A Study by Auger Electron and X-Ray Spectroscopies of Vacuum Brazing.

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A Thesis submitted for the degree of Doctor of Philosophy to the University of Surrey.

January 1986.
Summary.

Brazing may be described as more of an art than a science, there is little comprehension of the basic mechanisms governing brazing in air or vacuum. Consequently the behaviour of the Gold 18% Nickel brazing alloy in vacuum was studied using the novel techniques of hot-stage scanning electron microscopy with simultaneous bulk and surface analysis. The work demonstrates that careful control of experimental conditions allows both Auger electron and X-Ray spectroscopies (AES and EDXA) to be carried out at high spatial and energy resolutions, with good signal to noise in a realistic analytical time.

Combining post-brazing examination of samples heated in a UHV oven, with real-time studies of braze powder/substrate combinations on a heating stage in an Auger microprobe, revealed several important mechanisms. Vacuum brazing is a two-stage process; oxide penetration followed by wetting and spreading via a suboxide route. AES analysis showed that oxide penetration is achieved by reduction as a result of low oxygen partial pressures and high carbon activities, in the system as a whole, or locally (for example under or around a molten braze droplet), leaving an oxide-free surface, or a discontinuous, penetrable oxide.

After penetration has occurred wetting and spreading continues along the metal/metal-oxide interface. Flow may be impeded by residual oxide resisting the advancing liquid which is trying to disbond it. Alternatively, interdiffusion of the braze metal and substrate allows pick-up of elements which raise the melting temperature of the braze alloy and causes solidification. EDX analysis and digital element mapping during interdiffusion and solidification illustrates that the periphery of the braze pools are most affected, and that further elevating the temperature initially caused remelting, but eventually resulted in second phase formation in accord with the Au/Ni/Fe equilibrium diagram.
The use of Auger electron and X-ray spectroscopies to study vacuum brazing.

1 Introduction .......................................................... 1
2 Literature Survey ..................................................... 3

2.1 Vacuum brazing ...................................................... 3
2.1.1 Introduction .................................................... 3
2.1.2 Theory of wetting, spreading, and capillary flow .......... 10
2.1.3 Mechanisms of oxide displacement, wetting, and spreading 19
2.1.4 The interalloying of braze and parent metals ............. 25
2.2 Oxidation ............................................................ 29
2.2.1 Introduction .................................................... 29
2.2.2 Oxidation of iron in air and vacuum ....................... 31
2.2.3 Oxidation of iron-chromium alloys in air and vacuum .... 34
2.2.4 The influence of silicon and boron additions to the oxidation of iron and iron-chromium alloys ........ 43
2.3 Auger Electron Spectroscopy ....................................... 47
2.3.1 Introduction .................................................... 47
2.3.2 Auger electron spectroscopy - a short history ........... 47
2.3.3 Theoretical considerations .................................. 48
  2.3.3.1 The Auger effect ........................................ 48
  2.3.3.2 Production of Auger Spectra ............................ 54
  2.3.3.3 Pulse-counted vs. differential spectra for AES ...... 57
2.3.4 The development of high spatial resolution Auger spectrometers ......................................................... 61
2.4 Summary of literature survey .................................... 75

3 Optimisation of resolution for the V.G. MA500 ..................... 76

3.1 Introduction ....................................................... 76
3.2 Experimental ...................................................... 78
3.3 Results ............................................................ 82
3.4 Discussion ....................................................... 86
3.5 Conclusions ...................................................... 94

4 The oxidation and reduction of iron and iron-base alloys in air and vacuum ................................................. 95

4.1 Introduction ....................................................... 95
4.2 Experimental ...................................................... 96
  4.2.1 Oxide preparation ........................................... 96
  4.2.2 Heating stage studies ....................................... 97
4.3 Results and Discussion .......................................... 98
  4.3.1 Characterisation of native and prepared oxide films .... 98
    4.3.1.1 Native oxides ........................................ 98
    4.3.1.2 Films formed by heating in air ..................... 103
    4.3.1.3 Films formed by heating in a vacuum microbalance . 105
    4.3.1.4 Films formed by heating in a UHV environment .... 108
    4.3.1.5 Summary of oxide characterization ................ 112
  4.3.2 Hot-stage Auger spectroscopy of oxide covered surfaces 113
    4.3.2.1 The behaviour of oxides on chromium-free iron .... 113
      and iron alloys during heating in vacuum ...
    4.3.2.2 The behaviour of oxides on chromium containing .... 116
      iron alloys during heating in vacuum ...
5 Wetting and spreading of braze alloys on metal surfaces.............125

5.1 Introduction......................................................125
5.2 Experimental.....................................................127
  5.2.1 Ultra high vacuum oven spreading tests..........................127
  5.2.2 Heating stage studies........................................128
5.3 Results.............................................................133
  5.3.1 Ultra high vacuum oven spreading tests..........................133
    5.3.1.1 Orobraze 950 on Specpure iron............................134
    5.3.1.2 Orobraze 950 on Fe/Si (alloy 10)........................136
    5.3.1.3 Orobraze 950 on Fe12Cr (alloy 1).........................137
    5.3.1.4 Orobraze 950 on Fe12CrSi (alloy 5)......................139
    5.3.1.5 Orobraze 950 on Fe20Cr.................................140
    5.3.1.6 Orobraze 950 on Jethete M152............................142
    5.3.1.7 Orobraze 950 on 2328 Stainless..........................143
    5.3.1.8 Orobraze derivatives on Iron and Fe20Cr.................144
    5.3.1.9 Miscellaneous alloys on Iron and Fe20Cr................145
    5.3.1.10 Summary of UHV oven experiments........................147
  5.3.2 Heating stage studies.........................................148
    5.3.2.1 OB950 on specpure iron and Ferrosilicon...............149
    5.3.2.2 OB950 on alloy 1 (Fe12Cr) and Fe20Cr..................151
    5.3.2.3 Summary of heating stage studies.........................154
5.4 Discussion.......................................................155

6 Conclusions........................................................171

Appendix I - Preliminary data processing for optimisation of resolution work

Appendix II - Method for calculating the oxygen partial pressure in the presence of carbon.

Acknowledgements

References
List of figures

Figure 2.1 : The forces on a liquid droplet.
Figure 2.2 : The forces on liquid between two parallel plates.
Figure 2.3 : Diagram showing the principles of Auger electron and X-ray emission
Figure 2.4 : Relative probabilities of Auger electron and X-ray emission from a K-shell ionisation
Figure 2.5 : Depth dependence of electron emission
Figure 2.6 : Variation of the IMFP with electron energy
Figure 2.7 : Schematic diagram of an RFA
Figure 2.8 : Schematic diagram of the basic CMA
Figure 2.9 : Schematic diagram of an advanced CMA
Figure 2.10 : Schematic diagram of a CHA
Figure 3.1 : Spatial distribution of sources and detectors in the MA500
Figure 3.2 : General configuration of the V.G. MA500 (Plate I)
Figures 3.4-3.11 : Signal to noise versus 1/square root of peak counts.
Figures 3.12-3.19: Signal to noise versus square root of peak counts.
Figure 3.20 : Multiple element plot of S/N vs. square root of peak counts.
Figures 3.21-3.26: Pass energy versus count-rate curves.
Figure 3.27 : S/N vs. channel spacing at constant total count time and at constant time per channel.
Figure 3.28 : The effect of tilt angle upon the peak net integral.
Figure 3.29 : Pass energy vs. analyser resolution (FWHM).
Figure 3.30 : Pass energy vs. analyser resolution (XPS data only).
Figure 3.31 : Calculated pass energy vs. count-rate curves for Chromium.
Figure 3.32 : Log I/i vs. Log pass energy for copper and chromium.
Figure 3.33 : Resolution diagram for copper.
Figure 3.34 : Resolution diagram for chromium.
Figure 3.35 : Resolution diagram and value table for Nickel
Figure 3.36 : Resolution diagram and value table for Silver
Figure 3.37 : Resolution diagram and value table for Iron
Figure 3.38 : Resolution diagram and value table for Chromium
Figure 3.39 : Resolution diagram and value table for Gold
Figure 3.40 : Resolution diagram and value table for Copper
Figure 3.41 : Diagram showing the effect of variables on the resolution diagrams.
Figure 4.1 : Typical time-temperature profile for hot-stage tests
Figure 4.2 : XPS widescans typical of the native oxides on chromium-free iron alloys and iron
Figure 4.3 : Typical spectra showing the effect of ion-etching on the Oxygen 1s peak
Figure 4.4 : Typical spectra showing the effect of ion-etching on the Iron 2p3/2 peak
Figure 4.5 : Typical spectra showing the effect of ion-etching on the Silicon 1s peak
Figure 4.6 : Widescans typical of the native oxides on chromium containing iron alloys
Figure 4.7 : Typical spectra showing the effect of ion-etching on the Chromium 2p3/2 peak
Figure 4.8 : Typical spectra showing the effect of ion-etching on the Nickel 2p3/2 peak
Figure 4.9: Auger electron spectrum typical of the native oxide on Fe20Cr
Figure 4.10: Auger electron spectrum typical of the air-formed oxide on chromium-free iron alloys
Figure 4.11: Auger electron spectrum typical of the air-formed oxide on Fe20Cr
Figure 4.12: RBS spectrum typical of the oxide formed on Fe20Cr
Figure 4.13: Auger electron spectrum typical of the air-formed oxide on Jethete M152
Figure 4.14: Auger electron depth profile through the air-formed film on Jethete M152
Figure 4.15: XPS widescans of the microbalance rig oxide formed on alloy 1
Figure 4.16: XPS narrowscans of the microbalance rig oxide formed on alloy 1
Figure 4.17: Auger electron spectra typical of the surface of Fe20Cr heated in a vacuum microbalance rig
Figure 4.18: XPS spectra typical of the surface of Fe20Cr heated in a vacuum microbalance rig
Figure 4.19: RBS spectrum of the film formed on Fe20Cr heated for 7 hours at 712°C in a vacuum microbalance rig
Figure 4.20: Aluminium and magnesium XPS spectra of a typical film formed by heating alloy 1 in UHV
Figure 4.21: Aluminium and magnesium XPS spectra of a typical film formed by heating Fe20Cr in UHV
Figure 4.22: XPS spectra of a typical film formed by heating Fe20Cr in UHV
Figure 4.23: Auger electron spectra of a typical film formed by heating Fe20Cr in UHV
Figure 4.24: Auger spectra showing the behaviour of the air-formed oxide on pure iron during heating in vacuum
Figure 4.25: Free energy versus temperature diagram for iron, chromium, and silicon oxides
Figure 4.26: CO/CO₂ and H₂/H₂O ratios for iron, chromium, and silicon oxides
Figure 4.27: Auger spectra showing the behaviour of the native oxide on Fe20Cr during heating in vacuum.
Figure 4.28: Auger spectra showing the behaviour of the air-formed oxide on Fe20Cr during heating in vacuum.
Figure 4.29: Effective partial pressure of oxygen as a function of temperature and in the presence of carbon.
Figure 4.30: Auger maps showing the surface composition of partially spread OB950 on Jethete (Plate IX)
Figure 5.1a: Time-temperature profiles for UHV oven experiments carried out at ~1000 degrees centigrade.
Figure 5.1b: Time-temperature profiles for UHV oven experiments carried out to examine the effect of temperature.
Figure 5.2: Voltage versus temperature dependence for the MA500 hot-stage.
Figures 5.3-5.7: Orobraze 950 on spectroscopically pure iron
Figures 5.8-5.11: Orobraze 950 on Ferrosilicon (Alloy 10)
Figures 5.12-5.16: Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)
Figures 5.17-5.20: Orobraze 950 on Fe/11.21Cr/1.05Si (Alloy 5)
Figures 5.21-5.28: Orobraze 950 on Fe20Cr
Figures 5.29-5.33: Orobraze 950 on Jethete M152
Figures 5.34-5.35: Orobraze 950 on 2328 Stainless steel
Figures 5.36-5.39: Orobraze 950 derivatives on Specpure iron and Fe20Cr
Figures 5.40-5.42: Miscellaneous alloys on Specpure iron and Fe20Cr
Figure 5.43: Orobraze 950 on ferrosilicon (alloy 10) oxidised 25m at 400°C (Plate X)
Figure 5.44: Orobraze 950 on Specpure iron oxidised 10 mins at 400°C in air (Plate XI)
Figure 5.45: Auger spectra showing surface compositions of OB950 and Fe12Cr after vacuum brazing in the MA500
Figure 5.46: Orobraze 950 on Specpure iron oxidised 10 mins at 400°C in air (Plate XII)
Figure 5.47: Orobraze 950 on Specpure iron oxidised 10 mins at 400°C in air (Plate XII)
Figure 5.48: Orobraze 950 on Fe12Cr (alloy 1) native oxide (Plate XV)
Figure 5.49: Orobraze 950 on Fe20Cr oxidised 7 hours at 726°C (M) (Plate XV)
Figure 5.50: Orobraze 950 on Fe20Cr oxidised 7 hours at 726°C (M) (Plate XVI)
Figure 5.51: Orobraze 950 on Fe20Cr oxidised 25 mins at 575°C in air (Plate XVII)
Figure 5.52: Orobraze 950 on Fe20Cr oxidised 25 mins at 575°C in air (Plate XVIII)
Figure 5.53: Orobraze 950 on Fe20Cr oxidised 25 mins at 575°C in air (Plate XIX)
Figure 5.54: X-ray maps showing interdiffusion of Iron and Gold on alloy 1 (Plate XX)
Figure 5.55: Spectra showing sulphur on the surface of both braze and substrate prior to melting.
Figure 5.56: Figure showing Orobraze on Fe20Cr heated to , and analysed at four different temperatures (Plate XXI)
Figure 5.57: Auger maps showing phase separation in OB950 on Fe20Cr (air formed film) (Plate XXII)
Figure 5.58: X-ray maps showing phase separation in OB950 on Fe20Cr (air formed film) (Plate XXIII)
Figure 5.59: Isothermal sections showing the equilibrium between Gold, Nickel, and Iron at various temperatures.
List of Tables

Table 3.1: Table showing conditions used for Auger spectroscopy resolution studies.
Table 3.2: Conditions for the experiments examining the effect of channel spacing upon signal to noise ratio.
Table 3.3: Table showing the conditions for acquisition of magnesium X-ray excited Auger peaks at 60°tilt angle.
Table 3.4: Table showing the acquisition conditions for the Ag3d and Au4f XPS peaks at 60°tilt angle.
Table 3.5: Table showing the line fitting data for the pass energy vs. count-rate curves.
Table 3.6: Experimentally determined natural line widths for Auger peaks.
Table 3.7: Table showing the incidences of detector oversaturation.
Table 4.1: Substrates used for hot-stage and oxidation studies.
Table 4.2: Table showing oxidation treatments and analytical methods used.
Table 4.3: Substrate-oxide-braze metal combinations used for hot-stage Auger spectroscopy.
Table 4.4: Atomic percentage data for etch profiles and Al/Mg radiation depth studies on native and prepared oxide films.
Table 5.1: Table showing braze alloy compositions used for heating stage tests and UHV oven spreading tests.
Table 5.2: UHV oven runs carried out using Orobraze 950
Table 5.3: UHV oven runs carried out using brazing alloys other than unaltered Orobraze 950
Table 5.4: Table listing time, temperature, and substrate alloy combinations for the UHV oven runs.
Table 5.5: Table showing the incidences of effects seen on the UHV oven specimens.
Table 5.6: Weight percentage values from the areas shown in figure 5.56
**List of Plates**

| Plate I | General configuration of the VG MA500 (Figure 3.2)  
| Plate II | The heating stage in use in the MA500 (Figure 3.3)  
| Plate III |  
| Plate IV | Micrographs showing braze droplet (Figures 5.15-5.20)  
| Plate V | morphologies after brazing in vacuum. (Figures 5.21-5.26)  
| Plate VI |  
| Plate VII |  
| Plate VIII |  
| Plate IX | Auger maps showing the surface composition of partially spread OB950 on Jethete (Figure 4.30)  
| Plate X | Orobraze 950 on ferrosilicon (alloy 10) oxidised 25m at 400°C in air (Figure 5.43)  
| Plate XI | Orobraze 950 on specpure iron oxidised 10 mins at 400°C in air (Figure 5.44)  
| Plate XII | Orobraze 950 on specpure iron oxidised 10 mins at 400°C in air (Figure 5.46)  
| Plate XIII | Orobraze 950 on Fe12Cr (alloy 1) native oxide (Figure 5.48)  
| Plate XIV | Orobraze 950 on Fe20Cr oxidised 7 hours at 726°C (M) (Figure 5.49)  
| Plate XV | Orobraze 950 on Fe20Cr oxidised 7 hours at 726°C (M) (Figure 5.50)  
| Plate XVI | Orobraze 950 on Fe20Cr oxidised 25 mins at 575°C in air. (Figure 5.51)  
| Plate XVII | Orobraze 950 on Fe20Cr oxidised 25 mins at 575°C in air (Figure 5.52)  
| Plate XVIII | Orobraze 950 on Fe20Cr oxidised 25 mins at 575°C in air (Figure 5.53)  
| Plate XIX | X-ray maps showing interdiffusion of Iron and Gold on alloy 1 (Figure 5.54)  
| Plate XX | Figure showing Orobraze on Fe20Cr heated to , and analysed at four different temperatures (Fig. 5.56)  
| Plate XXI | Auger maps showing phase separation in OB950 on Fe20Cr (air formed film) (Figure 5.57)  
| Plate XXII | X-ray maps showing phase separation in OB950 on Fe20Cr (air formed film) (Figure 5.58)  
| Plate XXIII |  

(Figures 5.3-5.8)  
(Figures 5.9-5.14)  
(Figures 5.15-5.20)  
(Figures 5.21-5.26)  
(Figures 5.27-5.32)  
(Figures 5.33-5.38)  
(Figures 5.39-5.42)  
(Figures 5.43)  
(Figures 5.44)  
(Figures 5.46)  
(Figures 5.47)  
(Figures 5.48)  
(Figures 5.49)  
(Figures 5.50)  
(Figures 5.51)  
(Figures 5.52)  
(Figures 5.53)  
(Figures 5.54)  
(Figures 5.56)  
(Figures 5.57)  
(Figures 5.58)
1 Introduction

Vacuum brazing is widely used in industry as a high quality technique for joining incompatible or temperature sensitive materials, and for applications where the soundness of the final joint is of primary importance. A large number of vacuum brazed joints are made using precious metal containing braze compounds, the aerospace and nuclear industries being the main users. Precious metal filler metals fully satisfy the requirements of these industries, but their wider use is restricted by their prohibitively high cost. Most development work has been carried out empirically, since, as is the case with the entire brazing field, very little is known about the fundamental mechanisms which govern the behaviour of brazing alloys. Consequently the directions for further alloy development (for example to reduce the precious metal content and hence the cost) are unclear.

Any fundamental study of the brazing process will be primarily concerned with either how various parameters affect the formation of a joint, or how the properties of a finished joint might be affected by changing conditions. This work is concerned with the former; the effect of various factors upon the formation of a brazed joint. To make a strong, sound joint, the most important property of the braze metal is that, once it is molten, it can flow freely along the joint, and continue to flow until the joint is properly filled. The ability to fill a joint is dependent upon several factors, the most important of these being the wetting and spreading behaviour of the alloy on the chosen substrate. The theory of wetting and spreading is well developed, and it highlights further factors which are likely to affect wetting and
spreading, and hence the joint-filling characteristics. Amongst these further factors, the presence of an oxide film on the substrate, the segregation of species to the substrate surface, and interdiffusion of species between the braze and parent metal, are all liable to be important to the final behaviour of the braze-substrate system.

One of the main problems which faces researchers in brazing, is that the geometry of most joints means that nearly all useful information is hidden from view, and can only be inferred from post-brazing metallographic examination. For this study this problem has been overcome by looking at a 'half-joint' - i.e. the braze metal on a substrate surface. Obviously this approach cannot simulate the effect of capillarity within a joint, but it does allow visual examination, and surface and bulk analysis to be carried out at all stages during the brazing cycle. It is felt that the data acquired from such studies is directly applicable to conventional joint geometries.

Using the half-joint geometry with hot-stage Auger electron spectroscopy, X-ray analysis, and scanning electron microscopy, it is possible to build up a complete picture of the physical and chemical behaviour of a braze-substrate system with high image and spectral resolution, for all temperatures throughout the brazing cycle.

The next chapter reviews the current literature relevant to brazing, oxidation, and Auger spectroscopy in order to give an overview of the present level of understanding of these topics.
2 Literature survey.

2.1 Vacuum brazing.

2.1.1 Introduction.

Brazing, is perhaps the most ancient technique for joining metals, the Sumerians, a culture of the third millennium B.C. successfully brazed bronze, silver, and gold articles. Numerous ancient Egyptian brazed artifacts have been unearthed, and Pliny the elder (~60 A.D.) relates in detail the use of fluxes with gold-copper and gold-silver for the brazing of gold. In the 11th. century Theopilus describes the brazing of gold and silver with a near-eutectic silver-copper alloy and a flux - this technique actually being patented by Littledale in 1933(1).

The name brazing is derived from 'brassing', since copper-zinc, and copper-tin alloys were amongst the first to be widely utilised(2). Brazing may be simply defined as a process which joins a parent metal involving no fusion of the parent metal, but the fusion of a filler metal of differing composition which flows through a joint by capillary action. This 'definition' however, could equally well apply to soldering, so it has been suggested(3,4,5) that soldering is a reversible process that can be repeated at the same temperature ~450-500°C, whereas brazing is an irreversible process which is generally conducted above 450-500°C. Another suggestion(3) is that soldering relies upon adhesion facilitated by wetting, soldering leaves much 'bulk' solder in the joint and only interdiffuses at the parent metal surfaces. Brazing on the other hand involves diffusion of species throughout the bulk of the filler metal, and upon completion of the
joint very little of the filler metal is of unchanged composition.

At present more than 50% of all brazed joints are made with either 'easy-flo' or 'sil-fos' brazing alloys\(^6\), these commercial alloys are torch brazed and use a chemical flux. Silver soldering or hard soldering are both misnomers for brazing processes which use silver-base braze alloy compositions (such as the two commercial alloys mentioned above).

Filler metals are available in a wide variety of forms: wire, shims, powder, pre-forms, or clad to the parent metal. There are filler metals available to join virtually any type of parent metal, and one of the major advantages of brazing is that the process may be used to join dissimilar parent metals\(^4,5\). In any brazing process four things are necessary: clean parent metal, clean filler metal, a heat source, and a method of removing the surface oxides caused during heating. Cleanliness is imperative to the formation of a sound joint\(^2,3,7\). Heat may be applied via a gas-torch, induction heating, electron beam heating, or furnace heating, though recently the trend has been towards furnace heating methods. Oxide removal is of considerable importance for obtaining a metal-to-metal bond, bulk oxide may be removed prior to brazing by mechanical means (grinding, filing, shot blasting etc.), but during the brazing process itself the oxide must be removed by the use of chemical fluxes, reducing atmospheres, vacuum, or by using 'fluxless' brazing alloys.

The characteristics of a good brazing alloy are: adequate fluidity at the brazing temperature; the ability to wet and flow over the parent metal surface in the atmosphere used; sufficient chemical stability – there must be no loss of low melting point constituents (liquation), or
low vapour pressure elements at the brazing temperature; no excessive interalloying with the substrate (erosion); and the ability to form a good sound joint(5). Wettability is a term frequently used to compare the behaviour of brazing alloys on varying substrates, it is the ability of a liquid brazing alloy to flow (the property which determines the distance the alloy will travel away from its original position by capillary action(8)) over a base metal surface, whilst elements of the brazing alloy superficially diffuse into, and with the base metal(9).

Factors affecting the choice of brazing alloy obviously include their suitability for the base metal (manufacturers' data sheets, and experimental data(6,10) are usually sufficient for this aspect), the operating temperature and conditions of the brazed part, and the number of brazes necessary to complete the part (the solidus of the first braze alloy used, must be greater than the brazing temperature of any subsequent brazes(8)).

The recent move towards furnace brazing techniques has taken place for a number of reasons. Furnace brazing does not require skilled operators, so there is less reliance upon torch operators and welders, multiple defect-free joints may be made with only one brazing cycle, and control of the brazing atmosphere is fairly easy to maintain. Reducing atmospheres such as dry hydrogen or cracked ammonia, or the use of vacuum, also by-pass the need for fluxes, so whilst the capital cost may be high, multiple joints are easily made and costly post-brazing cleaning or oxide removal treatments are unnecessary.
Vacuum brazing is undoubtedly the 'Rolls-Royce' of the brazing methods available, the joint quality is far superior to other methods, but the capital cost is very high. Despite this, vacuum brazing is becoming widely accepted as a production technique. Most vacuum furnaces are of the cold-wall type\(^{(4,11)}\) - a heating element is contained within a cooled-wall vacuum vessel - these furnaces being originally developed for the aerospace and nuclear industries\(^{(4,5)}\) since the vacuum brazing technique is ideally suited for joining stainless steels, superalloys, refractory metals, and other difficult-to-join materials. Many authors have examined the numerous advantages of vacuum brazing\(^{(2-12)}\) and the main advantages are outlined below:

i) No gas or flux inclusions will remain in the joint.

ii) The finished joint is clean.

iii) Distortion of the finished work due to thermal stress is minimal.

iv) Many joints may be made simultaneously.

v) Full instrumental control of the brazing cycle ensures consistency.

vi) No skilled operators are required.

vii) Heat-treatments may be incorporated in the brazing cycle.

viii) The inevitable alloying that occurs on brazing may increase the remelt temperature so several re-runs may be possible without having to use different filler metals.

ix) Visual inspection of finished joints is sufficient to check that flow has occurred.

tax) Materials which cannot be brazed any other means may be joined by vacuum brazing.

xi) Strong sound joints are produced as a result of better wettablility.

xii) The technique may be used to repair mistakes - oversize or wrongly placed holes, leaks in UHV systems.
When vacuum brazing several factors must be borne in mind regarding the choice of filler metals\(^{8,13}\). The braze alloys must contain no low vapour pressure components (e.g., Cd and Zn), they must be able to wet and flow without the use of fluxes, and they must be of suitably high purity (i.e., free of dirt, carbon, oxide, and low vapour pressure components). In some cases high vapour pressure elements may be used for 'vacuum' brazing - if the furnace is backfilled with inert gas just prior to the filler metal melting\(^{2,11}\). The main interests of the aerospace and nuclear industries is the joining of high temperature materials (materials expected to operate at or above 500-600°C), consequently most of the vacuum brazing processes fall into the high-temperature alloy brazing category - brazing itself taking place in the temperature region of 950-1200°C\(^{9,11}\). The use of titanium and aluminium in many high-strength, heat-resistant alloys means that surface oxides can be very tenuous, and only the use of vacuum will prevent reformation after removal by the brazing process, oxide-free surfaces being essential if metal to metal contact between base- and filler-metals, and the subsequent formation of a strong bond is to be achieved\(^{14}\). A vacuum of \(1 \times 10^{-3}\) mbars has 0.5% of the original air of which 70% is composed of water vapour and organic vapours, at vacua of \(10^{-4} - 10^{-5}\) mbars the total oxygen content is less than 0.01 ppm\(^{2,5}\).

The most suitable high temperature brazing alloys for use in vacuum brazing fall into two main categories - the nickel-based, and noble filler metals. The aerospace industry is the largest user of heat-resistant brazing alloys\(^{15}\), and the demand for palladium, platinum, and gold-base brazing alloys is increasing annually, aerospace and nuclear components being the principal end products\(^{16}\). The main advantages of the noble filler metals are their high-temperature
strength, and above all their superlative high-temperature oxidation and corrosion resistance, this latter property being the main feature which makes noble filler metals preferable to nickel-based ones (17). Of the noble filler metals, one system has been particularly useful - the gold-nickel system. Alloys in this system contain 65-82% of gold sometimes including some chromium, but never more than 32% nickel. Gold-nickel-palladium (and gold-palladium) brazes are used for very high-temperature work, but the number of gold-nickel compositions is small and usually close to the pseudo-eutectic composition - 82.5% gold/17.5% nickel. The specification for the 'eutectic' alloy 'Orobraze 950' is 81.5-82.5% gold the balance nickel (AWS specification BAu-4)(15,18).

The Au/18Ni system has been used to join a very wide variety of metals: Inconel X, titanium to stainless steel, tungsten, molybdenum, and stainless steel to copper nickel and the glass-sealing alloys 'Kovar', 'Rodar', and 'Fernico' (3,5,8,10,15-17,19-21). More specific applications of Au/18Ni have been reported by many authors (6,15,16,18-22) and include: the Apollo lunar module reaction control system (where maximum resistance to the hydrazine/dimethylbenzine and nitrogen tetraoxide fuel was required); fixing of turbine compressor blades to the main shaft and the hydraulic supply lines in gas turbines; joining stainless steel hydraulic tubing in Concorde; and for load supporting members in the 'Phoebus IIA' reactors. The success of 'Orobraze 950' rests upon a number of its excellent properties which have been evaluated by a number of authors (3,5,6,8,15-17,20):
i) Excellent corrosion resistance and adequate mechanical properties at high temperatures.

ii) Only a small degree of interalloying with the substrate (gold often diffuses into the parent metal, but diffusion of elements such as chromium into the braze metal can further enhance the corrosion resistance).

iii) The alloy is free-flowing in hydrogen or vacuum.

iv) The alloy is workable, and available as powder, wire, foil and preforms (giving good flexibility for joint design).

v) There is a single melting point (950°C) which makes the alloy especially useful for joining metals of different thermal expansions, since cracks will not appear due to cooling through a 'pasty' freezing range.

vi) The alloy shows very little joint-gap dependence.

vii) The alloy contains no high vapour pressure components and is generally free from volatile bulk and surface contaminants.

Au/18Ni is particularly suited to joining stainless steel components - this being its main use since very little erosion occurs (and that which does tends to improve the corrosion resistance), and no refractory oxides or brittle phases are formed. The alloy wets stainless steel exceptionally well (very important for long, close-fitting joints), the surface finish is clean and smooth, and the brazing temperature can be as low as 970-980°C (meaning steels such as 'Jethete' which are used in the RB211 engine, and are heat-treated at 1000°C may be successfully brazed) (6, 19, 21, 22).
The main problem with 'Orobraze 950' (Au/18Ni) and other gold-rich brazing alloys is their cost - the price per ounce following very closely that of gold bullion! Furthermore delivery times are often quite long since suppliers aim to keep their precious metal stocks at a minimum (4,5). Consequently many alternative alloys have been tried, but generally without much success - either the corrosion resistance is poorer, or brittle phases form. Many of the 'alternatives' are only available in powder form, but planar flow casting has enabled such alloys as Ni-Au10.7-Cr5.8-Si5.3-B2.8 to be fabricated in foil and shims this alloy being 'nearly eutectic' and having similar properties to Au/18Ni(23).

The use of the noble filler metal braze alloys - notably Au/18Ni - has been largely restricted to applications where the cost of failure would be very high, either in terms of human life or expense, the cost of forming the joint is largely unimportant. Nevertheless several authors (3, 5, 24) have suggested that brazing is still carried out on a 'trial and error' basis, and that large areas of non-understanding still remain, examples being the behaviour of parent metal oxides in vacuum, and the precise way in which flow occurs.

2.1.2 Theory of wetting, spreading, and capillary flow.

In order for any brazing process to be successful, the liquid braze metal must first wet the parent metal, and then spread along the close-fitting joint by capillary flow. The ability to wet and then spread over the parent metal is dependent upon several factors, classical wetting and spreading theory allows examination of the conditions necessary to attain optimum spreading.
Any solid or liquid surface will exhibit a surface energy, which results from unsatisfied atomic bonds of the surface atoms leading to a net inward-acting force. The magnitude of this force is strongly dependant upon the type of bonding within the substance, for example, covalent materials have directional bonds which tend to align themselves perpendicularly to the surface so that the strongest bonds face inwards, hence the surface energy of covalent materials is usually lower than for materials with metallic bonds which are effectively symmetrical. A liquid droplet on a solid surface will try to reduce the overall energy of the system by minimising its surface area, thus a spherical outer surface is formed since this configuration yields the best surface area to volume ratio. Wetting has been studied by many authors, both from a theoretical viewpoint \((3,25-30)\), and from a practical approach \((9,14,19,24-26,29,31)\). It is useful to firstly consider the theory of wetting and spreading. Figure 2.1 shows the forces arising from surface energy, which act upon a liquid droplet on a solid surface. Where \(\gamma_{LV}\)

\[
\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}
\]

Figure 2.1: The forces on a liquid droplet

\(\gamma_{LV}\) is the liquid-vapour interfacial energy, \(\gamma_{SV}\) the solid-vapour
interfacial energy, and $\gamma_{SL}$ the solid-liquid interfacial energy. $\theta$ is the contact angle which is measured from the solid surface through the liquid and tangentially to the liquid surface. It is the value of $\theta$ which governs the wetting properties of the system:

$\theta < 90$ - wetting occurs
$\theta = 90$ - non-wetting
$\theta > 90$ - de-wetting
$\theta = 0$ - the condition for spreading

From the equation above it is possible to define a spreading coefficient 'S' (where $\theta=0$ therefore $\cos\theta=1$)

$$S_{LS} = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL})$$

Spreading occurs for positive values of $S$ which implies that $\gamma_{LV}$ must always be less than $\gamma_{SV}$ since $\gamma_{SL}$ is never negative. Thus low energy liquids on higher energy solids will spread (ie. a contact angle of zero). The curvature at the line of contact with the solid implies that there is a pressure difference across the surface of the liquid when compared to the equilibrium condition where a flat surface is present. The pressure difference $\Delta P$ across a droplet with principal radii of curvature $R_1$ and $R_2$ is given in an equation after Laplace:

$$\Delta P = \gamma_L \left[ \frac{1}{R_1} + \frac{1}{R_2} \right]$$
In the case of brazing the normal situation is a liquid between two parallel plates separated by a joint gap D. This situation is illustrated in figure 2.2, and it may be seen that the shape of the liquid surface, in this configuration, approximates to a cylinder, hence the pressure drop across the surface ($\Delta P$) may be derived.

**Figure 2.2: The forces on a liquid between two parallel plates**

\[ P = \gamma_{LV} \left[ \frac{1 + 1}{R_1/R_2} \right] \]

since \( R_1 = \frac{D}{2 \cos \theta} \)

and \( R_2 = \infty \)

then \( \Delta P = \frac{2 \gamma_{LV} \cos \theta}{D} \)

For vertical capillaries the low pressure region under the meniscus causes the column to rise until the weight of the column equals $\Delta P$ - ie. $\Delta P = h \rho g$, where $h$ is the height of the liquid column, $\rho$ the density of the liquid, and $g$ the acceleration due to gravity. The equilibrium height of rise is given by:
The rate of filling of a capillary gap is a complex quantity to predict, the fluid mechanics and fluid flow theories are fully explained in a paper by Milner (30), who gives the time (t) to fill a capillary gap of length 1 as:

\[
t = \frac{3\eta}{\gamma_{LV}\cos\theta} \cdot 1^2 \quad (\eta = \text{liquid viscosity})
\]

This equation assumes that streamline flow conditions prevail. A similar equation may be derived for the filling of a vertical gap, though in this more complex case the driving pressure (ΔP) has opposing it the hydrostatic pressure due to the increasing liquid column, and viscous friction, the equation is considerably more complex:

\[
t = \frac{12\eta}{\rho^2g^2D^3} \left[ -\rho g D - 2\gamma_{LV}\cos\theta n \cdot \frac{2\gamma_{LV}\cos\theta - \rho g D}{2\gamma_{LV}\cos\theta} \right]
\]

Hence for rapid spreading a high liquid surface tension (\(\gamma_{LV}\)) and high solid surface energy (\(\gamma_{SY}\)), are desirable, but the solid-liquid interfacial energy (\(\gamma_{SL}\)), the viscosity, and the contact angle should be low. The major factor affecting spreading is the solid-liquid interfacial energy, since under equilibrium conditions spreading will take place if \(\gamma_{SY}\) is more than \(\gamma_{LV}\) plus \(\gamma_{SL}\), the 'driving force' for wetting is therefore \(\gamma_{SV} - \gamma_{SL}\). It should be recognised however, that classical wetting and spreading theory assumes that there is no interaction between liquids and solids – in brazing operations this is
rarely the case. Furthermore it is assumed that all surfaces are plane and clean, again a condition seldom encountered. Consequently modifications to the 'thermodynamic theory' (which describes the equilibrium state outlined above) must be made in order to develop a 'dynamic theory' which estimates the degree of deviation from ideal conditions due to interactions, and to describe the rate at which equilibrium may (or may not) be reached. To date much of the 'dynamic theory' has still to be determined, but many of the effects of most interactions may be described qualitatively, and occasionally semi-quantitatively.

Many observations\(^{(9,24,25,29)}\) have shown contact angles significantly larger than zero for spreading systems. One reason for these non-zero contact angles is the effect of surface roughness, if a rough surface has an area 'r' times greater than its nominal area, then to calculate the contact angle on the rough surface - \(\theta\):

\[
\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta
\]

or more accurately:

\[
r\gamma_{SV} = r\gamma_{SL} + \gamma_{LV}\cos \theta \quad (\cos \theta = \cos \theta)
\]

In general terms any effect on a smooth surface is increased for a rough surface, for example, in spreading systems roughness will enhance spreading, whereas in non-wetting systems the contact angle will become even larger (and may even lead to de-wetting). Parker and Smoluchowski\(^{(26)}\) have developed a theory which considers the effect of the angle of capillary grooves on a metal surface upon the overall energy
of a metal-braze alloy system. They illustrate their theory using a system of silver on iron, and show that wetting will only occur if capillary grooves of suitable angle are present.

Unclean surfaces may also have a profound effect upon the contact angle, the presence of an oxide or grease film on the surface will change the surface energy of the metal and may cause the high-energy surface to behave as if it were a low-energy one, with the possibility of non-wetting.

The surface tension of the liquid (and the surface energy of the solid) may be altered by a number of factors — a change in any surface energy term will affect the final contact angle, either beneficially or detrimentally. If liquid vapour adsorbs onto the surface of the solid away from the liquid (molten metal) a spreading pressure results, which can cause non-zero contact angles to occur where surface energy data shows that zero angles should be attained. For conditions with no adsorption:

\[ \gamma_{SO} = \gamma_{SL} + \gamma_{LV}\cos\theta \]

Where \( \gamma_{SO} \) is the surface energy of a solid in vacuum. Since \( \delta_{SV} = \gamma_{SO} - \gamma_{e} \), then if adsorption occurs the equilibrium condition is:

\[ \gamma_{SO} = \gamma_{SL} + \gamma_{LV}\cos\theta - \pi e \]

The choice of environment may also affect the liquid surface tension, often controlled atmospheres or vacuum will improve wetting of the solid (although it should be appreciated that vacuum also suppresses oxide formation which will enhance wetting) since there may be an effective change in the \( \gamma_{LV} \) term. The temperature of the system will
affect the surface tension of the liquid - usually an increase of the temperature decreases the liquid surface tension without significantly reducing the solid surface energy - hence, contact angles lessen and spreading is enhanced. The use of plated-on 'easy to wet' alloys is fairly common, where difficult (or impossible) to wet substrates have to be joined.

Another major factor influencing the wettability of a system, is the degree of interalloying which takes place during the brazing cycle. Interalloying is examined in more detail in section 2.1.4, but its effect upon classical wetting theory will be examined here. Obviously a change in liquid composition will result in a change of the liquid surface tension, this change can be either beneficial or detrimental - a decrease in liquid surface tension usually improves wetting. In addition, interalloying may increase the amount of base-metal erosion (thereby changing the surface roughness), or change the viscosity and melting point of the liquid unfavourably which increases the time taken to fill a capillary gap, and can eventually cause solidified alloyed-liquid to 'choke' the joint gap. In the case of copper brazing of steel, iron diffuses into the braze metal and then saturates the solid steel surface with a thin layer of molten iron, the copper-iron braze metal then rapidly wets and spreads over the surface. Sharps and Tomsia suggest that the alloying interaction at the solid-liquid interface is very important in this and other systems in the attainment of zero contact angles. They surmise, that if a solid is undersaturated in a component relative to the liquid, the interaction at the interface results in a driving force which assists wetting. A further suggestion is that grain boundaries are often a source of non-equilibrium composition and may therefore facilitate wetting - there may also be an
effect due to thermal etching of the grain boundaries which can increase their capillarity. Several authors (14,31-34) have described the flow of liquid along the metal/metal-oxide interface, and whilst the mechanisms are described in detail in section 2.1.3, it is profitable to examine the theoretical requirements for such a mechanism to be viable. Obviously the metal/metal-oxide interface provides an excellent capillary gap, and the surface oxide is not wetted (so a sound metal to metal joint is formed), but for the suboxide spreading mechanism to occur, the following conditions must be met:

\[ \gamma_{SL} + \gamma_{L} + 2\gamma_{OX} < \gamma_{SOX} + \gamma_{OX} + \gamma_{L} \]

where \( \gamma_{OX} \) is the surface energy of the oxide, and \( \gamma_{L} \) is the contribution made to the overall energy by the liquid droplet before wetting (which is small compared to the area it later wets). Cohen et al. (33) state that for spreading to occur by the suboxide route the free energy of displacement \(-\Delta G_{\text{disp}}\) of the oxide must be negative where:

\[ \Delta G_{\text{disp}} = \gamma_{LOX} + \gamma_{SL} - \gamma_{SOX} \]

Hence the condition for spreading is when \( \gamma_{SOX} > \gamma_{SL} \) - a high metal/metal-oxide interfacial energy therefore favours the suboxide mechanism.

The classical wetting theory allows the conditions for wetting (zero contact angle) to be evaluated (ie. \( \gamma_{SV} > \gamma_{LV} + \gamma_{SL} \)), but the effect of non-ideal conditions - surface roughness and cleanliness, the brazing environment, interalloying, adsorption, and the nature of surface oxides - are only poorly understood, and mean that the 'thermodynamic theory' cannot be universally applied, the development of a more realistic 'dynamic theory' however, is still in its infancy.
For the reasons explained in the previous section, the formation of a strong sound joint depends upon both parent metal surfaces being clean and free from surface oxide. In practice an oxide free surface is virtually impossible to achieve in air, and consequently, whether the brazing operation is carried out in air, or with a controlled atmosphere, the surface oxide on the parent metal must be removed. For brazing in air either fluxes or the so-called fluxless brazes are utilised. Fluxes react chemically with the oxide, liquifying it so that it floats to the surface of the braze alloy, exposing the clean parent metal surface which may then be wetted by the braze metal. When brazing with controlled atmospheres or in vacuum however, no fluxes are used, it is the removal of oxide under these conditions which will be reviewed in this section.

The use of a controlled atmosphere - usually dry hydrogen or cracked ammonia - removes the surface oxide by a reduction reaction:

\[ \text{H}_2 + \text{MeO} \rightleftharpoons \text{Me} + \text{H}_2\text{O} \]

If dry flowing hydrogen is used, the water vapour produced by the reduction is removed and reduction continues.

Another method of oxide removal is by heating the assembly to be brazed in a vacuum. Several authors\(^{(4, 13, 14, 35)}\) report that metals are 'cleaned' by heating in vacuo, but, as has been admitted by others\(^{(3, 7, 30)}\) the nature of the process which reduces or removes the oxide film is still poorly understood. Thermodynamic data shows that the
oxygen partial pressures necessary for spontaneous decomposition of many of the oxides requires vacua many orders of magnitude better than are typically available. Reaction of the base metal with the oxide under vacuum conditions has been proposed (3, 8, 13, 14, 16, 25, 35), for example, dissolution of the oxide into the metal, or reduction of the oxide by carbon in the substrate. Alternatively the oxide may be removed by spallation as a result of thermal stress (35). These oxide removal mechanisms may well act in some systems, but in many instances (for example heat-resistant alloys and aluminium or titanium containing alloys) the oxide is not removed simply by heating in vacuum, and must still be removed during the brazing process. Exactly how this remaining oxide is removed is an area which has received very little examination.

Wall and Milner (14) studied a variety of substrate-filler metal combinations, they found that thin oxide films on Cu-Al, Ni-Al, and Fe-Al could be penetrated by liquid metals, whilst thick, or duplex films on these alloys could not. Tests on aluminium showed that liquid metal penetration would not occur until a pinprick was introduced into the oxide. Once oxide penetration had occurred there were three processes which could take place: spreading of the braze metal along the metal/metal-oxide interface (suboxide spreading); rapid bulk alloying and erosion of the parent metal; or neither of these processes - no spreading. Wall and Milner noted that oxide penetration took a finite time, they postulated that the penetration was attributable to pre-existent flaws in the oxide (or flaws introduced by thermal stresses), and hence the low probability of flaws being 'lined up' in duplex oxides prohibits penetration of, and spreading under duplex oxide scales. This theory requires a two-stage process, first oxide penetration, then suboxide spreading. It was suggested that optimum
spreading occurred when solubility of the liquid braze metal in the base metal was limited (but not zero - this prevented spreading), and that a critical pressure was necessary for wetting and spreading to occur, since too poor a vacuum resulted in the growth of inpenetrable films. The authors' summary states that their model relies upon a high metal/metal-oxide interfacial energy, also that penetration was enhanced by increased temperature, and that spreading was most successful for systems showing limited interdiffusion of species. The oxide was assumed to fragment after its detachment.

Siewert, Heine, and Lagally(36) working with Ag-Cu-Li on type 304 stainless steel showed that a 'halo' of copper-rich metal preceded the bulk of the liquid droplet whilst an invisible layer of copper (detected by Auger spectroscopy) preceded the halo. Their suggestion was that the copper and copper-rich liquid, having more similar properties to the substrate than the bulk braze alloy, assume a lower contact angle and therefore precede the bulk liquid. The 'halo' tended to favour grain boundary grooves, and the authors said that the invisible layer of copper both prepared the surface for wetting, and could react with the substrate oxide giving perhaps a copper-iron oxide complex. These types of diffusion processes by the copper and copper-rich liquid caused penetration of the oxide and the lifting of oxide 'islands'. This theory of oxide penetration is further substantiated by the increase in oxygen potential causing the inhibition of copper diffusion through the thicker oxides thereby preventing the production of a wettable surface.
Work by Rasmussen, Klarstrøm, and Weiss (32) has shown a suboxide spreading mechanism for 'fluxless' brazing of copper using a Cu-6%P braze. A 'corona' was seen to spread ahead of the liquid drop there also being 'fingers' between the corona and the main spreading drop. The model proposed is one where Cu₃P melts and reduces the underlying oxide and the main spreading front spreads over the oxide and with excess phosphate attacks, and detaches the oxide. In the corona region the detachment process is achieved by a corrosion cell - the copper phosphate material dissolves oxygen from the oxide at its surface, and dissolves copper at the metal-liquid (copper phosphate) interface so perpetuating the cell.

Fluxless brazing of aluminium has also been studied (37, 38). Early work by Winterbottom and Gilmour (37) using Auger electron spectroscopy (AES), showed that in clad materials vapour transport of magnesium through a porous oxide at temperatures exceeding 425°C (the temperature at which the aluminium oxide becomes porous), provided the means for the filler metal to be drawn through the oxide and to wet the metal surface. Magnesium is added as a 'promoter' to clad aluminium systems, its action is thought to involve removal of oxide and to exert a gettering effect upon residual oxygen and water vapour in the oxide. This work has recently been supplemented by McGurran and Nicholas (38). Using the technique of hot-stage scanning electron microscopy (HSSEM), the wetting and spreading of the system has been examined at high magnifications and in real time. At approximately 450°C the first stages of the wetting process began, and with increasing temperature the molten filler metal was 'exuded' through the oxide (alumina) - perhaps due to volume expansion of the eutectic liquid. The mechanism of oxide penetration is
not considered, but McGurran says that to join clad to unclad aluminium
the magnesium must be able to penetrate the alumina film on the workpiece,
this may be due to the oxide becoming porous (as inferred by
Winterbottom and Gilmour) or by reduction of the oxide. The oxide film
is then further removed by 'tunnelling' (suboxide spreading) of the
filler metal which eventually sweeps away the oxide.

The Gold-18%Nickel has been studied by Cohen et al(22,33), and
once again the technique of HSSEM was utilised, but in this work in
conjunction with AES and electron probe microanalysis (EPMA). The oxide
removal mechanism determined was one which involved a two-stage process
of first oxide penetration, and then suboxide spreading (the oxide
eventually fragments and floats on the filler metal surface as 'rafts').
The spreading braze alloy was seen to be preceded by a 'blister' caused
by the braze alloy spreading beneath the oxide. Liquid droplets never
spread over the oxide which could be seen floating as 'rafts' on the
molten braze alloy where it had been completely detached from the
substrate. A fine powder was used for the studies, and examination of
many micrographs showed that all but the smallest particles formed a
blister. This observation implied that penetration depended upon defects
being initiated in the oxide and not their pre-existence as previously
thought(14), furthermore the pre-existence of so many defects would be
most unlikely for the chosen substrate - a steel noted for its oxidation
and corrosion resistance. The hypothesis put forward to explain the
defect initiation, is based upon the assumption that when the powder
particles melt, they coalesce and slump, and, whilst they do not
actually wet the oxide, there is a significant decrease in oxygen
potential beneath the particles (even in a relatively 'hard' vacuum).
This means that more easily oxidisable elements enriched at the
metal/metal-oxide interface such as silicon, are able to reduce the oxide, and since the reduction products are liable to be particulate in nature, the oxide will be disrupted allowing the infusion of liquid filler metal:

$$3\text{Si} + 2\text{Cr}_2\text{O}_3 \rightarrow 3\text{SiO}_2 + 4\text{Cr}$$

The time taken for oxide penetration was seen to be related to the particle size, and in the work by Cohen et al. and later work \((34)\), this phenomenon was explained in terms of reduction of oxygen potential (ie. small particles have only a small reduction in oxygen potential beneath them and so the kinetics of the reduction reaction are slow, whereas for large particle which cause a large drop in oxygen potential, penetration is almost instantaneous). It was also noted that the blister volume varied linearly with the particle diameter, but the cause of this relationship was not isolated. Further work \((34)\) however, found that the failure of some particles to spread to completion, and the origin of the linear relationship was connected with the rate of change of composition of particles with differing volume - diffusion of parent metal species into the braze metal causing a substantial increase in the liquidus temperature thereby leading to solidification.

Recent work by Cohen and Castle \((39)\) using Au-18Ni and Ag-28Cu on heat-resistant and mild steels showed that for heat-resistant steel both braze alloys spread by a suboxide mechanism (in the silver alloy spreading of a very thin layer of silver along the interface caused spallation of the oxide well ahead of the braze pool), whereas for mild steel both filler metals appeared to wet the oxide.
2.1.4 The interalloying of braze- and parent metals.

When braze metals are melted on a base metal and wet the surface, there is a very strong possibility that some form of interdiffusion of species will occur. There may be some solid state diffusion before the braze metal liquifies, but this is relatively unimportant. The interalloying which occurs may take place in several different ways:

i) The liquid and solid form an alloy by diffusion of species into and out of the braze and parent metals.

ii) Species of the parent metal may diffuse into the braze metal.

iii) Species of the braze metal may diffuse into the parent metal matrix or grain boundaries.

iv) The interdiffusion of species (or one-way diffusion of species) may form intermetallic compounds in either the filler or parent metal.

The majority of successful brazing alloy-parent metal systems display some mutual solubility, and some authors\(^{(8,14)}\) believe that some interdiffusion of species is essential if wetting and spreading is to occur. Interalloying may be either beneficial or detrimental, for example in some systems\(^{(15,20)}\) diffusion of elements such as chromium into the braze metal can significantly improve the corrosion resistance of the filler metal, in addition, diffusion of elements such as boron, silicon, or lithium into the filler may cause a lowering of the solidus temperature and an improvement in the wetting and spreading behaviour. The use of boron, silicon, and lithium as melting point depressants is common in nickel-base brazing alloys, but the advantages must be offset against the tendency for such additions to penetrate and attack grain boundaries, and to form undesirable intermetallic phases\(^{(9)}\). Elements diffusing into the braze metal may however, increase the solidus
temperature, and solidification of the braze may occur before the joint is properly filled. This same effect though, can be advantageous if multiple brazing cycles are to be used, since the same filler metal may be used for all cycles because the 'alloyed' braze metal will remain solid at the temperatures at which the fresh braze metal will wet and flow\(^5,^{12}\). As a cautionary note, it must be appreciated that whilst a nominal amount of interdiffusion may (or may not) be beneficial, excessive alloying will very probably result in 'erosion' of the parent metal, which not only increases the effective joint gap, but also leads to very poor wetting and spreading characteristics.

Feduska\(^{40}\) in an extensive study of base metal-braze metal interface reactions concluded that when a brazing alloy contacts an oxide-free base metal a diffusion couple is set up due to the presence of a concentration gradient. In general elements in the base metal which are deficient in the braze metal will diffuse towards the substrate/braze interface and vice versa. This can have a number of effects, diffusion of species out of the braze metal can result in grain boundary penetration—especially with interstitials and elements of small atomic radii (eg. Si and B). If the braze is high in carbon with respect to the substrate, then carburization can take place due to interstitial diffusion. Braze alloy elements may also be able to undergo substituional diffusion with the substrate, resulting in solid solution formation at the interface.

The result of any interdiffusion process, is that equilibrium conditions are not achieved, so phase diagrams must be used with care. It has been suggested\(^{30}\) that the liquid with the lowest surface free energy in the pure state will attempt to segregate to the liquid metal
surface, and this will affect most alloying processes and wetting and spreading characteristics which both assume equilibrium conditions in their theory.

The conditions used during a vacuum brazing cycle are obviously of major importance to the brazing process. The usual procedure is to keep the brazing cycle to a minimum – to use the lowest temperature that ensures adequate fluidity, and for just long enough to fill the joint-gap. This means that the brazing temperature is generally 50-100°C above the melting point of the braze (unless conditions dictate otherwise), which means that the wetting, spreading, and gap-filling is rapid enough to avoid the majority of detrimental alloying effects. As inferred above, other factors which can affect the choice of times and temperatures are; whether the metal has been heat-treated – a process which may be usefully incorporated into the brazing cycle, or if 'active' elements like boron, silicon, lithium, and palladium are present which may segregate to grain boundaries or form intermetallic phases if too high temperatures, or too long times at temperature are used.

Most 'high-temperature' brazing processes are carried out between 1000-2000°C in vacua in the range 5x10⁻⁵ – 5x10⁻⁴ mbar. A typical time-temperature profile would involve heating at a slow rate to approximately 50-100°C below the melting point of the braze alloy, and then holding the temperature constant for a suitable time so that all components of the workpiece may attain the same temperature (this 'soaking' time will obviously depend upon the size of the article being brazed). There follows a rapid increase of temperature to the brazing temperature where the work is held for approximately 10 minutes, the
work is then allowed to cool with the furnace power off, either naturally, or by backfilling with cool inert gas\(^{(11)}\).

Such a 'typical' profile is not always feasible — often the particular braze metal or parent metal combinations used may require alternative conditions to restrict the amount of interdiffusion, or to ensure that long joints are totally filled. One such example of this is shown by the system upon which this work is based — the Rolls-Royce RB211 turbofan compressor unit can only be brazed at 30–40°C above the melting point of 'Orobraze 950' (Gold/18%Nickel) since the base metal (one of the heat-resistant 'Jethete' alloys) is pre-heat-treated at 1000°C\(^{(15)}\). Such conditions, whilst apparently acceptable, can lead to problems. Work on the effect of interdiffusion of the Gold-Nickel system at such low overheat temperatures\(^{(34)}\), based on the ternary Fe-Au-Ni diagram of Koster and Ulrich\(^{(41)}\) has revealed that at these temperatures the effect of interdiffusion of species can be very high, and could easily account for the unsatisfactory joint filling that can sometimes occur.
2.2 Oxidation.

2.2.1 Introduction.

Oxidation may be defined as the reaction of oxygen containing gases with metal surfaces. All metals, when exposed to oxygen containing atmospheres will form an oxide film, the thickness and nature of the film will depend upon many factors, temperature, the nature of the atmosphere and its partial pressure of oxygen, and the physical metallurgy of the metal (e.g. crystal orientation, grain size, surface finish, cold work, and purity\(^{(42,43)}\)). Oxidation processes are not normally equilibrium processes, but thermodynamics may be useful for the prediction of the composition of an oxide formed on alloys, although it must be appreciated that the nature of thin films is often markedly different than that of thick films. Kinetics govern the rate of oxide formation, and studies of oxidation have shown that the behaviour of the majority of systems may be fitted to one of the following empirical 'rate laws':

- **Linear** \( \Delta m = k_{Li} t \)
- **Parabolic** \( (\Delta m)^2 = k_{Pt} \)
- **Cubic** \( (\Delta m)^3 = k_{Ct} \)
- **Logarithmic** \( \Delta m = k_{Lln}(at+t_0) \)
- **Inverse logarithmic** \( 1/\Delta m = A-k_{Li} Lnt \)

where \( \Delta m \) = weight change, and \( t = time \)
The linear, parabolic and cubic rate laws are normally obeyed at higher temperatures (>500°C). A linear law is typical of a non-protective oxide whilst the parabolic and cubic laws are characteristic of protective films. Logarithmic and inverse logarithmic laws are generally associated with low temperature behaviour (room temperature and below, to approximately 500°C) and are characteristic of a protective film.

The nature of oxides formed on metal surfaces is of particular interest in the study of brazing, and indeed most metal joining techniques. The oxide thickness and composition may dramatically affect the brazeability and strength of components, firstly by the alteration of wetting and spreading characteristics, and secondly by the ease (or otherwise) and degree of oxide removal from the component surface. Oxide removal is of major importance during brazing, and consequently knowledge of the processes and mechanisms governing the formation, and eventual nature of oxides is important.

This review examines first the oxidation of iron—the base material for the majority of alloys—and then iron-chromium alloys which form the basis for stainless steels. Oxidation in both air and reduced partial pressures of oxygen are considered since both of these environments are relevant to brazing processes. The influence upon the oxide of silicon or boron additions to iron- and iron/chromium-base alloys, and their role in forming high energy interfaces is considered in the final section.
2.2.2 Oxidation of Iron in air and vacuum.

It is hardly surprising that iron has been the subject of a great many oxidation studies since it forms the base for numerous alloys. With any oxidation experiment it is important to fully characterise the specimen before, during, and after the study, in this respect iron is useful since the starting conditions can be very precisely specified.

The oxidation of iron in air has been extensively studied and most experimenters agree upon the nature and formation of oxides on pure iron\(^{(42,44-49)}\). The mechanism for growth is by the outwards diffusion of iron to the surface by diffusion through the oxide, where it reacts with the oxygen (cationic diffusion). The logarithmic rate law is obeyed at, or below room temperature\(^{(42)}\), but the parabolic law applies at higher temperatures\(^{(44)}\). At elevated temperatures a triple-layered oxide is formed, the outermost layer consists of a very thin layer of haematite \((\text{Fe}_2\text{O}_3)\), beneath which is a thicker layer of magnetite \((\text{Fe}_3\text{O}_4)\), the remaining 90% or so of the oxide consists of Wustite (non-stoichiometric FeO). Rahmel\(^{(45)}\) in his review paper, summarises the oxidation process as one in which iron ions travel through the Wustite via iron ion vacancies and defects, then through the magnetite and haematite layers via interstitial sites. Reaction may occur at the magnetite-haematite boundary since some inward diffusion of oxygen can take place through oxygen ion vacancies, dislocation pipes, and grain boundaries. The outward diffusion of iron creates vacancies at the iron-wustite interface - the vacancies may agglomerate and nucleate voids until the oxide and metal separate. If this happens however the oxidation does not cease, and several 'bridging mechanisms' have been proposed. The 'dissociative' mechanism\(^{(46,47)}\), suggests that upon
separation, the oxide dissociates freeing oxygen to react at the free metal surface, and slowly 'bridges' are built up and the oxidation mechanism reverts to cationic diffusion. Another mechanism proposes that oxygen transport across the separated region is via a CO/CO$_2$ or H$_2$/H$_2$O mixture in the pore, the entry of such mixtures being through microcracks in the oxide$^{(45)}$.

The oxidation of iron in reduced oxygen partial pressures or in vacuum has been far less closely studied, some of this work having been carried out using oxide free samples as a starting point$^{(42)}$. Such studies on single crystals of iron showed that after some induction period - thought to be due to oxygen dissolving in the iron - oxide nuclei rapidly appear and grow, the number and rate of growth of these nuclei depends upon temperature, pressure, and crystal orientation. Generally the effect of temperature was less marked than the effect of pressure, but increasing temperature, or pressure would increase the number of nuclei.

Graham and Cohen$^{(50)}$ in a comprehensive work on pure iron, studied the effect of oxygen partial pressures between 10$^{-6}$ and 60 Torr upon oxidation at 350° and 450°C. They found that the initial oxidation rate corresponded to a parabolic rate law, the length of duration of which became shorter with increasing oxygen pressure. After a period of intermediate oxidation kinetics, a second lower parabolic rate law takes over, and this second rate appeared to be largely unaffected by pressure. The authors propose that the lowering of the parabolic rate law is governed by, either the formation of a continuous Fe$_2$O$_3$ layer (which reduces ion flux), or by loss of contact at the metal/metal-oxide interface.
Hussey and Cohen\(^{(51,52)}\) have studied the oxidation of iron for a range of temperatures and pressures, and they too have found the oxidation kinetics to be strongly pressure dependant for partial pressures of oxygen less than around \(10^{-2}\) Torr. Initially oxidation follows a linear rate law which corresponds to magnetite growth, but the rate then slows due to haematite formation on the outer surface, although at temperatures in excess of \(460^\circ\text{C}\) haematite continually converts to magnetite. For vacua in the range \(10^{-4} - 10^{-6}\) Torr, and temperatures in the range \(450-550^\circ\text{C}\), Hussey and Cohen found a four stage oxidation process: an induction period (the length of which lessens with increasing pressure - the nucleation process); a period of increasing oxidation rate (the nucleii initially grow as hemispherical 'caps'); a period of linear oxidation (being associated with the coalescence of oxide nucleii to form a continuous magnetite layer); and finally a period of decreasing rate (caused by the reduction of easy diffusion paths for cations). The fourth stage is the most pressure sensitive, and for higher pressures \((10^{-4}\) Torr) haematite forms at the surface since the cation flux cannot support the magnetite formation, furthermore the rate may nearly slow to zero due to void formation at the metal/metal-oxide interface. For higher pressures haematite is always formed, and in general the induction period is too short to detect, and if temperatures or pressures are raised the oxidation rate increases. At higher temperatures still \((\sim800^\circ\text{C})\), Goursat and Smeltzer\(^{(53)}\) found Wustite to be stable and to form nucleii which grow to cover the surface - this gives an initial increasing rate, then a linear rate. Magnetite is then nucleated and grows to cover the Wustite with a decreasing rate. The rate of magnetite growth increases with increasing oxygen partial pressure. The oxidation mechanism remains one of cationic diffusion - that is iron ion diffusion to the surface.
Hot-stage studies by Castle and Hunt\(^{(49)}\), and Verma et al\(^{(48)}\) essentially verify the findings above. Castle's work on mild steel shows that manganese sulphide inclusions oxidise preferentially to pearlite, with ferrite being least easily oxidised. Further studies on iron single crystals revealed cracking of the magnetite layer early in the oxidation process, it is suggested that the cation flux leads to suboxide vacancies which cause the cessation of oxide growth. Spontaneous generation of ferric species at the surface leads to a large cation vacancy flux which rapidly reaches the level where magnetite is converted to haematite, the accompanying 10\% volume change leads to the film cracking. Verma used a vacuum of 3x10\(^{-4}\) at 500°C, and he too saw mixed haematite-magnetite films and in some instances the formation of Wustite.

The presence of interfacial voids at the metal/metal-oxide interface, and microcracks in the oxide, or loss of contact at the metal/metal-oxide interface during heating in air or vacuum, provides a potential means for the braze metal to contact the metal surface, either by introducing a preferred route for detachment of the oxide, or by providing paths which enable the braze metal to penetrate the oxide leading to its removal and allowing wetting and spreading processes to take place.

2.2.3 Oxidation of Iron-Chromium alloys in air and vacuum.

The oxidation of iron-chromium alloys in air has been extensively studied, the system being the basis for many heat-resistant steels. The behaviour of the system is strongly dependent upon the chromium content, a level of 12\% being the value which nominally separates stainless from
non-stainless steels\(^{(55)}\). A chromium content of 14\% or more means that a chromia (\(\text{Cr}_2\text{O}_3\)) film will form, but this film will not reform once it has broken down - film healing requires a chromium content of around 18\%\(^{(56)}\).

Chromia films grow by cation diffusion, and film breakdown occurs when the chromium concentration at the metal surface is too low to continually supply chromium ions to the oxide surface\(^{(56-58)}\). The film may well be irregular at high temperatures and may separate due to vacancy condensation at the metal/metal-oxide interface or at grain boundaries where diffusion is fastest\(^{(43,59)}\). The oxidation kinetics of chromia formers follow a parabolic rate law, at very high temperatures (>1100\(^\circ\)C) however, linear kinetics take over. Tedmon\(^{(60)}\) proposes that this is due to oxide volatilisation:

\[
\text{Cr}_2\text{O}_3 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{Cr}_3
\]

This reaction means that when the limiting scale thickness is reached, the supply of chromium ions to the surface, is equal to the loss of chromium by volatilisation. The linear rate constant will depend upon the chromium content of the alloy. Cox et al\(^{(60)}\) have seen that the initial oxidation of metals is substantially different than the later stages, an iron-15\%chromium steel first forms a chromia film, but after some hours the faster growing spinel oxide begins to become the dominant oxide. The proposed mechanism for this process, is one in which the cation flux enables vacancies to supersaturate at the metal/metal-oxide interface and form pores, the oxide above the pores thereby becomes mechanically unstable, and when it ruptures chromium deficient metal is exposed and the spinel oxide is formed.
The nature of oxide films on alloys with less than 12-13% chromium (the so-called nonchromia-formers), is somewhat more complex, but again the film formed depends heavily upon the chromium content, and to a lesser extent the temperature. Experiments have shown that a variety of different films may be formed, but the authors agree upon the underlying mechanism - the cationic diffusion of chromium ions - and how chromium content and temperature influence it. Olefjord studied oxidation at room temperature and found the outer layer of the oxide to be mainly iron oxide, with the amount of chromium increasing with depth into the film until it is slightly enriched in chromium (with respect to the parent metal) at the metal/metal-oxide interface. The outermost layer was thought to be haematite but ferric iron predominates at the interface. Olefjord proposes that the first oxide formed is formed very rapidly and comprises iron and chromium oxides, as more iron and chromium ions diffuse into the film, the chromium substitutes for the iron, which, once freed, diffuses to the surface to react with oxygen in the atmosphere.

At higher temperatures the oxide films formed possess a triple-layer structure, the outer layer is a very thin haematite film, overlying a much thicker magnetite layer, and finally a spinel layer of chromium content which increases as the metal/metal-oxide interface is approached. The composition of the spinel oxide may be expressed as:

$$Fe(2-x)Cr_xO_4$$

(where $0 < x < 2$)
For higher chromium contents (i.e., nearly 12%) \( x \) may be almost equal to 2 at the metal/metal-oxide interface. Iron and chromium diffuse throughout the scale, though chromium diffuses more slowly, such that iron is enriched at the surface whereas the oxide at the metal/metal-oxide interface is rich in chromium resulting from chromium substitution for iron freeing it to diffuse outwards. There may also be a little inwards diffusion of oxygen through the porous haematite outer scale and via short circuit paths (cracks, dislocation pipes, grain boundaries etc). At very high temperatures (>800°C) wustite becomes stable and replaces the haematite and magnetite layers\(^{46,47}\). For dilute chromium containing iron alloys the oxide cracks easily, and the cracks are quickly plugged, but with iron-rich oxide since the substrate is depleted in chromium after forming the first oxide, consequently the oxidation rate increases due to the non-protective nature of the iron oxide. Although an air formed oxide may be partially or totally reduced when heated in a vacuum, the final state of the metal surface may not necessarily be the same as the original condition since many of the diffusion processes are irreversible. This change in surface composition will affect the surface energy of the substrate and hence will alter the wetting and spreading characteristics of the iron oxide.

The effect of heating metals in vacuum is an effect that has been widely observed...but poorly understood. Several authors\(^{3,4,12-14,35,71}\) whilst studying vacuum brazing, have noted that metals when heated in a vacuum, emerge brighter than when they were introduced to the vacuum furnace. It has been noted that this 'disappearance' of the oxide film is dependent upon both temperature and pressure - a critical pressure exists below which no oxide forms (sic). The removal of the oxide film when brazing is of great importance, and consequently a
review of the ways in which oxide films may be thinned or removed by heating in vacuum is of particular relevance.

Lugsheider et al. (35) have studied the removal of oxide in vacuo using Auger electron spectroscopy and secondary ion mass spectrometry (SIMS). The work examined the surfaces of several nickel-base, and iron-base alloys before and after vacuum annealing at high and low temperatures. With the nickel-base alloy (similar to Inconel X) at first a layer of alumina formed a thicker oxide than the original air-formed film, but further annealing at 1150°C reduced the thickness to ~5Å and only nickel, chromium, titanium and carbon were present on the surface. Lugsheider suggests that the aluminium is volatilised as a suboxide due to the action of surface carbon - thermodynamics and experiments have shown the following reaction to be feasible:

\[ 2C + Al_2O_3 \rightarrow Al_2O + CO \]

Similar studies of an iron-base alloy showed that titanium in the alloy reacted with residual components in the vacuum to form thick surface layers of titanium nitride (TiN), titanium carbide (TiC), and titania (TiO₂).

Park, Houston, and Schreiner (72), have also noted that stainless steels when heated in vacuum, tend to lose their corrosion resistance. Their work with type 304 stainless steel using soft X-ray appearance potential spectroscopy, has shown that prior to vacuum annealing the surface contains only graphite and chromium oxide. After annealing for several hours at 500°C and <10⁻⁹ Torr however, the iron at the surface is greatly increased, and the chromium spectrum
changes from oxide to elemental. At very high temperatures (>1000°C) there is very pronounced depletion of surface chromium.

Experimental work has shown that the heating of metals and alloys in vacuum does indeed thin some oxides, but the oxide is rarely completely removed. Several mechanisms have been proposed - simple vapourisation of the oxide, increased solubility of the oxide in the parent metal, reduction by carbon in the base metal, reduction by more easily oxidised elements, and spallation due to cracking as a result of thermal stresses developing during heating, and whilst these mechanisms apply to certain systems where oxide is removed, for many other systems oxide removal does not occur and oxidation processes take place.

The oxidation of iron-chromium alloys in low partial pressures of oxygen has received considerably less attention than their oxidation at atmospheric pressure, and many of these studies have been carried out below 400°C. Under certain conditions alloying elements (e.g., chromium) may be selectively or preferentially oxidised and this process is often used as a pre-treatment. The mobility of chromium ions is much greater above 500°C, so in vacuum conditions it is possible to form chromia films with only a thin iron oxide overlayer with 'non chromia forming steels'.

Oleffjord showed that heating clean low-chromium alloys in ultra high vacuum conditions yielded a layer of chromia on the surface. Asami et al. have studied the heating of oxidised iron and iron alloys at 380°C in UHV conditions, their results show that heating in vacuo is accompanied by reduction of the oxidised iron, the decrease of O-H oxygen, and the oxidation of metallic chromium. The result is that
The surface films are rich in chromium - the degree of enrichment depending upon the chromium content of the alloy. The iron is reduced either by 'active carbon' or by the metallic chromium, which in turn then oxidises to form the chromium rich surface oxide. At temperatures greater than 300°C the surface oxide generally has the composition \( \text{Cr}^{(2-x)\text{Fe}}_x\text{O}_3 \), where \( x \) tends to zero with increasing chromium content.

Several workers\(^{75-82}\) have studied the oxidation and vacuum annealing behaviour of stainless steels. Early work by Hulquist and Leygraf\(^{75-78}\) considered the free energies of formation of various oxides, and proposed that the preferred order of oxide formation was \( \text{Cr} > \text{Ni} > \text{Fe} \). The type of oxide formed however depends upon the rate of supply of metal ions and oxygen to the oxide/gas interface. If the supply of oxygen to this interface is matched by the chromium ion flux, a chromia film will form. If however the supply of oxygen exceeds the chromium ion flux iron and nickel oxides (sic) are able to form. Furthermore if the temperature is too high a chromium oxide film will form, but its growth is very rapid and will result in the formation of a chromium depleted region beneath the scale, because the rate of chromium ion supply to the film exceeds the supply of chromium from the bulk to the subscale zone.

Gulbransen and Andrew\(^{79}\) working with type 304 stainless steel have examined the oxidation kinetics at 0.1 atm. pressure. They found that at 500-600°C a low parabolic rate was followed, but that at 800°C the rate becomes linear. At weight gains in excess of 90 \( \mu \text{g cm}^{-2} \) or temperatures greater than 900°C however, parabolic kinetics take over once again. The change of rate was thought to be attributable to
the vapourisation of chromium. A second rate law change was noted at 1150°C which was probably due to the evaporation of iron.

Wild(80) and Baer(81) have examined EN58A (18Cr/8Ni/1Mn) and 304 (18Cr/8Ni) steels using Auger electron spectroscopy to examine the surface composition at various temperatures and pressures. Both authors saw that slow heating in vacuo to ~500°C resulted in the removal of carbon, with chromium and oxygen becoming the major surface constituents. Wild also noted the segregation of sulphur and manganese to the surface with the removal of chlorine. Baer showed that rapid heating to 500°C did not remove carbon, but retained it as grain boundary carbide. On further heating Wild found that oxygen disappeared whilst iron and chromium levels became approximately equal to the bulk composition, and sulphur levels increased with increasing temperature. Wild noticed 'significant depletion' of metals at the surface, this was attributable to evaporation as follows: Manganese at >600°C, Chromium at >900°C, Iron at >1000°C, and Nickel at >1050°C. Baer also detected metal vapourisation, but the evaporation of manganese occurred at 800°C and was accompanied by the dissociation of grain boundary carbides removing the 'sensitisation' due to chromium at grain boundaries. Baer found chromium, iron, and nickel only to evaporate above 1000°C. Further work upon the oxidation of type 304 steel at pressures between 10^-1-10^-5 Torr revealed that at 850°C and 10^-5 Torr, oxidation to form chromia films could only take place once surface segregated sulphur had formed sulphur dioxide. At higher pressures (oxygen partial pressures of >10^-3 Torr) the formation of iron- or chromium-rich single or duplex films was strongly pressure dependant, the amount of chromium in the film increasing with decreasing pressure. No nickel oxides were ever formed, although nickel was slightly enriched just beneath the
metal/metal-oxide interface. The presence of surface segregants at the brazing temperature will result in a change in the surface energy, and the equilibrium spreading pressure, these will in turn affect the wetting and spreading characteristics of the braze/substrate system.

Greyling and Roux\(^{(82)}\) examined the oxidation of Fe/15.8Cr and Fe/18.8Cr/8Ni steels using Auger and X-ray photoelectron spectroscopy. They too found the removal of carbon and oxygen starting at \(\sim 350^\circ\text{C}\), with nitrogen, sulphur, and phosphorous appearing as surface segregants above \(400^\circ\text{C}\). For both steels chromium enrichment at the surface began at \(\sim 300^\circ\text{C}\) and maximised at \(\sim 500^\circ\text{C}\), the total enrichment being greater on the Fe-Cr alloy, probably due to the formation of grain boundary chromium carbides in the Fe-Cr-Ni alloy. The authors believe the role of temperature to be instrumental in the mobilisation of alloy components. Chromium is sufficiently mobile at \(500^\circ\text{C}\) to segregate to the surface and preferentially oxidise, but at lower temperatures chromium ions move only slowly and cannot fully match the supply of oxygen at the surface so less stable oxides (eg. iron and nickel) are able to form. The exposure (pressure x time) governs oxide formation given a particular ion mobility, hence by carefully adjusting temperature, pressure, and time conditions, it is possible to reduce iron oxides to chromium oxide.
The addition of small amounts of alloying elements to iron and iron-chromium alloys is often carried out to enhance the metal's corrosion resistance. At high temperatures the outer surface of the metal is often enriched in easily oxidisable elements, for example chromium and manganese, and careful heat treatments can often selectively oxidise these elements to form a more protective outer film. Strafford, in his review paper, cites the beneficial effects of rare-earth additions such as yttrium, samarium, vanadium, uranium, and zirconium to chromia forming iron alloys. One of the most widely studied alloy additions to steels (to enhance oxidation resistance) is silicon. Silicon is almost invariably present in steels due to its being added to 'kill' ingots, and some inevitable pick-up from the silicious refractories encountered during the iron and steelmaking process. The effect of further silicon additions has been studied by several authors, and it has been found that in the vast majority of instances silicon additions will enhance the oxidation resistance of iron and iron-base alloys.

In iron oxide, growth takes place by the outward movement of iron ions, and whilst silicon may initially be preferentially oxidised (it has a higher affinity for oxygen), it is rapidly overgrown by iron oxides. This process leads to an effective enrichment of silicon at the metal/metal-oxide interface, and the silicon present there can oxidise to form either fayalite (Fe$_2$SiO$_4$ or 2FeO·SiO$_2$) or silica (SiO$_2$) as a thin interfacial layer. In stainless steels layering occurs, with the most stable oxides nearest to the
metal/metal-oxide interface. The silicon oxide formed depends on the quantity of silicon present in the alloy, but both fayalite and silica have the effect of significantly reducing the iron ion flux. In pure iron silicon levels as low as 0.4% will yield a protective film (or at least a very low linear rate) for temperatures up to 900°C, above this temperature levels of around 1% are needed to give the same effect\(^{86}\). This enrichment of silicon at the metal/metal-oxide interface leads to a high energy interface which can act as a preferred route for detachment of the oxide. Film breakdown occurs when the oxide ruptures, exposing silicon deficient iron, and unless the silicon level in the iron is 3% or more, the newly formed scale is a non-protective mixture of iron oxides and fayalite. If oxygen diffuses into the bulk, subscale formation (or internal oxidation) may occur giving rise to silica particles in the metallic iron.

For iron-chromium alloys the effect of silicon additions are similar to that in iron, the outward diffusion of cations (iron and chromium ions) lead to an effective enrichment of silicon at the metal/metal-oxide interface and the formation of a protective film. For chromium containing alloys the amount of silicon necessary to give the improved oxidation resistance is smaller than for pure iron\(^{62}\), but since silica grows more slowly than chromia (or iron oxides), initial oxide nuclei are quickly overgrown. A thin layer of silica eventually coalesces at the metal/metal-oxide interface either as crystalline silica or coalesced amorphous silica particles, and these so-called 'healing layers' described by Wood\(^{56,65}\) slow the oxidation rate by impeding the cation flux, the layers however, are often difficult to detect due to their thinness. Whilst the oxidation rate is slowed or even halted, this does not mean that preferred oxides (eg. silicon or chromium oxides)
cannot grow at the expense of less stable ones (e.g., iron oxide), this sequential reduction of oxides provides the mechanism for oxide penetration proposed by Cohen et al. (33).

The incorporation of boron and borates into iron-chromium alloys has been examined by Hendy et al. (90) and Lea (64). Hendy found that treatment of alloys containing as little as 5% chromium with either borate solution or by volatilisation of boron compounds so as to incorporate boron into the scale, gave oxidation protection up to 600°C. Similarly treated alloys with 10% chromium gave oxidation protection at 800-900°C that could be maintained indefinitely. Boron was introduced simply by dipping samples into borate solutions (e.g., sodium metaborate, boric acid, 'borax', trimethyl borate) or by volatilisation of borosilicate glass ('pyrex'). With each form of treatment both Hendy and Lea found the surface to be enriched in chromium after oxidation, whilst untreated specimens had a surface layer composed of haematite and magnetite. Lea's Auger spectroscopy examinations showed that the very high surface chromium levels are associated with high levels of boron at the surface. The proposed oxidation mechanism (64, 90) is that boron enrichment at the surface (approximately 6% falling off to zero some 10 nm into the scale) introduces networks of \(-\text{O-}\text{O-}\) covalent bonds which impede oxygen diffusion and hence oxygen activity at the metal/metal-oxide interface. The restriction of oxygen mobility allows slowly diffusing chromium to reach the air/oxide interface. This situation can only arise if the outer layer remains coherent for sufficient time. The outer layer formed at 600°C may be \(\text{Fe}_0.2\text{B}_2\text{O}_3\) or \(\text{Cr}_0.2\text{B}_2\text{O}_3\), but the latter is more likely since is more stable. Chromium enrichment at the air/oxide interface means that the metal/metal-oxide interface is depleted in chromium, it is diffusion
through this depleted layer which governs the rate at which the protective film is built up. The presence of a braze droplet on the surface will also result in a restricted supply of oxygen to the surface, and can therefore encourage the reduction of less stable oxides by more stable ones. This may result in the formation of porous or cracked films (due to volume changes) which will allow the penetration of liquid braze metal. Alternatively, the sequential reduction process can cause the enrichment of certain elements at the metal/metal-oxide interface leaving a high energy, and therefore more easily separated interface.
2.3 Auger Electron Spectroscopy

2.3.1 Introduction

One of the most popular methods for the analysis of the surface of a material is Auger electron spectroscopy. Auger electron spectroscopy is now widely used for a vast and diverse number of applications - oxidation, adhesion, failure analysis, corrosion, tribology, electronics and many more. Despite its widespread use the technique is a fairly new one, having only been available since about 1967-1970. Since its 'birth' however, the technique has rapidly become established, with major advances being made in the fields of theory, instrumentation and application. It is beyond the scope of this thesis to give an exhaustive account of all these aspects - although a fine overview may be found in the recent book by Briggs and Seah (92). This survey will include a brief history of Auger electron spectroscopy, followed by sections containing the theoretical considerations pertinent to this work, and a brief review of the development of high spatial and energy resolution spectrometers.

2.3.2 Auger electron Spectroscopy - A Short History

Over the period 1923-1925, Pierre Auger discovered, and explained the effect which now bears his name (93). His experiments with a Wilson cloud chamber containing mixtures of hydrogen and argon (and later hydrogen with other noble gases), revealed that as well as photoelectron trails, there existed shorter trails which were attributable to a radiationless transition caused by atomic relaxation processes. Whilst this work by Auger was developed in the field of radioactivity to explain
the beta-decay of some elements\(^{91}\) its applicability to surface science was largely neglected until in 1943 Lander\(^{94}\) suggested that Auger electrons from solid materials (and not gases which Auger had used) could yield information relating to the surface. In 1967 Harris\(^{95}\) demonstrated that an Auger electron spectrum, when differentiated by an analogue technique could show surface components clearly with good signal to noise ratios. A short while later Weber and Peria\(^{96}\) and Shreiber and Thorp\(^{97}\) using converted LEED (low-energy electron diffraction) equipment succeeded in producing low resolution Auger spectra. The major step forward in the development of Auger spectroscopy as a surface analysis technique came with the advent of a cylindrical mirror analyser (CMA) built by Palmberg, Bohm, and Tracy\(^{98}\), which gave far better signal to noise than the retarding field analysers (developed from LEED optics) used until then. The development of reliable ultra-high vacuum systems was also taking place as the CMA was devised and Seah\(^{99}\) suggests that this was a major factor in the advancement of surface science. Since the 60's instrumentation has gradually improved allowing increasingly good energy and spatial resolution to be attained. These innovations have greatly enhanced the versatility and applications of the technique, and will be examined in more detail in a later section.

2.3.3 Theoretical Considerations

2.3.3.1 The Auger Effect

The initial work by Auger\(^{93}\) using a Wilson cloud chamber revealed that atoms exposed to ionising radiation were able to produce both photoelectrons and 'Auger' electrons, the latter resulting from a radiationless transition caused by atomic relaxation processes. Since
1925, our understanding of the nature of matter has increased immensely, and the Auger effect is now a phenomenon which can be readily explained.

Figure 2.3: Diagram showing the principles of Auger electron and X-ray emission

The process of Auger electron emission, along with what could be referred to as its sister process - X-ray fluorescence, is depicted schematically in figure 2.3. An incident beam of ionising radiation (either X-rays or energetic electrons) will cause inner, or core shell electrons to be removed leaving the atom in a singly ionised state. In
this state the atom is unstable, and this instability provides the driving force for the relaxation processes. The inner (core) shell electron hole is filled by an electron from one of the outer shells, which results in an excess of energy which may be lost in one of two ways. Firstly, and more simply, is the case of X-ray fluorescence - the excess energy is dissipated by the emission of a photon (X-ray) of characteristic energy. In the instance of Auger electron emission, the excess energy is given to an electron from either the same outer shell from which the electron to fill the original core-hole originated, or another outer shell, and this electron is then ejected with a characteristic kinetic energy. Briggs and Seah\(^{92}\) point out that for successful core shell ionisation the incident beam energy should be approximately five times greater than the binding energy of the electron it is intended to displace. It is apparent that both X-ray fluorescence and Auger electron emission cannot both take place from any given core hole, but as figure 2.4 shows, the probability of relaxation from K-shell ionisation by ejection of an Auger electron is far greater than that of X-ray photon emission up to an atomic number of \(^{\sim}32\). For Auger electron or X-ray emissions resulting from L, M, or N-shell core holes the relative probabilities are similar over similar kinetic energy ranges. In practise this means that strong Auger signals may be detected for all elements provided the relevant kinetic energy range is selected to ensure the resultant Auger electrons originate from the most favourable core shell ionisations.

At this point it is opportune to mention the nomenclature used to describe Auger transitions. Unfortunately there are several forms of nomenclature in current use but only two are commonly used: the 'chemical physics' and X-ray notations. By convention it has become
customary to refer to Auger transitions using X-ray terminology, but for completeness, an explanation of both X-ray and chemical physics terminologies will be given below.

Figure 2.4: Relative probabilities of Auger electron and X-ray emission from a K-shell ionisation

The electron orbitals about an atom allow discrete 'quantised' energy levels to exist, and these energy levels may be thought of as 'shells'. The principal quantum number 'n' defines these shells, and the total number of electrons which may exist in them (ie. \(2n^2\)). In X-ray notation the principal quantum numbers 1,2,3,4... are designated K,L,M,N... Within the shells described by the principal quantum number electrons can exist at different energy levels which can be thought of as subshells, these levels depend upon the velocity of the electron and the radius of its orbital. The total electronic angular momentum of any electron is therefore represented by the vector sum of its two principal momenta. These principal momenta are: the orbital angular momentum designated by the 'l' quantum number which may have values 1,2,3,4... which are designated s,p,d,f... in chemical physics nomenclature; and the spin momentum which is described by the 's' quantum number and has values of plus or minus one half. Although other summation methods are
available electron spectroscopists use a quantum number 'j' to describe the total angular momentum where \( j = l + s \) and therefore has values 1/2, 3/2, 5/2, etc. The table below shows the relationships between the various quantum numbers and the X-ray and electron spectroscopy suffices.

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Often the subshells (described by the 'l' quantum number) cannot be separately distinguished, for example in the L\(_2\) and L\(_3\) shells in which case the X-ray notation becomes L\(_{2,3}\). For an Auger transition arising from a core hole in the K shell being filled by an electron from the L\(_1\) shell and emitting an electron from the L\(_2\) shell the transition is described thus:

\[ KL_1L_2 = 1s_{1/2}^2s_{1/2}^2p_{1/2} \]
For a given primary beam energy both characteristic X-ray and Auger electrons will be produced. Taking once again, the transition shown by figure 2.3 (which by no means represents the only, or most likely transitions to take place), the energy of an emitted photon (X-ray) is given by:

$$E_K - E_{L_1} = h\nu$$

In the case of the Auger electron emission, the resultant kinetic energy of the emitted electron may be approximated as follows:

$$E_{KL_1L_2,3} = K_K - E_{L_1} - E_{L_2,3}^{*} [-W]$$

In this notation $E_i$ represents the binding energy of the i'th energy level (or electron shell). The value $E_{L_2,3}^{*}$ represents the value of the binding energy of the $L_{2,3}$ shell in the presence of a core hole - so its value is different to the value of $E_{L_2,3}$. When using a spectrometer to detect Auger electrons it is also necessary to subtract 'W' (the work function of the analyser) to obtain accurate kinetic energies. Figure 2.3 does not accurately represent the changes which occur during Auger electron or photon emission, since, once the core-hole has been filled the atom 'relaxes' (an inward collapse of the outer electron shells) in order to screen the hole in the inner shell. Similarly further relaxation occurs when the Auger electron is ejected since a second hole is created. Consequently in the case of Auger transitions it is difficult to predict with accuracy the energy of the ejected electron.

An approximate expression for the energy $E_{\text{wxy}}$ of an Auger electron from a WXY transition in an atom of atomic number Z is given by Briggs and Seah. The expression is based upon an empirical expression by Chung and Jenkins who assumed the binding energy change due to a core hole could be taken as being a mean value between the binding energy of the parent atom, and the binding energy of the next atom up in the periodic table.

$$E_{\text{wxy}}(Z) = E_{w}(Z) - \frac{Z}{2} [E_x(Z) + E_x(Z+1)] - \frac{Z}{2} [E_y(Z) + E_y(Z+1)]$$
Development of the expression above(93) gives a useful insight into chemical shifts in Auger spectra. These effects are small and produce a change in peak shape, in transition metals however, the energy changes are due to electrons in the incomplete 3d shell and are masked by the general broadness of the peak. It is not possible therefore, to deduce chemical state information from metals such as chromium and iron, whilst such data is available from elements such as silicon.

2.3.3.2 Production of Auger Spectra

Auger electrons and X-ray photons are generated throughout the ionisation volume induced by the incident radiation. In the case of an electron beam this volume depends upon the primary beam energy, and for beam energies in the region 10-25 KeV (the most useful range for microprobe analysis) the interaction depth is approximately 0.6-1.3 micrometres for most metals. X-rays are easily able to escape from depths of a few microns, and so X-ray photons will yield information reflecting the bulk composition of the fluorescing material. This means that by varying the primary beam energy it is possible to obtain a certain degree of depth resolution. Auger electrons however, are typically of low energy (in the range 20-2000 eV) and as such, are liable to interact with the material and lose energy due to inelastic collisions. Hence the detected Auger peaks will be representative of those electrons which have escaped the material without losing any of their energy, and this in turn implies that these electrons must be those from the surface layer of the material, since electrons generated in the bulk of the material can be expected to have lost energy. It is possible to excite Auger electrons for any primary beam energy which will successfully ionise the material under the beam, but typically energies
in the range 3-10 KeV are used because these values do not cause too severe differences in relative peak intensities between the upper and lower ends of the Auger spectrum. The thickness of the analysed surface layer is given by Seah\(^{100}\). in terms of the inelastic mean free path \(\lambda\) An electron has a probability of \(e^{-1}\) of travelling the distance characterized by the inelastic mean free path before being inelastically scattered. Seah expresses the characteristic depth from which Auger can be emitted (also known as the escape depth) as:

\[
\text{Thickness of analysed layer} = \lambda_M (E_{A}^{XYZ}) \cos \theta
\]

\(\lambda_M (E_{A}^{XYZ})\) is the inelastic mean free path of electrons of energy \(E_{A}^{XYZ}\) in a sample of matrix \(M\), whilst \(\theta\) is the angle to the surface normal of the electron detection system. The flux of emitted electrons from the material decays as \(e^{(-d/\lambda)}\) where \(d\) is the distance from the point of origin. This decay is more readily explained by the Beer-Lambert expression:

\[
I = I_o \exp(-d/\lambda \sin \theta)
\]
where \( I \) is the detected intensity, \( I_o \) is the measured intensity from a clean, pure, thick material, and \( d \) is the distance into the material. The implications of this relationship are that to a good approximation the following is true:

\[
65\% \ I = \lambda \sin \theta \\
85\% \ I = 2 \lambda \sin \theta \\
95\% \ I = 3 \lambda \sin \theta
\]

In practical terms this means that virtually all the detected signal comes from a sampling depth of \( 3\lambda \), this is illustrated by figure 2.5.

Figure 2.6: Variation of the IMFP with electron energy

Seah and Dench\(^{101}\) show the variation of \( \lambda \) with electron energy, their results for all the data which was available are shown in figure 2.6. The figure illustrates, that for elements yielding Auger electrons in the range 20-2000 eV, the inelastic mean free path varies between approximately 1-5 monolayers. Auger analysis is therefore a truly surface sensitive technique and for this reason it is necessary to maintain UHV conditions in a spectrometer so that contaminant layer
cannot build up and obscure the signal from the material beneath it.

### 2.3.3.3 Pulse-counted vs. differential spectra for AES

As will be outlined in the following section, modern high resolution Auger electron spectrometers are being increasingly used to collect pulse-counted (or direct) spectra rather than the traditional differential (or derivative) spectrum, so it is pertinent to examine the advantages and disadvantages of these two acquisition modes.

The use of analogue differentiation was first proposed by Harris (1995) since it allowed the small Auger peaks on their steeply sloping background to be presented with far superior visibility by effectively removing the background—its constant slope becoming a constant value.—(because of the larger amount of expansion possible for peak enhancement) that have made acquisition in the derivative mode so continually popular. Notwithstanding these advantages several authors (102-106) have recommended spectrum acquisition in the direct mode. Sickafus (102) presented Auger electron spectra as log N(E) vs. log (E) plots (ie. number of electrons detected at a given kinetic energy E vs. kinetic energy) and observed that whilst this form of presentation showed any Auger peaks that could be seen in derivative spectra, the reverse was not always true. He also pointed out that using the double log scales, the secondary electron background became a 'linear cascade', and that small changes in slope of this cascade were indicative of the source (ie surface or 'bulk') of the Auger signal. Strausser et al (103) used similar log-log plots and the same linear cascade approach in conjunction with standard spectrum subtraction methods to quantify overlapping copper, nickel, and cobalt peaks. They
commented that acquisition in the derivative mode would not have allowed contributions from the various peaks and more importantly their backgrounds to be separated. Madden\(^{104}\) argued that $N(E)$ data gives a far better basis for peak envelope synthesis, and better scope for energy loss corrections. This opinion is shared by Seah\(^{105,106}\) who agrees that the area under a pulse-counted Auger peak is clearly related to physical parameters, but adds that at present there are no truly effective means by which the contributions of background and energy loss events can be separated or removed. If accurate quantification is required Seah\(^{107}\) has found that a true derivative of the energy spectrum is only achieved if tiny modulation voltages are superimposed onto the detected electron current, because the relative peak intensities vary as a function of this modulation potential. Similarly a change in the energy resolution will also affect the relative peak intensities, and for some analysers such a change can come about merely by incorrect positioning of the specimen. Whilst these are real problems, they may be largely overcome by using published or experimentally determined standard data provided the acquisition conditions used for taking the standard spectra are faithfully duplicated when taking the spectra to be quantified. Seah also considers an alternative route to 'quantifiable' derivative spectra - acquisition in the direct mode followed by numerical differentiation. When measuring peak intensities he advocates the use of peak-to-background measurements (that is the distance from the maximum negative excursion to the [straight] base line) rather than the conventional peak-to-peak values, since the latter will contain distortions resulting from the energy loss signals on the low kinetic energy side of the peak.
Bishop\cite{108} has considered the information contained in the background and the separate constituents. Both he and Prutton et al\cite{109} realised that the background of direct spectra are affected by specimen topography, atomic number, and electron beam fluctuations, and hence they have proposed a signal normalisation technique by which their influence may be removed. Bishop et al\cite{110} have also noted that the background, and Auger signal may be subject to electron channelling effects if large-grained or single crystal specimens are analysed.

The use of pulse-counting for Auger electron spectroscopy is usually limited to the more modern high spatial resolution instruments. There are two main reasons for this, firstly, to achieve the high spatial resolution required for scanning Auger microscopy low specimen currents are necessary — typically a few tens of nanoamps. At such low specimen currents, the detected electron signal ceases to be a true current which can be differentiated, and instead becomes a series of discrete events as individual electrons arrive at the detector. Consequently the balance shifts in favour of pulse counting, since under these conditions the signal to noise in this mode is far superior to that attainable in the derivative mode. In addition to this most high spatial resolution instruments incorporate analysers which are more suitable for pulse counting. The second instance where pulse-counting is preferable, is where specimens which are susceptible to electron beam damage are to be examined. It is well known\cite{111-113} that the primary electron beam can damage some materials, and in some instances bring about electron stimulated desorption (ESD) of surface species. Furthermore the secondary electron yield (and hence the Auger background) is often affected by differences in composition and contamination level, so it is wisest to reduce the beam current and current density to a minimum,
thereby minimising damage and charging, but necessitating pulse-counting.

To summarise, acquisition in the differential, or derivative, mode is certainly faster, easier, and often cheaper than acquisition in the direct mode. In most circumstances the signal to noise of the latter mode is better, but it could be argued that derivative data is more easily and accurately quantified—especially given the wealth of published standard data. Differential mode acquisition however is not suitable for instruments using low beam currents—that is high spatial resolution machines—because a detector current is necessary, indeed such machines often configured so that it is impossible to reach the currents normally used in the derivative mode. Direct spectra undoubtedly contain more information than derivative spectra, this information being far less distorted, and although there is no simple way of distinguishing between the various components of the direct spectrum, it is possible to distinguish between components of derivative spectra. Direct spectra are more difficult to acquire, and, to achieve good signal to noise, require longer acquisition times than derivative spectra.

It seems likely that both acquisition modes will continue to be used, the derivative mode for 'everyday' work requiring non-stringent quantification, with the direct mode being restricted to use with Auger spectrometers operating at high spatial resolutions, and for physical studies requiring un-distorted data.
The development of high spatial resolution Auger spectrometers

Since 1925 Auger Electron Spectroscopy has evolved into a highly versatile and popular surface analysis technique. The first Auger electron spectra were produced in 1967 by what would now be considered very crude experimental apparatus, and this review endeavours to trace the various innovations and improvements which led to the high spatial and energy resolution spectrometers of the present day.

For his early work in 1957-68 Harris used an electron gun which was in effect a converted cathode ray tube, and had a spot size in the order of 2-4 mm at a beam current of several hundred microamps (μA) for a primary beam energy of 695-1910 eV. Consequently his spectra, which were detected by a 127° electrostatic sector analyser of 2.5″ mean radius enabling energy resolution (ΔE/E) in the order of 0.1% to be attained, contained peaks due to elastically scattered secondaries and plasmons. The major contribution of Harris however, was that he demonstrated that by differentiating the 'direct' Auger electron spectrum - small Auger peaks on a high background - the Auger peaks became far more prominent, the analogue technique 'differentiating out' the background upon which the peaks were superimposed. The derivative spectrum produced in this way gave very good signal to noise ratios, and meant that the technique was highly sensitive to small concentrations of elements at the surface. Following discussions with Harris, Weber and Peria showed that low-energy electron diffraction systems (LEED) could easily be adapted to produce Auger spectra. Their LEED optics used an electron gun running at approximately 3 μA giving a spot size of about 1 mm, the second derivative of the signal from a retarding field analyser.
provided the means of detection.

At this time Palmberg was also using a converted LEED system for Auger electron spectroscopy\(^{(115)}\) and his findings in 1968 using this arrangement showed that for solid materials the inelastic mean free path of electrons through the solid, was far shorter than had been accepted up to that time, and that it was proportional to the Auger electron energy, so that in silver for example, Auger electrons could only escape from a depth of around 4-8 Å. Auger spectroscopy had been recognised as a truly surface sensitive analytical technique!

The following year (1969) Palmberg, Bohm and Tracy\(^{(98)}\) published details of their high sensitivity Auger electron spectrometer. Their design was based upon the concept of a cylindrical capacitor as an energy analyser proposed some years earlier by Sar-eli\(^{(116)}\). Palmberg recognised that the sensitivity of retarding field analysers (used until then in converted LEED systems) and velocity analysers is limited primarily by the 'shot noise' - backscattered primary electrons reaching the detector. With retarding field analysers any electrons with energies greater than those applied to the retarding grids could reach the detector, so the detected signal is composed of backscattered primaries - giving a current of 0.3\(I_p\) (\(I_p\) is the primary beam current) - and of Auger electrons which only make up a small proportion of the detected signal, about \(10^{-4}I_p\). With a velocity analyser however, the current transmitted to the detector consists only of electrons with an energy \(\Delta E\) - the energy resolution of the spectrometer. Palmberg demonstrated that by careful positioning of the spectrometer exit slits the resolution could be as good as 0.5%. The major advantage of the 'coaxial cylinder velocity analyser' (now known as the cylindrical mirror
analyser or CMA) was that its transmission was very high, and it gave
signal to noise values several orders of magnitude greater than retarding
field analysers. By this time, electron gun design had also improved,
and Palmberg could use his CMA with a gun which gave a spot size of 0.1mm
(100µm) at 100µA beam current and 3KeV beam energy. The electron gun
however, was mounted to one side of the analyser which meant that only
grazing incidences of the electron beam onto the sample could be used,
and the beam had to be very carefully positioned to ensure that it was
centred within the acceptance area for the analyser.

By the early 1970's Auger electron spectroscopy had been eagerly
accepted as a surface analytical technique, and it found extensive usage
for a large variety of applications, but most notably for failure
analysis of steels. In those early years however, the system was
limited by its relatively poor spatial resolution, in the order of
50-100µm, and consequently there was a concerted effort to upgrade Auger
electron spectroscopy to a high spatial resolution technique.

The feasibility of incorporating Auger spectrometers into scanning
electron microscopes was first examined by MacDonald in 1970, and
Harris in 1971. Whilst neither of the microscopes used were
ideally suited to Auger spectroscopy (neither microscope could be
described as having a UHV environment), the studies did show that it was
possible to obtain sub-micron resolution with Auger electron
spectroscopy. In later work, MacDonald using a
computer-controlled SEM and AES experiment produced the first Auger
'maps' - spatial distributions of the surface chemical species. His work
used a high energy electron beam (15KeV) which gave good spatial
resolution, approximately 0.3µm for a beam current of 25nA. MacDonald
also pointed out that if 'Scanning Auger Microscopy' or SAM were carried out in conjunction with ion-sputtering and-or conventional X-ray microprobe analysis, it could yield a complete three dimensional analysis of the sample.

In the period 1971-76 there was considerable effort to develop both high spatial resolution AES and scanning Auger microscopy (SAM) as surface analysis techniques. Several workers (120-124) adapted current SEM's and UHV systems incorporating CMA's and electron guns with brighter sources - the outcome of this work was to underline the fact that high resolution SAM was a viable proposition. The first commercial scanning Auger microprobe was introduced in 1973 (125) and featured a CMA with a small internally mounted electrostatic electron gun. This arrangement overcame the problems associated with shadowing on rough samples due to the off-axis guns previously used, and gave a better Auger signal. The beam diameter of this instrument was only in the order of 5μm, and the spectrometer resolution (ΔE/E) was about 1%. At about the same time another manufacturer offered a concentric hemispherical analyser or CHA for use in Auger electron spectroscopy in conjunction with an X-ray photoelectron spectroscopy facility. Whilst this CHA was not incorporated on a high spatial resolution instrument (a choice of electron guns with spot sizes in the 5-40μm range were offered), it was able to record spectra at much higher resolution - 0.075% - but at the cost of far lower transmission. In 1975 the double-pass CMA was introduced and incorporated onto a commercial instrument. This analyser, in conjunction with a coaxial electron gun, gave an energy resolution of 0.7%, the improvement being due to the electron path through the analyser being effectively doubled, enhancing the rejection of electrons above or below any given energy. In 1976 Gerlach and MacDonald (126)
described a SAM which used a CMA with externally selectable apertures allowing the energy resolution to be manually set to either 0.3%, 0.6%, or 1.1%. The higher resolution available enhanced the suitability of the technique for the examination of low-energy Auger peaks, and when the system was used with the 0.5μm electron gun sub-micron SAM became possible. Two other notable advances in instrumentation described by Gerlach were the use of a LaB₆ electron source (which provided the high brightness, beam current, and longevity to enable the high spatial resolution to be achieved), and SAM electronics which allowed complete computer control of spectrum acquisition. In the same year Venables et al.(127), using a V.G. microscopes HB50 (which uses a field emission gun) fitted with a CMA carried out Auger spectroscopy at a spatial resolution of 30nm.

At this point it is pertinent to examine in more detail the various analysers and electron sources which are available. Electron energy analysers fall typically into one of three categories: Retarding field type, cylindrical mirror type, and concentric hemisphere type (although this type of analyser is almost always used in conjunction with a retarding grid). These three groups of analyser are shown schematically in figures 2.7, 2.8, 2.9, and 2.10, and whilst variations occur within these basic groupings the essence of the mode of operation is not changed. Similarly electron sources may be placed in groups: thermionic sources (tungsten and LaB₆), and field emission sources.

The retarding field analyser (figure 2.7) employs a number of grids (typically three or four) which can be independently set at a range of potentials. By adjusting the potentials of the grids, a particular pass energy may be set so that any electrons with kinetic energies greater
than this pass energy will reach the detector. Obviously this arrangement means that the signal to noise is poor, because the majority of the signal will be composed of electrons with energies greater than the pass energy.

Figure 2.7: Schematic drawing of an RFA

The cylindrical mirror analyser (figure 2.8) on the other hand, is a velocity analyser, and by means of a potential between the inner and outer concentric cylinders, is able to reject electrons with energies greater or less than the pass energy (ie. the potential between the inner and outer cylinders). This 'rejection' of electrons occurs because electrons with energies higher or lower than the pass energy will contact either the outer or inner cylinders (respectively), whilst electrons with energy equal to the pass energy will pass through the analyser in an arc to be registered at the detector. The CMA is able to accept electrons from a large solid angle of acceptance, although this advantage is lost if an off-axis electron gun is used. The CMA also offers very high electron transmission, so that spectra can be rapidly acquired in the derivative mode. Variations to the basic design of the CMA have included incorporation of coaxial electron guns (thereby
maximizing transmission and minimizing the effect of sample topography), inclusion of apertures just ahead of the detector to enable selectable energy resolution (this also allows angle dependent studies to be carried out), and doubling the electron path (the double-pass CMA) which enhances the energy resolution. All of these variations are depicted in figure 2.9. A disadvantage of the CMA is that, even with coaxial electron guns, there is very little workspace between the specimen and the analyser, and specimen positioning is critical — small shifts away from the focal point of the analyser will significantly alter the energy resolution of the system.

Figure 2.9: Schematic diagram of an advanced CMA

**Double pass CMA with coaxial electron gun**
The concentric hemispherical analyser, like the CMA, is a velocity analyser, and is illustrated diagramatically in figure 2.10. A potential is applied between the two hemispheres, and in the same manner as the CMA, electrons with energies greater or less than the pass energy contact the hemispheres, and electrons with energy equal to the pass energy pass through the analyser to reach the detector. As the dotted lines show, the solid angle of acceptance of the CHA is small and transmission through the analyser is poorer compared with the CMA, but to offset this, the energy resolution of this type of analyser is at least an order of magnitude better than the CMA. Problems associated with the small acceptance angle can be largely overcome by incorporating a transfer lens between the specimen and the analyser. Such a lens serves to collimate a beam of Auger or photo-electrons which may then pass into the analyser at a low entrance angle. The lens has the additional advantage that it isolates the analyser from fields associated with the column, and creates far more workspace around the specimen.

The most modern transfer lenses also incorporate elements to replace the...
conventional retarding grids, so that the field effects associated with these grids no longer affect electron detection. To offset the relatively low transmission of CHA's, large diameter analysers can be fitted with multi-detectors, but whilst this improves detection capabilities, a sophisticated computer acquisition system is needed to cope with the necessary energy offsetting of the detectors.

The other main area where Auger electron spectroscopy systems may differ is in the choice of electron source. Most commonly a tungsten 'hairpin' filament is heated so that it emits a stream of electrons (thermionic emission) which are accelerated via a charged grid. More recently Lanthanum hexaboride (LaB$_6$) filaments have become available, and whilst the electrons are still produced thermionically, they are produced more efficiently, so the source is 'brighter' than its tungsten equivalent. It should be borne in mind however, that LaB$_6$ sources are far more susceptible to changes in vacuum and emission current, more difficult to make, and need careful setting-up. Most manufacturers recommend that LaB$_6$ are differentially pumped. Notwithstanding these difficulties, LaB$_6$ sources are approximately 10x brighter than their tungsten counterparts, and, if correctly treated, will last far longer.

Field emission guns use a source which is fashioned to a point. A very high positive electrostatic field is applied between this point and an extraction electrode, this enables electrons at the tip of the pointed source to overcome the material's work function so that they can escape into the vacuum. Besides their high cost, field emission guns require extremely stringent vacuum conditions - differential pumping is mandatory - they are also very difficult to centre prior to their use.
The sources are however approximately two orders of magnitude brighter than tungsten filaments, and when set-up need little or no adjustment, in addition to this, the fact that no heating of the source is involved means that the sources are very long-lived.

Since 1976 there has been a gradual improvement of instrumentation, the double-pass CMA has remained virtually unchanged (and still offers only 0.3% max resolution), but the design of coaxial electron guns has improved greatly. CHA design has improved considerably and modern large diameter analysers offer far superior energy resolution. Notwithstanding this comparison the CMA is still very widely used, it has superior transmission (although multi-detector CHA systems may now rival this), and is relatively inexpensive compared to large CHA systems. The CMA however, when used with a coaxial electron gun has the clear advantage over the CHA (which always has an off-axis gun) in that it is far less sensitive to specimen topography - especially if spectra are taken in the derivative mode. This advantage is partially eroded however, if a transfer lens is used and positioned so that any shadowing effects are minimised.

Notable improvements have been made in the field of electron gun design allowing higher and higher spatial resolutions to be reached. Use is being made of LaB$_6$ and field emission electron sources enabling high beam currents to be maintained even for small spot sizes. For most purposes an electrostatically focussed electron beam is suitable. Early electron guns with their 1-2µm spot sizes were soon refined so that in the early 70's guns giving a beam diameter of 0.5-5µm were available. Since then electrostatically focussed guns which will produce a 0.1µm spot have been produced, although the spot size usually needs to be
increased to provide a sufficient specimen current for Auger spectroscopy in the derivative mode. The use of LaB$_6$ sources enables Auger electron spectra to be taken at around 0.25-0.5μm spatial resolution with an electrostatically focussed electron beam.

For maximum spatial resolution electromagnetically focussed electron beams, of the type commonly found in SEM's, need to be employed. This type of column can give better than 5nm resolution, but for AES work beam diameters of 30-50nm are typical for very high resolution instruments. Such gun and column assemblies are rather bulky, and consequently are unsuitable for mounting coaxially in a CMA (although Gerlach$^{(128)}$ reports this is now feasible), furthermore the use of permanent magnets in the column will introduce unwanted magnetic field which cause distortion in the low kinetic energy end of the spectrum. As a result of this electromagnetically focussed electron beams are usually used in conjunction with a CHA since both the column and analyser can be situated a 'safe' distance from the specimen (ie. beyond the influence of the magnetic field produced by the column). The low specimen currents involved with high spatial resolution instruments - even those with bright electron sources - mean that spectra must be collected in the direct (or pulse-counted) mode. In this configuration the advantages of the CMA in terms of transmission are largely negated, and the CHA provides a superior detection system, especially if multichannel detector electronics are incorporated. In principle the maximum spatial resolution available is governed by the electron beam diameter, it should be borne in mind however, that at very high resolution there is a considerable time penalty associated with the unavoidably poor count-rates. In addition to this backscattered electrons will excite Auger electrons from outside the electron probe 'footprint', and it is
this factor which determines the absolute maximum spatial resolution achievable.

It is interesting to look back over the last 15 years or so of development of high resolution Auger electron spectrometers, to highlight the trends which have come about. Auger electron spectroscopy is the most popular surface analysis technique in the U.S.A, and most manufacturers there find the CMA to be the analyser type most suited to Auger electron spectroscopy. The CHA is a relative newcomer to the field of Auger electron spectroscopy, its introduction being in about 1976 when it was incorporated into a British multiple-technique instrument. X-ray photoelectron spectroscopy (XPS) has been the more popular surface analysis technique in Britain and Europe, and spectrometer design in these countries has reflected this. The energy resolution required for XPS must be sufficiently good to enable small differences in peak shape to be determined, in order to obtain chemical state information. In the case of AES on the other hand, much of the early work was carried out on steels, and the iron Auger peak is broad so it does not yield any useful chemical information. Most of the early work on steels was purely qualitative too, so there was little need for good energy resolution detection systems.

The introduction of multi-technique instruments (ie AES and XPS plus others) therefore, reflected the trends which had been followed by different countries' manufacturers. American machines used CMA's with coaxial electron guns and off-axis X-ray guns, and were marketed as Auger electrons spectrometers with an XPS facility. British Machines tended to use a CHA with separate X-ray and electron guns, and were marketed as X-ray photo-electron spectrometers with an AES facility.
CMA based spectrometers are still unsuitable for high energy resolution work and as such are of limited use in XPS studies, in addition to this, there are problems in incorporating a retarding grid into a CMA - to do so means that the acceptance angle is significantly lessened. The CMA however retains its unsurpassed transmission properties, and is considerably cheaper than the CHA. If a coaxial gun is used conditions are really at their best for SAM because of the insensitivity of such a configuration to specimen topography.

CHA based spectrometers are much more suited to XPS, and as a result of this the performance of the analyser is optimised for acquisition in the direct mode (pulse-counting). Problems can therefore arise if large specimen currents are used (eg. for AES in the differential mode), since the CHA can give poor results at the low energy end of the Auger electron spectrum. This is because CHA's are particularly sensitive at low energies, and this may result in the Auger signal being masked by the 'true secondary' peak unless very careful sample positioning is carried out so as to maximise the signal from the low kinetic energy Auger peaks. The use of CHA's in Auger electron spectroscopy spectrometers however, did allow Auger electron spectra to be acquired in the pulse counted mode which meant that low specimen currents, and hence high spatial resolutions were feasible. The recent trends in high spatial resolution surface analysis are considered by Bishop (129), who also compares analyser types, electron sources, and focussing systems.
From the genesis of Auger spectroscopy in the late 60's to the present day, there has been a gradual improvement in spectrometer instrumentation. It is now possible to obtain Auger analyses and maps with a spatial resolution of ten nanometres or so which represents the smallest analysis volume of all the surface analysis techniques. To conclude, it is now more reasonable to regard very high spatial resolution Auger electron spectrometers as MICROSCOPES, which operate under UHV conditions and possess an Auger electron spectroscopy facility. The present thesis concerns the use of an instrument of this type.
2.4 Summary of the Literature Survey

The most important property of a brazing alloy is that it will flow, and continue to flow along a joint. This ability is dependent upon the wetting and spreading characteristics of the alloy. The literature survey considers the classical theory of wetting and spreading, and highlights the factors which can affect the braze alloy behaviour on a given substrate. The presence of a surface oxide on the substrate means that either the oxide surface must be wetted, which is unlikely, or that the oxide must be replaced by some means. Oxide displacement may be facilitated by the presence of high-energy metal/metal-oxide interfaces, or alternatively, by heating the metal in vacuo, local or total reduction of the oxide may result in an easily penetrable porous film, or a completely oxide free surface. Segregation of species to the surface of the substrate will affect the equilibrium spreading pressure, which can mean that wetting and spreading is impeded, or that it is enhanced by the formation of a more readily wetted surface. The pick-up of elements from the substrate by the molten braze alloy is an almost inevitable occurrence which can be beneficial or detrimental to the brazing process, but will certainly affect it in some way.

These phenomena may all be studied in 'real-time' using a half-joint geometry with the combined techniques of high resolution scanning electron microscopy and Auger electron spectroscopy (surface analysis), and X-ray spectroscopy (bulk analysis), on a heating stage in a UHV environment. Using these techniques it is hoped that the influence of the factors mentioned above, upon the wetting and spreading behaviour of brazing alloys will be determined.
3 Optimisation of Resolution for the V.G.MA500.

3.1 Introduction.

In order to study vacuum brazing at high resolution with both secondary electron imaging and Auger electron spectroscopy, whilst carrying out X-ray analysis for information regarding the bulk composition, it is evident that a UHV microscope with Auger electron and X-ray spectroscopy facilities is necessary. This requirement is met by the V.G. MA500 Scanning Auger microscope at Surrey University. The instrument has an electromagnetically focussed electron gun and can operate at accelerating voltages between ~2-30 KeV. This enables a maximum resolution of 50nm in the imaging (secondary electron) mode but due to the very low specimen currents such resolution entails, a practical maximum resolution for Auger electron spectroscopy is approximately 100nm. Electrons are detected via a transfer lens leading into a 4" concentric hemispherical analyser with a 'channeltron' detector. The spectrometer has been modified so that it will accept a solid state X-ray detector, and using software developed by Link Systems, simultaneous acquisition of both Auger electron, and X-ray spectra can be carried out. The datasystem also enables digital element maps to be acquired from either an Auger electron or X-ray signal. An X-ray source (Mg and Al) is also provided so that simultaneous X-ray photoelectron spectra (XPS) and X-ray fluorescence spectra (XRF) may be taken. The specimen may be ion-etched in-situ using an Argon ion gun. The spatial distribution of the various detectors and sources is shown in figure 3.1.
To enable the study of brazing processes, a vacuum-portable heating stage has been developed. The stage allows heating to approximately 1200°C with excellent temperature stability (±2°C), power is supplied via a voltage or current controlled D.C. power supply. The specimen temperature is recorded with a chromel-alumel thermocouple spot-welded to the specimen surface. Figure 3.2 shows the heating stage at a temperature of ~1000°C and figure 3.3 shows the general appearance of the V.G MA500.

The use of a high resolution microscope for imaging and surface and bulk analysis, means that data has to be collected in the direct (pulse counted) mode. Normally this presents no real problem, since the acquisition times are simply lengthened to counteract the less intense signal. The use of a heating stage however, means that a dynamic (rather than static) system is being studied, so as well as good resolution in energy and space, the shortest acquisition times possible are also required - i.e. resolution in time. To enable this criterion to be met a thorough knowledge of the way in which a change of operator-controlled spectrometer variables can affect the Auger spectra
Figure 3.2: General configuration of the V.G. MA500

Figure 3.3: The heating stage in use in the MA500
produced is required. This section develops a means for the optimisation of the spectrometer resolution in all three modes: time, energy, and space.

The object of this work is to determine the effect of the major operator-controlled spectrometer variables upon Auger spectra, and to devise a simple, empirical means by which the spectrometer may be set up to achieve optimum resolution in time, energy, and space, for a given set of experimental requirements. The pattern adopted in this work is felt to be of general application to this class of instrument.

3.2 Experimental.

Pure—better than 99.9%—samples of nickel, silver, iron, chromium, gold, tantalum, and copper were supplied by Johnson Matthey P.L.C. These materials were chosen since they represent the main elements of interest for work with silver/copper and gold/nickel brazes on ferrochromium. The metals were each approximately 10mm square and 0.5-2mm thick. The specimens were spot welded to MA500 stubs to ensure good conduction (with the exception of tantalum which had to be attached by silver 'dag'), and polished to a 1μm diamond paste finish. All specimens were degreased for at least five minutes by ultrasonic cleaning in 'inhibisol', and once in the microscope were argon-ion bombarded for up to 20 minutes in order to remove surface oxide and other adventitious surface contaminants. The cleanliness of each specimen, prior to carrying out the resolution optimisation analyses, was checked by taking an Auger spectrum paying careful attention to the carbon and oxygen levels.
Table 3.1: Table showing parameters used for Auger electron spectroscopy resolution studies.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ni, Ag, Fe, Cr, Ta, Au, Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant retard ratios</td>
<td>10, 4, 2 :1</td>
</tr>
<tr>
<td>Constant analyser energies (eV)</td>
<td>50, 20</td>
</tr>
<tr>
<td>Specimen currents (nA)</td>
<td>40, 20, 4</td>
</tr>
<tr>
<td>Acquisition times (secs)</td>
<td></td>
</tr>
<tr>
<td>For i = 4, 40</td>
<td>i.t = 1200, 4800</td>
</tr>
<tr>
<td>For i = 20</td>
<td>i.t = 400, 1200, 4800</td>
</tr>
</tbody>
</table>

Approximately 250 spectra were taken using all combinations of parameters shown in table 3.1. The acquisition times used were determined by making the product of the specimen current (i) and count-time (t) equal to one of three constant values representing 'slow', 'medium', and 'fast' acquisition times. Using this method the electron excitation remained constant so that spectra taken under different conditions could be more easily compared. The specimen current values chosen (4, 20, and 40nA) cover the range usually used in the acquisition of direct (pulse-counted) Auger spectra, similarly the constant retard ratio (CRR) and constant analyser energy (CAE) parameters were chosen to span the conditions used in both high and low energy resolution work. During the acquisition of these spectra the analysis chamber was consistently maintained at a vacuum of better than $10^{-8}$ mbar. An accelerating beam voltage of 10KeV was used throughout since this voltage has been shown by Bishop et al. to give optimum Auger signals for most experimental conditions and is sufficiently energetic to excite useful X-ray lines from the elements considered. The filament current was 0.1 mA, and the tilt-angle from the primary electron beam was kept at $45 \pm 5^\circ$ giving a take-off angle of $15^\circ$ from the surface.
normal. The largest (1000μm) aperture was used when taking the spectra, since it was with this aperture in place that the spatial resolution/beam current relationship was determined. The 4" hemispherical analyser was used with 4mm slits. All spectra were acquired under computer control over a range of 250 eV with a channel width of 0.5 eV using a parallel acquisition mode to distribute across the spectra any effect of the electron beam on the sample.

Table 3.2: Conditions for the experiment examining the effect of channel spacing upon signal to noise.

<table>
<thead>
<tr>
<th>eV / channel</th>
<th>scan width</th>
<th>total time</th>
<th>signal to noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>80</td>
<td>385</td>
<td>7.29</td>
</tr>
<tr>
<td>0.25</td>
<td>80</td>
<td>385</td>
<td>16.92</td>
</tr>
<tr>
<td>0.5</td>
<td>80</td>
<td>385</td>
<td>20.11</td>
</tr>
<tr>
<td>0.75</td>
<td>80</td>
<td>385</td>
<td>24.23</td>
</tr>
<tr>
<td>1.0</td>
<td>80</td>
<td>385</td>
<td>35.80</td>
</tr>
<tr>
<td>1.5</td>
<td>80</td>
<td>385</td>
<td>60.43</td>
</tr>
<tr>
<td>2.0</td>
<td>80</td>
<td>385</td>
<td>74.60</td>
</tr>
</tbody>
</table>

Group 2 - time per channel is constant at 0.1 secs.

<table>
<thead>
<tr>
<th>eV / channel</th>
<th>scan width</th>
<th>total time</th>
<th>signal to noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>80</td>
<td>800</td>
<td>19.61</td>
</tr>
<tr>
<td>0.25</td>
<td>80</td>
<td>320</td>
<td>14.55</td>
</tr>
<tr>
<td>0.5</td>
<td>80</td>
<td>160</td>
<td>14.04</td>
</tr>
<tr>
<td>0.75</td>
<td>80</td>
<td>106</td>
<td>16.39</td>
</tr>
<tr>
<td>1.0</td>
<td>80</td>
<td>80</td>
<td>13.14</td>
</tr>
<tr>
<td>1.5</td>
<td>80</td>
<td>53</td>
<td>15.30</td>
</tr>
<tr>
<td>2.0</td>
<td>80</td>
<td>40</td>
<td>19.09</td>
</tr>
</tbody>
</table>

Further Auger spectra were collected (according to the conditions of table 3.2) to demonstrate that although there is no effect of channel spacing upon signal to noise ratio when the time per channel is constant, there is a deterioration in signal to noise with increasing channel spacing when the total acquisition time is constant. A series of widescans were taken on the nickel specimen to assertain the effect of
A tilt-angle upon the Auger spectrum (10KeV beam, 20nA, CRR=4, 1000eV widescan, 1eV/channel, and 960secs count-time).

Table 3.3: Table showing the conditions for acquisition of MgKα excited Auger peaks at 60° tilt-angle.

<table>
<thead>
<tr>
<th>Element</th>
<th>Start KE (eV)</th>
<th>End KE (eV)</th>
<th>C.A.E. (eV)</th>
<th>Count-time (secs)</th>
<th>Channel spacing (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>805</td>
<td>875</td>
<td>50</td>
<td>600</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>835</td>
<td>855</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
<tr>
<td>Ag</td>
<td>335</td>
<td>375</td>
<td>100</td>
<td>300</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>365</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>685</td>
<td>715</td>
<td>50</td>
<td>600</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>685</td>
<td>715</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>450</td>
<td>500</td>
<td>50</td>
<td>900</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>500</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
<tr>
<td>Cu</td>
<td>880</td>
<td>930</td>
<td>50</td>
<td>900</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>925</td>
<td>905</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Magnesium X-ray excited Auger spectra were taken for nickel, silver, iron, chromium, and copper (but not gold whose Auger peaks cannot be excited by magnesium radiation) at pass energies (CAE) of 100, 50, and 10eV full acquisition details are given in table 3.3. These spectra produce well resolved Auger peaks from which the natural Auger peak widths (Full width at half maximum) may be determined, provided the natural peak width is greater than the 0.8eV FWHM of the magnesium Kα X-rays.
Table 3.4: Table showing acquisition conditions for Ag3d and Au4f XPS peaks (60° take-off angle).

<table>
<thead>
<tr>
<th>Element</th>
<th>Start KE (eV)</th>
<th>End KE (eV)</th>
<th>C.A.E (eV)</th>
<th>Count-time (secs)</th>
<th>Channel spacing (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (3d)</td>
<td>850.6</td>
<td>900.6</td>
<td>200</td>
<td>300</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>871</td>
<td>891</td>
<td>100</td>
<td>600</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>871</td>
<td>891</td>
<td>50</td>
<td>600</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>871</td>
<td>891</td>
<td>20</td>
<td>1200</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>871</td>
<td>891</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>871</td>
<td>891</td>
<td>5</td>
<td>3600</td>
<td>0.1</td>
</tr>
<tr>
<td>Au (4f)</td>
<td>1155</td>
<td>1185</td>
<td>200</td>
<td>600</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td>1185</td>
<td>100</td>
<td>600</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td>1185</td>
<td>50</td>
<td>600</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td>1185</td>
<td>20</td>
<td>1200</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td>1185</td>
<td>10</td>
<td>2400</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td>1185</td>
<td>5</td>
<td>3600</td>
<td>0.1</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectra were also collected for the silver 3d and gold 4f doublets at pass energies of 5, 10, 20, 50, 100, and 200 eV (see table 3.4 for full spectrum details) so that, in addition to peak width data at higher energies from electron excited Auger peaks the dependence of the energy resolution characteristics of the analyser with analyser pass-energy could be determined.

3.3 Results.

The Auger spectra acquired according to the conditions in table 3.1, were each individually examined, and the relevant data taken from them. The means of acquiring this data, and its preliminary processing are included in appendix 1.

Graphs were plotted for all elements to show the relationship between the signal to noise ratio, and the total number of counts at the peak maximum (signal) for each element. Where the signal is the number
of counts in the channel at the peak maximum, less the background contribution, which is taken as being the mean value of the counts in the channels at the high and low kinetic energy bounds of the peak envelope. The noise is taken to be the mean count value for a peak-to-trough measurement of channels which, in the eye of the operator, represented 'average' noise. The signal to noise ratio is simply the signal divided by the noise. Figures 3.4-3.11 show graphs of the signal to noise ratio versus the reciprocal of the square of the total peak counts - the two plots for silver (A and B) are for the large-lower energy peak (A) and the small-higher energy peak (B) of the silver doublet. Figures 3.12-3.19 show the variation of signal to noise ratio with the square root of the total peak counts, the straight line drawn on these graphs is one calculated by a least squares algorithm. Data from oversaturated peak signals has been included on the graphs, but excluded from the input-data to the fitting routine. Figure 3.20 shows a composite plot for the 'best-fits' from figures 3.12-3.19. No zero-weighting was applied, so whilst it is obvious that all lines should pass through the origin, this has not been forced.

Graphs were also plotted to show the effect of pass energy upon the count-rate for the standard elements, as may be seen from figures 3.21-3.26. These figures show solid curves which correspond to the calculated best-fit for one of the specimen current curves (the reference curve) with any oversaturated values plotted, but not included when fitting. The reference curve is then related to the other specimen current values as follows: a power-law curve has the form
\[ y = b \cdot x^a \]

hence by keeping 'a' constant the ratio of the curves' separation may be maintained by adjusting the 'b' values according to separation ratio. This has been carried out assuming the curves are separated by a ratio dependent upon the specimen current i.e. 4:20:40 or 1:5:10. Values from spectra in which the detector had oversaturated are noted by an unexpected drop in the signal to noise ratio. Table 3.5 shows the fitting data for the power-law curves.

Table 3.5: Table showing the line fitting data for the pass energy versus count-rate plots.

<table>
<thead>
<tr>
<th>Source of data</th>
<th>'a'</th>
<th>'b'</th>
<th>Correlation coefficient</th>
<th>Error in Gradient</th>
<th>Error in Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 4nA</td>
<td>1.33276</td>
<td>0.10874</td>
<td>0.933</td>
<td>0.18234</td>
<td>0.85166</td>
</tr>
<tr>
<td>Ni 20nA</td>
<td>1.81444</td>
<td>0.02378</td>
<td>0.708</td>
<td>0.50174</td>
<td>2.34327</td>
</tr>
<tr>
<td>*Ni 40nA</td>
<td>1.44984</td>
<td>0.43762</td>
<td>0.994</td>
<td>0.05751</td>
<td>0.26838</td>
</tr>
<tr>
<td>Ag 4nA</td>
<td>1.78357</td>
<td>0.04582</td>
<td>0.994</td>
<td>0.07007</td>
<td>0.28619</td>
</tr>
<tr>
<td>*Ag 20nA</td>
<td>1.57713</td>
<td>0.78336</td>
<td>0.994</td>
<td>0.05068</td>
<td>0.20307</td>
</tr>
<tr>
<td>Ag 40nA</td>
<td>1.79751</td>
<td>0.69773</td>
<td>0.995</td>
<td>0.07843</td>
<td>0.69773</td>
</tr>
<tr>
<td>*Fe 4nA</td>
<td>1.53176</td>
<td>0.04777</td>
<td>0.996</td>
<td>0.04545</td>
<td>0.20373</td>
</tr>
<tr>
<td>Fe 20nA</td>
<td>1.40211</td>
<td>0.63590</td>
<td>0.986</td>
<td>0.06568</td>
<td>0.29482</td>
</tr>
<tr>
<td>Fe 40nA</td>
<td>1.57004</td>
<td>0.56065</td>
<td>0.993</td>
<td>0.07617</td>
<td>0.31277</td>
</tr>
<tr>
<td>Cr 4nA</td>
<td>1.45261</td>
<td>0.09145</td>
<td>0.996</td>
<td>0.04427</td>
<td>0.19227</td>
</tr>
<tr>
<td>Cr 20nA</td>
<td>1.33304</td>
<td>0.89600</td>
<td>0.991</td>
<td>0.04921</td>
<td>0.21380</td>
</tr>
<tr>
<td>*Cr 40nA</td>
<td>1.39789</td>
<td>1.26698</td>
<td>0.998</td>
<td>0.04041</td>
<td>0.16126</td>
</tr>
<tr>
<td>*Au 4nA</td>
<td>1.59071</td>
<td>0.01631</td>
<td>0.998</td>
<td>0.03814</td>
<td>0.20096</td>
</tr>
<tr>
<td>Au 20nA</td>
<td>1.34242</td>
<td>0.37130</td>
<td>0.982</td>
<td>0.08058</td>
<td>0.38448</td>
</tr>
<tr>
<td>Au 40nA</td>
<td>1.69094</td>
<td>0.13189</td>
<td>0.993</td>
<td>0.10030</td>
<td>0.41923</td>
</tr>
<tr>
<td>Cu 4nA</td>
<td>1.74680</td>
<td>0.00968</td>
<td>0.995</td>
<td>0.06501</td>
<td>0.30711</td>
</tr>
<tr>
<td>*Cu 20nA</td>
<td>1.68182</td>
<td>0.08413</td>
<td>0.997</td>
<td>0.03803</td>
<td>0.17963</td>
</tr>
<tr>
<td>Cu 40nA</td>
<td>1.74550</td>
<td>0.12781</td>
<td>0.989</td>
<td>0.10898</td>
<td>0.46919</td>
</tr>
</tbody>
</table>

* Marks the curves used as 'reference curves' to calculate families of theoretical curves.
Data showing the effect of channel spacing upon signal to noise are shown in figure 3.27 which shows lines where the time per channel is constant at 1 second, and where the total acquisition time is constant at 385 seconds. The effect of tilt-angle upon the number of counts in the peak envelope (net integral) is shown in figure 3.28.

The values for the natural Auger linewidths for the elements considered are given in table 3.6, it should be noted that the linewidth for gold was measured from a 20eV pass energy electron excited Auger spectrum – the peak cannot be excited by magnesium or aluminium radiations. Figure 3.29 shows the effect of pass energy upon the analyser resolution characteristics, note that for pass energies greater than 200eV full width at half maximum values are taken from electron beam excited Auger peaks. Figure 3.30 shows only the XPS data – for pass energies less than 200eV.

Table 3.6: Natural line widths for Auger peaks.

<table>
<thead>
<tr>
<th>Element</th>
<th>Line Configuration</th>
<th>Linewidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>\text{L}<em>{3}\text{M}</em>{4\text{a}}\text{M}_{4\text{f}}</td>
<td>4.55 eV</td>
</tr>
<tr>
<td>Silver</td>
<td>\text{M}<em>{4\text{a}}\text{N}</em>{4\text{f}}\text{N}_{4\text{f}}</td>
<td>1.82 eV</td>
</tr>
<tr>
<td></td>
<td>\text{M}<em>{5}\text{N}</em>{4\text{f}}\text{N}_{4\text{f}}</td>
<td>3.18 eV</td>
</tr>
<tr>
<td>Iron</td>
<td>\text{L}<em>{3}\text{M}</em>{2\text{a}}\text{M}_{4\text{f}}</td>
<td>10.00 eV</td>
</tr>
<tr>
<td>Chromium</td>
<td>\text{L}<em>{3}\text{M}</em>{2\text{a}}\text{M}_{4\text{f}}</td>
<td>3.36 eV</td>
</tr>
<tr>
<td>* Gold</td>
<td>\text{M}<em>{3}\text{N}</em>{4\text{f}}\text{N}_{4\text{f}}</td>
<td>2.22 eV</td>
</tr>
<tr>
<td>Copper</td>
<td>\text{L}<em>{3}\text{M}</em>{4\text{f}}\text{M}_{4\text{f}}</td>
<td>1.36 eV</td>
</tr>
</tbody>
</table>

Values taken from spectra using MgKα X-rays at 10eV pass energy.

* Value taken from spectra using 10kV electron beam at 20eV pass energy.

85
DATA FOR PURE NICKEL

DATA FOR PURE SILVER (PEAK A)

Figure 3.4

Figure 3.5
DATA FOR PURE SILVER (PEAK B)

DATA FOR PURE IRON

Figure 3.6

Figure 3.7
DATA FOR PURE GOLD

DATA FOR PURE TANTALUM

Figure 3.8

Figure 3.9
Figure 3.10

DATA FOR PURE CHROMIUM

Figure 3.11

DATA FOR PURE COPPER

SIGNAL TO NOISE RATIO

1/SQRT(PEAK COUNTS) X10^-2

KEY
- 4nA Specimen Current.
- 20nA Specimen Current.
- 40nA Specimen Current.
DATA FOR PURE NICKEL (PEAK A)

DATA FOR PURE SILVER (PEAK A)

Figure 3.12

Figure 3.13
DATA FOR PURE SILVER (PEAK B)

DATA FOR PURE IRON

Figure 3.14

Figure 3.15
Figures 3.16 and 3.17 show plots of signal-to-noise ratio versus square root of peak counts for pure gold and pure tantalum, respectively. The graphs demonstrate how different specimen currents (4nA, 20nA, and 40nA) affect the signal-to-noise ratio. The key for the data points is:

- **+**: 4nA Specimen Current.
- **x**: 20nA Specimen Current.
- ****: 40nA Specimen Current.
DATA FOR PURE CHROMIUM

DATA FOR PURE COPPER

Figure 3.18

Figure 3.19
Figure 3.20: Multiple element plot of S/N vs. square root of peak counts.
Best Fit for three parabolae - Nickel data.

Reference curve is 40nA
\[ a = 1.44984 \]
\[ b = 0.43762 \]

Best Fit for three parabolae - Silver data.

Reference curve is 20nA
\[ a = 1.57713 \]
\[ b = 0.78336 \]

Figure 3.21

Figure 3.22
Figure 3.23: Best fit for three parabolae - Iron data.

Reference curve is 40mA
\[ a = 1.57004 \]
\[ b = 0.50000 \]

Figure 3.24: Best fit for three parabolae - Chromium data

Reference curve is 40mA
\[ a = 1.39789 \]
\[ b = 1.26698 \]
Best fit for three parabolae - Gold data.

Reference curve is 4nA
a = 1.59071
b = 0.01631

Best fit for three parabolae - Copper data.

Reference curve is 20nA
a = 1.68182
b = 0.08413
Figure 3.27: S/N vs. channel spacing at constant total count time and at constant time per channel.

- Total acquisition time = 385 seconds
- Time per channel = 1 second

Figure 3.28: The effect of tilt angle upon the peak net integral.

- Nickel
- Carbon

Net integral counts (arbitrary units)

Take-off angle (detector angle from surface normal)
Figure 3.29: Pass energy vs. analyser resolution (FWHM).

- Data from XPS Peaks
- Data from AES Peaks

Energy Resolution (eV)

Pass Energy (eV)

Figure 3.30: Pass energy vs. analyser resolution (XPS data only).

- Mean values from Magnesium X-ray excited silver 3d and gold 4f peaks

Energy resolution (FWHM) in eV

Pass energy (eV)
3.4 Discussion.

When varying the three resolution modes there are both instrumental and statistical constraints which govern the operating regime. The results have been reviewed in order to identify resolution boundaries for the elements studied. The way in which this aim has been achieved has been to define the relationship between the signal to noise ratio, and the number of counts recorded at the peak maximum.

In spectroscopy the normal operating regime is that in which the statistically derived noise varies proportionally with the reciprocal of the square root of the signal. Figures 3.4-3.20 show that, unless oversaturation of the detector occurs, this condition has been met for all of the experiments carried out in the work according to table 3.1. The use of peak counts (rather than net integrals) in the data shown is in accord with the manner in which many datasystems perform elemental analysis. Hence from figures 3.4-3.20 it is possible to ascertain the minimum number of counts necessary at the peak maximum to ensure a given signal to noise ratio.

Time resolution is determined by the count-rate - the upper boundary is fixed by saturation of the 'Channeltron' detector and its associated electronics, whilst there is, in principle, no lower boundary because counting may take place for as long as necessary provided time is no constraint.
Spatial resolution depends only upon the specimen current and will decrease as the count-rate increases, consequently its maximum value is set by the number of counts (to reach a given signal to noise ratio), and its minimum by count-rate (ie detector saturation).

Energy resolution is fixed by the analyser pass energy, and increases as the pass energy (and count-rate) decreases. The natural line widths define the upper limit, and provided the count-rate remains below the saturation level, the lower limit is determined by the analytical problem and the need to resolve adjacent or overlapping peaks. These three resolution modes will be considered below to quantify their interrelationships and boundary positions.

Figures 3.21-3.26 show that the count-rate increases with decreasing energy resolution (increasing pass energy) according to a power-law relationship, and that the increase in count-rate, at a fixed pass energy, is proportional to the specimen current (and hence the spatial resolution squared). The figures illustrate that the count-rate values for the 4, 20, and 40nA specimen current curves are in a 1:5:10 ratio. This is not unreasonable since the calculated beam areas for these specimen current values are also in the same ratio, and consequently the 'excitation areas' are in this ratio too. The fit attained by taking one specimen current curve as a reference, and using this to fit other power law curves, is clearly acceptable. The curves are fitted to a power-law ($y=bx^a$) using a fixed 'a' parameter, and varying 'b' according to the ratio given above. It is therefore possible to construct a series of power law curves representing pass energy versus count-rate for specimen currents other than those studied experimentally, simply by fixing 'a' at the predetermined value and setting 'b' proportionally to the specimen
current. A series of such calculated curves (calculated in this case for chromium) are shown in figure 3.31. Assuming this to be the case, then the curves of may be expressed as follows:

\[
\text{Intensity (count-rate)} = b \cdot E_{\text{pass}}^a
\]

From the curve separation ratios of figure 3.31, it is a reasonable assumption that 'a' is constant, and that the 'b' value is the product of the specimen current and a constant 'c', therefore:

\[
\log \frac{I}{i} = a \log E_{\text{pass}} + \log c
\]

Figure 3.32 shows plots for log(I/i) vs. log pass-energy for copper and chromium. The significance of the 'a' value is given in a paper by Seah\(^{(131)}\), who shows that for V.G. hemispherical analyzers in conjunction with a transfer lens - the configuration of the MA500 - the following relationship applies:

\[
\text{Intensity} \propto \text{Pass-energy}^{1.5}
\]

Our 'a' values reflect this instrumental factor being in the range 1.4-1.7 for the elements examined. The meaning of the 'c' values may be better understood if it is assumed:

\[
c = \sigma (1+r) \lambda G
\]
Where $\sigma$ is the probability of Auger emission per primary beam electron, $r$ is the backscattering ratio, $\lambda$ is the inelastic mean free path, and $G$ is the instrumental transmission function. $\sigma$ is the most important term and will differ from element to element so that the intercept should represent the experimental sensitivity factor for the element. The term $\lambda$ depends upon the kinetic energy of the electron, and $G$ upon the retarding potential. The retard potential however, varies with pass energy when using the constant retard ratio mode, and this may be responsible for the deviation from the slope predicted by Seah. For the purpose of this work, pass-energy and sensitivity-factor are taken as being the only important variables.

It is a straightforward exercise to combine the signal to noise versus peak counts, and pass energy versus count-rate graphs, to enable the conditions for any particular experiment to be calculated. The graphs in figures 3.21-3.26 and 3.31, yield a count-rate (counts per second) for any given combination of pass energy (energy resolution) at one of a range of specimen currents (spatial resolution). The number of counts necessary at the peak to achieve a particular signal to noise ratio may be found from figures 3.4-3.20. Hence to determine the count-time (time resolution) at a known count-rate, to obtain this given number of counts is a simple arithmetic exercise.

It must be realised however, that each of the three resolution modes are subject to either instrumental or practical constraints. Spatial resolution is governed only by the specimen current, and calibration on fracture edges shows that:

89
A practical lower limit for the spatial resolution is approximately 120nm which results from a specimen current of 4nA, below this arbitrary figure the Auger signal is so weak that all time resolution will be lost if even reasonable signal to noise is required (naturally the microscope can achieve far better resolution than this but only for use in secondary electron imaging). The spatial resolution also has an upper limit, which varies with the energy resolution (pass energy). Under conditions of poor spatial resolution (high specimen current) and poor energy resolution (high pass energy) the time resolution is excellent, but the count-rate induced by these conditions may be so large that it leads to the electron detector becoming oversaturated. Oversaturation of the detector begins when two electrons arriving almost simultaneously at the detector are counted as one, hence there is a net loss of signal. This effect is most evident at peaks, where oversaturation at the peak energy (but not the background) can result in flattening of the peak (or in extreme cases peak inversion), and thence an abnormal change in the signal to noise ratio. Oversaturation is dependent upon the condition of the detector (old detectors will oversaturate at lower count-rates than new ones) but was seen to have occured in several of the spectra taken—the effect being noted by loss of linearity in figures 3.12-3.20, a signal to noise decrease in the high counts region in figures 3.4-3.11, leading to a 'drooping over' of the hyperbola, and a loss of power-law dependence at high pass energies in figures 3.21-3.26. Instances where oversaturation has occurred are shown in table 3.7.
Table 3.7 Incidences where detector oversaturation could definitely be detected by an unexpected drop in signal to noise.

<table>
<thead>
<tr>
<th>CRR, i, t</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 4nA, 1200</td>
<td>Ni, Ag, Fe, Au</td>
</tr>
<tr>
<td>2, 4nA, 4800</td>
<td>Cu</td>
</tr>
<tr>
<td>4, 4nA, 4800</td>
<td>Cu</td>
</tr>
<tr>
<td>10, 4nA, 4800</td>
<td>Cu</td>
</tr>
<tr>
<td>2, 20nA, 1200</td>
<td>Ag, Au</td>
</tr>
<tr>
<td>4, 20nA, 1200</td>
<td>Ag, Fe, Cu</td>
</tr>
<tr>
<td>2, 20nA, 4800</td>
<td>Ag, Cu</td>
</tr>
<tr>
<td>4, 20nA, 4800</td>
<td>Cr, Cu</td>
</tr>
<tr>
<td>2, 40nA, 1200</td>
<td>Ag, Cr, Au</td>
</tr>
<tr>
<td>4, 40nA, 4800</td>
<td>Ag, Fe, Ta, Au, Cu</td>
</tr>
</tbody>
</table>

There is also a lower limit to the energy resolution which is reached when the analyser resolution is equal to the natural line width of the peak. Whilst in some instances it may be desirable to 'outresolve' the peak - for example to analyse the fine structure of the peak or to gain chemical state information - for dynamic systems, where only qualitative data is required, the time penalty incurred by using such analyser resolutions lessen the time resolution.

The Vacuum Generators Scientific MA500 has a number of instrumental limitations. In the constant analyser energy (CAE) mode continuously variable pass-energies are only available up to 200eV. If higher energies are required the operator is restricted to using the constant retard ratios (CRR) provided, this may often mean that to attain a particular count-rate for a fixed CRR, the specimen current must be altered.

Using the information above a 'resolution diagram' may be constructed. A series of calculated pass energy versus count-rate curves (cf. figure 3.31) are used to generate pairs of specimen current and
pass energy values for a constant count-rate. Hence for axes of pass energy and specimen current (energy and spatial resolution) a series of count-rate contours may be drawn. If a specific signal to noise ratio is chosen, these contours become a count-time contour. If these count times are divided by the natural peak width - the count-rate being based upon a peak net-integral (see appendix 1) - then time contours of seconds per eV may be put onto the diagram. Figures 3.33 and 3.34 show the resolution diagrams for copper and chromium at a signal to noise ratio of 5:1 with axes of; spatial resolution and specimen current, and energy resolution and pass energy. Whilst these figures illustrate the ways in which the resolution modes interrelate, of more practical use are the resolution diagrams in figures 3.35-3.40 which are used with their accompanying tables, where the constant time contours (numbered 1-6) may be matched to the desired signal to noise ratio to give the specific count-time per eV (time resolution) for any desired combination of specimen current (spatial resolution) and pass energy (energy resolution).

The diagrams are calculated for a channel spacing of 0.5eV which, as can be seen from figure 3.27, is as good a value as any, but if this value is changed without altering the count-time, the signal to noise ratio will vary according to the manner shown in the same figure. A reasonable estimation is that if the number of channels per eV is halved the signal to noise will be doubled. Hence, assuming that a 0.5eV channel spacing is used, then for point analyses the total acquisition time is the product of the seconds per eV value and the number of scanned channels, and for linescans or maps it is simply the seconds per eV value multiplied by the number of sampling points on the linescan or map. The diagrams are also calculated for single pure elements, consequently
if several elements were present the following equation might be used as a correction:

\[
\text{Corrected secs/eV} = \left(\frac{100\% \times \text{secs/eV from resolution diagram}}{\% \text{Element}}\right)^2
\]

The sensitivity factor for the element may be included on the bottom of the equation, but considering the differences that may be evident between bulk and surface compositions, this may not be important. Two final factors to consider are the effects of tilt-angle and temperature. Heating-stage studies must be carried out at 0° tilt-angle (ie. normal to the electron beam) hence the Auger signal will be affected in the manner shown by figure 3.28. This figure reveals that the low energy peaks appear to be less affected than do high energy ones, but the effect has not been quantified. Heating-stage studies have shown however, that the loss of signal due to the zero tilt-angle is counteracted very closely by the increased Auger signal that is produced in the temperature range 700-1000°C (the origin of this enhanced signal has not been investigated, but the effect is real, and is most likely associated with the surface carbon being 'burnt off'), so within the accuracy of this work the effect of tilt angle may be disregarded at temperature. Figure 3.41 shows the effect of some common variables upon the resolution diagrams. It should be pointed out that the 'a' value is a constant for any particular analyser configuration, and that the 'c' value is dependent upon the inelastic mean free path, the probability of Auger electron emission, the backscattering ratio, and the instrumental transmission function, hence it will vary from element to element.
Figure 3.33: Resolution Diagram for Copper - Signal to noise = 5

Figure 3.34: Resolution Diagram for Chromium - Signal to noise = 5
Figure 3.35: Resolution diagram and value table for Nickel

<table>
<thead>
<tr>
<th>Pass Energy (eV)</th>
<th>CRR = 10</th>
<th>CRR = 4</th>
<th>CRR = 2</th>
<th>CRR = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.09</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>5.0</td>
<td>0.10</td>
<td>0.20</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>7.5</td>
<td>0.34</td>
<td>0.47</td>
<td>0.31</td>
<td>0.24</td>
</tr>
<tr>
<td>10.0</td>
<td>1.71</td>
<td>0.85</td>
<td>0.57</td>
<td>0.43</td>
</tr>
<tr>
<td>15.0</td>
<td>3.93</td>
<td>1.97</td>
<td>1.31</td>
<td>0.98</td>
</tr>
<tr>
<td>20.0</td>
<td>7.07</td>
<td>3.54</td>
<td>2.36</td>
<td>1.77</td>
</tr>
</tbody>
</table>

Figure 3.36: Resolution diagram and value table for Silver

<table>
<thead>
<tr>
<th>SIGNAL TO NOISE</th>
<th>SECONDS PER eV REQUIRED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2.5</td>
<td>0.04</td>
</tr>
<tr>
<td>5.0</td>
<td>0.20</td>
</tr>
<tr>
<td>7.5</td>
<td>1.21</td>
</tr>
<tr>
<td>10.0</td>
<td>3.08</td>
</tr>
<tr>
<td>15.0</td>
<td>9.37</td>
</tr>
<tr>
<td>20.0</td>
<td>19.06</td>
</tr>
</tbody>
</table>
Figure 3.37: Resolution diagram and value table for Iron.

<table>
<thead>
<tr>
<th>NOISE</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>5.0</td>
<td>0.18</td>
<td>0.09</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>7.5</td>
<td>0.47</td>
<td>0.23</td>
<td>0.16</td>
<td>0.12</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>10.0</td>
<td>0.88</td>
<td>0.44</td>
<td>0.29</td>
<td>0.22</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>15.0</td>
<td>2.09</td>
<td>1.05</td>
<td>0.70</td>
<td>0.52</td>
<td>0.42</td>
<td>0.35</td>
</tr>
<tr>
<td>20.0</td>
<td>3.82</td>
<td>1.91</td>
<td>1.27</td>
<td>0.96</td>
<td>0.76</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Figure 3.38: Resolution diagram and value table for Chromium.

<table>
<thead>
<tr>
<th>SIGNAL TO NOISE</th>
<th>SECONDS PER eV REQUIRED</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
</tr>
<tr>
<td>2.5</td>
<td>0:05</td>
</tr>
<tr>
<td>5.0</td>
<td>0.22</td>
</tr>
<tr>
<td>7.5</td>
<td>0.52</td>
</tr>
<tr>
<td>10.0</td>
<td>0.96</td>
</tr>
<tr>
<td>15.0</td>
<td>2.21</td>
</tr>
<tr>
<td>20.0</td>
<td>3.99</td>
</tr>
</tbody>
</table>
Figure 3.39: Resolution diagram and value table for Gold.

<table>
<thead>
<tr>
<th>NOISE</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>5.0</td>
<td>0.23</td>
<td>0.11</td>
<td>0.08</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>7.5</td>
<td>0.56</td>
<td>0.28</td>
<td>0.19</td>
<td>0.14</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>10.0</td>
<td>1.05</td>
<td>0.53</td>
<td>0.35</td>
<td>0.26</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>15.0</td>
<td>2.48</td>
<td>1.24</td>
<td>0.88</td>
<td>0.62</td>
<td>0.50</td>
<td>0.41</td>
</tr>
<tr>
<td>20.0</td>
<td>4.50</td>
<td>2.25</td>
<td>1.50</td>
<td>1.13</td>
<td>0.90</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Figure 3.40: Resolution diagram and value table for Copper.

<table>
<thead>
<tr>
<th>SIGNAL TO NOISE</th>
<th>SECONDS PER eV REQUIRED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2.5</td>
<td>0.06</td>
</tr>
<tr>
<td>5.0</td>
<td>0.26</td>
</tr>
<tr>
<td>7.5</td>
<td>0.88</td>
</tr>
<tr>
<td>10.0</td>
<td>1.88</td>
</tr>
<tr>
<td>15.0</td>
<td>4.99</td>
</tr>
<tr>
<td>20.0</td>
<td>9.60</td>
</tr>
</tbody>
</table>
Figure 3.41: Diagram showing the effect of variables on the resolution diagrams.

Pass Energy (eV) - Energy Resolution

Specimen Current - Spatial Resolution

Long Count Times

Short Count Times

Total acquisition time is constant

Increased channel spacing

Increased temperature

Increased 'C'

Increased 'a'

Deviation from ideal tilt angle

Less than 100% of element

Increased multiplier age

Increased contamination

Poor vacuum
3.5 Conclusions.

Despite the assumptions which have been made when taking and processing the data, this work has shown that from a series of Auger and XPS spectra it has been possible to construct resolution diagrams which allow the operator to optimise spatial, energy, and time resolution for a given set of experimental requirements. The effects of detector oversaturation, natural peak width, channel width, element concentration, tilt-angle, and temperature have all been discussed, and their influence upon the diagrams outlined. The aim of the work was to provide a simple, empirical means of setting up the spectrometer to optimise resolution in the three modes - the resolution diagrams provide this means since experiments at Surrey University using the diagrams to set up the spectrometer show that they fulfill the primary requirement of actually being able to provide acquisition details from which spectra with 'optimum' resolution may be gained.
4.1 Introduction

The purpose of the following experimental work was to produce a number of different oxides upon a variety of iron and iron-base substrate materials, to characterise them, and to examine the chemical changes which take place during heating in a vacuum. The substrate materials with surface oxides of different thickness and composition, are produced for tests in both the Auger microscope, and in the ultra high vacuum oven. It is therefore important to be able to form well characterized oxides - the nature and history of the oxide must be well understood prior to the substrates' use for heating-stage or vacuum oven tests.

The substrates chosen for this work are listed in table 4.1 which also gives their compositions. The compositions of the alloys are representative of the major components found in the range of iron-based alloys for which Orobraze 950 is a commonly used brazing compound. The specpure iron was supplied by Johnson Matthey PLC, as were the base metals for the ferrosilicon and ferrochrome alloys which were vacuum cast at their research centre. Jethete M152 and 2328 stainless steel are commercial alloys, and the Fe20Cr steel was kindly supplied by Dr. Saunders at the National Physical Laboratory.
Table 4.1 Substrates used for hot-stage and oxidation studies.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specpure Iron</td>
<td>3 ppm Mn, 5 ppm Si, 2 ppm Mg, 1 ppm Cu, &lt; 1 ppm Ag</td>
</tr>
<tr>
<td>Goodfellow Iron</td>
<td>0.3% Mn, 0.1% Si, &lt;0.08% C, &lt;0.04% P, &lt;0.05% S</td>
</tr>
<tr>
<td>Alloy 1</td>
<td>11.67% Cr, 0.38% Si, balance Iron *</td>
</tr>
<tr>
<td>Alloy 5</td>
<td>11.21% Cr, 1.05% Si, balance Iron *</td>
</tr>
<tr>
<td>Alloy 10</td>
<td>0.35% Si, balance Iron *</td>
</tr>
<tr>
<td>Fe20Cr</td>
<td>20.00% Cr, balance Iron</td>
</tr>
<tr>
<td>Jethete M152</td>
<td>12.5% Cr, 2-3.0% Ni, 1.5-2.0% Mo, 0.35% Si, 0.08% C</td>
</tr>
<tr>
<td></td>
<td>0.02-0.04% N, 0.25-0.4% V, 0.5-0.9% Mn, &lt;0.03%P, &lt;0.025%S</td>
</tr>
<tr>
<td>2328 SS</td>
<td>24.1% Cr, 27.5% Ni, 2.6% Mo, 0.65% Mn, 2.7% Cu, 0.6% Ti</td>
</tr>
</tbody>
</table>

* Iron used to make the alloy was Goodfellow iron.
No analytical data available - estimated value.

4.2 Experimental

4.2.1 Preparation of oxides.

In order to prepare oxides of different thicknesses and compositions for each of the substrates four different preparation processes were available. The native oxide (film formed simply by leaving the specimen in air) was taken as one standard condition, and this condition was characterised using XPS and Auger spectroscopy. Secondly a range of oxides may be fairly rapidly and simply produced by heating the material in a conventional air furnace for any given time-temperature conditions. With the oxidation in air, the aim was to produce films with thicknesses in the 'interference' thickness range, and then to characterise these films. Further samples were prepared by annealing in an ultra high vacuum (UHV) oven for various times and temperatures in order to produce tenacious, non-porous, and 'pure' oxides. Finally some samples were annealed in a ground-glass grease-sealed diffusion pumped vacuum system, that had originally been used in conjunction with a microbalance (which no longer operates), but will henceforth, for convenience, be referred to as 'the microbalance rig', this vacuum system gave a total pressure in the range 10^-4-10^-5 for temperatures up to 900°C. The oxidation pre-treatments carried out are summarised in table 4.2 which also lists...
Table 4.2 Table showing oxidation treatments and analytical methods used.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Oxidation Treatment *</th>
<th>XPS</th>
<th>AES</th>
<th>RBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specpure Iron</td>
<td>Native oxide</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 mins @ 400°C (A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goodfellow Iron</td>
<td>Native oxide</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 1</td>
<td>Native oxide</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 hrs @ 900°C (M)</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 hrs @ 900°C (U)</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 hrs @ 850°C (U)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 5</td>
<td>Native oxide</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 10</td>
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</tr>
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<td></td>
<td>10 mins @ 400°C (A)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>20 mins @ 400°C (A)</td>
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<td></td>
</tr>
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<td></td>
<td>25 mins @ 400°C (A)</td>
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<tr>
<td>Fe20Cr</td>
<td>Native oxide</td>
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<td></td>
<td>✓</td>
</tr>
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<td></td>
<td>25 mins @ 575°C (A)</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
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<td>6.5 hrs @ 726°C (M)</td>
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<td>31 hrs @ 800°C (U)</td>
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<td></td>
<td>72 hrs @ 710°C (U)</td>
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<td>Jethete</td>
<td>Native oxide</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>5 mins @ 543°C (A)</td>
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<td></td>
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<td></td>
<td>1 min @ 543°C (A)</td>
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<td></td>
<td></td>
</tr>
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<td>2328 SS</td>
<td>Native oxide</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>10 mins @ 700°C (A)</td>
<td></td>
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</tr>
</tbody>
</table>

N = Native oxide
A = Air furnace film
M = Microbalance film (10⁻⁴-10⁻⁵ Torr)
U = UHV oven film (<10⁻⁵-10⁻⁶ Torr)
the analytical techniques utilised to characterise the films.

4.2.2 Heating-stage studies

The heating stage developed for the V.G MA500 has already been described in section 3. A typical time-temperature profile is shown in figure 4.1, analyses being taken as indicated where the temperature is relatively constant, and up to about 50°C below the melting point of the Orobraze (950°C). Beyond this temperature emphasis was placed upon observing the wetting and spreading behaviour of the system (which is described in section 5), and consequently analyses were not usually taken until these studies were completed. Table 4.3 sets out the substrate-oxide combinations examined.

Table 4.3 Substrate-oxide-braze metal combinations for heating-stage Auger Electron Spectroscopy (HSAES).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Braze alloy</th>
<th>Substrate</th>
<th>Oxidation treatment</th>
</tr>
</thead>
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<tr>
<td>BDS12</td>
<td>Orobraze 950</td>
<td>Specpure Fe</td>
<td>5 mins 400°C (A)</td>
</tr>
<tr>
<td>BDS13</td>
<td>Orobraze 950</td>
<td>Alloy 10</td>
<td>10 mins 400°C (A)</td>
</tr>
<tr>
<td>BDS14</td>
<td>Orobraze 950</td>
<td>Alloy 10</td>
<td>20 mins 400°C (A)</td>
</tr>
<tr>
<td>BDS15</td>
<td>Orobraze 950</td>
<td>Alloy 10</td>
<td>25 mins 400°C (A)</td>
</tr>
<tr>
<td>BDS16</td>
<td>Orobraze 950</td>
<td>Alloy 1</td>
<td>Native oxide</td>
</tr>
<tr>
<td>BDS17</td>
<td>Orobraze 950</td>
<td>Alloy 1</td>
<td>Native oxide</td>
</tr>
<tr>
<td>BDS18</td>
<td>Orobraze 950</td>
<td>Fe20Cr</td>
<td>31 hrs 810°C (U)</td>
</tr>
<tr>
<td>BDS19</td>
<td>Orobraze 950</td>
<td>Fe20Cr</td>
<td>7 hrs 726°C (M)</td>
</tr>
<tr>
<td>BDS20</td>
<td>Orobraze 950</td>
<td>Fe20Cr</td>
<td>25 mins 575°C (A)</td>
</tr>
<tr>
<td>BDS21</td>
<td>Orobraze 950</td>
<td>Fe20Cr</td>
<td>25 mins 575°C (A)</td>
</tr>
<tr>
<td>BDS22</td>
<td>Orobraze 950</td>
<td>Specpure Fe</td>
<td>10 mins 400°C (A)</td>
</tr>
<tr>
<td>BDS23</td>
<td>Orobraze 950</td>
<td>Alloy 10</td>
<td>25 mins 400°C (A)</td>
</tr>
<tr>
<td>BDS24</td>
<td>Orobraze 950</td>
<td>Fe20Cr</td>
<td>Native oxide</td>
</tr>
</tbody>
</table>

A = Air furnace film
M = Microbalance rig film
U = UHV oven film
Figure 4.1: Typical time-temperature profile for hot-stage tests.
4.3 Results and Discussion

4.3.1 Characterization of Oxide Films

Table 4.2 indicates the techniques which were used to characterize the films formed by the various pre-treatments. The types of oxide formed on the substrates may be divided into four categories: native oxides (ie. no heating in either air or vacuum), films formed by heating in air, films formed by heating in the vacuum microbalance rig (a 'soft' vacuum), and films formed by heating in a UHV oven ('hard' vacuum). The nature of the films formed by these treatments will be examined below.

The oxidation of metals in air, or low partial pressures of oxygen is fairly well documented (see section 2.2), although many of the previous studies have not considered the effect of the overall environment (eg. atmosphere, time at temperature, heating rate), and consequently there is little indication as to whether the oxide types described represent 'equilibrium' states, or whether an 'intermediate' film was described, which given more time in the same environment would gradually transform until the equilibrium oxide resulted.

4.3.1.1 Native Oxides

The types of native oxides formed by the substrates of table 4.1 essentially fall into two categories: films formed on chromium-free irons (ie. Specpure iron, Goodfellow iron, and Alloy 10 - ferrosilicon), and films formed on chromium containing substrates (ie. Alloy 1, alloy 5, Fe20Cr, and Jethete).
Figure 4.2: XPS widescans typical of the native oxides on chromium-free iron alloys and iron.
Figure 4.3: Typical spectra showing the effect of ion-etching on the Oxygen 1s peak.

Figure 4.4: Typical spectra showing the effect of ion-etching on the Iron 2p3/2 peak.

Figure 4.5: Typical spectra showing the effect of ion-etching on the Silicon 1s peak.
showing the effect of ion-etching on the Chromium 2p3/2 peak.

Intensity (Arbitrary units)

Binding Energy (eV)
Considering the films formed on the chromium-free substrates first, the spectra of figures 4.2-4.4 show that the film is an iron oxide with considerable amounts of carbon on the outermost surface. The oxygen peak (figure 4.3) is broadened at the very surface, probably due to the presence of a hydroxyl group which is most likely to result from an oxyhydroxide of some sort. The widescan of the unetched surface shows that the energy loss features associated with the iron peaks give rise to a steadily increasing background. This implies that iron is not a major surface component(132), but ion etching reveals that the carbon-rich outer layer is only very thin, since the widescan of the surface after 10 seconds ion etching shows an energy loss tail on the iron peaks, and the corresponding narrowscans show that the iron is present mainly as oxide—the metallic component of the iron peak being very small. After the first ion etch, the broadening of the oxygen peak is lost, leaving the pure oxide singlet. Further ion etching causes the iron peak to shift from the oxide position to the metal position (figure 4.4) until, for the longest etch time the oxide component of the iron peak is very small. The widescans of figure 4.2 also reflect the change from iron-oxide to iron, the carbon and oxygen peaks become smaller, and the energy loss features associated with the iron peaks become more prominent. The ferrosilicon alloy (alloy 10) behaves similarly to the pure iron, except that a small (and very noisy) silicon peak is visible (figure 4.5). The peak is too noisy to yield any chemical state information, but simple peak area measurements reveal that silicon may be slightly enriched in the scale with respect to the substrate. The silicon 2p peak was not used since it would be liable to clash with the iron 3s line.
For the ferrochromium alloys—alloys 1, 5, and Jethete (and although no XPS data is available for it, probably the Fe20Cr) the overall appearance of the carbon, oxygen, and iron peaks is the same as those for the chromium-free alloys (i.e., the same as figures 4.3-4.5). The iron peak showed a larger metallic component for the same etch time (when compared with the chromium-free alloys), perhaps implying that the film is thinner than that formed on the 'irons' (although beam induced reduction of iron oxide by chromium may also contribute to this). The widescans of figure 4.6 show the outer layer to be carbon rich as before, but beneath this is a mixture of iron, chromium, and oxygen. Narrowscans of the chromium peak (figure 4.7) shows that the peak gradually shows more of its metallic component with increasing etch time, although there is always a significant oxide component present but for the longer etch times this is probably due to metallic chromium re-oxidising). Silicon was detected most strongly in alloy 5, but it was also seen in Jethete and alloy 1, and in each case atomic percentage data implied that it was enriched at the metal/metal-oxide interface with respect to both the bulk metal and the bulk oxide. For the Jethete nickel was barely detected in the oxide film, but for long etch times the peak was fairly strong although not sufficiently so to allow determination of the chemical state (figure 4.8 shows the effect of etch time upon the nickel peak).

No XPS data is available for the Fe20Cr alloy, but Auger electron spectroscopy and Rutherford backscattering (RBS) have been used to characterize the film. The Auger electron spectrum (figure 4.9) shows the surface to contain mostly iron, oxygen, and carbon, with only a very small amount of chromium being detected. The rising background beneath the iron peaks is due to electrons which have lost energy due to
inelastic collisions, and indicates that iron is a major surface species. The RBS data shows virtually no oxide components in the spectrum, and the near equivalence of spectra taken normal to, and at $45^\circ$ to the accelerator beam implies that the film is only very thin.

The Auger data shows that on the chromium-free iron alloys an iron oxide is formed, the literature cites this oxide as being composed of a thin outer layer of haematite (approximately 10\% of the scale thickness) over magnetite, this cannot however, be deduced from the data presented. Silicon, when it is present in the substrate is seen to be present in the scale, although the noise in the data does not allow its chemical state to be determined. The literature suggests that the silicon will be present as fayalite (since there is only a low level of silicon) which will probably be most concentrated at the metal/metal-oxide interface.

For the chromium containing alloys, a thinner film is formed - assuming an etch rate of 3nm per minute (6KeV beam half focussed) then the films formed are approximately 2.5-3.0nm thick compared with 3.0-3.5nm for the chromium-free alloys. The data shows the outer surface of the film (ignoring of course the thin carbon and oxyhydroxide layer which was seen on both alloy groups) to be iron rich, but beneath this layer a mixture of iron and chromium oxides is seen. Atomic percentage data from peak area measurements (as shown in table 4.4) reveals a gradual increase in the amount of chromium in the scale as the metal/metal-oxide interface is approached, where chromium is found to be enriched with respect to the substrate. Silicon behaves similarly to the way in which it did for the chromium free alloys, and nickel was never seen in the scale.
Table 4.4 Atomic percentage data for etch profiles and Al/Mg radiation studies on native and prepared oxide films.

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<th>Cr</th>
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<td>0.0</td>
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<th>Fe</th>
<th>Cr</th>
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<td></td>
</tr>
<tr>
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<td>7.2</td>
</tr>
<tr>
<td></td>
<td>Aluminium</td>
<td>41.9</td>
<td>39.5</td>
<td>9.0</td>
</tr>
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<td>37.8</td>
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</tr>
<tr>
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<td>Aluminium</td>
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<td>42.0</td>
<td>8.7</td>
</tr>
<tr>
<td>Alloy 1:3 hrs</td>
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</tr>
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<td>at 900 microb</td>
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<td>36.8</td>
<td>8.2</td>
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<td>Aluminium</td>
<td>42.6</td>
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<td>9.0</td>
</tr>
<tr>
<td>Fe20Cr :5 hrs</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>at 820 microb</td>
<td>Magnesium</td>
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</tr>
<tr>
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<td>Aluminium</td>
<td>48.6</td>
<td>26.7</td>
<td>4.7</td>
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</table>
Figure 4.9: Auger electron spectrum typical of the native oxide on Fe20Cr.

Figure 4.10: Auger electron spectrum typical of the air-formed oxide on chromium-free iron alloys.

Intensity (Arbitrary units)

Kinetic Energy (eV)
The data correlates well with the literature, which explains the ways in which the films are formed as being a result of the fact that the more easily oxidisable elements (such as chromium and silicon) diffuse more slowly than the iron which therefore forms the first oxide. Chromium (or silicon) then substitutes for iron, freeing it to form fresh oxide at the surface.

From this study, and its good correlation with the literature, it may be deduced that the native oxides represent a quasi-equilibrium state, which is the result of kinetic conditions imposed by the oxidation in air. It follows that any subsequent changes due to heating in vacuum are wholly the result of the system moving from the kinetically determined quasi-equilibrium state, to a thermodynamic equilibrium appropriate to the temperature and alloy composition and vacuum conditions.

4.3.1.2 Films formed by heating in air

Auger electron spectra from the specpure and Goodfellow irons, and the ferrosilicon alloy show that, in common with the native oxides, the oxidation behaviour of this group of alloys is similar. The spectra are typified by the one shown in figure 4.10, and once again show iron and oxygen peaks on a rising background with a predominant carbon peak. Silicon was not detected on the surface of alloy 10 - the ferrosilicon alloy.

No data is available for the air-formed films on alloys 1 and 5, but for Fe20Cr the AES spectrum (figure 4.11) shows iron, but on an almost flat background, with strong carbon, oxygen and chromium peaks. The RBS spectrum (figure 4.12) shows features indicative of a fairly
thick film containing both iron and chromium oxides. Calculations and simulations using the RBS data, show that the oxide is approximately 25nm thick, and composed of 50% iron, and 50% chromium oxides. The AES spectrum for Jethete (figure 4.13) shows the surface to consist of mainly iron, oxygen, and carbon, with only a small amount of chromium. A depth profile through this film (figure 4.14) reveals a gradual enrichment of chromium at the expense of iron for a relatively constant oxygen concentration, until the interface is reached, at which point the levels of oxygen and to a lesser extent chromium decrease steadily whilst the iron level increases.

Whilst no depth profile information is available, it is likely that for the chromium-free alloys, the surface oxide is effectively the same as the native oxide, but thicker, sufficiently so for a blue interference colour to be visible. Most authors suggest that the degree of silicon enrichment at the interface is likely to be higher (than in the native oxide) and will lead to enhanced corrosion resistance. This is partially substantiated by the fact that to produce a 'blued' specimen the ferrosilicon had to be heated 4-5 times longer than the iron at the same temperature.

The film formed on the Fe20Cr is evidently chromium rich, although it is not completely iron free. RBS gives the composition as 50% iron oxides (haematite and magnetite) and 50% chromium oxides (chromia), although it is likely that spinel is present.
Figure 4.13: Auger electron spectrum typical of the air formed oxide on Fe20Cr.

Figure 4.11: Auger electron spectrum typical of the air formed oxide on Fe20Cr.

Intensity (Arbitrary units)

Kinetic Energy (eV)
Figure 4.19: RBS spectrum of the film formed on Fe20Cr, heated for 7 hours at 712°C in a vacuum microbalance rig.

Intensity (Counts)

Kinetic Energy

Relative percentages of Fe, Cr, and O.

Figure 4.12: RBS spectrum typical of the oxide formed on Fe20Cr.

Intensity (Counts)

Figure 4.13: AES electron depth profile through the film formed on Fe20Cr.

Etch time in minutes

Oxygen

Chromium

Iron

Relative percentages of Fe, Cr, and O.
Figure 4.16: XPS narrowscans of the microbalance rig oxide formed on alloy 1.
The film formed on Jethete is fairly typical of the type of film formed on the so-called 'non-chromia formers' and in consequence is probably equally representative of alloy 1 and 5. The outer surface is virtually all composed of iron oxide, but beneath the surface chromium is gradually enriched at the expense of iron, until the metal/metal-oxide interface is reached, where the chromium concentration is greatest, and often higher than the bulk concentration. Although there is no data available for the way that silicon behaves, the literature suggests that it will exhibit a similar concentration profile through the scale as chromium.

In common with the work on the native oxide films, this study shows a good correlation with other authors' work, which in turn implies that the films formed are in a kinetically determined quasi equilibrium state. Hence slow heating in vacuum will allow the oxide to move towards a true thermodynamic equilibrium, determined by the temperature, alloy composition and vacuum conditions.

4.3.1.3 Films formed by heating in the vacuum microbalance rig

This oxidation pre-treatment was only given to alloy 1 and the Fe20Cr but the characterization of these alloys was quite thorough. The XPS data for alloy 1 is shown by figures 4.15 and 4.16, which show analyses using magnesium and aluminium radiation. Atomic percentage data (see table 4.4) reveals that, whilst there is slightly more iron than chromium in the film (~0.5-1.0%), this situation is not changed by changing from magnesium to the more penetrating aluminium radiation, although the change is reflected by an increase of the metallic component in both the iron and chromium peaks.
For the Fe20Cr alloy several different oxidation times and temperatures were used, but the data shows no similarities between the resultant oxides. Firstly consider the Auger electron spectrum for the sample treated at 726°C for 6.5 hours (figure 4.17) which shows mostly chromium and oxygen on the surface, although a little iron and sulphur are also detected. The XPS data of figure 4.18 confirms this, showing mostly oxygen and chromium on the surface, although the latter has a significant metallic component (estimated at 20-30%) which suggests that the film is thin.

The specimen heated for 7 hours at 712°C gave confusing, but consistent results. The RBS spectrum (figure 4.19) indicates a gradual enrichment of chromium metal towards the outer surface of the scale which is calculated to be approximately 100nm thick. The Auger electron spectrum (figure 4.17) confirms this with oxygen and chromium being the predominant surface species. XPS data (figure 4.18) shows large quantities of carbon and oxygen, and a strong chromium peak with a dominant metallic component – virtually no iron was detected.

The diversity of the results does not really allow any firm general conclusions to be drawn, and a knowledge of previous work merely highlights the differences in behaviour from that which would be expected for the alloys studied. Alloy 1 gives a thin film considerably enriched in chromium, and the lack of any change in composition when more penetrating X-rays are used (ie. AlKα) suggests that the enrichment is not confined to the film, but is reflected in the bulk too.
Figure 4.18: XPS spectra typical of the surface of Fe20Cr heated in a vacuum microbalance rig.

Figure 4.17: Auger electron spectra typical of the surface of Fe20Cr heated in a vacuum microbalance rig.
For the Fe20Cr, the difference in behaviour is less likely to be due to the different times at temperature, but probably a result of the temperature differences between the two runs. The Auger electron spectrum from the higher temperature film is very similar in appearance to the air-formed film (figure 4.11), and both specimens exhibited interference colours, but whether this similarity is illusionary or actual can not be deduced from the data.

The gradual enrichment of metallic chromium towards the thin outermost oxide layer is difficult to explain. A thin chromia layer (<60Å) is seen to cover a thick region (~600Å) of chromium metal enriched substrate. This structure is shown well by the RBS results, and X-ray spectroscopy also shows an abnormally high chromium to iron peak ratio. The development of this surface composition is not at all clear, although two tentative explanations may be forwarded. There is a possibility that chromium from the substrate is evaporated (or volatilised) and the recondensed on the surface as the saturation vapour pressure is reached. Whilst there is some evidence for this mechanism - metal deposition on the vacuum tube wall, and a powdery, porous oxide - it is highly unlikely that steady state conditions would ever be attained and there is little reason why re-deposition should occur, especially to the extent seen in this study. The second possibility relies on the way the annealing is carried out - the specimen is slowly bought to temperature whilst under vacuum. Initially a thick oxide may form, but as the temperature is increased the environment could change from oxidising to reducing, and the largely chromia film is reduced to chromium metal. The eventual presence of a thin chromia layer is most likely to have formed upon removal of the specimen from the vacuum environment. The latter mechanism would also account for the film formed
on alloy 1, assuming that a similar concentration profile extended beyond the range of the aluminium X-rays.

The data presented here deviates markedly from what the current literature predicts, and illustrates the very great effect that non-equilibrium conditions can have upon the processes of oxidation and reduction.

It is evident that there is no proof for the proposed oxidation/reduction mechanism from the present data, but the explanation does elucidate a way in which films could form and then be removed. This in turn has important implications for vacuum brazing, since a slight alteration in brazing or soaking conditions could result in a change from detrimental to beneficial brazing conditions (i.e., oxidising to reducing) or vice-versa. Most vacuum brazing cycles are relatively rapid (not normally in excess of an hour), and it is quite possible that intermediate, non-equilibrium films, similar to the types described here could be formed during the brazing process.

4.3.1.4 Films formed by heating in a UHV environment

Once again the oxidation pre-treatments were only carried out on alloy 1 and Fe20Cr. Considering alloy 1 first, XPS spectra were taken using both aluminium and magnesium X-rays, for the specimen treated 4 hours at 900°C and the one heated at 850°C for 200 hours. The two sets of spectra are similar in appearance, iron, chromium, and oxygen being the dominant peaks and they are typified by figure 4.20. For the metal peaks, magnesium radiation gives only a small metallic component, but this component increases with the change to aluminium radiation.
Atomic percentage data (see table 4.4) shows that the film on the 4 hour specimen is slightly enriched in chromium with respect to the iron, but the opposite is true for the 200 hour specimen. In each case the oxygen and carbon levels are comparable to those in the air-formed film, but the iron is noticeably depleted, whilst the chromium is present in substantially higher concentrations — approximately twice as much for the 200 hour film and three times as much for the 4 hour film — when compared to the levels in the air-formed film. This illustrates clearly the effect that time plays in the oxidation process, and shows that for the test conditions used the approach to equilibrium is slow — resulting in oxide films which are inconsistent with those described in published data.

For the Fe20Cr alloy there are three specimens with different heat treatments. The data of figure 4.21, shows XPS spectra taken with magnesium and aluminium radiation for a specimen heated for 5 hours at 800°C. The magnesium radiation reveals that very little iron is present on the surface, the dominant surface species being carbon, oxygen, and chromium, the chromium peak displaying a significant metallic component. Aluminium radiation gives a larger mostly metallic iron peak, along with peaks for carbon, oxygen and chromium, the latter being mostly metallic in nature. Atomic percentage data (see table 4.4) shows that the oxygen level is low, and confirms that the film contains considerably more chromium than iron (this is especially true for the aluminium radiation).
Figure 4.20: Aluminium and magnesium XPS spectra of a typical film formed by heating alloy 1 in UHV.

Figure 4.21: Aluminium and magnesium XPS spectra of a typical film formed by heating Fe20Cr in UHV.
Figure 4.22: XPS spectra of a typical film formed by heating Fe20Cr in UHV.

Figure 4.23: Auger electron spectra of a typical film formed by heating Fe20Cr in UHV.
XPS data for a specimen heated for 31 hours at 800°C (figure 4.22) showed a large but broad oxygen peak. This is probably due to polar oxygen associated with carbon, although it is possible that some of the broadening may be attributable to a hydroxide, which could have been picked up upon exposure of the specimen to air during its transference from the UHV oven to the spectrometer. The iron peak had little or no metallic component, whilst the chromium peak showed both metal and oxide components. The Auger electron spectrum in figure 4.23 appears to show that the surface contains only a small amount of chromium, and mostly iron and oxygen, but this is not necessarily the case, because the chromium peak, whilst significant, is largely hidden due to its overlapping with a large oxygen peak.

For the specimen heated at 710°C for 72 hours the Auger electron spectrum (of figure 4.23) shows nearly all iron and oxygen on the surface (although, as before, the chromium peak, whilst present, is largely obscured). The XPS spectra (of figure 4.22) show metallic iron with a small chromium peak with both metal and oxide components. The oxygen peak is fairly broad implying that there is a second component, which is probably due to carbon bonded to oxygen, or possibly due to a hydroxide which formed on the specimens exposure to air.

The data from alloy 1 is somewhat strange in as much the results from the two heat treatments are the reverse to what would be expected. What is clear however, is that whilst the film is only thin (as shown by the increase in the metallic peak components for aluminium radiation) it is enriched in chromium when compared to the native or air formed oxides. This is due to the more easily oxidised, but more slowly diffusing chromium, being able to preferentially react with the small amount of
oxygen available, thereby forming a chromium rich film. The fact that the 4 hour film was richer in chromium than the 200 hour film may be due to the pumpdown times involved, the 4 hour specimen being exposed to a more oxidising atmosphere than the 200 hour specimen (which, though it may have initially been in an oxidising environment, may have spent several days in a reducing atmosphere as the vacuum conditions stabilised).

The Fe20Cr alloy treated for 5 hours at 800°C may have undergone a similar process to the specimens treated in the microbalance, that is, a change from oxidising to reducing conditions; resulting in a fairly thick chromium rich oxide being reduced to chromium and iron metal, the former in greater quantity than the latter.

For the specimens treated for 72 hours and 31 hours at 710 and 800°C respectively the films appear very similar to those from the native oxides (eg. figure 4.9). Assuming the films to be the same as the native oxide, how could such a situation have arisen? The simplest explanation is that the vacuum conditions were such that a reducing environment was present throughout the experiment, and hence the native oxide was first quickly reduced in the furnace, and then re-formed on re-exposure to air. This would lead to a small degree of chromium enrichment at the surface, but the difficulty in separating the chromium and oxygen Auger peaks means that this could not be verified.

Once again the data is different to what other workers have found, and it demonstrates once again, the degree to which the oxide can be affected by the environment. This is therefore of particular importance when non-equilibrium conditions (such as those found in most commercial
4.3.1.5 Summary of oxide characterization

The results from the oxide characterization show that for native oxides, and for air-formed films, there is good correlation with the data found in the literature. From this it can therefore be assumed for these types of oxidation process that a quasi-equilibrium film is formed quickly — the high oxygen concentration, and the constancy of the atmosphere (air) account for this. The data from films produced by heating in vacuum however, show a remarkable amount of variation, and often differ considerably from the films seen by other workers, which graphically illustrates the degree to which different conditions of time, temperature, alloy composition, and vacuum can affect the final oxide composition. It is obvious from this, that in reduced partial pressures of oxygen the attainment of equilibrium conditions occurs, but is slow, and becomes slower as less oxygen is available. The results also show that the environment in a vacuum enclosure can be subject to quite severe changes with time, until the equilibrium state is reached, a factor which can seriously affect the formation of the surface oxide.

The nature of the surface oxide is of great importance in vacuum brazing, tenuous chromium oxide films are excellent from the corrosion resistance point of view, but these more stable oxides are harder to penetrate and remove or reduce, and are therefore disadvantageous in vacuum brazing. The literature, and this characterization study both point to an area in which there is no clear understanding, namely the behaviour of metals when heated in vacuum or reduced partial pressures of oxygen. This area is of primary interest when vacuum brazing since a
typical brazing cycle often involves extended 'soaking' times at temperature, and this could lead to undesirable 'intermediate' film formation for the vacuum and temperature conditions. One of the drawbacks of the pre-treatment post-characterization approach is that in many instances the final film is so different from the initial film that it is virtually impossible to infer the processes which have taken place during heating in-vacuo. Using hot-stage Auger electron spectroscopy however, it is possible to study the changes which take place in a film of known initial condition during heating in-situ and in-vacuo. Hence HSAES is a very valuable tool in the study of oxidation and reduction processes in reduced partial pressures.

4.3.2 Hot-stage Auger spectroscopy of oxide covered surfaces

The results from the heating-stage studies are comparable in as much as they show the gradual disappearance of oxide from the surface — coupled with the segregation of sulphur to the surface. The oxide removal process can take place in several ways, and these are illustrated by the spectra in figures 4.24, 4.27, and 4.28. The way in which the oxide disappears from the surface of chromium-free, and chromium containing alloys is quite different, and consequently these two groups of substrate materials will be considered separately.
4.3.2.1 The behaviour of oxides on chromium-free iron and iron-alloys during heating in vacuum

The spectra of figure 4.24 are typical of the way in which the oxide upon chromium-free iron and iron alloys (e.g., ferrosilicon-alloy 10) is gradually removed by heating in vacuum. At room temperature iron, oxygen, and carbon are the only surface species, and the characterization work shows that both the native and air-formed films are mixtures of iron oxides, the only difference being their thickness. Carbon is present as a surface contaminant, and this is reflected by the way in which it is 'burnt off' at approximately 450°C, so that at around 500°C there is no residual carbon. The spectrum is otherwise unchanged until the temperature is in the region of 730-800°C when sulphur begins to be detected upon the surface. This gradual appearance of sulphur is mirrored by the gradual disappearance of the oxygen peak - which is clearly visible from the figure. In addition to the loss of oxygen, the iron peaks become more intense, and are superimposed upon a more steeply sloping background. There is no oxygen signal for the spectra taken above 830°C, and the lack of any energy loss features at the oxygen peak position, coupled with intenser iron peaks indicate that the oxygen has been completely removed, and hence the oxide has been reduced. The final surface condition prior to brazing is therefore composed of iron covered with sulphur. The sulphur is probably present as a monolayer, since the signal intensity levels out at a maximum value, and there is no significant attenuation of the iron signal - a thick layer of sulphur on the surface would suppress the energy loss tail associated with the iron. For the ferrosilicon alloy (alloy 10) some residual silica was detected on the surface of the cooled specimen after wetting and spreading had taken place. Silica is distinguishable from
silicon because the transition from Si\textsuperscript{0} to Si\textsuperscript{4+} involves a peak shift of 12eV in the silicon LMM peak. Silica was never detected as a continuous layer, but only in patches over the surface, and as 'rafts' on the braze metal surface. No silicon was seen during heating, although this could be due to either its relative scarcity (only 0.35% in the alloy), or due to the difficulty of detecting low energy peaks (76eV for Silica 92eV for Silicon) on the steeply rising background associated with direct spectra.

It is evident that the iron oxide is reduced by heating in vacuo, but cursory thermodynamic considerations show that the vacuum conditions necessary to dissociate the oxide at 850°C are pressures in the region of 10\textsuperscript{-16} atmospheres, which suggests that the spectrometer vacuum conditions (typically in the range 10\textsuperscript{-5} to 10\textsuperscript{-7} mbar) are not sufficient to reduce the oxide. The fact remains however, that the oxide is being reduced, so a more detailed examination of the thermodynamics is necessary. The major shortcoming of the approach adopted above, is that the oxygen pressure is considered in isolation, whereas in reality, the gases in the vacuum environment consist primarily of a mixture of carbon monoxide, carbon dioxide, hydrogen, and water vapour (there may also be hydrocarbon and other organic vapours, but these form only a very small proportion of the total gas). It is therefore important to determine the partial pressure of oxygen in the system, since this will govern whether the overall conditions are oxidising or reducing. Fortunately, using a free energy versus temperature diagram (Ellingham diagram) like the one shown in figure 4.25 this is a straightforward exercise. Figure 4.25 also shows the way in which such equilibrium data is attained, and figure 4.26 uses this data to plot graphs of the CO/CO\textsubscript{2} and H\textsubscript{2}/H\textsubscript{2}O equilibria for iron,
chromium, and silicon oxides. It is clear from figure 4.26, that at 850°C either a CO/CO₂ or H₂/H₂O ratio of approximately 3:1 results in a vacuum environment which is reducing towards iron oxide. Residual gas analyses of the gases in the spectrometer during a heating-stage run reveal that the reducing components (CO and H₂) are often 10 to 15 times more abundant than the oxidising ones (CO₂ and H₂O), and hence it is not surprising that iron oxides are so readily reduced.

4.3.2.2 The behaviour of oxides on chromium containing iron alloys during heating in vacuum

Figures 4.27 and 4.28 show the way in which the oxide on Fe20Cr behaves when it is heated in a UHV environment. It can be seen from table 4.3, that experiments were also carried out using alloy 1 with its native oxide film. The data from these experiments resembles closely that from the native oxide on Fe20Cr, but with less pronounced chromium peaks furthermore, the data for alloy 1 was in the form of a series of narrow scans and hence no information can be gleaned by studying backgrounds. The data was also subject to severe charging below 500°C which obscured the low energy peaks completely. Nevertheless the results which are available show that a comparison with the Fe20Cr (native oxide) results - which are described below - is valid. For the chromium containing alloys silicon was never detected during heating - Fe20Cr is silicon free, and alloy 1 has only small amounts of silicon. Notwithstanding the low silicon contents of the studied alloys, it is felt that silicon plays an important role in oxide breakdown (see reference 33 for example), and so its behaviour during heating in vacuo will be considered.
The native oxide on Fe20Cr

Figure 4.27 shows how the native oxide on Fe20Cr is reduced, and removed, as the temperature is increased. The previous section has shown the native oxide to be a thin mixed film composed of iron and chromium oxides, and the figure shows that this remains unchanged until 325-360°C. The energy loss tail associated with the iron peaks means that iron is a major surface component. Increasing the temperature, however, to 385-420°C causes this energy loss tail and indeed the iron peaks, to disappear, leaving only chromium and oxygen on the surface. The chromium signal is also slightly more intense, and the peak continues to grow larger as the temperature is further increased to 530-550°C. It is interesting to note that the carbon signal is still strong at this temperature whereas for the chromium-free alloys carbon was not detected above approximately 480°C. The previous argument for the reduction of iron oxide must be slightly modified, because in this instance, chromium is being substituted for any iron in the oxide — figure 4.26 shows that at all temperatures chromium oxide has a lower free energy than iron oxide, and will therefore reduce it. The presence of carbon at the higher temperatures indicates that it is in some way bound to either the oxide, or to the chromium metal as carbide — this has been shown to happen by Baer(81). Increasing the temperature to 570-600°C produces another change in the surface composition, the carbon signal diminishes, and the first traces of sulphur appear on the surface. There is also a reappearance of iron on the surface, although the absence of any associated energy loss features means that its concentration on the surface is low. A continued temperature increase brings about the removal of carbon, and increased intensity in the
chromium, iron, and sulphur peaks, the latter being matched by a decreasing oxygen signal. At approximately 700-730°C the iron and chromium peak intensities are nearly the same, and the sulphur has levelled out at a maximum value, above this temperature however, the iron signal intensity increases, whilst the chromium signal is more or less unchanged, until at 850°C iron is more abundant on the surface than is chromium. This is inferred from a simple comparison of the peak areas of the most intense iron and chromium peaks, but in addition, the chromium peaks appear to sit on the energy loss tail of the iron, rather than on their own distinct loss tail (compare the backgrounds at 850°C and 530-550°C) which shows that iron is considerably commoner on the surface than chromium. The events which occur between 550 and 850°C involve primarily the gradual reduction of chromium oxide, accompanied by the segregation of sulphur to the surface until it achieves monolayer coverage. The final surface condition reflects the bulk composition in as much as iron is present in greater quantity than chromium, except that no oxide is present, and the surface is covered by a thin layer of sulphur.

The air-formed oxide on Fe20Cr

The behaviour of the air-formed oxide on Fe20Cr is shown by the spectra of figure 4.28. The initial oxide condition, has already been described in detail (section 4.1), but briefly the film on the Fe20Cr alloy is a chromium-rich oxide containing only small amounts of iron (there is no real energy loss tail associated with the iron peaks). A trace of sulphur is visible at room temperature, and this almost certainly arises from its segregation to the surface during the oxidation pre-treatment. Heating the specimen causes a rapid reduction of the iron
oxide by chromium, so that at 520-550°C chromium, oxygen, and carbon are the main surface species, with only a trace of sulphur. Further heating results in greater chromium and sulphur signals both at the expense of oxygen, there is also a small reduction in the amount of carbon detected. At 660-670°C the sulphur peak has reached its maximum value, but unlike the spectra from the native oxide, oxygen is still detected, and the carbon level appears to have stabilised. At 750-760°C iron re-appears in the spectrum - albeit at a very low intensity. Oxygen is still detected at low levels, although these levels are misleading because much of the oxygen signal is obscured by the more intense chromium peaks. At higher temperatures the iron signal becomes stronger, and the oxygen signal weaker. The carbon signal decreases above approximately 880°C, but is not completely removed. At 885°C the surface is composed of sulphur, chromium, iron, and a little carbon. The surface is obviously considerably enriched in chromium, since the three chromium LMM peaks are present on a rising background caused by their energy loss tails being added - compare the spectra at 885°C and at room temperature (after cooling) with the final condition of the native oxide film. The carbon visible on the surface after cooling is the result of contaminant pick-up.

Like the native oxide, any iron in the film is reduced by chromium, until at approximately 500°C only chromium oxide is present on the surface. This chromia scale then begins to be reduced at ~600°C and the reduction process progresses steadily until no oxygen remains (at about 900°C). There appears to be a small shift in the carbon peak towards a lower kinetic energy, and this may be the result of carbide formation with metallic chromium. The chromium enriched final state is due to the thickness of the initial oxide - iron in the film is first
replaced by chromium, forming a thick chromia scale, which is then reduced to chromium metal so that the final surface has a chromium metal layer with a thickness related to the initial oxide thickness. In the case of the native oxide, the initial film was thin, so the degree of chromium enrichment after reduction is smaller than for the air-formed film.

Figure 4.25 shows that iron oxide reduction, by chromium, is to be expected, since the free energy of the latter is lower. The CO/CO₂ and H₂/H₂O ratios generated from the free energy vs. temperature diagram however, cannot account for the reduction of the chromium oxide, since this would require ratios in the order 10⁴-10⁵:1, and such values are in no way indicated by residual gas analyses. Once again therefore, a more sophisticated approach to the thermodynamics of the system is required.

For a UHV system, the total volume of gas can be assumed to be constant, the base pressure being a function of the leak and pumping rates. For a small leak rate (which is a valid assumption for UHV systems) the gases in the vacuum chamber can be considered to be in equilibrium. In the presence of a hot filament with a given carbon activity, the CO/CO₂ ratio, and hence the oxygen partial pressure will be influenced. If the gases in the vacuum chamber are assumed to be in equilibrium with the filament, then the equilibrium between the following two reactions, will determine the CO/CO₂ ratio.

\[
\begin{align*}
2\text{CO} + \text{O}_2 &= 2\text{CO}_2 \\
\text{C} + \text{CO}_2 &= 2\text{CO}
\end{align*}
\]

The way in which the ratio may be calculated is shown in appendix 2. Using this method it is possible to calculate for a fixed base pressure,
and for any values of carbon activity and temperature, the CO/CO₂ ratios and oxygen partial pressures. Figure 4.29 shows a plot of such data, and from the figure it is obvious that for the temperature range in which reduction has been seen to occur, even low carbon activities will result in oxygen partial pressures below those necessary for chromium oxide decomposition (i.e., reducing conditions). For the heating stage studies the carbon activity will be fairly high—carbides remain on the substrate surface, and contamination of the filament because of repeated exposure to air, carbon deposited on, or contained in the ceramic parts of the 'stage, and miscellaneous carbonaceous material in the vacuum system will all contribute to the carbon activity. It is apparent that there is an adequate carbon presence in the system to account for chromia reduction, indeed it has been assumed that equilibrium exists throughout the vacuum chamber, whereas in reality the conditions in the vicinity of the heating stage may result in an even more reducing conditions. This was verified by experiment BDS21 which was carried out at a base pressure of 5x10⁻⁶ mbar, this fairly high pressure was achieved by streaming pure oxygen into the spectrometer via the ion gun. Unfortunately the data from this run cannot be presented (a disc crash corrupted the files before they could be backed-up), but observations during the experiment showed sequential reduction like that of figure 4.28 to occur. The thermodynamic calculations presented here therefore account for sequential reduction process, and the reduction of chromium and iron oxides whilst heating in a vacuum. Further thermodynamic studies by Baer(133) show that for a theoretical starting condition where the total pressure of a UHV type enclosure is either wholly due to oxygen or water vapour, the final equilibrium is one which is strongly reducing at temperature and in the presence of carbon. Baer summarises his work by stating that for a system with good base pressure
Figure 4.29: Effective partial pressure of oxygen as a function of temperature and in the presence of carbon.

Equilibrium between:

\[ C + CO_2 = 2CO \]

\[ 2CO + O_2 = 2CO_2 \]
1000x 45° tilt angle 0B950 on Ferrosilicon

Oxygen Auger map

Iron Auger map

Chromium Auger map

Silicon Auger map
and low leak rate it is difficult not to reduce oxides at temperature, whereas for systems with lower base pressures (e.g., SEMs and vacuum furnaces), there can be a factor of almost $10^4$ difference in leak-rate causing a far higher effective oxygen pressure. Despite this, as is illustrated by experiment BDS21, it is the conditions local to the sample which are most important, and for most systems the local conditions will not be the same as the overall conditions, and this can often result in a reducing environment because of higher local carbon activities and temperatures. The experiments and calculations also indicate that it is possible to reduce silica in a good vacuum (silica has a decomposition potential of approximately $10^{-33}$ atm. at 800°C). This means that a sequential reduction of iron oxide to chromium oxide, and then chromium oxide to silicon oxide, and finally reduction of the silica would result in total oxide removal. Cohen et al (33) have shown that in a 'poor' vacuum (i.e., an SEM chamber) total oxide reduction does not occur, although the sequential reduction does take place at a slow rate. This means that in areas of low oxygen partial pressure, for example beneath a slumped braze droplet, sequential reduction to silica can occur. The silica is taken to be crystalline in nature, and can therefore be penetrated by the braze metal which contacts the substrate surface, and spreads by a suboxide route. Such a sequential reduction process, and the influence of local oxygen pressures is shown by figure 4.30. The micrograph shows Orobraze 950 that has been melted on oxidised Jethete using a heating stage in a scanning electron microscope. The accompanying Auger maps were taken in the MA500 after transferring the cooled specimen. The colours represent signal intensity, black denotes no signal, blue to green to red increasing intensity, and white 'full scale'. The maps clearly show that the metal substrate in the photograph, is covered by chromium and oxygen (i.e., chromium oxide), except in the
region of the braze metal, where only oxygen and silicon are detected. The oxide characterization studies have shown that there is a mixed oxide on Jethete which has been oxidised in air, iron rich on the outermost surface, so the figure demonstrates that iron oxide has been reduced by chromium, and in areas of low oxygen availability chromium oxide has been reduced by silicon. The surface of the braze metal is, in places, oxide free, and in others silicon, chromium, and oxygen are detected, this illustrates both oxide reduction, and the fact that spreading has occurred via a sub-oxide route. It should be appreciated that the experiment represents a 'frozen-in' condition since the specimen was rapidly cooled as soon as melting of the braze was noted (although this is a fairly good representation of actual brazing practise), and hence the data presented does not represent an equilibrium state. It is presumed that, given time the oxide on the braze metal surface would be reduced to form silica freeing chromium to diffuse into the braze metal, since there is no longer a source of chromium (ie from the substrate) to enable its competition with silicon for any available oxygen. Kubaschewski, Evans, and Alcock propose that in vacuo, and at temperatures below 1000°C, silica may react with hydrogen or silicon to form silicon monoxide, which under certain conditions may be liberated in gaseous form.

\[ \text{SiO}_2 + \text{H}_2 = \text{SiO} + \text{H}_2\text{O} \]
\[ \text{SiO}_2 + \text{Si} = 2\text{SiO} \]

The authors admit that the above reactions are the subject of quite heated debate, so temperatures are only approximate. Notwithstanding disagreements, a potential means of silica removal is available in vacuum systems, which in turn provides the mechanism for oxide removal, and eventually wetting and spreading.
The experimental and theoretical work both indicate that it is easier to reduce and remove oxides by heating in UHV conditions than is apparent from a cursory thermodynamic consideration. Either sequential reduction to a particulate oxide, or total oxide reduction, provide mechanisms which satisfy the first requirement for joint formation during vacuum brazing—oxide penetration. The presence (or otherwise) of residual oxide, however, can influence the second requirement—wetting and spreading, and this is examined in the next chapter.
5.1 Introduction

The previous chapter has explained the way in which the substrate oxide may be penetrated or removed, and how this initial process enables the second process of wetting spreading to take place.

The aim of this section of work is to examine the effect of the braze alloy and substrate compositions, of temperature, and of initial oxide condition, upon the wetting and spreading characteristics of the system. At this point it is useful to recap upon the meanings of the terms wetting and spreading. Section 2.3 describes a braze alloy as wetting the substrate if the contact angle is less than 90° and a spreading system as one where the contact angle is zero - although in practice, a near-zero contact angle will result in spreading conditions.

Oxides are not typically wetted by braze alloys (i.e., the contact angle is greater than 90°) so the first stage in the brazing process must be to by-pass the oxide. Once the oxide has been bypassed the braze metal wets the substrate surface, and if conditions favour the formation of near-zero contact angles, then spreading occurs. If the oxide has been penetrated (rather than removed) then spreading must progress via a suboxide route, which means that the mechanical properties of the oxide and metal/metal-oxide interface can affect spreading. If the braze metal spreads over a clean metal surface (i.e., total oxide removal), or along a sub-oxide route, then the liquid can dissolve components of the substrate - and to a lesser extent solid-state diffusion can occur. This interdiffusion may result in solidification of the braze, or in multiple
phase formation.

Two different techniques have been used to study wetting and spreading. An ultra-high vacuum oven allows many different braze alloy, substrate, and oxide combinations, to be studied at a fixed overheat temperature, but only by a post-brazing microscopic examination. The use of a vacuum-portable heating stage in the scanning Auger microscope means that for any starting condition, the way in which the brazing process develops as a function of temperature can be studied dynamically, and in-situ, with the facility for both bulk and surface analysis with high spatial resolution. The substrates used are the same as those used in the oxidation studies and are listed in table 4.1. The braze alloy compositions are given in table 5.1. With the exception of the Orobraze 950 which was supplied by Johnson Matthey PLC as <63μm powder, the alloys were argon arc cast from pure metal stock at the Johnson Matthey research centre.

The time-temperature profiles used for this work were chosen to reflect actual industrial practise - a short time at a 'soaking' temperature then a rapid increase to the brazing temperature which is held for 5-10 minutes prior to cooling.

Table 5.1: Table showing braze alloy compositions used for heating stage tests and UHV oven tests.

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orobraze 950</td>
<td>82.0% Au, 18.0% Ni</td>
</tr>
<tr>
<td>Orobraze 950 + 5% Fe</td>
<td>77.9% Au, 17.1% Ni, 5% Fe</td>
</tr>
<tr>
<td>Orobraze 950 + 10% Fe</td>
<td>73.8% Au, 37.5% Ni, 10% Fe</td>
</tr>
<tr>
<td>Gold-Copper</td>
<td>62.5% Au, 37.5% Cu</td>
</tr>
<tr>
<td>OB950 Replacement</td>
<td>Au, Cu, Pd, Ni, Cr, Ge</td>
</tr>
</tbody>
</table>
5.2 Experimental

5.2.1 Ultra high vacuum oven spreading tests.

A summary of the spreading tests carried out to date is given in table 5.2 which shows the experiments carried out using pure Orobraze 950, and 5.3 which shows experiments carried out using brazing alloys other than pure Orobraze 950. All specimens were in the form of 10mm diameter discs, with thicknesses varying between 0.2-1.0mm, and had been pre-oxidised, or simply left with their native oxides as indicated on the tables. Samples were polished to a 240 grit finish, unless they were to be pre-oxidised in the UHV oven or the vacuum microbalance in which case they were polished to a 1um diamond finish. Apart from the Orobraze 950 the braze alloys were in the form of filings, and in order to produce 'powder' (ie spherical particles like the OB950), some of the filings were placed on silica 'boats' in the UHV oven and melted. This caused the alloy filings to 'ball-up' - and alloys which have received this treatment, along with other Orobraze derivatives and alternative alloys, are tabulated in table 5.3. The 'boats' consisted of optical quality quartz discs approximately 20mm in diameter surrounded by a small 'wall' which had been fused to the disc. After heating in-vacuo, the powder often had to be scraped off the quartz, indicating that some form of reaction with the silica had taken place.

Time temperature profiles for each of the oven runs are given in figures 5.1a (which shows the experiments that were carried out at ~1000°C) and and 5.1b (which shows the experiments carried out at different temperatures to examine the effect of overheat upon spreading). The full details for each of the UHV oven runs are listed in table 5.4.
<table>
<thead>
<tr>
<th>Specpure Iron</th>
<th>Fe/Si (Alloy 10)</th>
<th>Fe12Cr (Alloy 1)</th>
<th>Fe12CrSi Alloy 5</th>
<th>Fe20Cr</th>
<th>Jethete</th>
<th>2328 S.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>sp 2 (N)</td>
<td>sp 2 (N)</td>
<td>XVI sp 4 (N)</td>
<td>V sp 1 (U)</td>
<td>VIII sp 1 (A)</td>
<td>VIII sp 3 (A)</td>
</tr>
<tr>
<td>VII</td>
<td>sp 1 (N)</td>
<td>sp 4 (N)</td>
<td>XVII sp 3 (N)</td>
<td>V sp 2 (M)</td>
<td>VIII sp 2 (N)</td>
<td>VIII sp 4 (N)</td>
</tr>
<tr>
<td>VIII</td>
<td>sp 5 (N)</td>
<td>sp 4 (N)</td>
<td>XVIII sp 4 (N)</td>
<td>VI sp 2 (M)</td>
<td>X sp 2 (N)</td>
<td></td>
</tr>
<tr>
<td>XI</td>
<td>sp 1 (N)</td>
<td>sp 2 (N)</td>
<td>IX sp 3 (N)</td>
<td>VI sp 3 (U)</td>
<td>XI sp 10 (N)</td>
<td></td>
</tr>
<tr>
<td>XII</td>
<td>sp 1 (N)</td>
<td>XVII sp 2 (N)</td>
<td>XIII sp 3 (N)</td>
<td>VI sp 4 (N)</td>
<td>XIII sp 5 (N)</td>
<td></td>
</tr>
<tr>
<td>XIII</td>
<td>sp 1 (N)</td>
<td>XVIII sp 2 (N)</td>
<td>XIV sp 3 (N)</td>
<td>VI sp 5 (A)</td>
<td>XIV sp 1 (N)</td>
<td></td>
</tr>
<tr>
<td>XIV</td>
<td>sp 5 (N)</td>
<td>XIX sp 2 (N)</td>
<td>XV sp 3 (N)</td>
<td>XI sp 2 (N)</td>
<td>XV sp 5 (N)</td>
<td></td>
</tr>
<tr>
<td>XV</td>
<td>sp 1 (N)</td>
<td>XX sp 2 (N)</td>
<td>XVI sp 3 (N)</td>
<td>XII sp 2 (N)</td>
<td>XVI sp 6 (N)</td>
<td></td>
</tr>
<tr>
<td>XVI</td>
<td>sp 1 (N)</td>
<td>XVII sp 4 (N)</td>
<td>XVIII sp 4 (N)</td>
<td>XIII sp 4 (N)</td>
<td>XVII sp 6 (N)</td>
<td></td>
</tr>
<tr>
<td>XVII</td>
<td>sp 1 (N)</td>
<td>XVIII sp 3 (N)</td>
<td>XIV sp 2 (N)</td>
<td>XIV sp 2 (N)</td>
<td>XVIII sp 5 (N)</td>
<td></td>
</tr>
<tr>
<td>XVIII</td>
<td>sp 1 (N)</td>
<td>XIX sp 3 (N)</td>
<td>XV sp 2 (N)</td>
<td>XV sp 2 (N)</td>
<td>XIX sp 7 (N)</td>
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<tr>
<td>XIX</td>
<td>sp 1 (N)</td>
<td>XX sp 3 (N)</td>
<td>XVI sp 5 (N)</td>
<td>XIX sp 5 (N)</td>
<td>XX sp 6 (N)</td>
<td></td>
</tr>
<tr>
<td>XX</td>
<td>sp 1 (N)</td>
<td></td>
<td>XVII sp 5 (N)</td>
<td>XVIII sp 6 (N)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: UHV oven runs carried out using Orobraze 950

KEY: VI sp 5 (A) = oven run no. VI, specimen no. 5, air furnace oxide

(N) = Native oxide
(A) = Air furnace oxide
(M) = Microbalance oxide
(U) = UHV oven oxide
<table>
<thead>
<tr>
<th></th>
<th>Orobraze 950 Pretreated on Silica</th>
<th>Orobraze 950 + 5% Fe Pretreated on Silica</th>
<th>Orobraze 950 + 10% Fe Pretreated on Silica</th>
<th>Orobraze 950 J.M. replacement alloy</th>
<th>Cold/Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specpure Iron</td>
<td>VII sp 5 (N) XI sp 8 (N)</td>
<td>VII sp 3 (N) XI sp 8 (N)</td>
<td>I sp 3 (N) XI sp 3 (N)</td>
<td>IX sp 4 (N) XI sp 7 (N)</td>
<td>XI sp 9 (N)</td>
</tr>
<tr>
<td>Fe20Cr</td>
<td>VII sp 6 (N) XI sp 6 (N)</td>
<td>V sp 5 (U) X sp 3 (N)</td>
<td>IX sp 5 (U) V sp 3 (U)</td>
<td>V sp 4 (U)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: UHV oven runs carried out using brazing alloys other than untreated Orobraze 950
Figure 5.1a: UHV oven time-temperature profiles
Figure 5.1b
UHV oven time-temperature profiles
For each of the oven runs, specimens were loaded so that the furnace could be pumped down overnight to give a typical starting pressure of approximately $10^{-8}$ mbar. During heating outgassing occurred, and the pressure at the brazing alloy's melting point was typically in the range $5\times10^{-6}$-$5\times10^{-8}$ and at worst $10^{-5}$ mbar. The spreading temperatures indicated for the test runs, represent the temperatures which were set on the furnace controller, which in practise meant the temperatures at which timing for the 'time at temperature' were started, so due to the inevitable overshooting, the highest temperatures reached before cooling were typically 6-10°C greater than the pre-set temperature. After the spreading tests the specimens were allowed to cool in vacuo and then removed from the oven and prepared for examination by scanning electron microscopy.

5.2.2 Heating stage studies

A typical time-temperature profile for a heating stage run has already been shown by figure 4.1, as have the hot-stage experiments carried out (table 4.3). In the earlier tests (ie. runs BDS12-17) polaroid photographs were taken at temperature to record the wetting and spreading phenomena, but for later experiments a video recorder was employed to provide a real-time record of the heating stage runs. Whilst the video image has far poorer resolution than the polaroid photographs, there is no 40 second frame time blackout which is associated with the slow scan oscilloscope, so short-lived events are not missed. This poorer quality is reflected in the figures from the later runs, since the only technique available to obtain a 'hard copy' of the video image, was to photograph the monitor screen using a 35mm camera. The aim of the hot-stage runs was to provide an opportunity to make a dynamic study of
the brazing process, and, if possible to determine the mechanisms of the various processes using bulk and surface analysis. Whilst the MA500 has a high resolution column, no corrections for working distance, beam energy, or amount of 'zoom' were available, and consequently all magnifications given are approximate, and are only included to give a sense of scale. The approximate scales for the magnifications used are given below:

<table>
<thead>
<tr>
<th>Magnification</th>
<th>Scale</th>
<th>Approximate Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>100x</td>
<td>10mm</td>
<td>100um</td>
</tr>
<tr>
<td>150x</td>
<td>10mm</td>
<td>75um</td>
</tr>
<tr>
<td>200x</td>
<td>10mm</td>
<td>50um</td>
</tr>
<tr>
<td>250x</td>
<td>10mm</td>
<td>35um</td>
</tr>
<tr>
<td>500x</td>
<td>10mm</td>
<td>20um</td>
</tr>
<tr>
<td>1000x</td>
<td>10mm</td>
<td>10um</td>
</tr>
<tr>
<td>2000x</td>
<td>10mm</td>
<td>5um</td>
</tr>
</tbody>
</table>

Temperature measurement proved extremely difficult, and for many of the runs a complete temperature record was not possible. Nevertheless the power response of the filament has been proven to be very consistent and in the event of thermocouple failure voltage control of temperature is satisfactory - the voltage versus temperature characteristics, estimated from 'successful' hot stage runs are shown in figure 5.2. A series of modifications to the 'stage have improved the temperature measurement behaviour provided only modest power increases are attempted!
Temperature (degrees C)

- Data from experiments BDS 18-24
- Gradient = 123.35
- Intercept = -74.34
- Correlation coeff. = 0.967

Voltage (Volts)
Table 5.4 Table listing time, temperature, and substrate alloy conditions for the UHV oven experiments.

[The numbers in square brackets designate the oven run from which the quartz-dish treated 'balled-up' powder originated]

<table>
<thead>
<tr>
<th>Oven run I</th>
<th>Fe12Cr (two specimens for oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Specpure iron + Orobraze 950</td>
</tr>
<tr>
<td>3</td>
<td>Specpure iron + OB950/5Fe/Si</td>
</tr>
<tr>
<td>4</td>
<td>Quartz dish + OB950/5Fe</td>
</tr>
<tr>
<td>5</td>
<td>Quartz dish + OB950/10Fe</td>
</tr>
<tr>
<td>6</td>
<td>Quartz dish + OB950/15Fe</td>
</tr>
</tbody>
</table>

4 hrs at 900°C, 8 mins >950°C, 5.5 mins >1000°C

<table>
<thead>
<tr>
<th>Oven run II</th>
<th>Fe12Cr (two specimens for oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 hrs</td>
<td>at 850°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oven run III</th>
<th>Fe12Cr (4 hrs in UHV at 900) + OB950</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Fe12Cr (200 hrs in UHV at 850) + OB950</td>
</tr>
<tr>
<td>3</td>
<td>Fe12Cr (3 hrs in microbalance at 900) + OB950</td>
</tr>
<tr>
<td>4</td>
<td>Fe20Cr (one specimen for oxidation)</td>
</tr>
</tbody>
</table>

5 hrs at 900°C, 13 mins >950°C, 10 mins >1000°C

<table>
<thead>
<tr>
<th>Oven run IV</th>
<th>Fe20Cr (six specimens for oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Fe12Cr (200 hrs in UHV at 850) + OB950/5Fe/Si [I]</td>
</tr>
<tr>
<td>3</td>
<td>3 hrs in microbalance at 900 + OB950</td>
</tr>
<tr>
<td>4</td>
<td>Fe20Cr (one specimen for oxidation)</td>
</tr>
</tbody>
</table>

31 hrs at 800°C, 9 mins >950°C, 6 mins >1000°C

<table>
<thead>
<tr>
<th>Oven run V</th>
<th>Fe20Cr (31 hrs in UHV at 800) + OB950</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Fe20Cr (31 hrs in UHV at 800) + OB950 repl.</td>
</tr>
<tr>
<td>3</td>
<td>Fe20Cr (31 hrs in UHV at 800) + Au/Cu</td>
</tr>
<tr>
<td>5</td>
<td>Fe20Cr (31 hrs in UHV at 800) + OB950/5Fe [VI]</td>
</tr>
<tr>
<td>6</td>
<td>Fe20Cr (four specimens for oxidation)</td>
</tr>
</tbody>
</table>

71 hrs at 710°C, 7 mins >950°C, 5 mins >1000°C

<table>
<thead>
<tr>
<th>Oven run VI</th>
<th>Quartz disc + OB950</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Fe20Cr (6.5 hrs in microbalance at 712) + OB950</td>
</tr>
<tr>
<td>3</td>
<td>Fe20Cr (71 hrs in UHV at 710) + OB950</td>
</tr>
<tr>
<td>4</td>
<td>Fe20Cr (native oxide) + OB950</td>
</tr>
<tr>
<td>5</td>
<td>Fe20Cr (20 mins in air at 575) + OB950</td>
</tr>
<tr>
<td>6</td>
<td>Quartz disc + OB950/5Fe</td>
</tr>
</tbody>
</table>

9 mins >950°C, 5.5 mins >1000°C
Oven run VII:  
1. Specpure iron (native oxide) + OB950  
2. Fe20Cr (native oxide) + OB950/5Fe/Si [VI]  
3. Specpure iron (native oxide) + OB950/5Fe  
4. Fe20Cr (native oxide) + OB950/Si [VI]  
5. Fe20Cr (7 hrs in microbalance at 710) + OB950/5Fe/Si [VI]  
6. Specpure iron (native oxide) + OB950/5Fe/Si [VI]  
7. Fe20Cr (7 hrs in microbalance at 710) + OB950/Si [VI]  
30 mins at 716°C, 9 mins >950°C, 5 mins >1005°C

Oven run VIII:  
1. Jethete (10 mins in air at 700) + OB950  
2. Jethete (native oxide) + OB950  
3. 2328 SS (10 mins in air at 700) + OB950  
4. 2328 (native oxide) + OB950  
5. Specpure iron (native oxide) + OB950  
6. Jethete (native oxide) + OB950 [VI]  
7. Specpure iron (native oxide) + OB950 [VI]  
22 mins at 700°C, 8.5 mins >950°C, 5 mins >1005°C

Oven run IX:  
1. Quartz disc + OB950/5Fe  
2. Quartz disc + OB950  
3. Fe12Cr (native oxide) + OB950  
4. Specpure iron (native oxide) + OB950/10Fe/Si [I]  
5. Fe20Cr (5 hours in UHV at 800) + OB950/10Fe/Si [I]  
4 hrs at 900°C, 9.5 mins >950°C, 5 mins >1005°C

Oven run X:  
1. Quartz disc + OB950  
2. Jethete (native oxide) + OB950  
3. Fe20Cr (native oxide) + OB950/5Fe/Si [IX]  
4. Quartz disc + OB950/5Fe  
5.5 hrs at 900°C, 10 mins >950°C, 5 mins >1005°C

Oven run XI:  
1. Specpure iron (native oxide) + OB950  
2. Fe20Cr (native oxide) + OB950  
3. Specpure iron (native oxide) + OB950/5Fe/Si [X]  
4. Fe20Cr (native oxide) + OB950/5Fe/Si [X]  
5. Specpure iron (native oxide) + OB950/Si [X]  
6. Fe20Cr (native oxide) + OB950/Si [X]  
7. Specpure iron (native oxide) + OB950 replacement  
8. Specpure iron (native oxide) + OB950/5Fe  
9. Specpure iron (native oxide) + Au/Cu  
10. Jethete (native oxide) + OB950  
30 mins at 900°C, 8 mins >950°C, 5 mins >1005°C

Oven run XII:  
1. Specpure iron (native oxide) + OB950  
2. Fe20Cr (native oxide) + OB950  
30 mins at 900°C, 10 mins >950°C, 4 mins >1047°C
Oven run XIII: 1 Specpure iron (native oxide) + OB950
2 Fe/Si - alloy 10 (native oxide) + OB950
3 Fe/12Cr - alloy 1 (native oxide) + OB950
4 Fe20Cr (native oxide) + OB950
5 Jethete (native oxide) + OB950

30 mins at 900°C, 7 mins >950°C, 5 mins >960°C

Oven run XIV: 1 Jethete (native oxide) + OB950
2 Fe20Cr (native oxide) + OB950
3 Fe/12Cr - alloy 1 (native oxide) + OB950
4 Fe/Si - alloy 10 (native oxide) + OB950
5 Specpure iron (native oxide) + OB950

30 mins at 900°C, 8 mins >950°C, 5 mins >980°C

Oven run XV: 1 Specpure iron (native oxide) + OB950
2 Fe20Cr (native oxide) + OB950
3 Fe/12Cr - alloy 1 (native oxide) + OB950
4 Fe/Si - alloy 10 (native oxide) + OB950
5 Jethete (native oxide) + OB950

30 mins at 900°C, 8 mins >950°C, 5 mins >1000°C

Oven run XVI: 1 Specpure iron (native oxide) + OB950
2 Fe/Si - alloy 10 (native oxide) + OB950
3 Fe/12Cr - alloy 1 (native oxide) + OB950
4 Fe/12CrSi - alloy 5 (native oxide) + OB950
5 Fe20Cr (native oxide) + OB950
6 Jethete (native oxide) + OB950

30 mins at 900°C, 9.5 mins >950°C, 5 mins >1020°C

Oven run XVII: 1 Specpure iron (native oxide) + OB950
2 Fe/Si - alloy 10 (native oxide) + OB950
3 Fe/12CrSi - alloy 5 (native oxide) + OB950
4 Fe/12Cr - alloy 5 (native oxide) + OB950
5 Jethete (native oxide) + OB950
6 Fe20Cr (native oxide) + OB950

30 mins at 900°C, 9.5 mins >950°C, 5 mins >1030°C

Oven run XVIII: 1 Specpure iron (native oxide) + OB950
2 Fe/Si - alloy 10 (native oxide) + OB950
3 Fe/12CrSi - alloy 5 (native oxide) + OB950
4 Fe/12Cr - alloy 5 (native oxide) + OB950
5 Jethete (native oxide) + OB950
6 Fe20Cr (native oxide) + OB950

34 mins at 900°C, 9.5 mins >950°C, 5 mins >1040°C
Oven run XIX:  
1 Specpure iron (native oxide) + OB950  
2 Fe/Si - alloy 10 (native oxide) + OB950  
3 Fe/12Cr - alloy 1 (native oxide) + OB950  
4 Fe/12CrSi - alloy 5 (native oxide) + OB950  
5 Fe20Cr (native oxide) + OB950  
6 Fe20Cr (native oxide) + OB950  
7 Jethete (native oxide) + OB950  
8 Fe20Cr (native oxide) + OB950  

30 mins at 900°C, 10.5 mins >950°C, 5 mins >1060°C

Oven run XX:  
1 Specpure iron (native oxide) + OB950  
2 Fe/Si - alloy 10 (native oxide) + OB950  
3 Fe/12Cr - alloy 1 (native oxide) + OB950  
4 Fe/12CrSi - alloy 5 (native oxide) + OB950  
5 Fe20Cr (native oxide) + OB950  
6 Jethete (native oxide) + OB950  
7 Fe20Cr (native oxide) + OB950  

30 mins at 900°C, 10 mins >950°C, 5 mins >1050°C

5.3 Results

5.3.1 Ultra-High Vacuum Oven Spreading Tests

The results from tests carried out in the ultra-high vacuum (UHV) oven are considered in the following manner: firstly the behaviour of Orobraze 950 on each of the substrates is described; then Orobraze derivatives (ie. OB950 pre-heated on silica and/or with iron additions) on 'specpure' iron and Fe20Cr; and finally the OB950 replacement alloy and a Gold-Copper alloy on specpure Iron and Fe20Cr.

Each sub-section is divided into a description of the substrate surface characteristics, and how these might be affected by temperature, a description of the type and extent of wetting and spreading and their temperature dependence, and to conclude a description of the type and degree of interalloying, evidence of which can be seen by the presence of extra phases in the cooled specimen, and its variation with
Example of the various forms of substrate surface effects, wetting and spreading behaviour, and interalloying effects are illustrated by figures 5.3-5.42, but it must be appreciated that, whilst the figures are for the most part representative of the results from the UHV oven experiments, they have been selected from over 450 photographs and cannot therefore be expected to depict all the variations of behaviour described in the text.

5.3.1.1 Orobraze 950 on spectroscopically pure iron

The wetting behaviour of Orobraze 950 on 'specpure' iron shows several distinctive features associated with the substrate surface and the filler metal. The substrate surface was, in virtually all experiments, covered with tiny crystallite particles - some of which were acicular in appearance, these particles may be seen in figure 5.3. The number of particles present was linked with the oxidation pre-treatment given the substrate, the thicker the initial oxide, the more numerous the crystallites. In addition to these particles the surface also showed thermal etching of the grain boundaries - grain boundary grooving, examples of which may be seen on figures 5.4-5.7. Around the edges of the braze droplets the surface was sometimes seen to be 'rumpled', and this effect is visible at the left of figure 5.4, and on figures 5.5 and 5.6.
At temperatures below approximately 1000°C (50 degrees overheat) the braze droplets wet the surface but with a contact angle of considerably greater than zero (ie. wetting, but not spreading conditions), in effect the braze droplets can be said to have 'slumped' on the surface. In most instances where low overheats are involved, the braze droplets appear to have sunk into the substrate leaving the perimeter of the droplets apparently below the level of the substrate surface. Figure 5.4 shows a droplet which has slumped on the surface with a high contact angle, and a sunken-edge. As the temperature is increased above ~1000°C the sunken-edge is slowly replaced with an edge which appears to be continuous with the substrate surface, the degree of replacement increasing with increasing temperature. This continuous-edge may be seen on the left-hand side of figure 5.5 and the right-hand side of figure 5.6. The gradual replacement of the sunken-edge with the continuous-edge is complete at approximately 1030-1040°C, and at these temperatures the contact angle is near-zero (spreading conditions). This allows the particles to spread irregularly over the substrate, and causes them to lose their domelike appearance (figures 5.4-5.6) so that they eventually form a thin flat braze pool roughly circular in shape - the condition shown by figure 5.7. The sunken edge effect was assumed to be a diffusion process on a macro scale a kind of Kirkendall effect, and hence the effect was dubbed the 'Kirkendall edge'.

For temperatures up to roughly 1000°C there is very little visible evidence for any interalloying having occurred... there being no second phases visible after cooling in the formerly single-phase brazing alloy. What little second phase is present is limited to the very smallest particles (<20um diameter) and the very edges of slumped droplets. Above ~1000°C as interdiffusion with the substrate increases, a second phase
which is generally lamellar in appearance, appears at the edges of the braze droplets, which can be clearly seen in figures 5.3, 5.5 and 5.6. As the test temperature increases, the amount of second phase seen towards the centre of the braze droplets increases, with the second phase at the edges becoming coarser, but it is not until temperatures in the order of 1050°C or more that a fine second phase may be seen in the very centre of large spread droplets.

5.3.1.2 Orobraze 950 on Ferrosilicon (alloy 10)

The substrate surface, in most instances, was free from any distinctive features except for grain-boundary grooving, although for a few of the samples which had been pre-oxidised to form thick films there was some evidence of retained oxide if the temperature did not exceed 980°C. Oxide, when retained, can be seen on the surface of the braze droplets as is illustrated by figure 5.8.

At temperatures below approximately 980°C the braze droplets slump on the surface with greater than zero contact angles. The Kirkendall-edge is prevalent (figure 5.9 and the same as for the iron eg.figure 5.4) although there are almost always regions where the edge is continuous with the substrate (eg.the same effect as that shown in figure 5.6). As with the specpure iron the contact angle, and degree of replacement of the Kirkendall-edge by the continuous-edge increases with increasing temperature, until at approximately 1000-1020°C when spreading takes place resulting in large, thin, and flat circular pools on the substrate surface - this is shown by figure 5.10. At approximately 1000-1020°C the surface of the substrate close to the edge of the braze droplet is seen to have small amounts of the braze
alloy upon it. The affected area extends a few microns beyond the edge of the braze droplet, and the extent of this 'pre-wetting' by the braze material increases with increasing temperature. Figures 5.9 and 5.11 show the pre-wetted area which can also be seen as a bright 'halo' around spread droplets when viewed at lower magnifications - as shown by figure 5.10.

At very low overheat temperatures (less than +10-20°C) no interalloying is visible on cooling, but as the test temperature is increased second phases first appear at the edges of the droplet (figure 5.9) and then as the temperature is further raised, they are seen more towards the centre of the braze pool (figure 5.11) until at 1020°C or so only the very centres of the largest braze droplets are free from second phases. Even at the highest overheat temperatures there is always a gradation of the extent to which interalloying has taken place throughout the droplets - the second phase being more plentiful and coarse towards the edges of the droplets.

5.3.1.3 Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)

In general the substrate surface showed no distinctive features other than the usual grain-boundary grooving, although the sample which had been pre-oxidised in the vacuum microbalance showed a martensitic type surface structure as shown by figure 5.12. The sample which had been pre-oxidised in the UHV oven for four hours (III sp1) retained an oxide which clearly showed cracks, and spreading by a suboxide route, and is illustrated by figure 5.13. The specimen pre-oxidised for 200 hours in the UHV oven did not show any indication of any oxide retention.
At low overheats the Kirkendall-effect dominates, the droplets wetting the surface, but slumping rather than spreading. At temperatures in the range 980-1000°C there is some 'disruption' of the substrate close to the edge of the braze droplet - the normally smooth appearance of the substrate surface is broken by very localised distortions near to the edge of the braze droplets - this disrupted region is shown in figure 5.14. Above approximately 1000°C the contact angle approaches zero and spreading over the surface takes place, this is associated by a small amount of pre-wetting by the braze metal. Above approximately 1020°C pre-wetting is very extensive and 'haloes' can be seen around fully-spread droplets, this spreading behaviour is the same as for 0B950 on ferrosilicon and is shown by figure 5.10. At very high temperatures (greater than 1050°C) very thorough spreading takes place and is accompanied by both pre-wetting and the braze alloy separating into two different 'bright' and 'dark' phases, this kind of behaviour is seen in figures 5.15-5.16.

For tests carried out at temperatures below 960°C interalloying is only visible at the very edges of the frozen braze metal, but as the temperature is increased the second phase becomes coarser and begins to extend further towards the centre of the droplet until, at temperatures between 980-1000°C the whole of the droplet shows signs of interalloying (i.e. the presence of a second phase). Above approximately 1040-1050°C the extent of interalloying is so great that separate phases are able to co-exist in equilibrium with each other. A bright single phase material is seen at the edges of the braze droplet (see figures 5.15 and 5.16), whilst a darker two-phase material is found at the centre of the spread droplet (see figure 5.16). Figure 5.16 shows that the centre of the spread droplet has a very rough 'semi-melted'
appearance, whilst closer to the edge (figure 5.16) this roughness or unevenness is gradually lost as the edge of the droplet, and the bright phase, is approached.

5.3.1.4 Orobraze 950 on Fe/11.21Cr/1.05Si (Alloy 1)

There is no information for the behaviour of this substrate/alloy combination below 1020°C but it is a fair assumption that the wetting and spreading characteristics would be similar to those of alloy 1. There is some evidence, in the form of bright crytallites on the surface of the braze and substrate metals, for a fair degree of oxide retention - the crystallites may be seen in figures 5.17 and 5.18. Between approximately 1020-1030°C a narrow disrupted region can be seen around the perimeter of the braze droplets, which may be seen in figure 5.17.

Spreading is seen to occur at around 1020-1030°C - the zero, and near zero contact angles are shown by figures 5.18 and 5.17 respectively. There was no pre-wetting visible for this braze/substrate system. At temperatures in the order of 1040°C or greater, spreading takes place very readily indeed - one sample was completely covered by a thin layer of the brazing alloy. 'Post-mortem' examination by SEM is rather unsatisfactory in such instances, since, as figures 5.19 and 5.20 illustrate it is virtually impossible to separate areas of still-exposed substrate from areas of two-phase braze metal.

At 1020-1030°C interalloying is seen throughout the solidified braze material. Figure 5.18 shows that there is some tendancy for the second phase to be preferentially distributed away from the edges of the droplet which consist of nearly all bright single phase material. When
spreading occurs to the degree shown by figures 5.19 and 5.20 it is very difficult to determine what interalloying effects have occurred. A tentative interpretation of the figures is that the bright areas consist of a bright, mobile, single-phase material which has spread unevenly over the substrate, leaving areas of the substrate exposed (figure 5.19 shows some evidence of grain boundary grooving). The dark areas could be composed of the braze alloy which has separated into bright and dark materials both of which appear to be single-phase from higher magnification photographs.

5.3.1.5 Orobraze 950 on Fe20Cr

The distinctive feature of the spreading of OB950 on Fe20Cr is the formation of a 'disrupted' region around the edge of all particles which have melted. The effect is neither dependent upon temperature, nor upon the size of the melted droplets, furthermore the width of the disrupted region always appears to be constant. The disrupted region, and its lack of droplet size dependence is illustrated by figure 5.21. Occasionally there is some continuation of the braze metal structure into the disrupted region, and this is shown by figure 5.22. There is a little evidence for oxide retention at temperatures below 1000°C but this is fairly exceptional and the retained film is only very thin - as shown by figure 5.23.

At temperatures below approximately 1000°C the braze droplets wet the surface and slump (figure 5.21) with the contact angles clearly greater than zero. As ~1000°C is approached the degree of interaction with the disrupted region (figure 5.22) increases, and at approximately 1010-1020°C the transition to spreading conditions takes place (the
contact angle becomes zero). Up to approximately 1040°C spreading occurs, but not to completion, whereas, above 1040°C spreading is very thorough and associated with the braze metal separating into several phases - see figures 5.24 and 5.25. At very high temperatures (1060°C and above) the separation of the braze metal is so marked that the brighter material may be seen as a ring around the edge of the darker material, this condition is shown by figures 5.26 and 5.27.

At very low overheat temperatures (<960°C) the solidified braze metal shows no evidence of second phase formation, but above this test temperature interalloying does occur to a visible extent, and a lamellar second phase may be seen distributed evenly throughout the braze droplets (ie. the same as figure 5.21). As the temperature is increased the second phase coarsens, until, at temperatures in the range 1020-1040°C the second phase shows preferential distribution towards the centre of the braze pool leaving only single-phase braze metal at the droplet edges - figure 5.28 shows this condition. Above ~1040°C the braze metal separates fully into two different materials, a bright, mobile, single-phase material, and a darker, static (and at the brazing temperature perhaps solid), two-phase material. The bright phase initially 'fills the gaps' between the dark material, and becomes more concentrated at the periphery of the pool (see figures 5.24 and 5.25), but as the temperature increases, the bright phase can only be found at the periphery leaving blocks of the dark, two-phase material in the centre of the braze pool - the condition shown by figures 5.26 and 5.27.
The surface of the Jethete has a characteristic martensitic appearance which is seen at all temperatures, but does not appear to be associated with retained oxide, figures 5.29-5.33 show this surface effect. In the proximity of droplets the surface often shows striations, similar in appearance to slip bands, and in addition to this, above ~1000°C grain boundaries which would otherwise have been thermally etched, are 'decorated' by the braze metal - both striations and grain-boundary decoration are visible in figures 5.30 and 5.31.

At low temperatures the braze metal does not spread over the surface but simply wets and slumps (figure 5.29), but at 980°C the contact angle approaches zero and some spreading takes place. Often spreading does not continue to completion (ie. a flat, thin, layer of braze metal over the surface), but the edges of the droplets spread, whilst their centres do not. This results in a droplet where the edges have spread, and form a flat thin layer, around a central unspread region which retains a domelike shape, the final droplet therefore resembles a fried-egg, and this is shown by figure 5.32. Spreading of this nature mainly occurs between 980-1000°C. Above ~1000°C the braze droplets spread to completion, and pre-wetting of the surface is very extensive so that the distinct droplet edges visible at lower temperatures are largely lost. At temperatures in the region 1030-1040°C spreading occurs very readily, and is usually associated with the separation of the braze metal into separate phases, the bright, mobile phase being present as a ring at the periphery of the droplet, as shown by figure 5.33.
At very low overheat temperatures (<960°C) there is no visible evidence for interalloying having taken place, but above these test temperatures a lamellar second phase is seen evenly-distributed throughout frozen droplets (figure 5.29). Up to approximately 1000°C the second phase simply coarsens and becomes more abundant as temperature is increased, but above this temperature the phases begin to separate, firstly at the pool edges (ie the same as figure 5.28), and then throughout the braze metal. A bright, mobile, single-phase material concentrates at the pool edges, and a darker two-phase material is left in the centre of the pool (figure 5.33).

5.3.1.7 Orobraze 950 on 2328 Stainless Steel

Data is only available for this alloy at a brazing temperature of approximately 1000°C (50 degrees overheat). The sample which had been pre-oxidised in air showed a fairly thick, particulate, retained oxide (figure 5.34), whilst the sample with its native oxide showed a much thinner, and non-particulate, retained oxide (figure 5.35).

For both samples spreading was very extensive, and appears to have taken place via a suboxide route, since, in both instances oxide particles could be seen on the surface of the braze metal. There was no visible evidence for interalloying having occurred.
All experiments were carried out at a temperature of \( \sim 1000^\circ C \), and the Orobraze derivatives studied (see table 5.3) were: OB950 + iron; and OB950, or OB950 + iron pre-heated on silica.

Firstly the behaviour of the Orobraze derivatives on iron will be considered. In almost all cases the iron showed thermal etching of grain boundaries, crystallites on the substrate surface, and often rumpling of the surface close to braze droplets (see figure 5.36). For OB950/5Fe and OB950/Si the droplets wet the surface and slumped, but did not spread, although there was often quite extensive surface rumpling and usually a continuous edge (figure 5.36). Addition of iron (5 or 10%) and pre-melting on silica however, significantly changes the spreading behaviour, zero contact angles are formed and the droplets spread. Spreading did not continue to completion since the droplet centres remained domed resulting in the characteristic 'fried-egg' shape of the spread droplets. Figure 5.37 shows this type of spreading, and although the substrate is Fe20Cr, the photograph is equally applicable to the spreading of OB950/Fe/Si on iron too. For all of the Orobraze derivatives interalloying is seen to occur, and in all but the OB950/10Fe/Si the droplet centres were free from second phases which were most plentiful and coarse at the pool edges.

On Fe20Cr all of the Orobraze derivatives showed a distinct disrupted region around the edges of the droplets, and in some cases there was a little pre-wetting or interaction with the disrupted region (figures 5.38 and 5.39). No oxide was retained and only thermal etching of the grain boundaries was noted on the surface. Figures 5.37, 5.38,
and 5.39 show grain boundary grooving and the disrupted region. For OB950/Si and OB950/5Fe spreading was fairly good, contact angles were small and the particles were not simply slumped on the surface (figure 5.38). For OB950 with both iron additions and the pre-melting on silica however, spreading was greatly enhanced. The contact angles formed were very low and spreading occurred readily, though not to completion since the droplet centres remained unspread resulting in the characteristic fried-egg appearance (figures 5.37 and 5.39). Interalloying was evident as a second phase which was lamellar or blocky, and evenly distributed throughout the droplets (figure 5.38) with the exception of the OB950/10Fe/Si alloy which remained as a single phase material. Some phase separation occurred in the OB950/5Fe/Si alloy, the edges of the droplets being single phase, and their centres two-phase as shown by figure 5.39.

5.3.1.9 Miscellaneous Alloys on Iron and Fe20Cr

All experiments were carried out at a temperature of ~1000°C, and the brazing alloys used were Gold/Copper and a gold-based Orobraze replacement alloy developed by Johnson Matthey - their compositions are given in table 5.1.

To begin, the behaviour of the gold/copper alloy on iron and Fe20Cr will be examined. The surface of the iron showed the distinctive particulate material, and grain boundary grooving. On the iron the degree of spreading is very extensive, the braze droplets wet the surface with a near-zero contact angle. Considerable grain boundary decoration takes place, and the micrographs suggest that the extent of pre-wetting is such that a continuous thin film of braze metal may be
present around the droplets some distance from the droplet edge (see figure 5.40). The braze alloy is clearly two-phase, the second phase being very acicular in nature, the material which decorates the grain boundaries is single phase. On Fe20Cr the surface shows no sign of retained oxide and only grain boundary grooving is evident. The braze alloy wets the surface, but with a non-zero contact angle, so that the droplets slump on the surface (see figure 5.41). Grain boundary decoration is very extensive indeed, very few boundaries remaining free from braze metal irrespective of their distance from a braze droplet. The braze alloy is clearly two-phase, the second phase being lamellar, and the grain boundary braze metal is single phase.

The behaviour of the Orobraze replacement alloy is very complex, and the small number of experiments carried out and micrographs taken mean that no firm conclusions can be drawn. On both iron and Fe20Cr spreading was very well advanced, and is associated with gross separation into phases of the braze metal. Grain boundary decoration is noticeable on both substrates, but is far more extensive on the Fe20Cr. Like the gold/copper alloy on iron, the surface around the braze pool is pre-wetted to such a degree that there is a continuous thin film of braze metal present, this is particularly evident on the iron substrate. Towards the 'centre' of the braze pool, the alloy separates into at least two phases, one dark, and one bright. The former material appears to be single phase, but the latter is composed of the 'matrix' material and two further phases - one blocky, one acicular. The typical appearance of this braze alloy after melting on iron or Fe20Cr is shown by figure 5.42.
Figure 5.3: Orobraze 950 on spectroscopically pure iron
Figure 5.4: Orobraze 950 on spectroscopically pure iron
Figure 5.5: Orobraze 950 on spectroscopically pure iron
Figure 5.6: Orobraze 950 on spectroscopically pure iron
Figure 5.7: Orobraze 950 on spectroscopically pure iron
Figure 5.8: Orobraze 950 on Ferrosilicon (Alloy 19)
Figure 5.9: Orobraze 950 on Ferrosilicon (Alloy 10)
Figure 5.10: Orobraze 950 on Ferrosilicon (Alloy 10)
Figure 5.11: Orobraze 950 on Ferrosilicon (Alloy 10)
Figure 5.12: Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)
Figure 5.13: Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)
Figure 5.14: Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)
Figure 5.15: Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)
Figure 5.16: Orobraze 950 on Fe/11.67Cr/0.38Si (Alloy 1)
Figure 5.17: Orobraze 950 on Fe/11.21Cr/1.05Si (Alloy 5)
Figure 5.18: Orobraze 950 on Fe/11.21Cr/1.05Si (Alloy 5)
Figure 5.19: Orobraze 950 on Fe/11.21Cr/1.05Si (Alloy 5)
Figure 5.20: Orobraze 950 on Fe/11.21Cr/1.05Si (Alloy 5)
Figure 5.21: Orobraze 950 on Fe20Cr
Figure 5.22: Orobraze 950 on Fe20Cr
Figure 5.23: Orobraze 950 on Fe20Cr
Figure 5.24: Orobraze 950 on Fe20Cr
Figure 5.25: Orobraze 950 on Fe20Cr
Figure 5.26: Orobraze 950 on Fe20Cr
Figure 5.27: Orobraze 950 on Fe20Cr
Figure 5.28: Orobraze 950 on Fe20Cr
Figure 5.29: Orobraze 950 on Jethete M152
Figure 5.30: Orobraze 950 on Jethete M152
Figure 5.31: Orobraze 950 on Jethete M152
Figure 5.32: Orobraze 950 on Jethete M152
Figure 5.33: Orobraze 950 on Jethete M152
Figure 5.34: Orobraze 950 on 2328 Stainless Steel
Figure 5.35: Orobraze 950 on 2328 Stainless Steel
Figure 5.36: Orobraze 950 derivatives on Specpure iron and Fe20Cr
Figure 5.37: Orobraze 950 derivatives on Specpure iron and Fe20Cr
Figure 5.38: Orobraze 950 derivatives on Specpure iron and Fe20Cr
Figure 5.39: Orobraze 950 derivatives on Specpure iron and Fe20Cr
Figure 5.40: Miscellaneous alloys on Specpure iron and Fe20Cr
Figure 5.41: Miscellaneous alloys on Specpure iron and Fe20Cr
Figure 5.42: Miscellaneous alloys on Specpure iron and Fe20Cr
Table 5.5: Table showing the incidences of effects seen on the UHV oven specimens.

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Key: yes - effect generally seen
no - effect not seen
960 - temperature (degrees C) at which the effect was first seen.
? - either no data, or uncertainty

Cry - Crystallites seen on surface
Rum - Rumpling seen on surface
GBG - Grain boundary grooving
SlB - Slip bands seen on surface
K.E - Kirkendall edge effect noted
Mar - Martensitic appearance of surface
R.O - Retained oxide noticed
S.S - Sub-oxide spreading noticed
Slu - 'slumping' of braze droplets
C.E - Continuous edge at droplet edge
Spr - Spreading of braze droplets
FrE - 'Fried egg' spreading
RSp - 'Runaway' spreading
P.W - Pre-wetting of surface
S.PE - Second phases seen at edges of droplets
S.PC - Second phases seen at centre of droplets
Die - Disrupted edge effect noticed
Phs - Phase separation noticed
GBD - Grain boundary decoration noticed

* - No data below 1020°C
** - All data at 1000°C
Table 5.5: Table showing the incidences of effects seen on the UHV oven specimens.

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<tr>
<td>OB repl. on Specpure Fe</td>
<td>no</td>
<td>no</td>
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<td>yes</td>
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<tr>
<td>OB repl. on Fe20Cr</td>
<td>no</td>
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<td>yes</td>
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All data from experiments at $\geq 1000^\circ C$. 
5.3.1.10 Summary of UHV oven experiments

The UHV oven experiments provide a convenient and fairly rapid means by which a number of substrate/brazing alloy combinations can be studied for a range of overheat temperatures. As tables 5.2, 5.3 and 5.4 show, the experiments carried out have been quite diverse, and the results reflect this by showing a remarkable variety of wetting, spreading, and interalloying characteristics! Table 5.5 shows the incidences of the effects mentioned in the preceding text, and it is clear that the experiments are invaluable for the provision of such qualitative data, and for the identification of general features resulting from the various braze substrate interactions. The fact remains however, that in many instances the data is of limited value, since, in isolation, a 'post-mortem' type examination cannot yield information relating to the ways in which the final state is arrived at during the brazing cycle. For many of the features illustrated by the micrographs, it is necessary to know how the braze metal, substrate, and substrate oxide interact with each other if the fundamental mechanisms of wetting and spreading, oxide penetration and removal, or interalloying are to be determined. For example some questions raised by this study are as follows: are the edge effects due to interaction with an oxide which is subsequently removed, or is the effect a result of gross erosion of the substrate? Are the 'fried egg' structures the result of a kind of framework around the droplet that is retained as a 'shell' once wetting and spreading has taken place? Is there a correlation between rate of spreading and extent of interalloying? Does the presence of a retained oxide mean that spreading is physically impeded, or is the solidification due to interalloying the factor limiting the amount of flow in the system? It is evidently not possible to answer such questions using only a
post-brazing examination technique, so it is necessary to combine such studies with a technique which allows the process to be examined at all stages throughout the brazing cycle, in real-time, and with the ability to analyse the surface and bulk composition of small areas. Hot-stage scanning Auger electron spectroscopy, when coupled with X-ray analysis fulfills this requirement superbly, and at Surrey University there is such a facility. The V.G. MA500 has been described elsewhere (section 3.1), and knowing its resolution limits in time, energy, and space, means that the entire vacuum brazing process may be fully examined. The fact that both the vacuum furnace and the Auger microscope are UHV instruments, and that both set-ups use 'single sided' joints, means that the results may be cross checked, thereby ensuring that the features noted using either technique can be verified as 'real' features, and not artifacts resulting from the equipment or experimental technique.

5.3.2 Heating Stage Studies

The studies carried out using the heating stage and UHV oven tests reveal that in many respects the wetting and spreading behaviour of specpure iron and ferrosilicon (alloy 10) are similar, and to a lesser extent, the behaviour of the chromium containing alloys (alloy 1, 5, and Fe20Cr), consequently these two groups of alloys - chromium free and chromium containing - will be considered separately. The heating stage studies carried out have already been listed in table 4.3. The following two sections consider the visual studies carried out during the hot-stage runs (the results from in-situ analysis will be considered later), and endeavour to illustrate the typical features seen during the wetting and spreading of the particular alloy groups. It is important to realise
that, in most cases the temperature measurement was poor, and hence temperatures on the figures are often inaccurate - being estimated from the voltage versus temperature characteristics of the 'stage. Similarly, the times given on the figures are only approximate, and serve only to give a feel for the duration of various effects. In common with the UHV oven studies, only a small fraction of the available micrographs are presented here, and hence cannot fully illustrate all of the effects noted during the heating stage tests.

5.3.2.1 Orobraze 950 on Specpure iron and Ferrosilicon

Figures 5.43 and 5.44 show the typical wetting and spreading behaviour of this group of alloys at low overheat temperatures - that is less than approximately 50°C above the melting point of Orobraze 950. Figure 5.43 shows OB950 on alloy 10, and 5.54 on Specpure iron. It is evident from the micrographs that the braze alloy is merely wetting the surface, spreading did not occur. It was noted that wetting was a very rapid process (a video frame-by-frame replay showed that the droplets wet the surface faster than the T.V scan rate - approximately 1/50th. second), but once an 'equilibrium droplet' had formed on the surface, its shape remained unaltered unless other particles melted. Despite the fact that OB950 is a near-eutectic alloy, not all braze particles melted at the same time since the stage design means that there is always a small temperature gradient across the substrate surface.

The major difference between the ferrosilicon and the specpure iron, was the presence of retained oxide on the ferrosilicon. 'Rafts' of debris could be seen on the surface of the still-molten braze, these rafts moving over the molten metal surface often breaking up in the
process (see figure 5.43 photos 3 and 4). Auger electron spectroscopy showed the rafts to be silica, and the point analyses from various regions on photo 4 of figure 5.43 are shown in figure 5.45.

Figure 5.44 shows, in photo 1, a braze pool which has solidified at the braze temperature, and the photos 2-6 show its behaviour as the temperature is increased. Photos 2, 3, and 4 show a liquid front moving across the droplet from 'bottom to top' - the still-solid braze alloy appearing darker than the liquid. It is notable that except where further remelting and wetting occurs, the braze pool does not spread, but remains as an 'equilibrium droplet'. Both figures 5.43 and 5.44 show that, once melting (or re-melting) and wetting have taken place, the edge of the braze pool begins to solidify. Solidification of the alloy is noted by the appearance of structure, on what was originally a smooth featureless liquid surface. The effect is the result of the solidifying alloy forming a 'skin' on the surface, which is then rumpled as the liquid beneath it solidifies and shrinks.

Figure 5.46 shows a short lived effect which was only noted in the case of the melting of OB950 on specpure iron (the area is incidentally the same as that shown in figure 5.44). As re-melting occurs, a dark region which behaved in a fluid-like manner, was seen on the surface of the molten braze. The source of the material appeared to be the top-left of the pool since a stream of it could be seen moving from top-left to the bottom of the droplet, gradually enlarging the darker region at the bottom of the pool. The effect is short lived, as the figure shows, and the 'final state' shown in the last photograph remained unchanged in appearance for the rest of the experiment.
Figure 5.47 shows the high-temperature behaviour of OB950 on ferrosilicon, although the figure is equally applicable to OB950 on specpure Fe (except that the transition from 'low' to 'high' temperature behaviour for iron is at 1030-1040°C compared with 1000-1020°C for ferrosilicon). Photos 1 and 2 show that as the temperature is increased spreading takes place, but then edge solidification halts this process. Upon further temperature increase, the braze remelts and spreads a little more, but as photo 4 shows, parts of the braze pool soon resolidify, and only limited spreading can take place between the solid regions, resulting in the irregularly shaped droplets seen in the UHV oven runs and photos 5 and 6. These last photos also illustrate very clearly, that solidification begins at the pool edges, after which the solidification front then moves slowly towards the centre of the braze pool.

5.3.2.2 Orobraze 950 on Fe12Cr and Fe20Cr

Figure 5.48 shows the low overheat spreading behaviour of OB950 over Fe12Cr which had been pre-oxidised in air (experiment BDS17). The behaviour is very similar to that of the chromium free alloys, the braze particles melt, and then rapidly wet the oxide free surface, forming 'equilibrium droplets'. There was no evidence of any retained oxide, no oxide rafts are seen on the surface and point analyses of the surface prior to melting showed the oxide to have been totally reduced. It may be clearly seen from the figure that soon after wetting the substrate, solidification at the edges begins (see for example the right hand edge of the large pool), until after approximately four minutes all edges had solidified despite the pool centre remaining molten.
Figure 5.49 shows the low temperature spreading sequence of OB950 on oxidised Fe20Cr (experiment BDS19). The surface of the molten pool has upon it an oxide raft which can be seen to move during the sequence. In photo 1 the braze particle at top left is unmelted, in photo 2 it is semi-molten, and in photo 3 it is fully molten (all surface structure having disappeared), but has not wetted the surface of the substrate...this happens in photo 4. The particle was molten but non-wetting for at least five seconds, although the eventual wetting took place in a few fractions of a second. Photos 5 and 6 show similar behaviour for the other braze particle. The figure illustrates that in this instance the surface has retained oxide, and the micrographs show that wetting cannot occur until this oxide is penetrated.

The low temperature sequence shown in figure 5.50 also shows that wetting cannot take place across an oxide. The particles at the bottom of photo 1, had sintered together during heating, and remained joined on melting. As particles around the two joined particle melted however, surface tension effects pulled them apart (photos 2, 3, and 4). As the particles part the surface is clearly de-wetted, the join being broken, and new 'equilibrium droplets' formed. Photo 6 shows the presence of many oxide rafts on the surface thereby confirming both the suboxide spreading mechanism, and the fact that the outer surface of the oxide cannot be wetted.

Figures 5.51, 5.52, and 5.53 typify the medium, and high temperature spreading of OB950 on Fe20Cr oxidised in air. Considering figure 5.51 first, photos 1 to 3 show two fairly large braze pools, both initially solid at their peripheries, which remelt allowing the pools to join. The edges of this new pool then solidify, and for no
further temperature increase, the solidification front gradually moves further and further towards the pool centre (photos 4, 5, and 6). Note the bright region at the edge of the braze pool, this 'halo' is retained throughout the sequence (although the contrast of the photos does not always show it), and will be considered later.

Figure 5.52 shows the spreading behaviour upon further increase of temperature. The solidified braze alloy gradually remelts, starting from the pool centre and finally melting the pool edges - this is shown by photos 1 to 4. Photo 5 depicts spreading over the surface with a near-zero contact angle, the extent of spreading can be gauged by the relative positions of the pool edge and debris on the substrate surface. Photo 6 shows the development of dark immobile 'islands' of second phase material a short distance behind the advancing liquid metal front. A second braze metal front is just visible at the top left of photo 6.

Figure 5.53 shows the continuing spreading behaviour of the system, photo 1 shows the braze pool visible in photo 6 of the previous figure, to have spread into the field of view. Second phase islands are still visible in the right-hand braze pool. The photos 2-5 illustrate how spreading progresses and photo 6 the final state of the alloy after cooling. Whilst it is not readily apparent from the micrographs, the real time studies showed that the dark second phase islands, precipitated at temperature, were immobile, and preceded by a bright apparently single phase material, which could not only spread over the surface, but could also flow around the solid islands, until finally the whole pool froze. If the temperature was increased, first the second phase islands, and finally the pool edges redissolved. After a short while similar islands reappeared a short distance behind the
spreading liquid front. In addition to this, it was noted that spreading was not a smooth process, but the liquid metal front moved forwards in a series of small jumps. At very high overheat temperature (>+150°C), the spreading/precipitation process became very rapid, the volume fraction of the dark phase being far larger than that of the bright phase and often following the bright front as a 'sheet' of dark material. This effect was noted during heating stage runs but has not been illustrated, since better quality micrographs have already been shown in the UHV oven spreading tests section.

5.3.2.3 Summary of heating stage studies

The real time brazing studies have proven particularly useful in providing data to elucidate the processes which take place during wetting and spreading, and to examine the effects which result in the end conditions already seen in the UHV oven tests. The combination of UHV oven experiments and heating stage studies allows a full picture of the events occurring during vacuum brazing to be built up. Neither technique, either in isolation, or combined, allows the mechanisms behind these events to be defined unless analytical information is available. Hot-stage Auger electron spectroscopy has already asserted the mechanisms which permit oxide penetration to happen, and the following section, using results from bulk and surface analyses carried out after (and in some cases during) heating, discusses the mechanisms which may be responsible for the effects described above and in section 5.3.1.
Figure 5.43: Orohaze 950 on ferrosilicon (alloy 10) oxidised 25 mins at 400°C.

- Photo 1: $x = 200$, $\approx 200^\circ C$
- Photo 2: $x = 100$, $\approx 960^\circ C$, time = 0 s
- Photo 3: $x = 200$, $\approx 960^\circ C$, time $\approx 50$ s
- Photo 4: $x = 200$, $\approx 960^\circ C$, time $\approx 95$ s
Figure 5.44: Graphene 950 on peapure Iron oxidised 10mins at 400°C in air.
1; x500, Temp = 960°C, time = 0 secs
2; x500, Temp = 965°C, time = 30 secs
3; x500, Temp = 966°C, time = 32 secs
4; x500, Temp = 966°C, time = 35 secs
5; x500, Temp = 966°C, time = 50 secs
6; x500, Temp = 966°C, time = 55 secs
Figure 5.45: Auger spectra showing surface compositions of OB950 and Fe12Cr after vacuum brazing in the MA500.

Iron surface
Debris on Gold surface
Gold surface

Intensity

Kinetic Energy (Ev)
Figure 5.46: Orobraz 950 on specpure iron oxidised 10 mins at 400°C in air.

1: x200, Temp = 965°C, time = 0 secs
2: x200, Temp = 970°C, time = 10 secs
3: x200, Temp = 970°C, time = 11 secs
4: x200, Temp = 970°C, time = 12 secs
5: x200, Temp = 970°C, time = 13 secs
6: x200, Temp = 970°C, time = 20 secs
Figure 5.47: Orobraze 950 on specpure Iron oxidised 10mins at 400°C in air.
1: x200, Temp = 1010°C, time = 0 secs
2: x200, Temp = 1015°C, time = 30 secs
3: x200, Temp. = 1020°C, time = 40 secs
4: x200, Temp = 1020°C, time = 50 secs
5: x200, Temp = 1020°C, time = 180 secs
6: x200, Temp = 1020°C, time = 420 secs
Figure 5.48: Orobraze 950 on Fe12Cr (alloy 1) native oxide.

photo 1
x 150
\(\approx 375^\circ C\)

time \(\approx 0\) s

photo 2
x 150
\(\approx 955^\circ C\)

time \(\approx 60\) s

photo 3
x 150
\(\approx 955^\circ C\)

time \(\approx 120\) s

photo 4
x 150
\(\approx 955^\circ C\)

time \(\approx 120\) s
Figure 5.49: Orobrase 950 on Fe20Cr oxidised 7 hours at 726°C (K)
1: x1000, Temp = 960°C, time = 0 secs
2: x1000, Temp = 960°C, time = 20 secs
3: x1000, Temp = 960°C, time = 25 secs
4: x1000, Temp = 960°C, time = 30 secs
5: x1000, Temp = 960°C, time = 50 secs
6: x1000, Temp = 960°C, time = 55 secs
Figure 5.50: Orobraze 950 on Fe20Cr oxidised 7 hours at 726°C (K)
1; x500, Temp = 965°C, time = 0 secs
2; x500, Temp = 965°C, time = 3 secs
3; x500, Temp = 965°C, time = 7 secs
4; x500, Temp = 965°C, time = 10 secs
5; x500, Temp = 965°C, time = 12 secs
6; x500, Temp = 965°C, time = 15 secs
Figure 5.51: Orobraze 950 on Fe20Cr oxidised 25mins at 575°C in air.
1: x500, Temp: 970°C, time: 0 secs
2: x500, Temp: 975°C, time: 30 secs
3: x500, Temp: 980°C, time: 40 secs
4: x500, Temp: 985°C, time: 70 secs
5: x1000, Temp: 985°C, time: 100 secs
6: x1000, Temp: 985°C, time: 120 secs
Figure 5.52: Oreobase 950 on Fe200r oxidised 25mins at 575°C in air.
1; x1000, Temp = 990°C, time = 0 secs
2; x1000, Temp = 1000°C, time = 5 secs
3; x1000, Temp = 1010°C, time = 8 secs
4; x1000, Temp = 1020°C, time = 10 secs
5; x1000, Temp = 1030°C, time = 35 secs
6; x1000, Temp = 1035°C, time = 70 secs
Figure 5.53: Grobzene 950 on Fe20Cr oxidised 25mins at 575°C in air.
1; x1000, Temp = 1040°C, time = 0 secs
2; x1000, Temp = 1045°C, time = 15 secs
3; x1000, Temp = 1050°C, time = 30 secs
4; x1000, Temp = 1055°C, time = 40 secs
5; x1000, Temp = 1060°C, time = 80 secs
6; x1000, Temp = 1000°C, time = 120 secs
5.4 Discussion

An overview of the results of the wetting and spreading studies from the UHV oven runs and the heating stage studies highlights two main areas which are likely to affect a brazing alloy when heated above its melting point in a vacuum. Both the presence of a retained oxide on the surface and the interalloying of braze and parent metals have been shown to affect wetting and spreading. These two factors both show a temperature dependence so it is hardly surprising that the wetting and spreading process is affected by temperature. This discussion aims to consider how the effect of oxide and of interalloying, in isolation and in unison, can explain the observed wetting and spreading behaviour.

It is perhaps easier to consider the effect of retained oxide first, since in UHV it plays a more minor role than interalloying. In the 'dirty' vacua typical of industrial vacuum brazing furnaces however, the effect of the surface oxide will be far greater. Figures 5.49 and 5.50 show unambiguously that the oxide is not wetted by the molten braze alloy. In one instance retained oxide prevented oxide penetration and wetting, and in the other, the presence of oxide on the surface caused de-wetting. Figures 4.30 and 5.43 showed that spreading, in the presence of retained oxide, was always by a suboxide route. The figures also imply that retained oxide can act as a physical barrier. The sequence shown by figures 5.52 and 5.53 showed that although spreading was occurring, the process was not a smooth one but took place in a series of small jumps. If one considers the strength of the metal/metal-oxide interface, it is obvious that it is fairly high, since spallation does not take place upon heating or cooling and the oxide is not easily removed. The interface energy, however, is
undoubtedly higher than the sum of the braze/substate and braze/oxide interfacial energies, since spreading is via the preferred suboxide route. It is quite probable though, that the oxide, which will not be spontaneously detached from the surface, can exert a mechanical force against the advancing metal front which is trying to lift it from the surface. Sufficient force would need to be generated by the liquid braze metal to detach the tenuous oxide, and it is reasonable to assume that it would take a short time to build up the necessary hydrostatic pressure. Such a process would explain the discontinuous advance of the liquid metal. The results from the previous chapter (4) reveal that oxide is sequentially reduced by heating in vacuo, until it is completely removed, or has formed an oxide stable in the prevailing vacuum and temperature conditions. Retained oxide is more common and more persistent on substrates containing chromium and silicon, especially if the oxide prior to heating in vacuum was thick - this is quite reasonable since both chromium and silicon form more stable oxides. In a 'real-life' brazing operation vacuum conditions fall well short of those used in the experiments described in this thesis, and the type of alloy for which OB950 is a commonly used braze metal (see chapter 2) are often rich in chromium or form a stable oxide. In consequence oxide effects will be far more pronounced, indeed oxides may even grow at various stages during heating and soaking, so their reduction will be slower and less complete. Thicker residual oxides, or more stable and tenuous ones, will result in greater difficulty in oxide penetration, and hence a greater impediment to wetting of the braze alloy. Even when wetting has occurred, and spreading begins, the oxide still plays a role, since it will exert a 'pressure' against the spreading braze, a force which will probably be greater for thicker and/or more stable oxides. Although the oxide is generally assumed to behave plastically at
temperature, it will resist bending. The pressure exerted against a spreading droplet therefore arises from oxide which has been partially detached. A portion of the oxide remains attached to the substrate, whilst some of it has been detached and bent upwards by the braze metal beneath it - resistance to this bending, by the oxide provides a resistive force.

The second major factor which affects wetting and spreading is interalloying between the braze and parent metals, but it must be emphasised that although the effect is being considered separately, it occurs in conjunction with oxide effects, and their combined action must be taken into account. In UHV conditions interalloying has proven the most important factor in the determination of wetting and spreading behaviour, but this is mainly because most oxide is removed by heating in UHV. In a commercial situation however, the two processes become equally important, primarily because of the poorer vacuum conditions found in most industrial vacuum furnaces.

The results show that interalloying begins as soon as the liquid braze metal contacts the parent metal surface - this means that in most cases wetting, a rapid process, will not be affected by interalloying. The driving force for interalloying relies upon a degree of solubility of parent metal species and braze metal species, which in turn sets up a concentration gradient between the braze and parent metals. This implies that the interdiffusion of species is a two-way process, and this is indeed the case, but the enormous differences in the mobility of atoms in liquid and solid matrices means that solid state diffusion (ie. from the braze into the substrate) can be disregarded in the majority of cases. Solid state diffusion does become important if braze metal
species show a particular affinity for grain boundaries, since this provides a rapid diffusion path. In many systems, and certainly for the system studied, diffusion of substrate species into the braze alloy, results in the melting point of the braze alloy being raised. The figures in the previous section show that solidification of the droplet or pool edges begins fairly soon after the surface has been wetted. Often the bulk of the braze pool remains molten, but for a fixed temperature spreading is effectively prevented. The reason why small droplets and pool edges solidify before the 'bulk' of a braze pool, is because the former areas have a higher surface area to volume ratio. Hence for a constant rate of diffusion of substrate atoms into the braze, the effective concentration is greater at the pool edges and in small droplets. It has already been shown (34), and the results presented thus far verify, that temperature increase causes formerly solidified areas to remelt, and perhaps spread over the surface. The spreading (or the existence of fully molten equilibrium droplets) continues until the molten braze dissolves enough of the substrate to push its melting point above the brazing temperature. Figure 5.54 shows X-ray maps taken of the region shown by the micrograph (the area is incidentally visible in the sequence of figure 5.48). The maps were taken in the scanning Auger microscope having cooled the specimen, but not removed it from the vacuum chamber, and hence, due to the rapid cooling rate of the heating stage, the composition at the brazing temperature has been 'frozen-in' to the droplet. The maps show that iron is enriched at the edges of the pool, whilst gold is slightly depleted in these regions, the higher concentration of iron at the pool edge means that the region will have a higher melting point than the bulk of the pool, therefore explaining solidification of the pool edges at a fixed temperature. The micrograph also shows the 'Kirkendall edge' effect which was seen on several of the
Figure 5.54: X-ray maps showing interdiffusion of iron and gold on alloy 1.

Gold X-ray map  
Iron X-ray map

1000x 45° tilt-angle 08950 on Fe12CrSi
hot-stage and UHV oven specimens (see table 5.5). It is proposed that the effect is due to the large difference in diffusion coefficients in liquids and solids, the convection transport on the liquid side of the liquid/solid boundary (of braze metal on a substrate) is approximately 1000x more rapid than diffusion transport of species, resulting in an enhanced Kirkendall effect. The movement of oxide rafts over the surface of molten braze pools indicates that there is considerable stirring motion in the pool, which will assist erosion of the substrate. Substrate atoms are constantly dissolved into the bulk, and solidification at the liquid/solid interface is prevented by stirring, so this allows the braze alloy to 'sink in' to the substrate as more and more of it is dissolved. The braze volume will increase slightly at the expense of the substrate surface but this effect is very slight since the edges reflect the shallow depth to which the substrate has been eroded—showing the characteristic Kirkendall edge. Preferential dissolution of substrate atoms (eg. if one or more substrate species is insoluble or only slightly soluble in the braze whilst another is readily soluble) will result in the same effect. In this case however, atoms diffusing from the substrate beneath the interface after the surface atoms have dissolved into the liquid, will leave vacancies, which given time, can condense to form voids into which the braze metal then 'sinks'. The interalloying process results in a highly alloyed region at the braze/substrate interface, and indeed a gradation of composition through both braze and parent metals, and so rapid cooling (typical of the UHV oven and hot stage) will result in stresses being set up due to differences in thermal expansion. This generation of stresses on cooling is felt to be responsible for the formation of slip bands, and rumpling which was seen on some of the specimens (see table 5.5). In the case of Jethete however, the martensitic appearance of the alloy (and perhaps
the slip bands) is more likely to be due to the shear transformation associated with martensite formation, as the matrix is rapidly cooled from an FCC region to a BCC region.

The type of interalloying behaviour discussed so far is typical of low, to medium overheat temperatures, i.e. up to approximately 80-100°C above the braze alloy's melting point (950°C). The UHV oven runs indicate that for such overheats, the presence of silicon and/or chromium in the substrate appears to enhance spreading — namely that spreading occurs at a lower temperature than for the chromium or silicon free substrates, there are several possible reasons for this. In the case of silicon, its dissolution into the gold-nickel braze may result in a reduction of its melting point, or alternatively silicon enrichment at the metal/metal-oxide interface or at the surface (where the oxide has been fully removed), can result in a more easily detached interface or more easily wetted surface. For chromium, dissolution is likely to be deleterious (the braze's melting point would increase), but chromium enrichment at the interface or the surface, either of which could occur as a result of sequential reduction, might still result in a more easily wetted surface. This is because, whilst chromium dissolution encourages solidification, the degree to which the melting point is raised for a given uptake of chromium may be less than for other metals, or alternatively chromium may be taken up more slowly than other metals, so its enrichment at the interface could result in an overall slowing down of solidification. The other possibility is that a chromium enriched surface would have a higher surface energy than the unenriched surface, and this too would encourage formation of a low contact angle.
In addition to the apparently beneficial effects of chromium, and silicon, increasing the overheat temperature also enhances wetting and spreading - although very high overheats can result in unexpected, and potentially bad behaviour. The effect of temperature could be due to the surface energy of the liquid braze, decreasing with increasing temperature, but a decrease in liquid viscosity would also account for the enhanced spreading. The only low to medium overheat spreading effect which has not been discussed so far, is the presence of 'two-liquids' seen only on the surface of 08950 on specpure iron. Careful examination of the video record revealed a dark mass moving over the surface in a fluid manner (see figure 5.46), but it is unlikely that the movement is associated with the flow of immiscible liquids since the gold-nickel-iron phase diagram (figure 5.59) does not predict a miscibility gap. Analysis of the dark fluid is impossible because the effect is short lived. The iron surface is known to be oxide free, and whilst sulphur has segregated to its surface, the AES results of figure 5.55 show that sulphur is present on all surface prior to melting, and hence is unlikely to cause the effect. The fluid like behaviour of the material, however, could be achieved by a micro-particle mass moving under the influence of surface tension. The UHV oven experiments show that iron always exhibits tiny crystallites on its surface after heating in vacuo, and it is proposed that these numerous particulates could be responsible for the two-liquids effect. Whether the crystallites are formed during heating, or upon re-exposure of the oxide free surface to the atmosphere is not known, and therefore the cause of the 'two liquid' effect is still not certain. Although no miscibility gap is predicted by the phase diagram (figure 5.59) it is possible for a concentration gradient to exist within a liquid, consider for example the formation of dense solution at the bottom of a beaker in which a substance is dissolving -
Figure 5. Spectra showing sulphur on the surface of both braze and substrate prior to melting.

Surface of Fe20Cr at 800°C (prior to melting)

Surface of Au18Ni at 800°C (prior to melting)
naturally or electrochemically. If this principle is applied to OB950 dissolving iron, then an explanation of the 'two liquids' effect, in accordance with the phase diagram may be postulated. Low density iron-rich material formed as iron dissolves into the gold at the liquid/solid interface, could be swept to the surface by swirling due to a convection (or Marangoni(136)) effect. Once at the surface the low density iron-rich liquid would show surface tension effects since the surface energy of the iron and gold rich liquids would be different. Furthermore, since the emissivity of iron is much less than that of gold, the iron-rich areas would appear darker. The effect eventually disappears as a result of convection mixing and diffusion.

The effects discussed so far have been typical of low to medium overheat temperature behaviour (up to 80-100°C above the braze alloy's melting point). At higher overheat temperatures, the braze alloy, which was essentially single phase at the lower temperatures, begins to form separate phases. The figures from the UHV oven runs show that the gross separation into a dark two-phase material, and a light single-phases material, is confined to OB950 melted on substrates containing both iron and chromium, and that the effect is often associated with considerably enhanced spreading. Figure 5.53 shows the gradual phase separation with OB950 on Fe20Cr - the fact that the effect is more marked, and occurs at the lowest overheat temperature on Fe20Cr, and that it is only noted on the chromium containing alloys, implies that the presence of chromium results in the phase separation. The phase separation effect is associated with interalloying, and so experiment BDS24 was devised to examine it in greater detail. The aim of the experiment was to heat the braze to a fixed temperature above its melting point, to allow interdiffusion and edge solidification to take place,
and then to 'freeze-in' the composition by rapid cooling to 10-20°C below the melting point. The bulk and surface composition at various points on the surface could then be found using EDXA and AES. The process was then repeated, heating to above the alloy's new, higher, melting point, allowing wetting, spreading, and edge solidification to occur again, and then re-freezing and re-analysing. Four melts were carried out in all, and the appearance of the frozen alloy after each melt, and indicators showing at which points EDXA analyses were taken, are shown in figure 5.56. Semi quantitative data from these, and similar regions are given by table 5.6. The data were calculated using the analyses from the Fe20Cr and Au18Ni as 'standards' from which relative concentrations could be calculated. It was decided not to carry out a full 'ZAF' correction for several reasons; no standards were available to enable absorption coefficients or sensitivity factors to be determined, the dead-time correction of the detector is not provided, the 10KeV beam barely-excites some of the elements studied and hence accurate quantification is not wholly valid, and most importantly, the specimens were neither flat so the take off angle could not be determined, nor homogeneous meaning that the application of a ZAF correction would be dubious. Instead, analyses on the 'pure' Fe20Cr and Au18Ni were used to provide relative sensitivity factors, taking their compositions to be accurate and the samples homogeneous. Consequently the results should not be taken as being strictly quantitative, rather that they provide a semi-quantitative means of assessing the overall manner in which the concentrations in braze droplets and pools change with temperature and position in the droplet or pool.
Table 5.6 Weight percentage values from the areas in figure 5.56

<table>
<thead>
<tr>
<th>Position</th>
<th>%Gold</th>
<th>%Nickel</th>
<th>%Chromium</th>
<th>%Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - substrate</td>
<td>-</td>
<td>-</td>
<td>20.00</td>
<td>80.00</td>
</tr>
<tr>
<td>B - pool edge</td>
<td>75.17</td>
<td>15.71</td>
<td>1.33</td>
<td>7.79</td>
</tr>
<tr>
<td>C - pool centre</td>
<td>86.22</td>
<td>12.70</td>
<td>0.11</td>
<td>0.79</td>
</tr>
<tr>
<td>D - pool outer edge</td>
<td>37.65</td>
<td>33.10</td>
<td>4.90</td>
<td>24.35</td>
</tr>
<tr>
<td>E - pool edge</td>
<td>83.53</td>
<td>10.48</td>
<td>1.27</td>
<td>4.72</td>
</tr>
<tr>
<td>F - pool centre</td>
<td>82.70</td>
<td>13.20</td>
<td>0.76</td>
<td>3.34</td>
</tr>
<tr>
<td>G - substrate</td>
<td>-</td>
<td>-</td>
<td>20.00</td>
<td>80.00</td>
</tr>
<tr>
<td>H - pool edge</td>
<td>83.83</td>
<td>5.12</td>
<td>2.18</td>
<td>8.85</td>
</tr>
<tr>
<td>I - pool centre</td>
<td>75.77</td>
<td>14.22</td>
<td>2.28</td>
<td>7.73</td>
</tr>
<tr>
<td>J - substrate</td>
<td>-</td>
<td>-</td>
<td>20.00</td>
<td>80.00</td>
</tr>
<tr>
<td>K - bright edge</td>
<td>79.03</td>
<td>0.00</td>
<td>5.23</td>
<td>15.74</td>
</tr>
<tr>
<td>*bright edge</td>
<td>80.16</td>
<td>0.00</td>
<td>5.36</td>
<td>14.48</td>
</tr>
<tr>
<td>*bright edge</td>
<td>79.39</td>
<td>0.00</td>
<td>5.56</td>
<td>15.07</td>
</tr>
<tr>
<td>L - dark phase</td>
<td>42.94</td>
<td>9.98</td>
<td>8.41</td>
<td>38.65</td>
</tr>
<tr>
<td>*dark phase</td>
<td>14.12</td>
<td>10.21</td>
<td>12.89</td>
<td>62.78</td>
</tr>
<tr>
<td>*dark phase</td>
<td>13.03</td>
<td>14.62</td>
<td>12.27</td>
<td>60.08</td>
</tr>
<tr>
<td>Orobraze 950</td>
<td>82.00</td>
<td>18.00</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* X-ray spectrum acquired at 15 KeV - all other spectra at 10 KeV

Careful observations during the experiment, and of videos from other O950 on Fe20Cr experiments which showed the phase separation, revealed that, as the UHV oven micrographs implied, the dark phase formed immobile solid 'islands' around which the bright phase could flow freely. The dark islands always formed a short distance behind the advancing liquid front, although when very rapid spreading occurred the areas of the light single phase material were much narrower and the darker two-phase material was seen behind the bright phase as a solid 'sheet' rather than as isolated islands. The analyses of the areas shown in figure 5.56 and the data from these areas shown in table 5.6, clearly indicate that the light areas are gold rich (with respect to the dark areas), and contain little or no nickel, its place being taken by iron.
and chromium in an approximate 80:20 ratio. The dark areas contain less gold, and hence are nickel-rich with respect to the light phase, they are also strongly enriched in iron, and contain fairly large amounts of chromium. It is evident that not only does the gold rich phase have a higher melting point than the dark two-phase material (it is liquid whereas the dark phase is solid at a given temperature), but that it wets the substrate surface very well. It is likely therefore that the gold rich phase is responsible for the 'pre-wetting' which was seen on some systems. In addition to this, it is probably responsible for the 'disrupted edge' effect seen on the Fe20Cr and to a lesser extent some of the other chromium containing alloys. It is proposed that the 'halo' seen preceding the spreading braze pool at fairly high overheat temperatures, is due to a film of the highly fluid gold rich phase. The thin film will of course alloy rapidly with the substrate, but there is always an enormous reservoir of fresh gold from the braze pool. On cooling the gold film de-wets, leaving only an alloyed region around the periphery of the braze pool - the disrupted edge. This model would account for the results from Auger and X-ray spectra taken from the disrupted edge region. Auger electron spectroscopy reveals no oxygen at the edge, or on the substrate, thereby dismissing suboxide spreading as a possibility, and shows only iron and chromium peaks. X-ray spectra from the same area however show iron, chromium, and gold. The results are at first sight contradictory, until the low sensitivity of AES, in the pulse-counted mode, for gold is taken into account - the low energy peak cannot be separated from the 'true secondaries' contributing to the background, and the high energy gold peaks are only very feeble even on pure gold. The sensitivity of X-ray spectroscopy for gold however, is very high, a significant peak can be obtained from even the lowest gold concentrations. It is worth mentioning that the width of the disrupted
edge (10-20 microns) is sufficient to ensure that the gold signal does not originate from gold in the main pool being excited. The Auger and X-ray maps of figures 5.57 and 5.58 illustrate the final condition of a braze pool that has spread, and has separated into phases. The Auger maps show that the entire surface is covered by sulphur (point analyses indicate monolayer coverage), and through this thin overlayer iron is seen to be concentrated on the surface of the substrate, and on the dark regions, whereas it is less abundant, but nonetheless present on the surface of the light phase. The distribution of chromium is similar, but the signal is generally less intense, hence the noisy image. Gold is seen to be enriched in the light phase regions, and it is just detected around the periphery of the pool on the disrupted edge. The X-ray maps (figure 5.58) show the enrichment of gold in the light phase, and also suggest that chromium may be enriched in these areas too. The dark phase areas on the other hand are clearly enriched in iron and nickel, although gold and chromium are still detected. Both sets of maps support the point analysis data, and strengthen the argument for the spreading process which has been proposed.

The discussion so far has highlighted the importance of interalloying in wetting and spreading, and the way in which it is responsible for the cessation of spreading due to solidification, and for the separation of the braze metal into separate phases. It is therefore worthwhile to consider the equilibrium of the system more carefully. The gold/nickel/iron diagram of Koster and Ulrich\(^{41}\) has been used to demonstrate why solidification occurs at a fixed overheat temperature\(^{34}\), but calculation of the liquidus and solidus of the system by Saunders\(^{135}\) from thermodynamic data allows more informed conclusions to be drawn. The calculated isothermal sections are shown by
2000x 0° tilt-angle OB950 on Fe200r

Gold Auger map

Iron Auger map

Chromium Auger map

Sulphur Auger map
Figure 5.58: X-ray maps showing phase separation in 08950 on Fe20Cr (air-formed film)
Isothermal sections showing the equilibrium between gold nickel and iron at various temperatures.

(The upper contour is the solidus, above it the material is solid, below it solid is in equilibrium with liquid until the lower contour - the liquidus, is crossed. Below the liquidus the alloy is wholly liquid)
All phases are FCC.
Examination of the diagram immediately confirms the previous work\(^{(34)}\) showing that for only small additions of iron to the 'eutectic' composition (Au18Ni) the liquidus can be raised by a significant amount, which will result in solidification. The main improvement of the new diagram, compared with the original by Koster and Ulrich, is that a freezing range is predicted, and this, in turn, allows the formation of phases, and their approximate compositions to be determined. To illustrate how heating stage analysis and observation can be related to the equilibrium phase diagram, consider figures 5.56 and 5.59, and table 5.6. Photo 1 of figure 5.56 shows the braze pool after heating to 970°C (maximum) then cooling by twenty degrees or so for analysis. Analysis A shows the unchanged substrate composition, whereas B, and C show that iron (and to a lesser extent chromium) are enriched at the pool edges, but only present at very low concentrations in the centre of the pool. The edge was seen to solidify at the test temperature, and examination of the equilibrium diagrams puts the compositions at the edges in the 'solid' region for the approximate values calculated from the X-ray data. The pool centre on the other hand contains so little iron, that it is able to remain liquid. Moving on to photo 2, analyses from D and E show iron enrichment and solidification whilst F, with less iron, remained liquid at the test temperature. Analysis D shows very significant take-up of iron and chromium, although in this instance iron and chromium from the substrate are probably being detected through the thin braze alloy overlayer, giving a false impression of the degree of uptake of substrate components.
Photos 3 and 4, and their analyses should be considered together, since the compositional evidence suggests that photo 3 represents the composition immediately before gross phase separation (photo 4). Analyses H and I (photo 3) show that the outer edge of the pool is gold rich compared with the central region (which is therefore nickel enriched) whilst the iron and chromium levels are roughly even. The micrograph represents a region which was spreading fairly quickly (albeit in small distinct steps) immediately prior to cooling, and hence cannot be considered in quite the same way as the effectively static conditions of photos 1 and 2. In this instance the phase composition of the alloy must be considered rather more carefully. Figure 5.59 shows that if the alloy contains more than ~10% nickel, then upon cooling through a 'pasty' freezing range (i.e. the gap between the liquidus and solidus) a nickel-rich solid will be in equilibrium with a gold-rich liquid. The conditions, however, are not static, and hence whilst the nickel-rich solid is immobile, the gold-rich liquid is still able to spread over the surface, and it will therefore leave the solid phase behind. The result is that the fluid gold-rich phase becomes concentrated at the edges of the pool, leaving nickel-rich material at the pool centre. Photo 4 and analyses K and L (and also spectra taken at 15KeV on similar regions) show the eventual result of the process which began in photo 3. Photo 3 showed no evidence of gross phase separation, merely a change in concentration between the pool edges and the pool centre (in effect the solid present acted to slow the spreading of the nickel rich areas by forming a kind of slurry). Photo 4 however, shows that the solid phase is fully precipitated (and presumably fused to the substrate), and heavily iron and nickel enriched. This enables the fluid gold (gold-rich phase) to flow around it and over the surface. As the fluid gold spreads it inevitably picks up more iron and chromium, which in turn leads to
more solid phase precipitation. The very rapid spreading seen in some of
the hot-stage experiments (and viewed on some of the cooled UHV oven
experiments) is also the result of phase separation. In this instance
the fluid gold spreads quickly over the surface in a thin layer, which
means that alloying not only happens rapidly, but also has a gross
effect. The conditions rapidly reach the stage where the second phase
may be precipitated, and this occurs laying down the nickel rich solid
as a sheet, allowing more fluid gold to spread over the surface.

The data which has been acquired from the heating stage studies and
from the post mortem examination of brazed samples (UHV oven runs), in
conjunction with examination of the relevant equilibrium phase diagrams,
allows the various processes involved in vacuum brazing to be not only
observed, but in most cases it is also possible to determine the
mechanisms involved. The present work is in accord with previous studies,
but goes further to provide a greater understanding of previously
unknown mechanisms and processes.

The various effects mentioned in this discussion are all liable to
be encountered during actual brazing processes, and in most instances,
poor control of brazing conditions will result in badly made joints. If
for example the surfaces to be joined are covered in oxide, then wetting
will be prevented until the oxide has been either penetrated or removed,
indeed poor vacuum conditions during heating, soaking, or brazing might
allow oxide growth which will add to the difficulty of producing a sound
joint. Retained oxide could have particularly serious consequences if
one side of a joint were wetted (the oxide having been penetrated or
removed) whilst the other were not. In such a circumstance the problem
is compounded by interalloying, because the side in contact with the
substrate may result in solidification (due to substrate element pick up) before the second half of the joint has wetted - the net result being no joint at all! It is generally accepted that some interalloying is inevitable during brazing, but if the extent is too large then there are several problems which can arise, for example; change of workpiece dimensions or joint gap size, change of brazing alloy's physical and mechanical properties (which can be good or bad), and solidification at the brazing temperature. All of these problems are made worse by increasing the temperature, simply because the potential for interalloying is greater. It is evident therefore, that this work, whilst a scientific study under somewhat unreal conditions (e.g., the half-joint geometry, and in UHV) has a direct relevance to actual vacuum brazing practise, and has served to tie-down several of the facets of the vacuum brazing process which were previously uncomprehended, or at worst unnoticed or ignored. Perhaps the 'bottom line' of the work is to point out that Orobraze 950 is generally regarded as an excellent brazing alloy, its widespread use being prevented only by price. This means that the problems found with this alloy are liable to be worse with other alloys, underlining the importance of to understanding the processes and mechanisms involved with vacuum brazing, to ensure the production of a sound brazed joint.
The work presented in this thesis shows that the use of Auger electron and X-ray spectroscopies, both at ambient and elevated temperatures, and in conjunction with ambient and elevated temperature electron optical observations, are valuable and effective techniques for the observation of vacuum brazing processes, and the determination of their mechanisms.

Hot-stage Auger electron and energy dispersive X-ray spectroscopy have provided invaluable results, and it has been demonstrated that careful calibration and setting-up of the spectrometer enables high spatial and energy resolutions to be realised during spectroscopy for realistic analytical times. The use of a high resolution scanning Auger microscope with a heating stage illustrates that it is possible to observe brazing at high temperatures, with good spatial resolution, in-situ, and in vacuo, with the capacity for analysis, although it is more or less essential to employ a video recorder to capture short-lived events despite the difficulty in producing high quality images from the video record.

Post-mortem examination of brazing alloys melted on substrates in an ultra-high vacuum oven provides a fairly rapid means for examining a wide range of brazing alloy and substrate combinations at different temperatures, and for different substrate surface preparations. Data acquired from such studies enables trends to be found, and different features, with their conditions of occurrence to be established, thereby allowing a more informed approached to time-consuming and difficult mechanistic studies using hot-stage microscopy and
The combination of the techniques mentioned above, all of which use the easy to examine 'half-joint' type of specimen, has allowed conclusions to be drawn regarding the nature of processes involved with vacuum brazing using Orobraze 950. The brazing process is a two-stage process involving first oxide penetration and then wetting and spreading. The second process is influenced by both retained oxide, and interdiffusion between the parent and substrate species.

This study has shown that Orobraze 950 never wets the surface oxide, and that this otherwise inpenetrable layer, is rendered penetrable by reduction processes associated with both the oxide composition and the vacuum conditions. In conditions of low oxygen partial pressure for example under a braze pool, more stable oxides reduce less stable ones, eventually resulting in a fine, particulate, and therefore penetrable, oxide. In UHV conditions the presence of carbon in an effectively leak-free system, will result in oxygen partial pressures low enough to totally reduce all but the most stable oxides.

Once the oxide has been penetrated, either by sequential reduction due to low local oxygen pressures and a mixture of stable and unstable oxides, or by the atmosphere, or by a combination of the two, spreading takes place along the metal/metal-oxide interface - a suboxide route. Any oxide left on the surface represents an impediment to wetting and spreading either by preventing wetting until penetration occurs, or by exerting a resistive mechanical force against the liquid braze reducing its ability to wet or spread over the surface. Once the oxide has been fully displaced, it floats on the surface of the liquid braze.
metal - in a joint this would result in its being flushed out of the gap.

As soon as the liquid braze metal is in contact with the substrate surface, a two-way interdiffusion of braze and parent metal species takes place (although in most instances braze metal diffusion into the substrate is slow compared with the diffusion of substrate atoms into the liquid, so the former may be disregarded). Interalloying represents a limiting factor to the degree of spreading, since the high surface contact area to volume ratio in small droplets, or at the edge of braze pools, results in solidification due to an increase in the alloy's melting point, and therefore the cessation of wetting or spreading. Very extensive interalloying may result in multiple phase formation which changes not only the wetting and spreading properties of the braze alloy, but also its mechanical properties. Interalloying inevitably causes erosion of the substrate, and whilst this can be beneficial (e.g. enhanced corrosion resistance), it effectively leads to a change in size of the workpiece, and the joint-gap.
Preliminary data processing for optimisation of resolution work

Peak net integral (shaded)

Signal

Signal at half maximum

Kinetic energy (eV)

Peak Position (eV) - Value of (3) on the Kinetic energy scale

Net Integral (counts) - Shown cross-hatched on the diagram, the Link system simply calculates the integral between points (1) and (2) using a straight line background. For silver the net integral of the doublet was split proportionally to the two peak heights.

Background (counts) - \( \frac{(1) + (2)}{2} \)

Signal (counts) - \( \frac{(3) - (1) + (2)}{2} \)

Noise (counts) - \( (4) - (5) \)

Signal at half maximum (counts) - \( \frac{(signal) + background}{2} \) (this value was then used to find points (6) and (7))

Full width at half maximum (eV) - \( (6) - (7) \)

Signal to noise ratio - \( \frac{signal}{noise} \)

Signal to background ratio - \( \frac{signal}{background} \)

Count-time (seconds) - From run-time statistics

Count-rate (counts per sec) - \( \frac{Net \ integral}{count-time} \)

Specimen Current (nA) - From digital multimeter on MA500

Pass energy (eV) - CAE reads direct, CRR = peak position = \( E_{pass} \) retard ratio
APPENDIX 2  Method for calculating the oxygen partial pressure in the presence of carbon.

Consider the equilibrium between the following two reactions:

I  \( 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \) \( \quad k_I = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}} \cdot P_{\text{O}_2}} \)

II  \( \text{C} + \text{CO}_2 = 2\text{CO} \) \( \quad k_{II} = \frac{P_{\text{CO}}^2}{aC \cdot P_{\text{CO}_2}} \)

If the standard free energy changes for equations I and II are given by \( \Delta G^0_I \) and \( \Delta G^0_{II} \) then:

\[
\begin{align*}
  k_I &= \exp\left(-\frac{\Delta G^0_I}{T \times 2.303}\right) \quad \text{and} \quad k_{II} = \exp\left(-\frac{\Delta G^0_{II}}{T \times 2.303}\right)
\end{align*}
\]

For a constant total pressure \( (P_t) \) the following is true:

\[
P_t = P_{\text{CO}} + P_{\text{CO}_2} + P_{\text{O}_2}
\]

From II : \( P_{\text{CO}_2} = \frac{P_{\text{CO}}^2}{aC \cdot k_{II}} \)

and From I : \( P_{\text{CO}_2} = \frac{P_{\text{CO}}^2}{P_{\text{CO} \cdot k_I}} = \frac{P_{\text{CO}}^2}{aC \cdot k_{II}} \)

\[
\begin{align*}
   \text{therefore} \quad P_t &= P_{\text{CO}} + \frac{P_{\text{CO}}^2}{aC \cdot k_{II}} + \frac{P_{\text{CO}}^2}{aC \cdot k_{II} \cdot k_I} = P_{\text{CO}} + P_{\text{CO}} \quad 1 \quad + \quad 1 \\
   \text{let} \quad P_t &= C \\
   \text{and} \quad P_{\text{CO}} &= B \\
   \text{and} \quad A_I = \frac{1}{aC \cdot k_{II}} \quad \text{and} \quad A_{II} = \frac{1}{aC \cdot k_{II} \cdot k_I} \quad \text{and} \quad A = A_I + A_{II}
\end{align*}
\]
then : \[ P_{CO} = \frac{-B + \sqrt{B^2 - 4AC}}{2A} \]

and \[ P_{CO_2} = P_{CO}^2 A_I \]

and \[ P_{O_2} = P_{CO}^2 A_{II} \]

Therefore, knowing \( k_I \) and \( k_{II} \) (from free energy calculations) as a function of temperature, then for a fixed base pressure, and given values of carbon activity the carbon monoxide partial pressure may be derived, and from this the partial pressures for oxygen and carbon dioxide.
Acknowledgements

I would like to thank Johnson Matthey Metals PLC for sponsoring this work, for their provision of the precious metal brazes and specpure substrate materials, and for technical details about industrial brazing practice. I am indebted to Doctors John F. Watts and Donald R. Baer for their valuable help and support, and comments when proof-reading parts of this thesis. I also wish to extend my thanks to Professor James E. Castle for initiating this work, for his encouragement, supervision, and frequent helpful suggestions. I am grateful to the staff and students who made my time at the department of Materials Science and Engineering so enjoyable and profitable, finally I wish to thank Mrs. Jackie Larmour for typing many of the more difficult Tables and equations, and for her valued assistance with the 'last-minute jobs' at Surrey which I was unable to carry out after having started work in London.

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