applied to other situations with similar geometry where an anode is between two cathodes. This is a situation that exists with adhesively bonded HDGS where the zinc coating behaves as an anode and is analogous to Melville’s scratch with possible cathodes either side in the form of exposed iron and covered zinc at the edge of the overlap, Figure 8.2 (a). In this scenario the exposed zinc becomes analogous to the scratch in Melville’s model with a thickness of 10 $\mu$m, i.e. $\ell = 5$ $\mu$m. Melville’s model determines whether it is possible for the covered zinc be vulnerable to any significant cathodic activity and if so make some estimation of the distance into the overlap (away from the joint edge) that cathodic influence may play any role in the formation of the initiation zone.

In order for any electrochemical activity to occur an electric current must be able to flow between the proposed electrodes and so an electrolyte must be present. In a hostile environment such as 98% relative humidity it is not unreasonable to assume that a layer of water will have condensed over ageing lap joints, modifying Figure 8.2 (a) and completing a circuit between the proposed electrodes, Figure 8.2 (b). With electrochemical cells set up an estimation of current flowing between the two sets of
electrodes may be determined to give another indication of the likelihood of significant cathodic activity under the adhesive.

![Diagram of cathodic activity](image)

Figure 8.2 Schematic of the cut edge of HDGS; analogous to Melville’s scratch. Exposed under (a) dry conditions and (b) high relative humidity.

In order to estimate the flow of current between the respective sets of electrodes certain assumptions must be made, however, it is anticipated that the calculations will give an indication of the electrochemical situation that exists for the scenario of Figure 8.2 (b).

Current can be calculated using Ohm’s law:

\[ V = IR \]

\[ I = \frac{V}{R} \]

Where: \( V \) = potential difference across the electrodes

\( R \) = resistance between the two electrodes
Considering the exposed zinc and iron electrodes first the resistance may be calculated as follows:

\[ R = \frac{\rho l}{A} \]  

8.5

Careful consideration of the definition of these terms must be taken; the resistivity (\( \rho \)) of the electrolyte, condensed water, will be high. Condensed (pure) water contains no ions and so has a resistivity similar to well distilled water. Although ions will of course contaminate the condensed water on contact with the lap shear joint the resistivity of the electrolyte will still be high, initially and the usual value for the resistivity of distilled water, has been taken at \( 5 \times 10^4 \, \text{\Omega m} \). \( l \) is given as the width of the scratch, i.e. the thickness of the zinc coating, 10 \( \mu \text{m} \). The cross-sectional area perpendicular to the direction of the current \( (A) \) has been considered as a unit length (cm) and so only the thickness of the electrolyte layer is really required. This has been taken as 100 \( \mu \text{m} \), 1mm would clearly have been too thick/wet. The cross-sectional area, therefore, may be taken as \( 100 \times 10^{-6} \times 10^{-2} \, \text{m} = 10^{-6} \, \text{m} \). These values may now be substituted into Equation 8.5 to estimate a value of the resistance between the exposed zinc and iron electrodes.

\[ R = \frac{\rho l}{A} \]

\[ = \frac{5 \times 10^4 \times 10^{-5}}{10^{-6}} \]

\[ R = 5 \times 10^5 \, \Omega \]

The potential difference between the exposed zinc and iron electrode is 0.32 V and was determined using standard electrode potentials. Using Equation 8.4;

\[ I = \frac{V}{R} \]

\[ = \frac{0.32}{5 \times 10^5} \]

\[ I = 0.64 \, \mu\text{A} \]

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In calculating the possible current flow between the exposed and covered (by adhesive) zinc general assumptions have once again been made. A similar approach has been taken as before, however, here the electrolyte is the epoxy adhesive that has adsorbed water. No value of resistivity for the epoxy is given, however, Kajda in his PhD thesis [132] measured the resistance of an epoxy coating and this value of $5 \times 10^{-6}$ $\Omega$ is used. Any experimental measurement of the potential difference between the covered and exposed zinc would be extremely difficult to measure, however, by simplification of the Nernst Equation the potential difference can be related to the concentration of oxygen at the possible corrosion sites:

$$E' = E^{\circ} + \frac{R.T}{nF} \log_e \frac{P'}{P_0}$$

Where; 
- $R$ = the gas constant
- $N$ = the number of electrons involved in the half cell reaction
- $T$ = absolute temperature
- $F$ = the Faraday constant

$$\Delta E = \frac{0.059}{4} \log_{10} \frac{P'}{P'}$$

$$\Delta V = 0.015 \log_{10} \frac{P_0}{P_0'}$$

Where $P'(P_0)$ and $P'(P_0')$ may defined as the partial pressure of oxygen in atmospheres saturated and depleted in oxygen respectfully.

It is clear that a very small potential difference will exist and if a 10 fold difference in oxygen pressure is assumed a potential difference of 0.015 V will exist. These estimated values of $R$ and $V$ allow a current to be calculated:
Thus, within the bounds of the various assumptions made above, the current flowing between the exposed zinc and iron is at least two orders of magnitude greater than that between the covered and the exposed zinc. This suggests that practically all electrons produced by the anodic zinc will be consumed at the cathodic iron and very little, if any, cathodic activity will occur at the edge of a lap joint which would result in classical cathodic delamination, (anodic activity at a defect leading to alkaline peeling of a coating) or adhesion.

Returning to Melville’s approach to the distribution of potential around a scratch, he plotted a series of curves showing the variation of potential as a function of distance from the centre of the scratch for different values of $\lambda$, Figure 8.3. The value of $\lambda$ is defined by Equation 8.9.

$$\lambda = \frac{\ell}{L_c}$$ \hspace{2cm} 8.9

where: $\ell =$ half the width of the scratch and $L_c$ is the polarisation parameter defined by Equation 8.10.

$$L_c = \sigma h_c$$ \hspace{2cm} 8.10

The value of $\lambda$ is inversely related to the polarisation parameter ($L_c$) and therefore also inversely related to conductivity of the electrolyte ($\sigma$). The conductivity of both electrolytes discussed above are very low and whilst slopes of the cathodic polarisation curve ($h_c$) are not known, values of low conductivities will result in $\lambda$ values tending towards unity and above.
Figure 8.3. Variation of potential along electrode with distance from the centre of a scratch for different $\lambda$ values [131]. (a) Linear distance axis showing the effect of $\lambda$ on the zone of potential over short distances and (b) logarithmic distance axis showing that lower $\lambda$ values result in a larger zone of potential.

From Melville’s charts it is clear that high values of $\lambda$ represent small regions of potential variations. Plausible curves for the potential distributions around the cut edge of HDGS have been added to the schematics of Figure 8.2 and are represented in Figure 8.4. The shape of the lines plotted have been used for illustrative purposes and merely give an indication of zone of potential influence. As a result of the higher conductivity of the electrolyte between the exposed zinc and iron couple a larger distribution of potential has been predicted, the dotted red line shows how distribution
may increase as the conductivity of the electrolyte increases over time. This agrees with the calculations of current that implied that the iron cathode dominates all cathodic activity by consuming all electrons generated by the anodic dissolution of zinc. Figure 8.4 also indicates that the zone of potential distribution across the covered and exposed zinc cell does not reach the covered zinc at the edge of the overlap. This infers that cathodic activity as a result of this corrosion cell is not responsible for the formation of the initiation zone. Later in this chapter data will be presented on the kinetics of the development of the initiation zone. Values as large as 2 mm are recorded for the longer exposure times, a value which is certainly too large for cathodic activity which has resulted from the dissolution of the exposed zinc anode. The calculation of current flow and prediction of distribution of potential at the covered and exposed zinc have been made independent of the presence of a relatively large iron cathode the other side of the “zinc” scratch. If the presence of exposed iron was taken into account one would intuitively expect the current and zone of potential influence to be even smaller.

![Figure 8.4. A schematic of the predicted zones of possible electrochemical activity at the exposed cut edge of adhesively bonded HDGS.](image)

The surface analysis results reported in Chapters 6 and 7 have shown that the formation of the initiation zone is a result, in part, of cathodic activity. The calculations, however, estimating corrosion currents and predicting potential
distributions, have indicated that this cathodic activity is not the result of a corrosion cell being set up between exposed and covered zinc, in contrast to the situation observed with mild steel lap joints [33]. A more plausible explanation for cathodic behaviour within the initiation zone is water diffusing through the polymer to the substrate and setting up electrochemical cells. A micro-anode, possibly caused by heterogeneity on the surface, could well lead to cathodic activity spreading out a certain distance from a small anodic central region. There are a number of ways that water may penetrate the well-ordered polymer layer adjacent to the substrate, including imperfections such as differences in cross link density as discussed by Mayne and Mills in their observations of D and I type paths for water transport through organic film [35]. Another possible route for water to penetrate to the substrate may be along the sides of ballotini beads added to the adhesive bond system during joint fabrication. Ballotini are absent from the failure surfaces, presumably ejected on mechanical testing, indicating poor adhesion with the organic phase. If this is the case the presence of ballotini may offer an accelerated route for water diffusion and thus allow the reactants for cathodic activity to penetrate to the substrate interface. Evidence for the involvement of ballotini in the failure mechanics was given in Chapter 6 showing ballotini to be the source of diagnostic cathodic marker ions. This observation supports the concept that the ballotini provide a route for water transport to the metal substrate, with magnesium leaching from the ballotini and subsequently cathodically deposited on the metal substrate. The specific role of the ballotini in the overall failure mechanism is discussed in more detail in the next chapter.

Having been able to discount traditional cathodic delamination effects, the importance of water ingress seems more important to the overall failure mechanism of the joint. A study of the mechanical data generated over periods of up to 12 months and the growth rate of the initiation zone, the next section sets out to determine whether the formation of initiation zone is driven by water ingress or subsequent cathodic disbonding.
8.4. The Significance of the Initiation Zone on the Mechanical Performance of a Joint

8.4.1. Introduction

The main aim of this project has been to determine the failure mechanisms of adhesively bonded HDGS in both the as received and pretreated state. Bearing this in mind little attention has been paid to the complicated fracture mechanisms of lap shear joints, although mechanical data for all joints tested has been collected. At a very early stage of the project the initiation zone was identified and thought to have a significant effect on the performance of the joint. The size of the initiation zone increases over the ageing period and by comparing the size of initiation zone with load to failure and assessing the load bearing capacity of the joint system the significance of the initiation zone on the residual strength of the joint will become apparent.

8.4.2. The Growth Rate of an Initiation Zone

The size of the initiation zone was measured using an optical microscope with a calibrated graticule on a set of joints aged over periods of up to 12 months. The phosphated substrate with epoxy adhesive system was chosen and each month of ageing produced three joints, i.e. six failure surfaces. Seven measurements were made along each of the six initiation zones as shown in the schematic of Figure 8.5. It is already known that the initiation zone does not move into the overlap of a joint as a uniform front on a microscopic level, and this was very evident on inspection under an optical microscope. As a result a great deal of variation was observed in the measurements taken, however, as 42 measurements were taken per set of joints a mean measurement gave a representative indication of actual initiation zone size. A graph of size of initiation zone versus time is plotted in Figure 8.6 and a linear relationship is displayed with no sign of a plateau after 12 months.
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Figure 8.5. Schematic showing the seven positions from which size of initiation zone measurements were taken.

Figure 8.6. Graph showing the relationship between size of initiation zone and time.

The straight line obtained in Figure 8.6 is a little surprising, as water ingress is known to play a large part in the formation of the initiation zone. If the diffusion of water was the dominating failure mechanism a non-steady state diffusion graph would be observed, with the concentration of water at a particular point in the polymer varying with time according to Fickian diffusion behaviour. This may infer that it is the
development of cathodic delamination areas that is the rate determining step for
growth of the initiation zone with their existence either affecting water transport
through the adhesive or accelerating or retarding the growth of the initiation zone
compared to water ingress alone.

After 12 months exposure the size of the initiation zone has grown to more than 2
mm. Returning to Melville's model, the predicted area of cathodic activity resulting
from the cut edge of galvanised steel was certainly no greater than a few micrometers,
as with an electrolyte of very low conductivity a high $\lambda$ value is expected. For the
observed electrochemistry to have been the result of edge effects a low value of $\lambda$
would be required, around $10^{-3}$, requiring an electrolyte with a reasonably high
conductivity. With cathodic activity 2 mm into the joint further evidence for the
existence of local cathodic cells on the substrate within the initiation zone is provided.

Watts has reported disbondment rates of 5 nm s$^{-1}$ for propagating cathodic
delamination fronts in coatings [133]. The initiation zone disbondment rate for the
system represented in Figure 8.7 is around 0.1 nm s$^{-1}$, an order of magnitude slower
than the value given by Watts. This not entirely unexpected, as Watts studied a
system that observed a true interfacial failure driven purely by cathodic delamination,
in this project water ingress is also partly responsible for weakening the initiation
zone. Cathodic weakening is not as aggressive as traditional cathodic delamination
and so the rate and effect of disbondment cannot be expected to be as great. Although
true interfacial failure is not observed throughout the whole of the initiation zone
knowledge of its rate of growth allows an estimation to be made on the rate at which
bonds are broken and therefore comment on the charge involved in driving the
initiation zone forward.

From the graph in Figure 8.6 after 8 months the initiation zone has grown 1.656 mm.
Using this data it is possible to estimate the number of bonds broken:
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8 months \( \Rightarrow \) (8x30x24x3600) \( \Rightarrow \) 2.1 x 10^7 s.

If the assumption is made that one bond is approximately 0.1 nm

\[ 1.656 \text{ mm} \Rightarrow 1.656 \times 10^6 \text{ nm} \]

Number of bonds broken after 8 months = 1.656 x 10^7

Number of bonds broken per s

\[ = \frac{1.656 \times 10^7}{2.1 \times 10^7} \]

\[ = 0.8 \text{ bonds s}^{-1} \]

Number of bonds broken per unit length (cm) per second.

\[ = 0.8 \times 10^2 \times 10^{10} \]

\[ = 0.8 \times 10^8 \]

With of the rate of disbondment of the polymer adhesive estimated it is possible to elucidate to the charge required for cathodic disbondment to maintain the rate of initiation zone growth. If one hydroxyl ion is required to break one bond conversion to charge is calculated by:

Number of bonds broken (cm\(^{-1}\)s\(^{-1}\)) x charge on an electron

\[ = 0.8 \times 10^8 \times 1.6 \times 10^{-19} \]

\[ = 1.28 \times 10^{-11} \text{ Coulomb s}^{-1} \]

Converting to charge per day

\[ = 1.28 \times 10^{-11} \times 86400 \]

\[ = 1.10 \times 10^{-6} \text{ Coulomb day}^{-1} \]

By converting to charge per day, necessary to drive the initiation zone forward, a comparison can be made with Leidheiser's theoretical value for the rate to sustain cathodic delamination; 1.7 x 10^{-6} Coulomb per day [30]. The calculated value above
is very close to Leidheiser's limiting charge per day and is close enough to suggest that cathodic activity is the dominating factor responsible for growth of the initiation zone and may explain why Figure 8.6 does not follow established laws of diffusion. The estimated charge also supports the low propagation rate compared to Watts' much faster delamination rate.

The complex stress distribution in a lap joint was briefly referred to in Chapter 6 and it was noted that stress concentrations exist at the ends of the overlaps. This often leads to initial locus of failure occurring at the edge of an overlap at or close to the adhesive/substrate interface before switching to the opposite substrate interface where propagation will continue until meeting a corresponding crack travelling from the other side of the joint. The formation of the initiation zone, therefore, could simply be as a result of stress concentration at these points. The surface analysis discussed in Chapters 5 and 6 have conclusively shown this not to be the case and Figure 8.6 showing that the initiation zone continuously increases over a period time of exposure to a hostile environment, also showing the simple fracture mechanics explanation not to be valid. If this were the case, no significant increase in initiation zone size would be observed.

8.4.3. The Effect of the Size of Initiation Zone on Load to Failure of the Joint

Having shown that the growth of the initiation zone is directly proportional to time it follows that its size must have some effect on the load to failure of the adhesive bond. Figure 8.7 shows that initiation zone, once again, is directly related to the load to failure. This highlights the durability problem of the adhesive bond system, with no sign of the size of the initiation zone starting to reach a plateau the load to failure will continue to fall.
Another method of analysing the significance of the initiation zone on overall joint performance is assessing the load bearing capacity of an adhesive bond. This involves the determination of load carried by the cohesively failed areas of the overlap and is calculated by dividing the load to failure by the visually cohesive area of the failed interfaces, a schematic of the method is given in Figure 8.8. The intention is to demonstrate whether the whole of the cohesively failed area shares the applied load or if certain areas are weakened and unable to carry the load. The term initiation zone has been used to describe the interfacial failure areas at the ends of the overlap throughout this project. They have been considered as possible interaction sites for crack propagation on mechanical testing. On occasion, however, visual degradation has been observed around the whole of the overlap, as with the photograph in Figure 6.2. With this in mind the load bearing capacity of tested joints have been considered with a weakened area around the whole edge of the overlap, as shown in the schematic of Figure 8.8.

Figure 8.9 shows how the load bearing capacity of the cohesively failed interfaces vary with time, interestingly, the line of best fit is close to horizontal giving a constant load bearing capacity of approximately 25 N mm\(^2\). This infers that no weakening of the joint exists outside the initiation zone and that the existence of the initiation zone is responsible for loss in joint strength. This is somewhat surprising as the horizontal
best-fit line suggests that diffusion of water into the overlap has not travelled further than the length of the initiation zone possibly indicating that transport of water may determine initiation zone size. It has already been proposed, however, that water ingress is not the dominating factor involved with the formation of the initiation zone as Figure 8.6 shows that size of the initiation zone is directly related to time exposed to a hostile environment and is not diffusion controlled.

\[ d = b - (a - c) \]

<table>
<thead>
<tr>
<th></th>
<th>Load to Failure (N)</th>
<th>Load Bearing Capacity (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Joint</td>
<td>x</td>
<td>x/ab</td>
</tr>
<tr>
<td>Aged Joint</td>
<td>y</td>
<td>y/cd</td>
</tr>
</tbody>
</table>

Figure 8.8. The methodology used to determine the load bearing capacity of an adhesive bond.

Figure 8.9. Graph showing the relationship between the load bearing capacity of a joint and time.
One reason why the growth of the initiation zone does not follow a non-steady state diffusion curve may be related to alternative diffusion paths within the polymer. Mayne's I and D type areas have been considered but the presence of ballotini may also affect diffusion rates. The relatively large, smooth glass spheres, may provide a preferential route for water transport thus affecting the rate of overall water ingress into the joint. Small area XPS has already shown that the ballotini are responsible for providing the balancing cations in the cathodic corrosion equation, which is responsible for regions of interfacial failure within the initiation zone. Ballotini may well provide a path for water to penetrate to the substrate surface and set up local corrosion cells, resultant cathodic activity will ensue leading to areas of disbondment. The aggressive cathodic behaviour could also provide a reason why Fickian diffusion does not dominate initiation zone growth with delamination effects actually driving the crack forward. The most significant observation from the graphs plotted in Figures 8.7 and 8.9 is that overall performance of the joint seems to be dependent on initiation zone size; whilst not unexpected, the graphs do confirm that in order to improve the durability of the adhesive joint system the control of failure in the initiation zone is critical.

8.5. Effect of Cathodic Activity on Alternative Adhesive Systems and Ageing Conditions

The mechanical data presented in section 8.4 has shown the significance of the initiation zone on joint performance and theoretical predictions inferred that cathodic disbonding is the dominating mechanism of the formation of the initiation zone. The mechanical data given was for a phosphated HDGS substrate with an epoxy adhesive aged in 98% relative humidity. Other systems have been aged under various conditions and it is interesting to see how the mechanical data compares with theoretical predictions and the surface analysis diagnoses for failure mechanisms. A comparison of the load to failure for three types of treated HDGS, with an epoxy adhesive, is plotted in Figure 8.10 including the phosphated pretreatment already discussed along with alkaline cleaned and a mixed oxide pretreatment.
Figure 8.10. Graph showing a performance comparison of differently treated HDGS, using an epoxy adhesive, versus time at 98% relative humidity and at 35°C.

Figure 8.10 shows conclusively the importance of using a pretreatment. Surface analysis and visible examination of the alkali cleaned joints, discussed in Chapter 6, indicated that the locus of failure passes through a zinc corrosion product layer. This is the result of the anodic dissolution of zinc, cathodically protecting exposed steel, and leads to the formation of a weak boundary layer. This has a dramatic effect on the load to failure of the joints, to the extent that after a period of 8 months joints would fall apart on placing in the test machine and hence actual load to failure could not be recorded. Despite the very poor durability performance of alkali cleaned joints initial bond strengths were interestingly higher than for both pretreatment systems. Both the phosphating and mixed oxide pretreatments appear to inhibit anodic dissolution of the zinc having visually similar failure interfaces, predominantly cohesive failure with characteristic initiation zone at either end of the overlaps. Whilst the mixed oxide pretreatment does not yield as great a load to failure as phosphated HDGS a better retention of initial bond strength is observed, a reduction of 35% compared to 46% after 9 months. This may suggest that the mixed oxide coating inhibits cathodic behaviour more efficiently.
In order to provide a controlled ageing environment two sets of joints were immersed in Milli-Q water in filled 250 cm³ glass jars at 35°C. Alkali cleaned and phosphated joints were tested with sets of three joints removed from testing after 1, 3, 6 and 9 months. Milli-Q water provides a relatively clean ageing media with a low oxygen concentration and the glass jars were washed out to leach out as much contamination as possible. Figure 8.11 shows how performance of the milli-Q water tested joints varies over time, once again the pretreated substrate out performs the alkali cleaned HDGS. An improved retention of bond strength for the alkali cleaned system is observed with load to failure never falling below 3 kN. Oxygen supply for corrosion reactions was limited during ageing since the glass jars were filled to capacity prior to ageing. The resultant effect, as expected, is reduction in the amount of electrochemical activity and thus prevents gross corrosion, an approach to testing developed by Davis [33]. A low oxygen ageing media may explain the improvement in retention of initial bond strength for the phosphated system, with oxygen being a key ingredient for cathodic activity, Figure 8.11. This improved performance is yet another indication that cathodic activity is the dominating mechanism responsible for the formation of the initiation zone. A comparison of the phosphated joint strengths under different ageing conditions is shown in Figure 8.12, the relative humidity aged samples, where oxygen is readily available to supply the cathodic corrosion equation, display a lower load to failure.

Figure 8.11. Graph showing the performance of alkali cleaned and phosphated HDGS joints aged in Milli-Q water at 40°C.
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Figure 8.12. Graph showing the effect of different ageing environments on the performance of adhesively bonded phosphated HDGS.

Returning to Figure 8.11, it is interesting to note that the alkali cleaned substrate has a higher initial load to failure than the pretreated system. This is not totally unexpected, phosphate pretreatments have been used for many years in the paint industry and offer good corrosion protection, however coatings are not generally expected to withstand heavy loads and interfacial contact has been seen to be more significant than bond strength. Phosphate pretreatments may not be ideally suited to the world of adhesive bonding, they present a surface made up of acicular crystals that protrude from the basal plane and despite providing a large area for interfacial contact, they can be mechanically weak and offer a locus of failure on loading, where the crystals meet the basal plane, as discussed in Chapter 2. SEM analysis of 1 month aged joint (immersed in milli-Q water) shows this to be the case with the epoxy adhesive showing a mixed mode of failure through the polymer and phosphate crystals, Figure 8.13. There is a distinct difference between the phosphate free areas, observed in Chapter 7 and the mixed failure mode displayed in Figure 8.13. Here, a trace of where the phosphate crystals were can be seen as they have fractured close to the basal plane on mechanical testing. Indeed SIMS analysis actually confirms the presence of phosphate on both failure interfaces, where failure was a result of cathodic activity dissolution of the phosphate crystals had taken place removing all trace of them.
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Figure 8.13. SEM micrograph showing the mix mode failure of a phosphated/epoxy adhesive bond aged for 1 month in Milli-Q water.

So far the only mechanical data shown has concerned the failure of adhesive bonds using the structural epoxy type of adhesive. In Chapter 7 small area XPS identified that cathodic disbondment was also observed within the initiation zone with the use of a sealant adhesive. A graph relating the load to failure versus time for the sealant adhesive bonds is plotted in Figure 8.14. Understandably the loads given are considerably lower than for bonds fabricated with the epoxy adhesive and the initiation zones are less well defined. Another difference in joint behaviour between the two adhesive systems is that initially the sealant adhesive seems to show an improved joint strength on ageing.

Figure 8.14. Graph showing the relationship between load to failure and time for adhesive bond fabricated with a polybutadiene sealant type adhesive.
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Despite exhibiting poor loads to failure a superior retention of initial bond strength is observed with only about a 25% loss in strength for both treatment systems. This may well be a result of the superior resistance to water, however, a more likely explanation is that the cohesive properties of the adhesive are so weak that the failure mechanisms described previously have little effect on joint strength. This is highlighted by the alkali cleaned HDGS system, previously, at a reasonably early stage of ageing, failure occurred through a weak zinc corrosion product, with the polybutadiene adhesive a cohesive failure through the polymer is generally observed. The load to failure of the polymer cohesive failure is lower than the failure through the corrosion product and so gross corrosion of the zinc coating may not necessarily affect bond strength. It should be noted that mechanical data was collected over a twelve month period, which was not possible with the epoxy adhesive, and electrochemical activity may well be slowed by the inhibitors in the adhesive.

8.6 Concluding Remarks

Experimental work reported in Chapters 6 and 7 identified initiation zones at either ends of joint overlaps for phosphated HDGS. Surface analysis carried out within these regions determined that a combination of cathodic activity and ingress of water was responsible for the formation of the initiation zone on mechanical testing. This failure mechanism has been termed cathodic weakening with cohesive and interfacial failed regions existing in the initiation zone. The effect of the exposed iron cathode has been investigated by calculating possible corrosion currents and predicting regions of potential distribution around the cut edge of HDGS. The basic calculations made predict that virtually all electrons produced at the exposed zinc will be consumed at the relatively large iron cathode with it being very unlikely that electrons would consumed at the covered zinc. By applying an established model to predict potential distribution at the cut edge of HDGS, it becomes clear that the zone of electrochemical potential available for cathodic activity under the polymer covered zinc is extremely small, if indeed it exists at all. The electrochemical activity observed by surface analysis is too far away from the cut edge of the overlap for any possible zone of potential to have any impact on a failure mechanism. These predictions confirm that that the cathodic activity observed is not a result of
electrochemical activity that has originated from the exposed edges of HDGS, indeed, the iron cathode may act to slow formation of the initiation zone by attracting cathodic activity.

The growth rate of the initiation zone does not follow standard diffusion kinetics inferring that water diffusion is not the dominating mechanism. By comparing the rate of cathodic delamination with Leidheiser's predicted rate of charge per day it is possible for cathodic activity to be responsible for driving the initiation zone forward. The size of the initiation zone has been shown to be related to bond strength, for a structural epoxy system. Further evidence to suggest that electrochemical activity is the dominating factor is provided by analysing the joints immersed in pure water with low partial pressures of oxygen. Limited oxygen supply has slowed the rate of growth of initiation zone and retention of bond strength has improved over time. Oxygen is key requirement for the cathodic corrosion half equation and so limiting its availability, in the case of immersing joints, has a severe effect on the rate of joint degradation, indicating the importance of cathodic activity.
Chapter Nine

The Failure Mechanisms of Hot Dipped Galvanised Steel

9.1. Introduction

The previous chapters have discussed various aspects of the mechanism of failure of adhesively bonded galvanised steel. The heterogeneous nature of the substrate has been characterised and the effect of aluminium on acid-base interaction sites evaluated. Chapter 6 identified thin strips of apparent interfacial failure at either ends of failed overlaps, termed initiation zones. Selected area XPS was carried out within regions and determined that electrochemical activity played a part in initial bond degradation. The development of an imaging ToF-SIMS methodology allowed the role of the adhesive within the initiation to be characterised, taking advantage of the molecular sensitivity of SIMS. Small area XPS considered the effect of electrochemical activity on the phosphate pretreatment, identifying denuded areas which were characteristic of cathodic activity. Both of the surface analysis techniques have identified cathodic weakening mechanisms within the initiation zone, combining cathodic disbondment and a thin cohesive failure as a result of water ingress.

A simplistic modelling approach has shown that any electrochemical activity is initiated as a result of local cells set up at the substrate/adhesive interface and not as a result of exposed zinc at the overlap edge. Mechanical data generated from the structural adhesive system confirmed the importance and relevance of the initiation zone on overall joint performance, with load to failure related to size of initiation
zone. The purpose of this chapter is to consider the conclusions from the previous experimental chapters and to not only determine a failure mechanism for adhesively bonded HDGS, but also to document the steps involved and also speculate on possible ways of improving durability. At appropriate points in the text additional analytical data are included to further support a well developed hypothesis or to provide a rebuttal to an alternative scenario.

9.2. Failure Mechanism for the Two Adhesive Systems

9.2.1. A Comparison of Structural and Sealant Type Adhesives

Surface analysis has been carried out on failed lap shear joints that have been fabricated using two different adhesive types; a commercial structural epoxy and a polybutadiene sealant adhesive of known formulation. Chapters 6 and 7 studied the locus of failure through the initiation zones of these different adhesive systems using ToF-SIMS to study the epoxy joints and small area XPS to analyse the sealant joints. The complementary analysis techniques of SIMS and XPS were used to identify similar failure characteristics responsible for the formation of an initiation zone despite different adhesive systems being used. SIMS identified cathodic markers and specific polymer molecular ions whilst XPS established that the dissolution of the phosphate pretreatment had occurred. The quantitative nature of XPS was exploited to show the presence of polymer within the initiation zone. Small area XPS (20 μm) carried out within the initiation zone of the structural epoxy joints confirmed that the failure mechanism proposed for the two adhesive systems was compatible. Once again light and dark areas were observed within the initiation zone and closer inspection of these areas revealed denuded regions of phosphate pretreatment, Figure 9.1. One possible conclusion from these complementary findings infers that, for the phosphate pretreatment, the failure mechanism appears to be independent of adhesive type, this is also discussed in the next section.
Figure 9.1. Small Area XPS (20 μm) within an initiation zone of a 11 month aged phosphated HDGS with a structural epoxy adhesive acquired from (a) dark region with pretreatments and (b) bright area showing a clean zinc surfaces.

The mechanical data generated by the of the different adhesive type systems, however, is markedly different. As was seen from the plots of load to failure against time in Chapter 8, Figures 8.10 and 8.14, the epoxy adhesive initially carries a load to failure approximately six times greater than the polybutadiene system. The structural adhesive out performing the sealant adhesive is not a great surprise (the respective adhesives are designed for very different applications), however, the respective load to failure also seems to be reflected in the locus of failure through the joint. For the sealant adhesive system by far the weakest path for the locus of failure appears to be through the middle of the adhesive yielding a cohesive failure, Figure 9.2 and yielding
little if any plastic deformation to the substrate. For the stronger structural adhesive system, however, fracture propagates close to the substrate/adhesive interface and at approximately the mid-point of the overlap switches from one interface to the other, Figure 9.2. In the case of the phosphate pretreatment fracture can actually occur through the mechanically weak phosphate crystals, this was observed in this study and has also been reported in the literature [134]. Whilst the mechanism of failure for the initiation zone appears to be similar for both adhesives the initiation zone is much less well defined in the sealant system than in the structural joints. This may once again be related to the weak nature of the polybutadiene adhesive allowing failure to occur through the adhesive at lower loads and thus controlling stress concentrations at the ends of the overlap.

Figure 9.2. Schematic diagram showing the general loci of failure through failed joints of the different adhesive types.

**9.2.2. The Effect of Different Pretreatments**

Whilst the majority of the study has focussed on the failure mechanisms of phosphated HDGS, four pretreatments have been employed throughout the course of the project:

(a) Yttrium (alkali cleaned HDGS treated with aqueous Y(NO₃)₃
(b) Control (alkali cleaned HDGS)
(c) Mixed Oxide (Co/Ni/Fe) with a chrome rinse
(d) Phosphated HDGS with a chrome treatment
Relatively routine surface analysis was all that was required to determine the failure mechanisms for the first two pretreatments. For the yttrium pretreated joints, failure was found to occur at the yttrium/adhesive interface, suggesting that poor or non-existent intrinsic bonding between the respective interfaces had occurred. Previous work with yttrium has shown it to be extremely dependent on adhesive type and most encouraging results that have been obtained using the rare earth treatment have generally been coupled with silanes [110]. The control system was found to be susceptible to anodic dissolution of the zinc with XPS showing that failure occurred through a weak zinc corrosion product, this was in strong agreement with the literature [45].

Whilst previous work has shown the performance of yttrium pretreated substrates to be a function of adhesive type, the phosphated HDGS in this study showed a similar mechanism of failure with two very different adhesives. The fourth pretreatment to be tested was a mixed oxide (Co/Ni/Fe), ultimately this was used as a comparison for the performance of the phosphate treatment. Although lower loads to failure were achieved reasonable retention of initial bond strength was observed, Figure 8.10. The lower initial bond strength was a little surprising as a smoother substrate could possibly be expected perform better under a mechanical load compared to phosphate crystals, which are considered to be weak at the basal plane. Previous results from British Steel Strip products had found the mixed oxide treatment to out perform the phosphate treatment, [60]. The mixed oxide system was only tested using the structural adhesive, previously reported initiation zones were observed on the failed overlaps and imaging ToF-SIMS was carried out within the initiation zone of a 9 month aged joint. Figure 9.3 (a) and (b) shows the resultant images for m/z 24, characteristic of the cathodic marker magnesium and m/z 135, the characteristic marker for epoxy adhesive. An overlay of these two images, Figure 9.4, shows a remarkably similar result to the images shown in Chapter 6 and it would appear that a similar mechanism is responsible for the formation of the initiation zone despite a change in substrate pretreatment.
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Figure 9.3. Positive ToF-SIMS images showing (a) $^{24}\text{Mg}^+$ (cation rich areas) and (b) m/z = 135 (polymer rich areas).

Figure 9.4. Positive ToF-SIMS in showing that the cation rich and polymer rich areas do not coincide (green = $^{24}\text{Mg}^+$ and red = m/z 135).

Once again cathodic activity is seen to play a major role in the formation of the initiation zone, leaving areas of true interfacial failure and separation between adhesive and substrate prior to mechanical testing. Electrochemical activity is thought to occur as a result of local cells set up on the substrate surface, as demonstrated by a series of simple electrochemical equations in Chapter 8. This seems to agree with SIMS images but does pose problems such as the lack of an anode and how does the route by which the reactants for the corrosion half cells arrive at the interface. A mechanism for the formation of the initiation zone and hence failure characteristics of adhesively HDGS has been proposed and the next section will address the outstanding points, such as those raised above by providing a series of schematic diagrams and concluding with some suggestion for improvement to the adhesive system.
9.3. The Role of Electrochemistry in the Formation of the Initiation Zone

Considerable importance has been attached to the presence of an initiation zone in the failure surfaces of adhesively bonded HDGS, the mechanical data displayed in Chapter 8 has justified the care and attention taken over its analysis by showing that joint performance is related to its size. Three mechanisms for failure have been proposed for the formation of initiation zones; water ingress, responsible for a thin cohesive failure close to the substrate interface and two mechanisms associated with cathodic activity resulting in a true interfacial failure either through delamination of the organic phase or dissolution of the pretreatment, Figure 9.5. The three mechanisms observed are all identifiable with the failure mechanisms introduced and discussed in Chapter 2, an interfacial failure and cohesive failure of the polymer has been identified by imaging ToF-SIMS. The dissolution of phosphate crystals (characterised by small area XPS) may be compared to Ritter’s observations on the dissolution of oxide films under cathodic conditions [26].

![Figure 9.5. Schematic diagram illustrating the proposed failure mechanisms responsible for the formation of the initiation zone.](image)

The electrochemical activity appears to be the more significant of the failure mechanism. Delamination or dissolution characteristics are irreversible, however, if
allowed to dry out wet adhesion failures are believed to recover up to 80% of their lost strength [25]. The calculations concerning the origin of any possible electrochemistry within the system showed that any anodic activity generated at the edge of the overlap would be balanced by all electrons produced being consumed at the large exposed iron cathode. Thus, in order for any electrochemistry to take place within the initiation zone local cells must be set up at the substrate surface. For cathodic activity to prevail reactants such as oxygen and water must still reach the substrate interface and a mechanism must be postulated for this in order for the overall failure process to be fully understood. The relatively simple explanation of diffusion of water through the polymer is not satisfactory, water will diffuse in the molecular form, however, to act as reactant for electrochemical activity it must be present in liquid form and so would require a surface to nucleate on. A likely host for nucleation of water may well be the ballotini, which are randomly sprinkled throughout the overlap area during joint fabrication. Ballotini have already been identified as the source for the magnesium which acts as a marker for areas of cathodic activity during SIMS imaging and so magnesium may be leached out of the glass ballotini on nucleation of water, transported to the substrate and involved in subsequent corrosion reactions. The presence of ballotini may also accelerate the transport of “electrolyte” by providing what Funke has described as a non-activated transport path [135]. Funke proposes that coatings with pores much larger than the mean jump distance of diffusing molecules or ions can generally be defined as multiphase systems, as they will include additives such pigments or in this case ballotini. These additives provide preferential transport paths for water within the organic phase towards the metallic substrate as shown in Figure 9.6.

![Figure 9.6. Possible diffusion path for water within the organic phase.](image-url)
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This proposed transport path explains the existence of local corrosion cells, however, a major concern with the present mechanism of failure is the apparent lack of any ions diagnostic of anodic activity in the surface analysis. Naturally for any cathodic activity to occur, anodic activity must take place as well; however, no real signs of anodic corrosion products have been detected within the initiation zone. One possible scenario could be that magnesium leaches out into the nucleated water and creates an alkaline liquor that actually bring about delamination of the adhesive and dissolution of the phosphate pretreatment. This idea becomes more plausible considering that no corrosion process is involved, i.e. no anodic activity is required, and would lead to areas of interfacial failure similar in size to the ballotini, i.e. in the order of 100 μm, the areas hitherto thought of as indicative of cathodic activity. This possibility is very easily investigated. The pH required for the delamination of polymer from a substrate is very high, 12 and above, the values achieved by cathodic activity [30]. In order for an alkali solution to strip adhesive off a substrate a condition of extremely high pH must be reached. This possibility was investigated by monitoring the pH of the water over a period one month and placing a relatively large volume of glass ballotini with milli-Q water in sealed containers at a temperature of 40°C, Figure 9.7. Whist initially the pH of the solution does increase it reaches a plateau quickly and never rises above 9, thus the kind of value required to cause delamination of polymer and phosphate dissolution is never achieved.

![Figure 9.7](image_url)

Figure 9.7. A graph showing the effect of ballotini on the pH of water as a function of time.
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Although the idea of alkaline liquor may not be valid there is still the problem of the lack of identifiable anodic activity within the initiation zone. This cannot be the case and another alternative could be the presence of a micro-anode, possibly caused by discrete heterogeneities or imperfections at the substrate interface [136]. A micro-anode would be difficult to detect but would explain the restricted size of the cathodic activity observed in the SIMS images, Figure 9.8 (a). The comparatively large consumption of electrons at the exposed iron of the free cut edge of the substrate may also contribute the restricted size of cathodic activity. However, the growth of the initiation zone appears to be almost directly related to time and so is not completely restricted to the very outside of the overlap, a small anode seems a more reasonable explanation for the restricted cathodic activity.

Figure 9.8. A schematic representation of (a) a micro anode with surrounding cathodic region and (b) a proposed mechanism for cathodic activity within the initiation zone.

The main experimental chapters of this thesis suggest mechanisms of failure for adhesively bonded HDGS. This section has concentrated on some of the issues proposed by the previous chapters and attempted to provide credible explanations for the observed phenomena. It is suggested that ballotini plays a significant role in the proposed failure mechanism, providing a nucleation site and transport path for water, Figure 9.8 (b). The existence of micro-anodes at the substrate would explain the relatively little amount of anodic activity observed but more importantly explain the restricted size of the deleterious cathodic activity which appears to be the dominating mechanism of the initiation zone. The restricted regions of cathodic activity “leaves room” for a second mechanism of failure within an initiation zone; a “wet adhesion”
type failure resulting in a thin cohesive failure close to but not at the substrate interface.

9.4. Further Work

The failure mechanisms of adhesively bonded HDGS have been established. The first stage of any durability study is to understand why a system fails, then suggestions and work for improvement in performance can be started and so the aims of the project have been met. This work has been funded by Corus, with a view to expanding the use of adhesively bonded HDGS in automotive applications and so the greatest control over changes within this particular system lies with modification of the substrate. This is fortunate as on the basis of this work it has been shown that initial modification of the substrate has already led to a substantial improvement in performance, compared to the poor durability performance of alkali cleaned HDGS.

In the previous section the role of ballotini was discussed at length, whilst they cannot cause cathodic delamination, a result of local electrochemical cells at the substrate surface, it does appear that they have an effect on the overall mechanism. One possible effect of ballotini may be the acceleration of bond degradation and the formation of the important initiation zone by aiding the transport and acting as a nucleation site for water. An interesting short-term investigation, therefore, would involve a durability study using an alternative form of fixing the glueline thickness; this should obviously exclude methods that may have an effect on any possible electrochemical activity such as copper wire, the careful use of a precise jig or nylon wire could be a possibility. Joint performance could be examined by monitoring the load to failure and also the growth of any resultant initiation zone. A more rigorous study could also include the use of surface analysis techniques.

An alkali cleaning methodology was employed to remove both hydrocarbon contamination and surface segregated species. A systematic and reliable methodology has been developed for the surface preparation of as received HDGS suitable for adhesive bonding. Quantitative XPS has been used to determine the chemical nature of the cleaned HDGS substrate. The water break test, widely used in
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industry to assess metallic substrates following alkali cleaning, is not appropriate and can inadvertently imply that a heterogeneous surface is clean and suitable for bonding, which in turn can have serious ramifications on adhesive joint performance. This is particularly relevant where unpretreated HDGS is adhesively bonded or a pretreatment that does not involve metal attack is employed. It may not be practical for industry to employ XPS to inspect an alkaline cleaned surface, however, an improvement in the industrial protocol for the alkali cleaning of HDGS should be considered.

Work carried out on alkali cleaned HDGS revealed that anodic dissolution had a severe effect on joint performance. By treating the surface with a phosphate conversion coating durability was improved greatly, although initial bond strengths were actually lower than the initial bond strengths of the alkali cleaned system. This observation was not wholly unexpected; whilst phosphate treatments have in the past acted as pretreatments for coatings their use in adhesive bonding has been somewhat limited due to fears that they are mechanically weak and do not perform under load, acting as a weak boundary layer. A pretreatment that provided the durability performance of a phosphate-based pretreatment with no penalty to initial bonded strength would be preferred.

A chromate treatment was used to inhibit corrosion, however, analytical data has identified cathodic behaviour responsible for initial bond degradation in this study. A non-uniform chromium treatment, however, would leave the substrate open to electrochemical attack and coverage of the pretreatment should be investigated. Mechanical damage of the phosphate crystals has been reported in this study, which may well affect the chrome treatment as well. The effect of cracks, observed by the SEM investigation, on the pretreatment stability under cathodic conditions should be explored. A series of electrochemical experiments holding respective substrates at anodic and cathodic potentials in appropriate solutions with marker ions would, hopefully reveal the yet undetected anodic sites. One possible method of analysing a pretreatment's resistance to cathodic activity may be to determine polarisation curves and monitor cathodic current, a low cathodic current may indicate a resistant coating.
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The improved performance of the phosphated joints does not aid the development of an environmentally friendly pretreatment, phosphating lines generate toxic wastes, along with the problem of carcinogenic hexavalent chromium employed in chromating [137]. The development of an yttrium pretreatment in this study did not yield encouraging results, however, the main thrust of the project was to understand the failure mechanism of already established pretreatments and attempts to improve the poorly performing system were not made. Whilst results from this study indicate that yttrium does not produce a durable joint its behaviour with adhesion promoters such as silanes may well give improved adhesive joint behaviour. Further investigation of rare earth metal pretreatments should not be discounted.

The adhesives industry has an increasing need for environmentally friendly pretreatments and whilst this project has not furthered the development of any “green” pretreatment it does highlight some of the major issues that must be addressed in the development of a pretreatment for adhesively bonded galvanised steel. Cathodic activity has been identified on failed substrates and found responsible for initial degradation for different adhesive systems. Condition of the substrate surface plays a major role in adhesion, influences electrochemical activity and in turn bond durability. The conclusions from this study must be used to develop a tenacious pretreatment capable of producing improved durability performance for adhesively bonded HDGS and improve its position within the automotive industry. This project has recognised certain durability issues in adhesion by employing surface analysis. It is hoped that the methodologies used can be exploited in any subsequent stages of this project as well as elsewhere in the world of adhesion and spectroscopy.
Chapter Ten

Conclusions

10.1. Introduction

The work described in this thesis has studied the failure mechanisms of adhesively bonded HDGS. Lap shear joints have been fabricated and exposed to 98% relative humidity for up to 12 months. The durability performance of a series of joints with various pretreatments has been monitored. Surface analysis has been used to characterise components of the adhesive system, defined the exact locus of failure and interrogate specific failure regions of interest. The analytical data generated has been used successfully to derive a failure mechanism for adhesively bonded HDGS. The principal analytical techniques employed in this study have been ToF-SIMS and XPS. Both have potential shortcomings when used to study an adhesive system however, used together they have produced unambiguous and complementary data. The two surface specific techniques have been used in a novel manner in this study, which potentially could be employed in many areas of research and not just adhesion.

10.2. The Surface Characterisation of HDGS

Standard area XPS carried out on as received HDGS used in this study identified aluminium present at the surface. Prior to coating or adhesive bonding industry uses an alkali cleaning solution on HDGS to remove mill oils and other deleterious contamination. Alkali cleaning is also known to attack the metal surface causing
dissolution and thus the removal of the aluminium. This project has demonstrated that reduction of the surface concentration of aluminium by alkali cleaning does not bear a straightforward relationship to the process parameters of the process. Furthermore the water break test, employed by industry to characterise the surface condition of HDGS, merely gives an indication of the wettability of the substrate and does not ensure that complete removal of aluminium has taken place.

The presence of aluminium on the surface of HDGS has been found to affect the density of acid base sites available for interaction with an organic phase. Despite the amphoteric nature of both aluminium and zinc only basic sites were observed. As the surface concentration of aluminium decreases the number of strong basic sites available for interaction decreases, indicating that presence of aluminium will indeed affect the adhesion properties of HDGS. The effect of aluminium on phosphate deposition was also investigated, however, no changes in crystal structure or morphology were observed even when the surface concentration of aluminium was as high as 13 atomic percent. Whilst there are concerns over the presence of aluminium on HDGS for adhesive bonding no aluminium was found on fracture surfaces throughout the subsequent durability study.

10.3. The Deposition of Cathodic Yttrium as a Pretreatment for HDGS

The use of yttrium as an environmentally friendly pretreatment for adhesively bonded HDGS has been investigated. Deposition conditions were found by establishing solution kinetic and concentration requirements, with surface concentration determined using quantified XPS data. A 10 minute exposure to a solution of $10^{-2}$ M yttrium nitrate was found to yield maximum uptake of yttrium. On inspection by EDX, however, a strong yttrium signal is obtained, implying the rare earth pretreatment exists as a thick layer, not ideal for adhesive bonding. Scanning Auger microscopy has also shown that cathodic yttrium is deposited in an island like formation. Joints fabricated using an yttrium pretreatment produced very poor durability, the results obtained were inferior to the control samples assembled from alkali cleaned HDGS. Failure occurred at the adhesive/yttrium interface in both dry
and aged joints, indicating a low level of adhesion between the pretreatment and adhesive layer. Yttrium has shown both encouraging and poor durability results with other substrates and in the past has been found to be adhesive dependent [128]. The use of a coupling agent with a rare earth pretreatment should not be discounted either, having given reasonable performance on mild steel in the past [110].

10.4. Surface Analysis of Failed Interfaces

Alkali cleaned phosphated HDGS adhesive bonds have been aged, mechanically tested and their failure surfaces interrogated by XPS and ToF-SIMS. In agreement with previous studies the alkali cleaned samples failed cohesively through a layer of a weak zinc corrosion product. At the exposed cut edge of the substrate zinc will act as a sacrificial anode protecting the iron cathode, resulting in anodic dissolution of the zinc and the development of a weak corrosion product, (zinc oxide).

On the phosphated joints a thin strip of visually interfacial failure has been identified at the ends of the failed overlaps, termed an initiation zone. Extensive surface analysis has shown that the formation of the initiation zone is the result of environmental degradation. Surface analysis has identified two distinct regions of failure within the initiation zone:

i) Wet adhesion failure; resulting in a thin cohesive failure.
ii) Local cathodic cells; resulting in true interfacial failure.

ToF-SIMS imaging has demonstrated molecular specificity and good detection limits by identifying traces of adhesive in the initiation zone (characteristic of a wet adhesion failure) and magnesium in areas deficient in polymer which provide elemental markers for cathodic activity (interfacial failure). Cathodic activity generates aggressive hydroxyl ions that can cause delamination of an organic phase. In work with mild steel joints, cathodic activity has been shown to drive a delamination front forward leading to complete separation prior to mechanical testing. This is not the case with the HDGS systems of this study; cathodic rich areas do exist,
however, these are complementary to adhesive rich areas leading to the introduction of the term cathodic weakening rather than classical cathodic delamination.

Advances in small area XPS in recent years have allowed specific areas within the initiation zone to be interrogated and in particular has shown the effect of cathodic activity on a phosphate pretreatment. A zoom microscope fixed on the spectrometer has identified bright and dark patches within the initiation zones of failed joints. Small area XPS at a spot size of 20 µm, has shown the bright regions to be denuded phosphate regions. Cathodic activity within the initiation zone has resulted in the dissolution of the phosphate crystals. Small area XPS analysis across an initiation zone has also identified traces of adhesive within the initiation zone. ToF-SIMS and XPS have produced complementary data indicating that the formation of the initiation zone is the result of cathodic weakening with mechanical loading.

10.5. The Origin of Electrochemical Activity within the Initiation Zone

The significance of the initiation zone is indicated by the mechanical data generated throughout the durability study. The size of the initiation zone is directly related to the load to failure of the joints tested. Examination of the kinetics of the development of the initiation zone indicates the absence of a diffusion controlled phenomena. Thus it is not the migration of water, alone, within the adhesive which is primarily responsible for the formation of this zone. Loss in joint performance due to water ingress may be reversible, however, cathodic delamination effects are permanent and considered more pernicious. Based on an established electrochemical model and theoretical considerations the origin of electrochemical activity has been identified as local corrosion cells set up on the HDGS surface. It is thought that glass ballotini not only provide nucleation sites for molecular water but also a diffusion route for subsequent liquid water. This explains the patchy nature of initiation zones, with cathodic activity leading to interfacial failure in a similar spatial distribution to that of the ballotini in the adhesive. Whilst ballotini are not responsible for the formation of the initiation zone it is believed they have played an important role in identifying the deleterious affects of cathodic activity at the failed interface. With arguably
fortuitous hindsight the use of ballotini has benefited the project; by providing a source of marker ions identifying cathodic activity, a sight for water nucleation and a transport path for liquid water to arrive at the substrate surface. Considering the above point the presence of ballotini may appear detrimental to durability performance, however they only affect the kinetics of failure and not the overall failure mechanisms.
References

3. E. Lawley, "The Use of Adhesives in the Automotive Industry: Case Studies" Published report by Land Rover Ltd. UK.
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