A STUDY OF STRESS CORROSION IN ALLOYS OF ORTHOPAEDIC INTEREST

by

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of Doctor of Philosophy

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SUMMARY

A number of failed surgical implants have been examined and a brittle type of fracture shown to be a major cause of failure. It was not possible to establish unequivocally the mechanism of fracture from these examinations but the evidence suggested the importance of mechano-chemical effects.

Static stress corrosion tests on both smooth and notched specimens of currently used and potentially useful implant materials were performed. The materials tested being iron, cobalt and titanium based alloys. Tests were run for long periods (up to 10,000 hrs) and elevated temperature used as an accelerant. These tests showed that stress corrosion was not a major cause of failure in present implant devices.

The problem of predicting the likelihood of SCC failure in very long term implantation eg up to 50 years for a hip joint has been investigated using a dynamic strain test. In this test specimens were strained at a constant rate in 0.17M NaCl solution; the potential of the specimen was controlled and the corrosion current flowing during the test monitored. Stress corrosion susceptibility was revealed by a reduction in mechanical properties in the stress corrosion environment compared with those in air.

Data obtained on 316S16 stainless steel have been interpreted in terms of a slip-step dissolution model. Extrapolation of susceptibility to long exposure times has been made on a semiquantitative basis. The theory predicts that 316S16 should be free from SCC in implant conditions for the periods of use envisaged.

Slight susceptibility has been observed in cobalt based alloys which was dependent on the pre-existence of a stress concentrator eg a notch root. A model for cracking based on grain boundary attack has been developed for Co-Cr-Mo and metallurgical treatments to minimise cracking suggested.

The effect of strain-rate, environment, alloy structure and alloy hydrogen content on susceptibility of titanium alloys to SCC was investigated and a mechanism based on slip step dissolution and titanium halide hydrolysis postulated. The development of a critical crack tip deformation rate has
been shown to be the most important mechanical parameter. Alloy structure, environment composition and alloy hydrogen content are also significant, the effect of hydrogen being via its influence on the stability of the oxide film rather than any bulk metallurgical effect. Using the model, heat treatment conditions which may induce susceptibility have been predicted for the commercially important alloy Ti-6Al-4V. The deleterious effect of these conditions has been shown experimentally and recommendations made for their avoidance during implant manufacture.
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INTRODUCTION

1.1 The Surgical Implant Problem

Metallic surgical implants may fail in service. Although the incidence of failure is low the cost in terms of patient suffering and hospital time is significant. Failure may be due to corrosion which releases metallic ions into the body causing tissue reaction and necessitating removal of the device. Alternatively mechanical failure may occur where the implant fails to support the stresses imposed upon it. This may take the form of bending, or more seriously sudden fracture.

Some metals in specific environments are susceptible to failure by the combined action of stress and corrosion. As a result cracks may form and propagate at stresses much lower than those causing failure in the absence of the corrosive environment; this phenomenon is known as stress corrosion cracking (SCC). Chloride containing media are known to cause SCC in some alloys of the type used for surgical implants. There is a possibility therefore that implants in the dilute saline body environment may fail by stress corrosion cracking.

1.2 Scope of the Current Research

As part of a programme of biomedical research carried out at AWRE under the sponsorship of The Department of Health and Social Security a contract was placed with the Materials Department to investigate the causes of surgical implant failure.

Initially a number of failed implants were metallurgically examined. As a result of observations of these failures various programmes of laboratory study were undertaken.

This thesis reports the work performed on stress corrosion of implant materials.

1.3 Examination of Failed Implants

Described below is an examination of seven failed surgical implants. Implants which had fractured were often chosen for investigation because this form of catastrophic failure seemed potentially the most serious. A more detailed report of these and other examinations can be found in references 1 and 2.

Fracture and other surfaces were examined by scanning electron microscopy (SEM) or optical microscopy (OM). Metallographic sections were examined by optical microscopy.
1.3.1 Vitallium Eggers Plate

The Eggers plate (figure 1) was fractured at opposite ends of the same slot. The plate was also bent laterally by about 15°. Screw markings on the fractured slot edges suggested that the screws were placed near to the slot centre. The counter-sunk portions of the screw heads acted as wedges exerting a much greater bending moment on the sides of the plate in the fractured slot than that caused by the screws in the unbroken slot.

Figure 1a shows the surface of the fracture close to the end of the plate, changes in fracture topography were observed across the fracture as shown in the figure. Figures 1b and 1c show these areas in greater detail and are probably typical of different grains.

Optical metallography near the fracture showed considerable amounts of porosity and inclusions (figure 1d). Ghost dendrites were visible in slightly unfocussed specimens. The fracture path was transgranular and the grain size generally very large (2-3 mm dia.).

The other fracture in this implant, close to the centre of the plate, is shown in figure 1e. The fracture was mainly by cleavage, although at the bottom right hand side there was an area of intergranular fracture. In this region the detail of the fracture topography indicated propagation from bottom to top. The central area appeared to be cleavage steps with considerable quantities of non-metallic material which may have been corrosion product or wear debris (figure 1f). Analysis (Table 1) has shown that the material satisfied B.S.3331: 1962 and 1968.

1.3.2 Stainless Steel (EN58J) Steinmann Intramedullary Pin

The pin was of "clover leaf" section and was 252mm long to the fracture (figure 2). The fracture surface showed "clam shell" markings indicative of fatigue failure which originated from the topmost point in figure 2a from a surface notch.

Analysis (Table 3) showed that the alloy was as specified by BS.3531: 1962 and 1968.

This failure was a direct result of fatigue initiated from a notched surface. This damage may have occurred during surgical insertion but scratches running around the pin suggested that many were manufacturing defects.

1.3.3 Titanium Intertrochanteric Nail and Plate Assembly

The nail (a type of pin used to repair hip fractures) is shown in figure 3, fracture had occurred across the slot at the nail end of the plate. A detailed view is shown in figure 3a. The rim at the top right hand fracture face was crossed by a series of steps, one of which has extended into the crack shown in figure 3b. Figure 3c shows a region close to the left hand rim of figure 3a of ductile tear fracture, the rest of the fracture surface was mainly cleavage (figure 3d).
Optical metallography revealed subsidiary transgranular cracking associated with the main fracture and revealed a two phase structure (figure 3e) abnormal for commercially pure titanium.

Analysis (Table 2) showed that the iron content was above specification but none of the alloying additions used to stabilise the β phase in commercially available titanium alloys were detected.

The two phase acicular structure had probably been produced by hot working titanium in the β field followed by subsequent working in the α+β field and slow cooling. This is against normal commercial practice which recommends that the forging temperature should not be above the α+β/β transus because the structures produced by β forming lead to poor mechanical properties. Thus it seems probable that the failure of this implant was largely due to bad forging practice.

1.3.4 Titanium Jewett Nail and Plate

The implant fractured across the junction between the nail and plate, the fracture embracing part of the machined groove around the threaded hole, figure 4. All four bone screws were broken and abrasion markings around the countersinks of the screw holes indicated that the screws were not inserted normally to the plate.

The initiation of failure appears to have been in a damaged region in the groove. On the groove close to and pointing directly at the damaged region, was a deep score mark, figure 4a. A crack running along the groove and across the fracture is shown in figure 4b, figure 4c shows the fracture surface close to these cracks. The fracture followed the groove and then moved away from it to follow a path through the thinnest section. Subsidiary cracking was also observed in the area of the groove.

Analysis (Table 2) of the material showed that the alloy met BS 3531 (1962 & 1968).

The failure of this implant appears to have been initiated by the failure of the screws which led to increased stressing at the junction of the nail and plate. This region was both the most highly stressed and the thinnest section of the implant. Brittle failure occurred at the nail plate junction, initiated by cracks introduced into the material around the groove by damage occurring probably during insertion.

1.3.5 Vitallium Screw

This screw failed on insertion about 6 mm from the screw head. Figure 5a shows the fracture surface to be brittle and predominantly intergranular. The elongated (columnar) shape of the grain together with porosity at the screw core is typical of a cast structure in this material. Optical metallography showed a complete grain boundary network of lamellar carbide precipitate, and precipitation within the grains (figure 5b).
Particles of refractory material picked up from the mould during casting were also present. The fracture follows the path of the grain boundary precipitate. Regions of porosity were also observed along the fracture path.

Chemical analysis, Table 1, showed that carbon at 0.48% exceeded the 0.35% maximum of the revised specification BS 3531, 1968.

The main structural features of this screw were the grain boundary precipitate and central porosity. The former can be attributed to reheating the cast material close to the melting point causing localised grainboundary melting; the latter to poor casting technique. The failure of the screw was due to the application of too high a stress to a material weakened by grain boundary precipitation and casting defects.

1.3.6 Jewett nail

The Jewett nail was a two piece construction, the plate being bent over at its shaft end and the two parts arc welded together so that the head of the shaft was formed from the plate. No screw was used in hole 4.

Corrosion was observed in the countersinks of holes Nos. 1 and 3, no corrosion was observed on the screws.

Analysis of both the nail shaft and plate, Table 1, showed the material to be within the BS 3531 : 1962 specification. The shaft was about 209 HV and the plate about 230 HV hardness (equivalent to about 5% reduction of area by cold work). Both plate and nail were softened to 150-160 HV in the region of the weld, despite this the failure occurred in the harder and therefore stronger region of the plate.

The plate fractured across screw hole 4, i.e. the hole in which no screw was used. Figure 6 shows one of the fracture surfaces the abraded areas indicate that the two fracture surfaces had rubbed together after fracture. A section through the fracture (figure 6b) showed that it occurred with little deformation until the final ductile tearing through the concave side of the plate. A crack was observed in the angle between the plate and
the shaft in the central region of the plate and lying normal to the length of the plate. Figure 6c is a section through this crack which was transgranular with a slight tendency to branch.

Figure 6d shows the crack running across the upper surface of the plate with deformation markings on the plate surface and corrosion debris along the path of the crack. Figure 6c shows part of the fracture surface in which the abraded area is shown in contrast to the striated structure of the original fracture surface.

Figure 6f is a section through the head of the shaft parallel to its length and half way across its diameter. The shaft was threaded internally and the plate joined to the shaft by the welded region. Weld penetration was only about 30% on one side and zero on the other, the weld having "run out" to be completed in the shaft rather than at the shaft-plate interface.

Abraided areas and a striated surface indicated a fatigue failure in a region of reduced section where the stresses were at a maximum. There was evidence to suggest that corrosion was active in the region of the fracture: corrosion pits were observed on the screw hole countersink which could have initiated a fatigue crack and corrosion products were associated with the subsidiary crack. The subsidiary crack was transgranular with some tendency to branch, i.e., characteristic of a stress corrosion crack in stainless steel.

The evidence was therefore that a stress corrosion or corrosion-fatigue mechanism was operative in causing the failure of the Jewett nail. That failure occurred in the plate rather than at the very poor weld can only be explained by the presence of a relatively low stress in the region of the weld. This is confirmed by the position of the Jewett nail in the femur observed on the X-ray photographs of the implant in the patient.

Venable Plate

The device is shown in figure 7. The screws from the plate, numbered 1–6 (figure 7a) are adjacent to the holes into which they were inserted. The plate was cracked from the edge of the plate to screw hole 3. Severe pitting was observed around holes 2, 3 and 5 and to a lesser extent around holes 1 and 6. This corrosion was mainly associated with the countersink region of the holes but extended to the concave face of the plate around holes 2 and 5. Corrosion was also observed beneath the heads of screws 2, 3, 5 and 6, figure 7a, and on one side of the head of screw 3.

Figure 7b shows the fracture surface after the plate had been sawn in two and figure 7c shows in more detail the striated structure of the
fracture surface. The final parting of the two fracture faces occurred near the bottom of the screw hole by ductile tearing when the section was reduced. (figure 7d).

The structure produced by intense attack in the crevice conditions between the screw head and plate countersink is shown in figure 7e.

1.3.8 Conclusion

The examination of these and other failed implants led to the following conclusions:

(i) Corrosion was often present, particularly in crevices and regions of contact of two components. This corrosion may be attributed to the low pH developed in the occluded corrosion cell in a crevice and/or to fretting removing the protective oxide film. The deposits observed in such regions may be metallic wear debris, oxide film wear debris, adventitious organic material or true corrosion product.

(ii) Defects caused by poor manufacture were often a cause of failure.

(iii) Defective surgical technique may contribute to failure. In this context a defective surgical technique is one which is deleterious to the implant.

(iv) Fractures and cracking usually occur with an absence of macroscopic and often microscopic ductility, this suggests corrosion fatigue or stress corrosion as a cause of failure. Impact fracture may however be a possible failure mode particularly for the low ductility cast alloy Vitallium.

Although these conclusions were drawn on the basis of observations on a limited number of implants they have been substantiated by a large amount of subsequent work by Hughes and Jordan [3, 4] at AWPRE and by other authors [5, 6, 7]. A further important mode of failure has been observed in this subsequent work: torsional failure of screws during insertion or removal. This appears to be the only type of implant failure commonly due to simple overstressing.

The correction of defects due to poor manufacturing or poor surgical technique was considered to be outside the scope of any laboratory investigation. Failure due to these causes are a large part of the total number of failures however, and efforts were made to bring to the attention of surgeons and manufacturers the existence of these defects and ways of avoiding them. The deleterious effect of such phenomena as sensitization
at welds, high inclusion content, poor surface finish and highly localised plastic deformation is metallurgically well recognised and means of avoidance well known. Effort was concentrated on less well understood problems where the solutions were not immediately obvious. Programmes of laboratory work were begun on:

(a) Electrochemical corrosion studies of implant materials.
(b) Insertion characteristics and failure of surgical screws.
(c) Impact properties of implant materials.
(d) Corrosion fatigue properties of implant materials.
(e) Stress corrosion properties of implant materials.

Separate programmes of work were necessary on stress corrosion and corrosion fatigue because it was not possible from fracture examination to attribute failure unequivocally to one or the other of these mechanisms. It is possible that either mechanism may operate according to the mode of stressing. Alternatively in the complicated and varied stress situation existing in service different parts of the fracture may propagate by different mechanisms. A final consideration is that in the very low cycle fatigue regime applicable to implants subjected to varying stresses due to walking, etc, a fracture mechanism intermediate between the high cycle corrosion fatigue and static stress corrosion normally studied in the laboratory may be applicable.

1.3.9 References


### TABLE 1 Analyses of Vitallium Implants

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### TABLE 2 Analysis of Titanium Implants

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</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Jewett Nail (Shaft)</td>
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<td>19.4</td>
<td>8.9</td>
<td>2.9</td>
<td>0.53</td>
<td>0.88</td>
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<td>6</td>
<td>Jewett Nail (Plate)</td>
<td>0.057</td>
<td>19.4</td>
<td>10.8</td>
<td>2.7</td>
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<td>1.65</td>
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<td>Venable Plate</td>
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<td>20.0</td>
<td>8.1</td>
<td>0.2</td>
<td>0.45</td>
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<td>0.072</td>
<td>18.5</td>
<td>9.6</td>
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Figure 3
Intertrochanteric Nail and Plate Assembly x1

Figure 3a x6 (OM)

Figure 3b x150 (SEM)
Figure 3c x750 (SEM)
Figure 3d  x40 (SEM)  

Figure 3e  x200 (SEM) 

Figure 4  Jewett Nail and Plate x1. Inset - fracture surfaces x3.
Figure 6  Jewett Nail and Screws x1

Figure 6a  x6 (OM)

Figure 6b  x60 (OM)

Figure 6c  x60 (OM)

Figure 6d  x200 (SEM)
Figure 6e  x850 (SEM)

Figure 6f  x5 (OM)

Figure 7  Venable Plate and Screws  x1\frac{3}{4}

Figure 7a  x4 (OM)
2. SURVEY OF THE RELEVANT SURGICAL AND METALLURGICAL LITERATURE.

This survey is divided into four sections.

The section on surgical implants is intended to give background and lend perspective to the stress corrosion investigation.

The other sections review the stress corrosion literature on the three main classes of implant materials in environments relevant to the implant problem.

The stress corrosion literature on each class of alloy has been considered separately because although useful correlation and comparison between different systems can be made, greater clarity can be achieved by considering them individually.

2.1 Survey of the Literature on Surgical Implants

2.1.1 Introduction

This survey based on a fuller review published in the literature (1) is concerned almost exclusively with metallic surgical implants. Ceramics, reinforced polymers etc. have to date found little use as load bearing materials in orthopaedic surgery.

The study of implants covers a wide field touching on aspects of medicine; physiology, corrosion science, metallurgy and engineering; to simplify the study this survey has been divided into four parts:

(a) The properties required of an implant and the implant material.
(b) The characteristics of currently used implant materials and the reasons for their use.
(c) Possibilities for improvement in implants and implant materials.
(d) Methods of measuring implant and material performance and their correlation with service in humans.

2.1.2 Properties required of an Implant and the Implant Material

Suitable mechanical properties are listed by Morral (2) as:

(a) High elastic limit and strength, remaining constant with time.
(b) High Young's Modulus.
(c) Good fatigue resistance.
(d) A freedom from stress corrosion and corrosion fatigue.
The problem of compatible mechanical properties for bone and implant is a difficult one; a requirement for similar Youngs Moduli, Strengths, Fatigue resistances etc., cannot be fulfilled without imposing mutually exclusive requirements on the metal. Also a coefficient of friction of \( 0.01^2 \) (that obtaining in articular cartilage) is difficult to achieve with metal surfaces.

**Corrosion Resistance**

Corrosion is important for two reasons. Firstly, the implant may be so severely corroded that it is weakened and fails or becomes loose. Secondly corrosion may cause irritation to the body resulting in non-union of the fracture and other deleterious clinical effects. These may be listed as:

(a) The metal ions released into the body by corrosion may be toxic to the tissues.

(b) Wright and Axon have suggested that both the corrosion products and the galvanic currents produced during corrosion affect the bone and tissue. They have increased corrosion rates and resultant bone dissolution by passing an electric current between two stainless steel screws inserted in dead bone in saline solution. Although it is debatable whether or not corrosion interferes directly with bone union (the tissue inflammation being usually some way from the site of fracture) corrosion may interfere indirectly by loosening screws and thereby removing support from the fractured area. Work by Grazisti and Guelfi has also indicated that the microcurrents set up by corrosion may interfere with bone growth.

(c) Ions released into the tissue may be carcinogenic. This is not generally thought to be a problem as large numbers of implants have been used over the years without these effects arising. However, if the present trend for implants to stay in the body for longer periods continues (allowing a build up of metal ions in the tissues) carcinogenic effects may become important.

(d) Metal ions released from the implant may cause an allergenic or hypersensitive response from the patient.

Two factors are concerned in the tissue response due to corrosion in the body. Firstly there is the actual severity of corrosion, the more corrosion present in the tissue the more severe the reaction; secondly
there is the toxicity of the corrosion product. Some metal ions are less well tolerated by the body than others and cause a more severe reaction.

Many theories have been put forward to account for corrosion of implants within the body. The difficulties of carrying out in vivo experimental work or a sufficiently detailed statistical analysis of clinical results make it difficult to draw firm conclusions as to the validity of these theories. The major ideas put forward are:

(a) Metallic transfer of material from surgical tool to implant allows microscopic electrochemical cells to be set up. Bowden, Williamson and Laing\(^{(6-9)}\) using radioactive tracer techniques measured the amount of transfer occurring. Transfers of metal to 10 μgm were commonly found in stainless steel although transfers of up to 2000 μgm were possible in certain extreme conditions. Hicks and Cater\(^{(20)}\) however after a clinical survey, came to the conclusion that metallic transfer is not significant: they considered fretting or crevice corrosion more important.

(b) A differential concentration of electrolyte over the implant may cause corrosion\(^{(11)}\). This is especially true of different oxygen tensions over the implant\(^{(12)}\). Anaerobic conditions occur particularly inbetween the countersinks of screws and screwholes.

(c) Fretting corrosion or surface abrasion which cause the destruction of the protective oxide layer on stainless steel allows corrosion of the underlying steel. Scales and Zarek\(^{(13)}\) have suggested that this may be an important factor in implants of several components. This is supported by the experimental work of Cohen\(^{(14)}\).

(d) Mixing of different metals in a multicomponent device, variation in composition of a metal or variation in the degree of work hardening of a metal have all been suggested as causes of corrosion. Such variations could allow cathodic and anodic regions to be set up with subsequent corrosive attack\(^{(14)}\). The use of mixed metals seems to have been a cause of corrosion\(^{(15)}\) when several different grades of steel were commonly used for implant fabrication but, as Hicks and Cater\(^{(10)}\) point out, mixing of the more corrosion-resistant materials such as vitallium and
Titanium, does not lead to corrosion. Local plastic
deformation causing work hardening has often\(^{4, 9, 13, 16}\) been
cited as a possible cause of corrosion although Scales, Winter
and Shirley\(^{17}\) in their clinical survey of implant removals
found no support for this.

\((e)\) The most serious manifestation of corrosion is stress
corrosion or corrosion fatigue which may cause catastrophic
failure of the implant. Failures attributable to corrosion
fatigue have been observed by several authors\(^{17, 18, 19, 20}\).
Some work on corrosion fatigue of implant materials has been
performed by Hodges\(^{21}\) and more recently by Wheeler and James\(^{22}\)
and Colangelo\(^{23}\).

A report by Zappe\(^{24}\) attributed an implant failure to stress
corrosion, this prompted the Armco Steel Corporation\(^{25}\) to carry out
simple bend SCC tests on AISI 316 steel in human serum at room temperature
for 60 days. No cracking was observed at the end of this time.

In general the work reported on corrosion of implant materials
has been performed without the benefit of modern electrochemical theory
or testing techniques. Work on mechanochemical properties has been limited
largely to corrosion fatigue.

Effort has been concentrated on particular aspects of specific
materials. No overall comparison of materials or work on basic mechanisms
of failure seems to have been performed.

**Economic requirements**

Ideally implant materials must be easily shaped by conventional
methods, stainless steel is particularly good in this respect. Vitallium
however suffers from the disadvantages of having to be fabricated by the
complicated lost-wax casting process. Vitallium as a raw material is
about 8 times more expensive than stainless steel. The new wrought vitallium\(^{+}\)
does not have to be cast but it is not easily worked and has been used
mainly for intermedullary pins. It is also more expensive than cast
vitallium. Titanium and titanium alloys can be fabricated in a similar
manner to stainless steel and are comparable in price to cast vitallium.

**Design**

The surgeon is faced with a large number of implant designs and
variations many of which fulfill the same purpose. Very few of these
have been examined for suitability from an engineering point of view.

\(^{+}\)A ductile Co-Cr-Ni-W alloy - loosely called wrought vitallium
It seems likely that considerable improvement could be made in design leading to devices of higher strength with better fatigue resistances (26). Important points to consider are (27):
(a) The design should be dimensionally suitable for its purpose ie it should fit.
(b) The design should be simple, to facilitate manufacture.
(c) The design should be such that an extensive operation is not required for the insertion of the implant.

One of the greatest problems in implant design is that the mechanical forces to which the implant is subjected in service are not fully understood (28). The work of Marts (29) and Patrick and Tosien (30) in this field has shown that the implant/bone combination in the case of hip prostheses is usually much weaker than either the individual prosthesis or bone. Bynum et al (31) have tested the performance of current designs of bone fixation plates investigating the effect of such variables as plate length, width and screw size. In no case did they observed capacities above 33% of the strength of unfractured bone.

2.1.3 The Characteristics of the Major Implant Materials and the Reasons for their use.

The materials in use at present may be classified into four categories:
(a) Cobalt-chromium alloys containing cobalt, chromium and molybdenum or cobalt, chromium, nickel and tungsten, the most important of which is "vitallium" produced by the Howmet Alloy Plant for the Austenal Laboratories Inc.
(b) Various stainless steels. The most commonly used comply with the standards AISI 316/317, BS 316S16/317S16 or their low carbon modifications eg AISI 316L etc.
(c) Commercially pure titanium and titanium alloys.
(d) Miscellaneous other alloys which are little used because they have limited application or high cost eg, tantalum, zirconium, ticonium [a high modulus cobalt based alloy] etc.

Cobalt base alloys

Besides vitallium two other cobalt based alloys have recently found use: a Co-Cr-Ni-W Alloy, HS25, often loosely known as wrought vitallium and a Co-Cr-Ni-Mo alloy known as MP35N.

Vitallium is normally available only in the cast form but Co-Cr-Ni-W and Co-Cr-Ni-Mo may be wrought although they are not easily worked because of their hot strength properties. A great advantage of these materials is that by a combination of mechanical deformation and thermal ageing they can achieve extremely high strengths (33, 34, 35). This combined with their high modulus of rigidity may be desirable where volume of the implant is
The newer cobalt based alloys have the drawbacks that they are expensive, difficult to work and their corrosion resistance and tissue tolerance has not yet been established by long usage, in particular the crevice corrosion behaviour of Co-Cr-Ni-W has been questioned by Devine et al (36) who have investigated the hot working of HS21, a similar material to vitallium. Wrought HS21 has better mechanical properties (particularly ductility) than the cast material but whether the improvement is worthwhile in view of the difficulties of working the material has yet to be established.

Co-Cr-Mo alloys were first used in implant surgery because of their corrosion resistance. However early in their use problems were encountered due to difficulties in production. These problems have now largely been overcome by improved casting and control techniques (37). Current problems in the production of implants from Co-Cr-Mo alloys are the difficulty in producing complex shapes and the occurrence of large grain sizes even when special casting techniques are employed (38). This is particularly important in small components such as nails and screws where the grain size may be comparable with the cross-sectional area.

Austenitic Stainless Steels

The most common implant material in Britain is stainless steel complying with the British Standard on surgical implants (39, 40). Steel to an equivalent AISI specification is used in the USA. These steels are fully austenitic containing 2-5% Molybdenum which confers added resistance to pitting corrosion.

It is generally agreed that stainless steel is inferior to vitallium in corrosion resistance although this is claimed as an advantage in certain circumstances eg microcorrosion inhibits bone growth into the flutes of selftapping surgical screws and makes their subsequent removal much easier.

The advantages of stainless steel are:

(a) It has a low cost compared with other implant materials.
(b) It is readily available in many shapes and forms from many sources.
(c) It is easily shaped and worked at low cost.
(d) It has superior strength and fatigue resistance to vitallium.

Titanium

Titanium is a relatively new implant material. In May 1964 an amendment was made to BS 3531 to include titanium as an implant material and now it is finding widespread application.
Titanium is probably the most inert material yet used for implants, Boethe, Becton and Davenport (41) who studied titanium implants in cats, reported the response of bone to titanium as good as, if not better than, other implant materials. More recent work by Gottlieb and Leventhal (42) and Beder and Eade (43) confirm these findings. Ferguson, Laing and Hodge have found that implanted titanium contaminates tissue only to a very small extent and that this small contamination causes very little tissue reaction (44, 45).

Titanium can be forged, welded and machined relatively easily. Tensile strengths of up to 770 MPa can be obtained with annealed titanium but the modulus of elasticity is low, about 103 GPa compared with 193-207 GPa for vitallium and stainless steel. Some surgeons think the low coefficient of elasticity a disadvantage especially in the fixation of long bone fractures where maximum rigidity is required (46). A further disadvantage is the poor friction and wear properties of titanium on titanium, this precludes its use in all metal joint replacement. Some of these disadvantages have been overcome in recent years by the use of alloys, particularly Ti-6Al-4V. They have corrosion properties comparable to the pure metal in conditions pertinent to implant applications but have greatly improved mechanical properties. This is particularly useful in small highly stressed members such as surgical screws. Some alloys are hard enough to be useful in restricted wear situations and Ti-6Al-4V has been used in conjunction with high density polythene for elbow and hip replacements.

2.1.4 Possibilities for Improvements of Implants and Implant Materials

Three major areas of implant production where improvements could be made are:

(i) Design
(ii) Fabrication methods
(iii) Materials

Design

The problems of design have already been commented upon. Connected with these problems is the problem of standardisation. At the moment there is a bewildering variety of implants many fulfilling the same requirements. More standardised designs, which had been tested from an engineering and clinical point of view, and would minimise the possibility of implant failure in use.

Fabrication Methods

Various authors have suggested the use of advanced fabrication techniques in the production of prosthetic devices. However many of these techniques may be too expensive for general implant fabrication. The stellite alloys in particular could benefit from improvement in fabrication methods.
Zarek, Smith and Wilkinson (38) have reported improved and more consistent mechanical properties for Co-Cr-Mo alloy made by powder sintering rather than casting.

Vacuum melting and casting (47, 48) may also be usefully applied to Co-Cr-Mo alloys. A higher purity alloy with increased corrosion resistance and a 50% improvement in the fatigue endurance limit has been reported.

A problem in long term implantation eg for joint replacement is to obtain a strong mechanical bond between implant and bone. Plasma spraying has recently been used to coat a titanium substrate with a porous titanium surface (49). Using this technique it is possible to provide a suitable pore size for bone growth into the implant surface thus producing a strong mechanical bond. This technique may find use in future implant applications not only to provide porous surfaces but also to provide wear or corrosion resistant surfaces.

Materials

Substantial improvement in implant performance could be attained by the use of better materials. Although new cobalt based alloys may be developed they will probably be relatively difficult to work because of their hot strength properties. Improvements in the corrosion resistance of stainless steels or the introduction of a totally new material are alternative approaches to the problem.

The corrosion resistance of 25 Cr-20 Ni steel has been substantially improved by surface diffusing molybdenum, nickel or tantalum into the steel (50). It is thought that 18 Cr-8 Ni steel may also benefit from this treatment.

It is likely that titanium alloys will replace pure titanium where high strength is important eg surgical screws. There is a possibility that the wear characteristics of titanium may be improved either by surface treatment (51) or by the production of new wear resistant alloys (52). If the galling problems in titanium alloy implants can be overcome, or avoided by the use of Co-Cr-Mo or plastic bearing surfaces, these alloys may find use in joint prostheses where high strength and maximum corrosion resistance are important because of the length of time this type of implant has to remain in the body and the high stresses to which it is subjected.

In recent years there has been renewed interest in non-metallic materials for load bearing orthopaedic implant use. These are of two main types: ceramics, normally based on calcium aluminate (53, 54, 55, 56) or polymers, normally based on epoxy resins (57). Most work has been concentrated on ceramic systems as these display excellent tissue compatibility combined with a porous surface which allows tissue ingrowth.
Non-metallic materials have serious deficiencies however, their mechanical properties are poor and they are difficult to fabricate into complex shapes (49). Their mechanical properties may be improved by reinforcement with metallic, quartz or carbon fibres (57), this technique allows the mechanical properties of the resulting composite to be varied according to the concentration and orientation of the reinforcing phase thus limited attempts to match properties to service requirements may be made. Ceramics may replace metals in orthopaedic surgery only for very limited applications eg in skeletal replacement devices where maximum physical and chemical compatibility is required over long periods and high mechanical properties are of secondary importance.

2.1.5 Methods of Measuring Implant and Material Performance and Their Correlation with Service in Humans

There are two methods of assessing implant and material performance. (a) In vitro experiments where an attempt is made in the laboratory to simulate the effect of body environment on the implant material. (b) In vivo experiments where laboratory animals or exceptionally humans are used.

Often in vitro and in vivo experiments are both performed and a correlation of results attempted. More commonly the results of implant performance in humans are obtained by a survey or clinical case histories and examination of failed implants.

The types of in vitro corrosion testing may be broadly classified as:

(a) Weight loss measurements on specimens which have been standing in simulated body fluids for long periods.
(b) Electrochemical measurements of corrosion.
(c) Detection of corrosion product by chemical means.
(d) Various specialised investigations eg metallic transfer measurements, corrosion fatigue and stress corrosion experiments.

Weight Loss Measurements

Some of the earliest corrosion tests (58) were of the weight loss type. A careful test procedure was employed as weight changes were low (0-0.4 mg dm$^2$ day$^{-1}$ were recorded). Little difference was found between the materials tested or in the effect of the corroding solution used. Clarke and Hickman (58) did similar weight loss experiments, however the weight changes obtained were always small making their significance uncertain.
Electrochemical Measurements

Clarke and Hickman (59, 60) carried out the first electrochemical measurements on corrosion implant materials. They carried out tests in equine serum and found that measurements of static potential, weight losses due to electrolysis, and potential difference per unit current density bore no relation to the known corrosion-resistance of the materials used. Finally they found that a parameter they call the anodic back e.m.f. (A.B.E.) bore a close correlation to known corrosion-resistance. The A.B.E. was found by measuring the potential difference across a cell with the material as anode and a calomel cathode in a bath of equine serum. The "IR drop" across the cell was then subtracted to give the A.B.E. The results were independent of current over a wide range and correlated well with weight loss experiments carried out by the same authors (60).

Although Clarke and Hickman think the Anodic Back E.M.F method suitable for "screening" possible implant materials before expensive animal testing Hensler (61) reported that he has found the A.B.E. varied widely with current density and specimen dimensions, he suggested further work is necessary if the test is to be used as a quality control for implant material.

More orthodox electrochemical measurements have been carried out by Hoar and Nears (50) on a range of materials in 0.17M Sodium Chloride Solution, buffered Sodium Chloride Solution, and Hank's solution (a solution of inorganic salts with glucose, designed to simulate body fluids).

Their measurements included potential/time curves for isolated specimens, potential/current curves for anodes and current/time curves for anodes maintained at constant potential. It was concluded that stainless steels and nickel alloys were unlikely to resist pitting corrosion indefinitely in the body, that Cobalt based alloys of the vitallium type should withstand exposure for a very long time and that titanium and some of its alloys should resist corrosion indefinitely.

These findings have been confirmed by subsequent similar work by Bultitude and Morris (62) and Mueller and Greener (63). The recently devised transient linear polarisation technique has been used to make corrosion rate measurements in vivo (64, 65) and the results correlated with in vitro electrochemical testing (65). In addition to performing basic tests to compare the corrosion characteristics of implant materials electrochemical methods have been used to investigate the role of organic compounds in passivation (66) and the effect of microstructure on the corrosion characteristics of alloys of orthopaedic interest (67, 68).
Emmëus has applied the ferroxyl test to corrosion of stainless steel (69, 70) and Co-based alloy implants (94). The test consists of exposing the specimen to a gel of 0.9% NaCl solution, potassium ferricyanide and gelatin. With free metal ions the ferricyanide forms coloured complexes. Any corrosion site on the metal is attached by the gel (the test is provocative) forming coloured "bubbles". The results are qualitative but Emnëus found general agreement with the results of in vivo tests (71, 72) although the ferroxyl test seemed to be more severe, giving positive reactions at times where there was no biological reaction.

Specialised Investigations

Bowden, Williamson and Laing suggested that transfer of metal from tool to implant during insertion may be an important factor in causing corrosion. In a series of papers (6, 7, 8, 9) this was tested by simulating surgical operating procedures and measuring the amount of transferred metal using a radioactive tracer technique. Autoradiography was also used to determine the distribution of the transferred metal.

Transfers of approximately 20 μg were common between stainless steel tools and stainless steel screws. Contamination with the harder Co-Cr-Mo alloys was much lower (about 0.5 μg). Particular trouble was encountered when drilling a pilot hole through a plate when milligram amounts of metal could be transferred from the drill.

Pathological observations and spectroscopic analysis of biopsy samples (9) revealed a correlation between the severity of handling of an implant during insertion and the subsequent concentration of metal ions in the surrounding tissues. Bowden, Williamson and Laing interpreted this as being due to the increased metallic transfer occasioned by the more severe handling.

Work on the combined effects of corrosion and fatigue has been done at King's College, London (21). Electrochemical measurements were made on alternately stressed specimens of stainless steel, Co-Cr-Mo alloy, and titanium in Fink's solution. The fatigue resistance of all the materials was found to be reduced by the corrosive medium although Titanium was found to be least affected in this respect.

More recently Wheeler and James (22) and Colangelo (73) have performed fatigue crack propagation studies on 316L stainless steel using precracked specimens and a stress intensity analysis. There are however inconsistencies in their results and the fact that the important initiation step is omitted from this mode of testing makes the application of the results to a service situation unsure.
The small amount of work performed on SCC of implant stainless steels has already been described.

**In Vitro Mechanical Testing**

A major difficulty in this field is deciding what forces act on an implant in service; the stress pattern may be particularly complex at fracture sites (74). These complicated stresses are difficult to reproduce experimentally and work has been confined to simple stressing.

In spite of the difficulties valuable work has been done by Martz (29) on the mechanical properties of implant bone combinations. Martz measured the strength of bone, implant and bone-implant combinations in tension, bending, compression and torsion. In torsional tests Martz found that a 3" Sherman plate failed at 15 inch pounds and a Lane Plate at 66 inch pounds; considering a torque of more than 60 inch pounds is required to tighten a screw Martz considered the devices inadequate. In transverse bonding tests all implants were found to be weaker than bone, and bone with implant fixation was often only a fifth or a tenth as strong as intact bone. These findings were later verified by the results of Bynum et al (31).

**In Vivo Corrosion Experiments**

The most comprehensive in vivo corrosion experiments have been performed by Ferguson, Laing and Hodge (45). They implanted specimens in rabbits, sacrifice the rabbits four to six months later and measured the concentration of metal ions in the surrounding tissues and major organs (75, 76) spectroscopically. Cobalt and Nickel from implanted material was found in high concentration in body organs. In a more recent paper (44) the authors have estimated the severity of the tissue reaction by the thickness of the membrane around the implant. (This membrane forms even when there is no obvious corrosion and is thought to be a major factor in the implants acceptance by the tissues (77)). Several alloys which have not found use as implant materials gave outstanding results in these experiments and may be useful as future materials eg Hastelloy C and 17 Cr-7Ni precipitation hardened steel. Titanium and its alloys were also found to behave very well.

Recently Hoar and Mears (50) performed a different kind of in vivo investigation in that they made electrochemical measurements on a human finger pin and also, via catheters, on a femoral plate fitted in a goat. They found general agreement with their in vitro determinations.

**Clinical Surveys and Metallurgical Examinations**

Cohen (78) in a paper on 300 removed implants found that corrosion was much more common than mechanical failure. The corrosion was usually of the crevice type but examples of erosion-corrosion, electrolytic corrosion at junctions of dissimilar metals, and pitting corrosion were also claimed to be observed.
The earlier work of Hicks and Cater (10) and Scales et al (79, 80) in this field in general supports the findings of Cohen, their major conclusions were:

(a) Co-Cr-Mo alloy implants are satisfactory and superior in corrosion resistance to implants of En 58J steel.
(b) The metallic transfer effect did not appear to be important.
(c) The mixing of metals did not lead to corrosion if the metals had a high corrosion resistance but did so if the metals were of inferior corrosion resistance.
(d) Variations in hardness were found in different areas of an implant but did not seem to correlate with corrosion.
(e) Counter-sink corrosion was found to be common in stainless implants.
(f) Intercrystalline corrosion and fatigue failure were found in some steel implants.

The full value of a clinical survey cannot be realised unless accompanied by some metallurgical examination of the failed implants, this has been done by Scales et al (80) and other authors; it has been found that:

1. Mechanical failure usually occurs with the absence of macroscopic ductility and is normally ascribed to fatigue or corrosion fatigue. This is a major cause of failure in stainless steel implants (19, 20) and is often initiated from notches, metallurgical defects or inclusions (20).
2. Intercrystalline corrosion is sometimes present, in steels which have a high carbon content and are unstabilised. The occurrence of this phenomenon can be readily controlled by use of the correct steel, avoidance of welding and correct heat treatment.
3. Faulty manufacturing technique and poor quality material may lead to failure. Carburisation of the cannulae of hip nails (80, 81) and faulty casting without adequate heat treatment are examples of this (82). There has been an improvement in the quality of implants over the years and gross defects are now normally absent, however metallurgical defects in the material are still common. Cahoon and Paxton (20) have examined unused 316L16 stainless steel and vitallium implants, over 50% of them were considered to be metallurgically defective. High inclusion contents were often found in the stainless steel and porosity in vitallium implants. Inclusions, particularly of the MnS type have a deleterious effect on corrosion resistance (84).
2.1.6 Conclusions

Although presently used implants are not unsatisfactory the possibility of significant improvements exists. Some of the requirements of a suitable implant material are obvious but there is disagreement among surgeons about other requirements eg high or low modulus of elasticity. Once clinical opinion has established what combination of properties is ideal a compromise has to be made and a material chosen taking into account other factors such as availability, cost, fabricability etc.

Economics have meant that alloys have not been developed and produced specifically for the implant market. Instead, materials have been adopted from other technologies eg chemical engineering and the aerospace industry where corrosion resistance and high strength are important. The future development of metallic implant materials may be expected to depend on the development of alloys for these technologies.

Much of the early work on the appraisal of implant material properties was performed by surgeons concerned with immediate practical solutions.

Relatively little basic work using modern techniques has been done until recently. Work of this type leading to a more rational understanding of the mechanisms of corrosion and fracture will be required to further advance the technology of implant materials.
2.1.7 References


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40. Proposed new Standard to replace B.S. 3531 (B.S.I. Technical Committee SGC/18).


70. P Peterson, H Emnëus, "The Ferroxyl Test as a General Test of the Corrosiveness of Surgical Applicances Made From Stainless Steel or Cobalt-based Alloys of the Stellite Type mainly Vitallium and Neutriliun", Acta Orthopaedica Scandinavica, Vol. 29, No. 4, pp 331-340.


or titanium or niobium stabilised stainless steels. For this reason only transgranular stress corrosion will be considered in this survey.

In recent years a large amount of work has been done on stress corrosion of stainless steels in nuclear reactor systems. Failures at low temperatures have largely been due to sensitisation effects, transgranular cracking only occurring at high temperatures in relatively pure water (\(\sim 300^\circ C\)). Much of this modern work is therefore less relevant to the problem of stress corrosion in implant conditions than older work in more concentrated chloride environments at lower temperatures. The survey will therefore concentrate on this older work.

2.2 Phenomenology

Before considering possible mechanisms for SCC in the austenitic steel-chloride system it is necessary to review the effect of such variables as alloy composition, environment, temperature etc. on cracking susceptibility. Most of the work reported has been done on commercially available alloys in saturated magnesium chloride solution at 154\(^\circ\) C. As SCC has been found to be sensitive to small variations in experimental conditions and procedures, it is often difficult to compare different authors' results. However, the more important effects are well defined.

Alloy composition has a marked effect on susceptibility.

Copson (10) and others (11 - 14) have demonstrated the beneficial effect of increased nickel content (figure 1), austenitic alloys with nickel contents greater than 45\% are generally considered to be immune. This generalisation has recently been brought into question by the observations of Oriou et al (15) of cracking in high nickel Inconel alloys exposed to high temperature pressurised water. Its applicability to lower temperature environments with higher chloride contents is well established however.

Chromium has less effect than nickel on susceptibility (16) and there is disagreement between various authors as to whether chromium improves or lowers SCC resistance. One possible explanation of this is that it is the nickel plus chromium content which is important (10, 12). This view is supported by the findings of Hines and Jones (17) who observed that the combined concentrations of some alloying elements correlated well with SCC susceptibility.

Of the elements present in lower concentrations the following features are reasonably well established: silicon (12, 18 - 20) and manganese (19) lower SCC susceptibility in small amounts (<2\%) although manganese lowers the general corrosion resistance. Small concentrations of copper (16, 19), molybdenum (18, 20, 21) niobium, titanium (17, 21, 23) and sulphur (20) either have no effect or are slightly deleterious. Phosphorous lowers SCC resistance (20, 1, 24). Interstitial solutes play an important role, increased nitrogen content heightens susceptibility (20, 23, 21, 25, 26) whereas carbon has a complex effect. Extra low (ELC) grades of steel have relative immunity to SCC with susceptibility passing through a maximum at carbon contents from 0.065 - 0.085\% (17). At higher carbon contents susceptibility again decreases (0, 23, 25, 26).

Attempts will be made later to explain these effects of composition susceptibility in terms of the various theories proposed for the mechanism of cracking.
Large additions of ferrite stabilising elements (e.g. Mo, Cr) may increase SCC resistance through changing the alloy structure; ferritic Fe-Cr steels are immune and ferrite grains in austenitic steels do not propagate cracks (27). Grain size also has an important effect, SCC susceptibility increasing with grain size. This seems a general effect; having been observed in a variety of SCC metal/environment systems. This effect adds to the difficulty of comparing the work of different authors and may account for disagreements on the effect of alloying elements. As variations in alloy composition seem to affect crack initiation rather than propagation (28) surface roughness is another variable which can mask compositional effects (the time to initiate cracks from a smooth surface can be four times longer than from a rough surface (29)).

The effect of stress on time to cracking has been found to be semi-logarithmic with a steep slope above the yield stress and a much shallower slope below (9); higher stresses lower both the initiation and propagation time of cracks (25). The minimum stress at which cracking occurs (threshold stress) is very dependent on environmental factors and has been reported to be as low as 1000 - 2000 psi (30) and as high as 50,000 psi (31) according to conditions. A further reason for the wide variation in results is the difficulty of defining an exact threshold; failure occurring below a short term threshold stress after long periods of time, this long term effect is of obvious practical importance. Birchon and Booth (32) have interpreted the threshold stress in terms of a strain threshold necessary to initiate slip bands. On this basis threshold stress should be no more than the yield stress of the material in the environment of interest. This idea does not seem to have been investigated, however.

The movement of dislocations is probably the important feature in SCC initiation because static dislocations in the form of cold working do not have a large effect on susceptibility.

The chemical environment is a major factor in stress corrosion cracking. Although this survey is concerned mainly with cracking in chloride containing media the fact that cracking will also occur in high purity water containing oxygen, lead or hydroxyl ions and in concentrated sulphuric acid-sodium chloride solutions is important when considering cracking mechanisms.

SCC seems relatively insensitive to chloride concentration except at very low concentrations. Frey and Staehle (9) have reported that cracking is stifled for [Cl\(^-\)] < 10 ppm at temperatures above 200°C because the thickened oxide film can maintain structural integrity at these low chloride concentrations. Cations present in the solution exert an important influence (33); if stainless steel is resistant to corrosive attack in the medium e.g. MgCl\(_2\), CaCl\(_2\), ZnCl\(_2\), then SCC can easily occur. In situations where pitting occurs, e.g. NaCl, KCl, NH\(_4\)Cl, cracking occurs only after long exposure times. Solutions causing heavy corrosion attack, e.g. CrCl\(_3\), FeCl\(_3\), HgCl\(_2\), give no SCC.

It can be seen that SCC is an extreme form of localised corrosion being present only in conditions where most of the material surface is resistant to attack. Water in the liquid phase seems necessary; in autoclave experiments (34) cracking is rapid only near the dewpoint and is greatly inhibited by 20°C superheat; Rhodes (35) could not obtain cracking in ZnCl\(_2\)/KCl.
melts without the addition of 2.5% H₂O. There has been some disagreement over the necessity of oxygen for chloride cracking. Oxygen seems necessary in neutral solutions where the reduction of oxygen is the primary cathodic reaction, in these conditions cracking can be inhibited by sulphite additions which lower the oxygen concentrations to 0.01 - 0.1 ppm (9). Other oxidising agents, e.g Na₂Cr₂O₇, H₂O₂, Fe³⁺, Cl₂, Br₂ providing alternative cathodic reactions may accelerate cracking. In boiling magnesium chloride at 154°C the oxygen concentration has been estimated at 0.3 ppm (35); in these conditions the cathodic reaction is probably hydrogen evolution (20, 35).

As a corollary to the accelerating effect of oxidising agents, reducing agents inhibit or prevent cracking (36). Lowering the pH accelerates cracking in MgCl₂ (37, 38) unless the pH is too low, when general corrosion occurs rather than SCC (39). This is in line with the requirement for most of the surface to remain passive for SCC to occur. As a corollary raising the pH lowers susceptibility (40, 41). SCC is most severe at higher temperatures but cracking of AISI 304 and 347 type steel has been reported by Scharfstein and Brindley (42) in the range 165 - 200°F. The slow rate of crack propagation at lower temperatures makes it difficult to derive a temperature threshold for cracking.

Many of the effects of alloy and environment composition can be explained on an electrochemical basis, therefore it is instructive to consider directly the effect of anodic or cathodic polarisations on cracking. Stress corrosion in MgCl₂ is found to occur only in a relatively narrow potential band at about −0.15V (SHE) (36, 37, 43-46) cathodic polarisation at current densities of the order of microamps per square centimetre strongly inhibit cracking (7, 37, 45, 47). Anodic polarisation at 50 - 100mV more noble than the initial isolated corrosion potential causes rapid cracking in susceptible alloys (37, 46), the initiation time seems to be eliminated, and the density of initiation sites and subsequent cracks increased by 10² (37). Higher anodic polarisations do not accelerate cracking so strongly but rather cause a general corrosion attack on the material.

The morphology of cracks is significant in mechanistic explanations of SCC. When the initial crack reaches a critical length (which is dependent on stress) the branches lengthen and produce further branches to give a network of cracks. This network spreads laterally more quickly than it penetrates (48, 28). It is generally agreed that cracks consist of short segments on the (111) planes (48, 43, 49, 50); this is supported by observations of crack-like defects and localised corrosion attack on the (111) planes of thin film sections (51-53). Once the crack has started to propagate the plane of propagation is less easy to identify because of attack at the crack sides (54); this combined with the small size of the crack segments (about 1μ (43)) may explain why some authors have reported that they can find no relationship between propagation path and crystallographic structure (48, 33). Other authors have reported cracks on (100) planes in 20 Cr-20 Ni steel (55) and on (110) in 18 Cr - 18 Ni and 18 Cr - 10 Ni steels (56).

### 2.2.3 Mechanisms

Cracking may be divided into two stages:

(a) Initiation

(b) Propagation
Initiation is rate controlling in stainless steels and the great majority of "time to failure" is required for initiation. In spite of this, most of the work on stress corrosion has been concerned with propagation, possibly because this stage is more amenable to experimental observation and theoretical treatment. However, many of the ideas put forward are applicable to both stages.

**Initiation**

Cracks are thought to initiate in the austenitic steel/chloride system from local defects in the passive oxide film. These defects in certain situations seem to nucleate cracks directly and in others to produce sharp corrosion pits from which the crack subsequently grows. The defects suggested by various authors are of two types:

1. Inherent defects in the film
2. Defects caused by the metal substrate

Nuclei for defects may be present in an incomplete or defective film (57); Hoar (58) has postulated that breakdown of passivity occurs by clustering of chloride ions at such singularities, removal of a cation to give a chlorocomplex (later decomposed), causing film thinning and raised dielectric field. This process continues until catastrophic breakdown. In this context it is interesting to note the beneficial effect of silicon on stress corrosion susceptibility; silicon is known to improve the resistance of the film to chloride attack (93) and therefore may inhibit SCC by making initiation more difficult.

Regarding the metal substrate, attack has been postulated at α-ferrite, hydride or "quasi-martensite" produced by straining, such singularities presumably affect the oxide layer and thus initiate attack. Smialowski et al (60) have presented more convincing evidence that cracks initiate from pits caused by mixed manganese and ferrous sulphide inclusions. It has often been suggested, particularly when cracks start without pre-existing pits, that initiation occurs through structural defects in the metal which rupture the overlying film. Emergent slip bands have been commonly suggested as initiation sites (28, 33), the number of sites increasing with cold work (28, 61). Subgrain boundaries (62), dislocation pileups (53, 63), moving dislocations (64), stacking faults (63) and areas of short-range order (22, 63) have all been suggested as initiation sites. Pitting is normally reported to precede cracking, indeed in NaCl, KCl and NH₄Cl solutions pits seem to be a necessary precursor to cracking. The pits however are not the normal saucer shaped or angular type observed in unstressed situations but are sharp fissures (62): Lea and Helle have observed (33) that cracks will only propagate from sharp pits and not from rounded ones. In MgCl₂ cracking is normally seen to propagate directly from a surface defect without a prior pit; some authors however (33, 49) have observed "micropits" on slip bands from which cracks propagate and it is possible that these must form prior to crack propagation.

As initiation is the rate determining step the initiation (or induction) time is an important measure of stress corrosion susceptibility; unfortunately the induction time varies considerably with experimental conditions such as size and form of specimen, mode of stressing, surface
oughness etc (28). For these reasons the use of initiation time as a practical measure of stress corrosion resistance is unreliable. The majority of workers consider that the initiation time is required to produce pits (or micropits) on the surface from which cracks subsequently grow. Uhlig and his coworkers (25, 65, 66) take a different view; they report that pre-pickling specimens before exposure had no effect on time to failure, in addition heat treatment at 154°C in air prior to exposure had the same effect on induction as pre-exposure in MgCl\textsubscript{2} at 154°C. They interpret these results in terms of an initiation time necessary for interstitial carbon and nitrogen to diffuse to dislocations thus making them electrochemically active. It is difficult to reconcile these ideas with the findings of other authors and the effects of cathodic protection, pH, surface roughness etc on initiation time.

Airman has commented however (67) that a difference in composition must be noted, Uhlig looked at 20 Cr - 20 Ni and 25 Cr - 20 Ni alloys instead of the more often examined 18 Cr - 8 Ni or 18 Cr - 10 Ni materials; the small additions of nitrogen may have a major effect in these materials of borderline stress corrosion susceptibility.

Propagation

Once cracks have initiated they start to propagate; rates, typically of several millimetres per hour, have been observed by a variety of techniques (68, 167, 169). The propagation rate is much faster than a normal corrosion process and much slower than ordinary brittle failure.

There are three main theories of SCC in the austenitic stainless steel/chloride system:

(a) The electrochemical mechanism

(b) Stress sorption cracking

(c) Hydrogen embrittlement

Electrochemical Mechanism

The electrochemical mechanism was first suggested in 1940 by Dix (6) who proposed that cracks followed paths in the metal especially sensitive to corrosion. A theory which postulated a brittle fracture step initiated by an electrochemical attack was put forward by Keating in 1948 (8). These two similar but distinct ideas known as the continuous electrochemical mechanism (CEM) and the periodic electrochemical mechanism (PEM) were widely developed by subsequent authors. The PEM model was first suggested because the observed crack growth rates seemed too large to be accounted for by corrosion alone. An corrosive attack which triggered a short brittle fracture step was suggested with subsequent attack at the tip of the arrested crack to reinitiate a further brittle step. A problem to be resolved was the origin of the mechanical fracture step; Lea and Helle (33) and Kirk et al (104) have suggested chemical sharpening of the crack tip followed by crack advance due to notch brittleness, this mechanism in such an inherently ductile material as austenitic stainless steel seems doubtful. Forty (71) has shown that a brittle fracture may advance into ductile material if the crack velocity is greater than the velocity of deformation of the alloy. To achieve such a high velocity the crack must start in brittle material and Forty suggests that the corrosion step must embrittle the material.
although the exact mechanism is obscure. Forty and Humble (72) postulated
that at the crack tip the corrosion process produces a thick tarnish film
which mechanically ruptures due to yielding, the exposed metal retarnishes
and cracking of the film again occurs (the brittle mechanical step). This
model has proved very useful for copper-based alloys in ammoniacal solutions
but its applicability to Fe-Cr-Ni alloys is questionable since no thick
oxide film is generally observed in the conditions in which cracking occurs.
It has more recently been recognised that dislocation structure may be
significant in a mechanical fracture step because of the restriction of
deformation to certain crystallographic planes in materials with planar
dislocation arrays. The importance of dislocation arrangement in stress
corrosion will be amplified later. If propagation is periodic rather than
continuous it should be possible to detect the discontinuous nature of
cracking experimentally; four main methods have been used:

(a) Discontinuities in corrosion potential
(b) Sudden elongation steps
(c) Acoustic emission from the brittle crack propagation
(d) Microscopic observation of sudden crack extension on
the metal surface

Such methods have been successfully used in other systems to observe the
periodic nature of propagation. When applied to the austenitic steel/
chloride system electrochemical measurements with sensitive equipment have
failed to show any sudden voltage jumps (62, 31); similar negative results
have been obtained in attempts to measure sudden extension steps (62, 67,
73, 74). Fairman (67) has used equipment which he claims would detect
extension steps down to 50 Å and has obtained negative results. Neilson (75)
has heard sounds during cracking which he attributes to acoustic emission
from sudden crack extension; Van Rooyen (76) however was unable to reproduce
these results. Bursts of crack extension on the surface have been noted in
an 18 Cr - 8 Ni steel at 205°C in NaCl solution under conditions of wetting
and drying (70) but such observations are open to the criticism that the
crack is propagating continuously but breaking through the fracture surface
intermittently due to alternative pinning and releasing of the crack front
where it intersects the specimen surface. Striations on stress corrosion
fracture surfaces have been observed (67) typically with a separation of
0.3 - 0.5 µm; these markings can be interpreted as being due to sudden
crack extension and arrest but an alternative explanation is that the crack
path is changing from one slip plane to another, the slip plane separation
in these alloys is about 0.3 - 0.5 µm (77). In general if crack propaga-
tion is periodic the mechanical step must be extremely small (probably <50Å)
to have escaped detection. One of the important points to be resolved if
Dix's ideas are to be applied is the origin of a pre-existing sensitive path
along which cracks propagate. One of the more obvious ideas was the possibi-
ility that a second, corrosion susceptible, phase exists in the austenitic
structure. Edeleanu (78) and Rochär (79) have suggested that "quasi-
martensite" may be initiated by the strain at the crack tip and preferentially
dissolved. Edeleanu has shown that needles of martensite are preferentially
attacked by MgCl₂ and that cracks and martensite are often spatially associat-
ed; he later accepted the criticism (76) that cracking occurs at temperatures
too high for normal martensite formation in many austenitic steels (80).
addition Uhlig, White and Lincoln (66) found that prestraining to precipitate martensite actually improved SCC resistance. It is true that martensite is often observed but it seems to be produced incidentally to the strain field around the crack tip and not directly associated with cracking.

Dislocations may be important in creating a crack sensitive th in fcc metals such as austenitic stainless steels. Results by Swann and others (77, 81-83) indicated that materials containing planar arrays of dislocations were susceptible to SCC whereas materials with a tangled dislocation structure were immune. The dislocation structure depended on the stacking fault energy (SFE) of the material (84). Alloys with a low SFE produce pairs of dissociated dislocations with an energy of stacking fault in between; it is difficult for the dislocation to change its slip plane (cross-slip) because to do so the partial dislocations must have to recombine annihilating the stacking fault area, this is energetically unfavourable and so the dislocations tend to segregate and lie up on certain slip planes giving a characteristic planar arrangement. Ease of cross slip in an alloy of high SFE (no dislocation dissociation) results in a cellular arrangement of dislocations (63). Stacking fault energies can be calculated from measurements of dislocation node separation in thin foil electron microscope specimens using the method of Whelan (5). Most of the SFE measurements for austenitic stainless steels have been carried out at room temperature and at strains of 5%. Thomas et al. (6), noting observations in nickel alloys (87) that the magnitude of the strain and temperature could control the type of dislocation arrangement, obtained measurements of SFE at 154°C at various strains to reproduce conditions experienced under stress corrosion testing in boiling saturated MgCl2 solution. In the materials examined, AISI 304 steel and coloy 800, the found that changing the conditions led to an increased dislocation density but did not change the arrangement.

More recent work has shown that the correlation between dislocation arrangement and SCC susceptibility is not as strict as was earlier believed. Douglas et al. (72) have observed that Nichrome has a planar dislocation array yet is highly resistant to SCC. Incoloy 800 is more typical in that it has a high SFE (< 30 erg/cm²) yet it has a planar dislocation structure but is resistant to SCC. In addition Swann (77) showed that phosphorus additions to a 20 Cr-20 Ni austenitic steel results in planar dislocations and susceptibility to SCC while the SFE falls at 30 erg/cm². These results show that SFE is not the only factor affecting dislocation arrangement and also that dislocation arrangement is not the only structural factor affecting SCC susceptibility. A rather confused picture may be clarified by considering the results of Swann (77) who, on the basis of his work in Cu, Au and austenitic alloys, concluded that short range order (SRO) exerted an effect. The motion of a dislocation in a slip plane will destroy the SRO present in that plane and so lower the stress necessary to move further dislocations over the same plane (88), thus slip is confined to close parallel slip planes. Because the dislocations are close together the node radii are low and the SFE obtained by Whelan's method are high. Thus, it is possible have planar dislocations in a material of apparently high stacking fault energy through the presence of strong SRO. It has further been observed that planar dislocations destroy areas of SRO or clusters of solute atoms to produce areas of disorder, which are anodic sites. Thus, SRO or solute clustering is necessary for SCC susceptibility. Pure metals and totally random solid solutions are predicted to be immune.
Swann (77) introduced a further refinement where he considered the effect of reordering. If an area disordered by planar dislocations can rapidly reorder then the anodic site is lost and stress corrosion does not occur; alternatively with slow reordering the anodic site persists sufficiently long for anodic attack and crack extension to occur. This complicated system of structural effects is shown schematically in figure 2; information on some important materials is given in table 1.

The theory that lattice imperfections have a critical effect on stress corrosion as outlined above has had a great deal of success; many authors have observed a close correlation between dislocation substructure and susceptibility to cracking (21, 53, 77, 81-83, 86, 89) also many of the phenomenological features can be explained by the theory. The decrease in susceptibility as nickel content increases may be ascribed to the change of dislocation structure from planar to cellular as the nickel content is increased. The deleterious effect of phosphorous and nitrogen can be explained by their strong affinity for chromium; it is probable that strong SRO exists which produces the observed planar dislocations and cracking susceptibility in annealed material. In cold worked material the dislocation network becomes tangled and cracking is not observed (77). In spite of the success of the dislocation theory it depends on postulates of SRO and reordering rates, direct evidence for ordering in the Fe-Cr-Ni system being sparse. There is evidence for ordering in the Fe-Ni system (90, 91) and in the Ni-Cr system (92, 93). The detection of order by X-ray or electron diffraction methods in Fe-Cr-Ni alloys is difficult because of the similar atomic scattering factors; it presence is often inferred from electron microscopical observations of the type mentioned earlier. Although lattice imperfections are important in SCC they are only part of the phenomenon; the significance of planar dislocation arrays lies in the fact that they give massive localised slip through the surface which exposes a large area of fresh metal. This is of importance in the electrochemical theory where extremely rapid anodic dissolution of this step is expected, however, it may be argued that such a slip would rupture a brittle oxide film or provide a clean surface for absorption or entry of H ions. Thus, the dislocation ideas outlined above have application to more than one theory of SCC and the correlation of planar dislocations with SCC provides no unique test of the validity of any stress corrosion theory. Other factors such as alloy repassivation rates, environment composition etc are of equal importance; a widely held view is that a suitable dislocation structure is necessary but not sufficient for stress corrosion cracking.

The continuous electrochemical theory has been developed on a macroscopic scale by Hoar and his coworkers (61, 62, 38, 45, 94, 95). They believe that the high rate of strain at the crack tip produces "strain-depolarisation", i.e., the freshly exposed atoms in the plastically strained region have a high internal energy and are preferentially dissolved, the crack tip is anodic to the crack sides and rapid dissolution occurs at the continually advancing tip. They have performed experiments on rapidly strained wire electrodes in an attempt to simulate the conditions prevailing at the crack tip; susceptible alloys show a sharp increase in corrosion current on straining, eg, with 18-3 steel at $10^4$ times increase has been observed (96). With non-susceptible alloys the effect is much smaller, perhaps an 8-17 times increase (96). Some of Hoar's work on wires has been repeated by Hines on rod specimens (28); similar work has also been done by van Rooyen (73) and Graf and Springe (97).
Crude estimates of the crack tip current density required to produce a crack propagation rate of 2 mm/hr by dissolution give values of 500 mA/cm² (28, 62). There is an anodic current limitation of ~100 mA/cm² to concentration polarisation for unstrained stainless steel at 154°C MgCl₂ (98). Yielding of the metal and streaming of the electrolyte lowers current densities of the order required for cracking however (94, 95). At potentials where unstrained material showed no dissolution, Hoar suggested (2) that concentration polarisation does not occur in a C situation because crack yawning continually draws fresh supplies of reactant to the crack tip. Hines has commented (43) that concentration polarisation may be kept low only by certain anions and this may explain the specificity of anion which is a major feature of SCC. A point of doubt was the nature of the regions cathodic to the crack tip; it was originally thought that oxide covered crack sides and/or specimen face were the cathodic area, it is now known that austenitic steels undergo slow active dissolution in saturated MgCl₂ solution at 154°C (5, 37, 46, 95). Although an oxide film of the classical type does not at low and Uhlig have observed (99, 100) a partially hydrated Fe(OH)₃ about 4500 Å thick which correlates with a reduction in the overall corrosion rate and a shift of potential to more anodic values ie into a region where SCC occurs. This potential drift however may be explained by an alternative mechanism of preferential dissolution of iron and chromium to leave an ennobled nickel rich surface. It has been postulated that slip steps breaking through such a surface expose an anodic area which preferentially dissolved until re-enabled; subsequent slip steps re-tiate this cycle until a crack with nickel rich cathodic sides is formed. 

(a) With increase nickel content cracking should be inhibited as the composition of a surface and step become more similar.

(b) Elements with similar nobility to nickel should have a similar effect.

is observed that cracking is indeed stifled by increasing nickel content and that copper additions have a similar effect to nickel.

Other suggestions for the cathodic reaction are that the sides the crack are dissolving actively but very slowly, the cathodic reaction involving oxygen reduction on the metal surface (2). Other authors noting the equilibrium oxygen concentration in MgCl₂ solution at 154°C have observed bubbling from SCC cracks (97). In this context the crack is significant; Marek and Biman (101) have cracked AISI 304 steel in MgCl₂ at 154°C, frozen the cimen and broken open the crack; they observed that the pH at the crack tip may be 1 or less while the pH in the solution farther down the crack is about 4.5 which is the same as the bulk solution. The low pH at the crack tip would enhance the probability of hydrogen evolution at or the crack tip as a cathodic reaction.

The existence of the "strain depolarisation" effect and its significance to SCC has been well established, however, the mechanism a microscopic basis is less well defined. The importance of planar location arrays has been emphasised but stresses in the lattice surrounding dislocations have been calculated to exert negligible
The thermodynamic effect on the reversible potential \((102, 103)\), therefore the effect must be a kinetic one. Scully \((104)\) has commented that cracking in general occurs when an area of metal is produced which is too large (or produced to rapidly) for the environment to repassivate in a critically short time; he postulates that the height of an emergent slip step is important in denuding the environment of important passivating species. Although these ideas are attractive their applicability to the austenitic steel-magnesium chloride system is not well developed.

The presence of alloy solute atoms exert a critical effect; reviews by Vermilyea \((105)\) and Regel \((106)\) have emphasised that solute atoms are necessary to "decorate" dislocation lines before attack will occur, the effect of carbon and nitrogen concentration on SCC susceptibility supports this idea. In general according to the electrochemical theory the emergent slip steps at the crack tip are anodic because of composition differences; this may be due to solute segregation, disordering, surface enrichment or other reasons. Attack at these steps propagates the crack along the slip \((111)\) plane. Some authors \((107, 108)\) through observations in various systems believe that the crack does not advance uniformly but that corrosion "slots" or "tunnels" form which join by ductile rupturing of intervening material to give cracks. Armijo and Wilde \((109)\) however have criticised the suggestion that such tunnels are necessary for cracking in the stainless steel-chloride system because they have observed tunnels in the absence of stress in a non stress corroding medium.

**Stress sorption cracking**

Several workers \((110, 111-113)\) have advanced the idea that adsorption at the highly stressed regions of the crack tip causes a reduction in cohesion of the metal bonds. Such an adsorption-decohesion mechanism is thought to be operative in liquid metal \((114)\) and complex ion \((115)\) embrittlement. Proponents of the stress sorption theory point out that it explains the brittle nature of cracking better than the electrochemical mechanism which might be expected to produce a fracture surface showing more signs of corrosion dissolution than is actually observed. They also claim that the specificity of anion observed in SCC fits in better with an adsorption mechanism.

Uhlig and Cook \((36)\) have obtained experimental support for their adsorption ideas in their work on the inhibition of SCC by the addition of small amounts of sodium acetate, nitrate, iodide or benzoate to boiling \(\text{MgCl}_2\) test solution. Although these salts had no major effect on anodic or cathodic behaviour and also little effect on solution conductivity, in concentrations of only a few percent they greatly reduced or in the case of nitrate and acetate totally inhibited SCC. It was observed that the salt addition acted through shifting the critical potential for cracking to a more noble value than the corrosion potential. Uhlig and Cook postulate that the inhibitor anions which do not themselves cause cracking compete with chloride anions for available sites, the potential has then to be made more noble to achieve the higher \(\text{Cl}^-\) concentration within the double layer necessary for absorption.
Coleman et al. (110) have presented evidence which they claim supports the adsorption theory. They measured the dependence of fracture stress, \( \sigma_F \), on grain diameter, \( d \), for an 18-8 steel and compared the results in air with those in magnesium chloride. Using the Petch relationship (116):

\[
\sigma_F = \sigma_0 + k d^{1/2},
\]

where \( k = \frac{6\gamma G}{\sqrt{1 - \nu}} \)

\( G \) = shear modulus,

\( \gamma \) = surface energy,

\( \nu \) = Poisson ratio,

values of \( \gamma \) were calculated. They obtained values of 157 erg/cm\(^2\) in \( MgCl_2 \) as compared with 1000 erg/cm\(^2\) in air. Armstrong et al. (117) criticised these results on the basis that flow stress, which is a function of the ease of dislocation movement, is also dependent on grain size. The correct correlation may therefore be between flow stress and SCC susceptibility rather than surface energy and SCC susceptibility. Results are open to a more fundamental criticism however in that it is difficult to see how \( \sigma_F \) can be sensibly measured on specimens in \( MgCl_2 \) because of cracking due to SCC; this makes an accurate knowledge of cross-sectional area required for \( \sigma_F \) calculation impossible.

Finally the possible inter-relationship of adsorption and anodic solution theories cannot be ignored; adsorption may be important in aging anodic dissolution from general to specific. Westwood (118) has forward the idea that certain species may act as step poisons and \( d \) to corrosion tunneling which some authors think is part of the SCC process in stainless steels.

**Hydrogen embrittlement**

Early suggestions by Edeleanu (78) that hydrogen embrittlement play an important role in SCC suffered from two serious objections: firstly, the solid state diffusion rate of atomic hydrogen in the fcc lattice was low making permeability into the metal from the crack tip difficult; secondly, polarisation results showed that cracking accelerated by anodic polarisation and inhibited by cathodic polarisation, the opposite effect would be expected in a classical hydrogen embrittlement situation. These objections have been overcome to some extent by the work of Holsworth and Louthan (119) who have shown that cathodic hydrogenation of stainless steel leads both to internal strain to expansion of the \( fcc \) lattice and a lowering of the stacking fault energy; this lowers the activation energy barrier inhibiting phase transformation and allows martensitic transformation even of AISI 310 steel which normally does not undergo strain induced transformation at temperatures as low as 4 K. Rhodes (35) has suggested that rapid hydrogen fusion can occur along martensite platelets and so advance ahead of the crack tip more quickly than would be calculated for a model of hydrogen fusion in austenite. Rhodes meets the second objection, that cathodic polarisation inhibits cracking by a consideration of the special conditions prevailing at the crack tip. He has calculated that the motion of very small amounts of anodic oxide product within the small volume at the crack tip will result in acid concentrations of 1M, which is supported by the experimental work of Marek and Hockman already cussed.
This low pH favours hydrogen liberation as a cathodic reaction. Although cathodic polarisation increases the rate of hydrogen evolution or other cathodic reactions on the specimen surface (the major cathodic site), this model predicts that the inhibition of the anodic reaction at the crack tip decreases the solution acidity and reduces the cathodic hydrogen evolution reaction in adjacent areas. In addition a high electrolytic resistance between specimen surface and crack tip would prevent the applied cathodic current having a substantial effect on potential near the crack tip. Similar arguments show an increase in hydrogen evolution near the crack tip with anodic polarisation, such an increase was visibly noted in Rhodes' studies.

Although it has been suggested that hydrogen may embrittle metal by an adsorption-decohesion effect or by the build up of high pressure hydrogen gas in voids the two mechanisms usually considered in a stress corrosion context are:

(a) The precipitation of a brittle phase which advances the crack by brittle fracture

(b) The precipitation of an anodic phase which advances the crack by preferential localised dissolution.

Whiteman and Troiano (120) have shown that thin sections of cathodically charged austenitic steel have lowered ductility and Benson et al. (121) have further shown that brittle fracture occurs in martensitic platelets formed in the presence of hydrogen. The effect of hydrogen is twofold: firstly, it enables the phase transformation to take place; secondly, it may embrittle the resultant martensitic phase. Vaughan et al (59) take the other view that a hydride precipitate is anodically dissolved. In their electron microscopical observations on hydrogen charged austenitic steels they observe that an alloy hydride with a hcp structure is precipitated. In susceptible alloys the effect of stress is to cause diffusion of hydrogen and orientation of the hydride precipitate at the crack tip, in immune materials this effect is absent, the alloy-hydride phase precipitates immediately and is not orientated. On boiling the specimens in MgCl₂ the alloy hydride is rapidly dissolved with the evolution of hydrogen. It is postulated that in a stress corrosion crack this hydrogen may be evolved (as is often observed) or may react with the surrounding matrix and repeat the diffusion-precipitation-reaction cycle.

2.2.4 Conclusions

Each of the three main theories outlined above has its strengths and weaknesses, however, many of the finer points of SCC are difficult to explain on any theory (e.g in FeCl₂ solution in the temperature range 289 - 342°C Pickett and Wilson have observed that cracking changes from wholly transgranular to wholly intergranular as the temperature is raised (91). No theory seems sufficiently sophisticated to explain results such as this.) Part of the problem in deciding the validity of any theory is the difficulty of devising tests which will allow predictions of different results by different theories; another problem is that varying one experimental parameter can consequently vary others and make controlled experimentation difficult, e.g compositional changes in the material may affect:
(a) Stacking fault energy
(b) Short range order, long range order or clustering
(c) Reordering rates
(d) Solid state diffusion rates
(e) Anodic polarisation characteristics
(f) Cathodic polarisation characteristics
(g) Repassivation rates
(h) Adsorption characteristics, or any combination of these

Thus, it is unwise when observing the effect of compositional variations in one of these parameters to take this as support for a particular theory without considering the effect of such variations on other parameters. The picture is complicated by the possible interrelationship of theories; anodic attack at the crack tip, an integral part of the electrochemical mechanism, is necessary in the hydrogen embrittlement theory; adsorption effects may also serve to localise anodic attack.

The possible effect of environment on the stress necessary to cause crack advancement has largely been ignored. It is generally assumed that dislocations reach the crack tip through creep, and creep parameters have been used in the discussion of stress corrosion results (122, 123). However, work on the effect of alloying elements in 18-8 steels shows that creep behaviour does not correlate well with SCC susceptibility: electrochemistry, dislocation, coplanarity etc seems more important (124). Actual stresses at the crack tip may be difficult to estimate from the macroscopic tensile stress because of the corrosion product wedgeing effect observed by Nielson (75) and Pickering et al (125) but it does seem possible for any particular stress that plastic flow may be enhanced in the crack tip region because anodic dissolution continually removes dislocation pile ups. A potential will exist for dislocation movement to this "sink" thus making plastic flow easier. Some results by Spretnak and Griffis (126) are of interest here - they have found that the environment at the crack tip can affect the critical train at which flow is channelled along slip directions and also the nature of plastic instabilities mounted along these lines (weak instabilities lead to slow stable crack growth, strong instabilities to unstable fast fracture).

It would seem a fruitful line of stress corrosion research to attempt to simulate the mechanical and chemical conditions prevailing at crack tip and study their interaction. This should provide more mechanistically useful information than the studies of bulk properties previously performed.

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Figure 1. Effect of Nickel on SCC Susceptibility
(Adapted from Copson (10))
FIGURE 2. INTERRELATIONSHIP OF STRUCTURAL EFFECTS IMPORTANT IN STRESS CORROSION CRACKING
The first incidence of SCC in Titanium was reported by Kiefer and Harple in 1953 who described cracking of commercially pure Titanium in red fuming nitric acid. Work on creep in turbine blades in the mid 1950's led to the discovery of cracking in the presence of chloride salts at temperatures above 250°C. Major interest was aroused by Brown in 1966 when he reported SCC in Ti-8Al-1Mo-1V alloy when tested in aqueous 3.5% NaCl solution at room temperature. Although SCC of Titanium Alloys is rarely seen in service the use of these materials in aerospace and submarine applications where stress corrosion may be the cause of catastrophic failure has led to intensive study of the problem since 1965.

The reason why Stress Corrosion under the relatively mild conditions of low chloride concentration and low temperature had not been recognised before was the difficulty of initiating cracks. Titanium is normally immune to pitting in these conditions and so the pits, which are a common initiator of Stress Corrosion cracks in other systems (eg austenitic steel/chloride), do not form. This difficulty of "natural" initiation does not mean that the problem is not of practical importance, in large structures the presence of cracks due to welds, fatigue etc may initiate Stress Corrosion. Brown overcame the problem of initiation by performing his tests on a cantilever notched beam containing a fatigue crack. Stress Corrosion susceptibility was measured by a lowered resistance to further slow crack propagation; although this approach had been used before Brown used a specimen geometry and method of stressing which greatly simplified the experimental arrangement. His method and presentation of results using linear elastic fracture mechanics to express Stress Corrosion susceptibility in terms of reduced fracture toughness has been widely used by subsequent workers. The use of a fracture toughness approach has distinguished Stress Corrosion testing of Titanium Alloys from much of the earlier Stress Corrosion work on Copper and Aluminium Alloys and various types of steel where nominal stress and time to failure were the parameters used. This has occurred because of the initiation difficulty mentioned earlier and also the growing widespread use of fracture toughness as a mechanical property parameter for high strength materials. The applicability of the stress intensity factor (K) to Stress Corrosion of Titanium Alloys has been convincingly demonstrated by Smith et al: they tested a centre cracked sheet under wedge force loading conditions where crack extension causes reduced stress intensity at the crack tip but increased net section stresses. Stress Corrosion crack growth was found to arrest under these conditions, demonstrating its dependence on stress intensity; furthermore the stress intensity at arrest was found to agree closely with threshold K values for Stress Corrosion crack propagation (known as Kp) obtained by conventional Brown type tests. It is interesting to speculate on the results of stress corrosion tests performed by fracture toughness methods on classical stress corrosion systems where time-to-failure has been the variable normally measured. Effects due to specimen configuration, surface finish and the long period of time required for initiation would be nullified, making results more reproducible. Also when considering the wide variation in threshold stresses for initiation reported in these systems it may be more instructive to consider threshold stresses for propagation from a pre-existing crack either in terms of net-section stresses or stress intensity values.

Before considering the mechanisms postulated for the cracking of Titanium in aqueous chloride environments it is necessary to review the effect of such variables as alloy composition, structure, environment, stress etc on cracking susceptibility and also to examine their influence on crack path and fracture morphology.
Composition

The stress corrosion susceptibility as measured by the $K_J/K_{J,SCC}$ ratio ($K_J$ is the fracture toughness of the material in air and $K_{J,SCC}$ in the stress corrosion medium) has been measured for a large number of commercially available and experimental alloys. Table 1 gives an example of the type of information obtained. The dependence of susceptibility on alloy composition is often obscured because of the powerful effects of variables such as preferred orientation and grain morphology resulting from different rolling procedures and heat treatments applicable to each alloy. In spite of this, several important trends can be discerned:

(a) Isomorphous $\beta$ stabilisers such as Niobium, Molybdenum, Vanadium and Tantalum reduce or eliminate susceptibility. It has been suggested that these additions affect susceptibility through increasing the amount of $\beta$ phase present; the $\beta$ phase being immune in these alloys and acting as a ductile crack arrester. It should be noted however that the eutectoid $\beta$ stabilisers Manganese and Cobalt increase susceptibility. (For reviews of Titanium metallurgy and phase equilibria see McQuillan and McQuillan, Seagle and Bartlo, or Jaffee.

(b) Aluminium in concentrations of approximately 5 W/O and above increases susceptibility. This effect seems to be dependent on the existence of an ordered phase, Ti$_3$Al, which exerts an influence on the dislocation structure. Alloying elements which behave similarly to Aluminium such as Tin, Indium and Gallium may have a similar effect. Although Aluminium is a major constituent in many alloys which suffer from SCC its presence is not necessary for cracking eg, Ti-6Al-4V alloy is very susceptible.

(c) A high Oxygen content increases susceptibility. Unalloyed Titanium with 0.38 W/O Oxygen is susceptible. The effect probably operates through a dislocation mechanism similar to that occurring in the case of Aluminium additions.

(d) Hydrogen content, besides affecting the inherent fracture toughness of Titanium Alloys, has been reported by some authors to also have an effect on SCC susceptibility. This will be discussed more fully when considering Hydrogen embrittlement as a possible mechanism of stress corrosion.

Structure

A combination of plastic deformation with solution treating and ageing generally improves $K_{J,SCC}$ values by refining transformed structures and reducing the grain size. Rolling texture (preferred orientation) is an important variable, the difference in SCC susceptibility of thick and thin gauge plate is partly due to differences in rolling texture and partly due to different stress states at the crack tip. Differences in rolling texture and heat treatment can give a wide variation in results from nominally the same material and this confused the interpretation of early work. However these effects can be rationalised by considering the microstructures produced.

The majority of Titanium Alloys are $\alpha + \beta$ alloys consisting mainly of $\alpha$ phase, small amounts of $\beta$ stable at room temperature and retained metastable high temperature $\beta$. Various grain morphologies may be formed by combinations of heat treatments in the $\alpha + \beta$ or $\beta$ fields and plastic deformation. The structure
May be further complicated by the presence of martensitic phases, a complex hexagonal transition phase known as \( \omega \), or ordered phases e.g., Ti-4Al. It is generally reported that the \( \beta \) phase in \( \alpha + \beta \) alloys acts as a ductile crack arrestor [6, 14, 15, 16]. Heyn using electron microprobe analysis [17] has found that steps between areas of cleavage in Stress Corrosion fracture surfaces of Ti-8Al-1Mo-1V correspond to sheets of \( \beta \) phase, the \( \beta \) phase presumably interrupting the stress corrosion cleavage process in the susceptible \( \alpha \) phase. \( \beta \) is not always efficient as a crack arrestor, Piper et al. [18] have reported that the structure of \( \beta \) is important: equiaxed \( \beta \) resulting from processing in the \( \alpha + \beta \) field is less effective than the lamellar and randomly oriented \( \beta \) produced by \( \beta \) processing. Precipitation of a second phase within the \( \beta \) grains can lower SCC resistance, \( \alpha \), \( \omega \) and intermetallic compounds such as Ti\(_2\)Cu and Ti\(_3\)Si\(_2\) have been reported to have this effect [12, 13] possibility by nucleating cracks in \( \beta \) and embrittling it to such an extent that it can no longer act in a ductile manner. Finally the \( \beta \) phase is not immune in all instances - it is susceptible in Ti-Mn alloys and in the \( \beta \) alloy Ti-13V-11Cr-5Al [12] where cracking may be inhibited by \( \alpha \) precipitation. This does not necessarily mean that \( \alpha \) is immune in this case because cracking occurs on \{100\} planes of the \( \beta \) phase and near the \{0001\} plane in the \( \alpha \) phase cracking may be expected to be inhibited because of the relationship \{110\} \( \beta \) // \{0001\} \( \alpha \). Blackburn has identified two martensitic phases \( \alpha' \) and \( \alpha'' \) produced when the \( \beta \) phase of Ti-8Al-1Mo-1V is quenched from temperatures above 870°C, these phases are immune to SCC and raise \( K_{isc} \) values in the material [12], similarly martensite in Ti-6Al-4V has been reported to be immune [6], however martensites formed in Ti-5Al-2.5Sn [6] and Ti-8Al [12] are susceptible. A further complex hexagonal phase, \( \omega \), may be formed by prolonged low temperature ageing, the presence of \( \omega \) phase lowers \( K_1 \) and \( K_{isc} \) values and has a general embrittling effect.

In addition to the phases present, grain morphology and size are important, Lane et al. [26-28] have shown for Titanium alloys containing Aluminium that a matrix containing coarse long platelets is more susceptible than one containing fine platelets and \( \alpha \) dispersions. An increase in SCC susceptibility with increasing grain size has been noticed in Ti-5Al-2.5Sn [12], Ti-Al alloys [12] and Ti-4Al-4Mo-2Sn-0.5Si [13], increasing amounts of cold work on the other hand have the opposite effect, decreasing susceptibility in Ti-5Al-5Sn-52r, Ti-7Al-2.5Mo and Ti-4Al-4Mo-2Sn-0.5Si [13].

Alloys containing Aluminium or Aluminium and Tin show greatly reduced \( K_{isc} \) values when aged in the temperature range 500°C-700°C, this seems due to the precipitation of ordered particles Ti\(_2\)Al or Ti\(_3\)(Al,Sn), which may exert their influence either through affecting the dislocation structure or hydrogen transport kinetics, these effects will be discussed later.

**Stress State**

A feature peculiar to the Stress Corrosion of \( \alpha + \beta \) Titanium alloys is that susceptibility is less in thin gauge material than in thick gauge and that immunity may be achieved if the gauge is thin enough [18, 19, 20]. This phenomenon is partly due to the difference in structure found in different thicknesses but this is not a total explanation of the effect, Wald [19] tested plate remachined to thin specimens and found that a true thickness effect occurred. A second important feature is that a pre-existing crack is usually necessary for initiation. These two effects operate through their influence on the stress state existing at the tip of a SCC crack, in a sufficiently thick plate with a sufficiently deep crack a triaxial stress state exists, this has the effect of preventing plastic deformation which would blunt the crack. The result is a sharp crack with large areas of fresh metal exposed by the local plane strain conditions [20]. Although a fatigue crack is usually required to initiate SCC (e.g., SCC in Ti-6Al-4V will not initiate from tear or shear cracks [21]) some highly susceptible alloys require a less severe stress raiser;
Notable exceptions to the requirements outlined above are:

(i) Plane strain conditions do not seem necessary for cracking in many organic solvents. Smooth thin specimens will crack in these environments.

(ii) Stress corrosion effects have been observed in dynamic strain [23] and potentiostatically controlled dynamic strain [24, 25] tests.

(iii) β alloys will crack in a smooth condition [16] and are more susceptible in thin sections than in thick sections [6].

Crack Path

Cracking in the α phase of α+β alloys occurs by cleavage near the (0001) plane [6]. The crack velocity is high (1 to 50 mm/min have been reported [26, 27] and Blackburn and Williams [12] have observed a continuous current/time plot during cracking of Ti-8Al-1Mo-1V indicating continuous propagation.

The angle between the fracture and basal planes has been measured by Meyn [28] and Hockman and Starke [29] for Ti-7Al-2Nb-1Ta as 15° to 16°, similar results have been obtained in Ti-8Al-1Mo-1V [17, 30, 31] and Ti-8Al [12, 31]. The conclusions of these investigations are that cracking occurs by cleavage on the {1017} or {1018} planes [6].

β alloys are again atypical in that cracking occurs on or near {100} planes [6].

Fracture Morphology

The fracture morphology is generally a mixture of cleavage and dimple modes. Cleavage occurs through susceptible α phase and ductile failure in β or transformed β [15], in addition ductile tear ridges corresponding to thin β lamellae may occur [15]. The degree of SCC susceptibility is qualitatively related to the areal fraction of cleavage fracture [15]. As a crack propagates and the K_I value approaches K_{JC} an increase in the amount of dimple failure is observed and the crack velocity increases, Feige and Murphy [20] suggest that the increased dimpling is due to the crack velocity outstripping the electrochemical reaction rate at the crack tip with a consequential reduction in stress corrosion (cleavage) fracture.

Corrosive Environment

Although this survey is mainly concerned with cracking in chloride environments at room temperature other environments are of interest because of the bearing they may have on Stress Corrosion mechanics.

Table 2 [32] give some of the environments in which cracking occurs. Halogen ions are an important class of SCC agents, cracking occurs in the presence of Cl^-, Br^-, I^-, and ClO^2^- at room temperature [33] but not in a large number of other anionic species examined [33, 34]. Feige and Murphy [33] made the important observation that cracking occurs only in the presence of ions which will cause
Titanium to pit at potentials of less than 20V indicating that penetration of the oxide film is important in SCC. This is supported by the fact that the concentrated acids and organic media which cause cracking at room temperature also remove the film on titanium. The presence of chloride does not seem necessary for cracking in organic environments eg cracks form in methanol with no detectable Cl\(^-\) contamination \[35\], however the presence of decomposition products such as formaldehyde may be important \[35\].

Cations present during cracking in chloride bromide and iodide seem to have no effect \[34\] but the anion concentration affects both \(K_{SCC}\) and subcritical crack velocity \[36\], a high concentration being the most severe condition. Raised temperature also increases crack velocity but has little effect on \(K_{SCC}\) \[36\]. Cracking can be inhibited by a variety of additions \[20, 34\]: \(\text{AgNO}_3\), \(\text{HNO}_3\), \(\text{Na}_2\text{SO}_4\), \(\text{NaF}\), \(\text{NaOH}\), \(\text{K}_2\text{Cr}_2\text{O}_7\), \((\text{COOH})_2\), \(\text{Na}_2\text{PO}_4\) in various concentrations prevent cracking at low chloride concentrations eg distilled water but are ineffective at higher chloride concentrations except in massive amounts \[34\].
P\(H\) seems to have negligible effects on cracking; Leckie \[37\] has observed that a pH of 14 has no inhibiting effect on the cracking of Ti-7Al-2Nb-1Ta in chloride solution. Several authors \[25, 34, 37, 38\] have investigated the effect of electrochemical potential on susceptibility, there seems to be a region of cathodic protection at potentials of less than \(-1000\text{mV (SCE)}\) between \(-1000\text{ mV and } +1000\text{ mV}\) susceptibility passes through a maximum and decreases again, at higher potentials than \(+1000\text{ mV}\) pitting occurs and susceptibility again increases. These effects will be considered more fully later.

**Microstructural Effects**

Before considering in detail the two main types of mechanism proposed for SCC in Titanium ie Electrochemical Dissolution and Hydrogen Embrittlement it is necessary to review the large amount of work done on microstructural features such as dislocation arrangements, ordered phases etc which are significant in any mechanistic interpretation of SCC phenomenology.

The presence of an ordered phase Ti\(_3\)Al is known to have a dramatic effect on the stress corrosion susceptibility of Titanium alloys. Diagram 1 shows the Titanium-Aluminium equilibrium diagram obtained by Crossley \[39\]. The Ti\(_3\)Al phase boundary occurs at 4.4 W/0 Al at 500°C; earlier authors had located this boundary at somewhat higher Aluminium contents eg 7.5 W/0 Al. Ageing of an Aluminium containing alloy such as Ti-6Al-4V or Ti-8Al-1Mo-1V around 500°C may be expected to precipitate coherent Ti\(_3\)Al particles from the \(\alpha\) matrix although the temperature range will depend on the effect of other alloying elements and the extent of precipitation will be governed by such factors as composition, time, temperature, prior cold work etc \[22\]. Tin has a similar effect to Aluminium but Ti\(_3\)Sn does not precipitate homogeneously and seems less effective than Ti\(_3\)Al in promoting susceptibility \[40\]. However alloys containing approximately equal parts of Al and Sn to a total of 12-13 atomic per cent can exhibit homogeneous precipitation of ordered Ti\(_3\)Al\(_x\) particles which do promote susceptibility \[40\]. A major effect of such precipitation is to alter the dislocation substructure in the \(\alpha\) matrix. For concentrations of Aluminium of less than approximately 5 W/0 cross-slip is easy and a cellular network of dislocation tangles results \[12, 41, 42\], at higher concentrations of Aluminium cross-slip is prevented and dislocation pairs increasingly occur. In a homogeneous material (ie no Ti\(_3\)Al precipitates) the presence of planar dislocations may be attributed to the stacking fault energy (SFE) being raised above a critical value \[43, 44, 45\], a high oxygen concentration in commercially pure Titanium has this effect \[12, 13, 15\] the dislocations become planar and stress corrosion susceptibility occurs. The induction of susceptibility by Oxygen additions to the immune unalloyed material is a strong argument for the importance of the dislocation structure on SCC.
Ageing to precipitate Ti₃Al accentuates dislocation coplanarity through the existence of strong short range order, the Ti₃Al particles are sheared during deformation /12, 46/ thus promoting dislocation coplanarity through the mechanism proposed by Cottrell /47/. Once coplanar arrays of dislocations are formed they may promote stress corrosion susceptibility by causing dislocation pile-ups against grain boundaries or α/β interfaces /42/ which result in high stresses normal to the cleavage plane and promote fracture according to Stroh’s theory /48/. An increased slip length will maximise the stress at the head of the pile up, this may be a reason why susceptibility is lowered by a small grain size or fine dispersion of β phase which will keep the slip length low /13/. A similar explanation may be provided for the beneficial effects of cold work, this increases the dislocation density and again reduces the effective slip length /13/. Alternatively coplanar slip may be important in providing massive slip through the surface on deformation and so affecting repassivation in a way suggested /49/ for other systems. It has been reported that the critical current density for repassivation increases with increasing Aluminium content /50/, also Sanderson and Scully /51/ have observed a change of attack for Ti-Al alloys in boiling Magnesium Chloride solution from pits joined by wide fissures to narrow cracks as the Aluminium content is raised.

A second major effect of Aluminium is to promote the formation of Titanium Hydride. This effect has been widely reported /42, 52, 53/ but the literature is somewhat confused on the details of the mechanism, the most thorough work seems to have been done by Boyd et al /42/ who studied the absorption and solubility of Hydrogen and the nucleation of hydrides in several Ti-Al alloys. They found that the equilibrium solid solubility of Hydrogen in Titanium is negligible but that increasing amounts of Aluminium allowed greater supersaturations of Hydrogen in the α matrix; ageing to precipitate Ti₃Al accentuates this effect, ordered material absorbing Hydrogen more readily than disordered material; Boyd et al consider this to be due to Hydrogen absorption by Ti₃Al but this is not necessarily so, the microstructural changes brought about by the presence of Ti₃Al may aid the absorption of Hydrogen. Once supersaturation of Hydrogen in the matrix reaches a critical value rapid precipitation of Titanium Hydride occurs, the hydrides appear to nucleate randomly and grow rapidly on the {1010} planes until they impinge. Aluminium, then, increases the non-equilibrium solubility of Hydrogen in the matrix so allowing rapid growth of large hydrides /52/ once critical saturation is reached. The nucleation barrier for hydride formation may be overcome by a large supersaturation of Hydrogen as we have seen but it may also be overcome by plastic deformation. The function of Aluminium in Stress Corrosion susceptibility may then be to allow Hydrogen to reach a sufficient concentration in the material at the crack tip to allow rapid growth of massive hydrides rather than allowing the Hydrogen to be dissipated at lower supersaturations in the production of small random hydrides. Hydrides and the effect Aluminium has on their formation will be discussed further when considering a Hydrogen Embrittlement mechanism for SCC.

The restriction of slip to certain planes caused by the presence of Ti₃Al or Titanium Hydride may be of critical significance to stress corrosion susceptibility /54/. The planar arrays caused by Aluminium contents of greater than 6 WO occur on the prismatic {1010} and pyramidal {1011} planes and rarely on the basal {0001} plane /55/, i.e increasing the Aluminium content impedes basal slip. Titanium hydride forms on the prismatic and pyramidal planes /56/ probably nucleating and growing along the {1010} 1/3 <1120> and {1011} 1/3 <1120> dislocations /57/. The hydrides effectively block dislocation movement on these planes either by the incoherent Titanium Hydride/Titanium boundary /56/ or by the stress field generated in the α matrix due to the larger specific volume of the hydride /58/. Thus Ti₃Al and Titanium Hydride may inhibit slip on all of the major slip systems; this allows a less dominant system, {1122} 1/3 <1123> to become important. This system has been observed in several cph metals /59/.
as well as Titanium and Titanium Alloys \( 60 \). The idea that slip is largely confined to \([1122] 1/3 <1123>\) during SCC has been developed by Mauney and Starke \( 59 \) to explain the observation that cracking occurs by cleavage on the \{1017\} or \{1018\} planes. If pile-ups occur on \{1122\} \( 1/3 <1123>\) due to dislocations meeting grain-boundaries, \( \alpha \) /\( \beta \) interfaces or other blocked slip-planes then Stroh's theory of fracture \( 48 \) predicts that the cleavage plane (i.e., the plane across which maximum tensile stress occurs) is at \( 70.5^\circ \) to the pile-ups slip-plane. \{1017\} is at \( 70.76^\circ \) to \{1122\} and \{1018\} is at \( 69.4^\circ \) to \{1122\} giving good agreement with the theoretical \( 70.5^\circ \). Although it is difficult to find experimental verification for this model it is attractive in that it provides an explanation for the peculiar crack path. The Hydrogen Embrittlement and Anodic Dissolution mechanisms in their simple forms cannot predict the crack path. Even if Mauney and Starke's ideas are not accepted in full the fact that slip can be highly restricted by Ti-Al and Titanium Hydride is of significance in any mechanistic explanation of cracking.

It is interesting to note that a high oxygen content (e.g., 0.1 - 0.2 w/o) raises the critical resolved shear stress on all three major slip systems but has the greatest effect on the pyramidal and prismatic \( 61 \) i.e., it has a similar effect to Titanium Hydride.

### Electrochemical Mechanism of Cracking

The dependence of SCC on applied potential in Titanium alloys has been well established by several authors \( 24, 25, 33, 34, 37, 38 \). Generally a region of cathodic protection is observed at potentials of less than \(-1000\) mV (SCE), susceptibility is at a maximum at \( 0\) mV (although Beck \( 34, 38 \) has reported a somewhat lower value) thereafter a region of anodic protection occurs up to \(+1000\) mV. At higher potentials pitting attack occurs and susceptibility increases. These results confirm that electrochemical effects are of primary importance in the mechanism of cracking.

The Electrochemical Theory of SCC where rapid anodic dissolution of an advancing crack tip is the mechanism of cracking has been widely developed for other systems. Three major variants of the Electrochemical Theory have been proposed for Titanium Alloys:

Feige and Murphy \( 33 \) have emphasised the importance of passive film rupture. Applied stress ruptures the protective oxide film and halogen ions delay repair allowing dissolution of the exposed Titanium, repassivation then occurs and repetition of film rupture, anodic attack and repassivation advances the crack. The reaction rate is dependent on the rate of slip and the rate of repassivation. Coplanarity and restriction of slip may be expected to enhance susceptibility, this is in accordance with the results discussed earlier, but this model is not able to explain why cracking occurs on \{1017\} and \{1018\} in an apparently cleavage mode. Some environmental effects are correctly predicted however: \( \text{Cl}^- \), \( \text{Br}^- \) and \( \Gamma^- \) are well known for their deleterious effect on passivity and their specificity as stress corrosion agents in this system is probably due to their ability to prevent repassivation in the manner suggested \( 33 \). The effect of the electrochemical stability of the oxide on Stress Corrosion susceptibility has not been widely considered by other authors, Leckie \( 37 \) has commented that the stability may be affected by alloying additions and it is interesting to speculate that some of the compositional effects interpreted through microstructural changes may have an alternative explanation on this basis. The inhibiting effect of certain anions can be explained on the basis of a competition between the inhibitor and \( \text{Cl}^- \) on the emergent slip step, this may be why an excess of inhibitor over \( \text{Cl}^- \) is required.

Finally Feige and Murphy \( 33 \) explain anodic inhibition by the thicker oxide film present at anodic potentials: a thick oxide when fractured by the same amount of slip as a thin oxide exposes a smaller amount of bare metal surface thus minimising attack (See Diagram 2).
Hydrolysis of Titanium halide following reactions such as

\[ \text{Ti}^{4+} + 4\text{Cl}^- \rightarrow \text{TiCl}_4 \]

\[ \text{TiCl}_4 + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{Cl}^- \]

may be critically important in cracking \( [20] \), the net effect is that \( \text{Cl}^- \)
becomes reavailable for reaction and is attracted by the intense electrical
field to the edge of active slip planes. The \( \text{H}_2^+ \) ions produced may be cathodically
discharged or may form Titanium Hydride, thus this type of reaction is significant
in an anodic dissolution mechanism where

\[ \text{Ti}^\text{III}_\text{me} \rightarrow \text{Ti}^{\text{III}_\text{me}} \]

is the overall crack propagating reaction or in a Hydrogen embrittlement
mechanism where a supply of \( \text{H}_2^+ \) is a necessary prerequisite. Beck \( [62, 63, 64] \)
has developed a semiquantitative continuum electrochemical model for cracking
where halide recycling is an important step. He has developed the model to comply
with the following experimental data \( [24, 64] \):

1. SCC occurs only in the presence of \( \text{Cl}^- \), \( \text{Br}^- \) or \( \text{I}^- \).

2. SCC velocity is approximately linearly related to potential over a
range of about 2000 mV with a zero-velocity intercept at -900 mV (SCE) for
duplex annealed Ti-8Al-1Mo-1V.

3. Anodic current flowing into the crack is approximately linearly related
to potential with zero-current intercept at about -800 mV (SCE).

4. Under potentiostatic conditions SCC velocity is relatively independent
of the cations present or pH of the bulk solution.

5. Velocity is proportional to the 1/4 power of the bulk halide concentration
becoming asymptotic to a limiting velocity at zero bulk concentration.

6. Activation energy for velocity is about 3.5 kcal mole \(^{-1}\).

7. On removing an externally applied potential from a propagating crack
the initial open circuit potential is only slightly below the previously applied
potential for a range of applied potentials up to +200 mV (SCE). At more anodic
applied potentials the value of the initial open-circuit potential approached
+200 mV (SCE) asymptotically. Thereafter the open circuit potential decays over
a period of \( 10^{-2} \) to \( 10^6 \) seconds finally approaching -800 mV (SCE).

Beck then formulated a model where he divided the crack into three zones:

(i) Tip zone where the cracking process takes place,
(ii) Monolayer zone where the first monolayer of oxide is formed,
(iii) Multilayer zone where the oxide increases in thickness.

By considering the mass transport and kinetic requirements of each zone
together with continuity and conservation requirements Beck was able to express
his model in a set of differential equations. Only reasonable, fundamental
assumptions concerning the applicability of quasi-steady state conditions, a
continuum treatment and the importance of halide ions as the SCC agent were made
up to this stage.
To solve the resulting differential equations numerical methods implemented by computer were used. It was necessary now to assume values for many of the variables present, these values were obtained from the literature, from separate experiments and where necessary by estimation. In the course of the development of the model several alternative sets of assumptions were tried and it is significant that none of these models for any reasonable parameter values yielded calculated behaviour even roughly corresponding to experimental observations. In particular, models with (i) no halide tip current and no $\text{H}^+$ reduction and (ii) halide tip current and $\text{H}^+$ reduction but no halide recycling were unsuccessful. The final model whose formulation was guided by failures in alternative models and the results of additional experimentation included terms for a halide current to the crack tip, the existence of $\text{H}^+$ reduction and the conservation of halide. Beck achieved conservation by the displacement of Titanium Halide by Oxide during crack propagation to give the monolayer oxide zone although he makes the point that hydrolysis is a feasible alternative. Some recycling mechanism is also necessary to explain cracking of Titanium Alloys in distilled water by a halide mechanism, it is postulated that residual Chlorine in the metal resulting from the Kroll manufacturing process is the source of halide here but to maintain a sufficient concentration at the crack tip some recycling mechanism is required.

The model excludes two other postulated cracking mechanisms. Firstly the hydride mechanism is excluded on the grounds of (i) Hydrogen ion discharge near the crack tip must be small because if the Hydrogen ion discharge current were comparable to the halide current there would be no potential gradient down the crack and the driving force for halide transport would be lost, (ii) The crack "out runs" diffusion of Hydrogen from the crack tip into the metal because the discharge rate is low compared to the crack velocity.

Secondly the oxide wedging mechanism is excluded because calculations show that the oxide thickness on the crack walls is always considerably less than the crack width.

It is instructive at this point to consider how the results calculated from Beck's Theory agree with the experimental data quoted earlier:

1. SCC occurs only in $\text{Cl}^-$, $\text{Br}^-$ or $\text{I}^-$: The explanation of this effect is outside the scope of Beck's model.

2. Linear relationship of velocity and potential: because of the limitations on the mass transport of halide ions in the monolayer zone the model predicts a potential drop which is linear with tip current, this tip current is equivalent to the rate of creation of new surface i.e velocity. The zero velocity intercept is more negative than the mixed potential for the anodic reaction

$$\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (I)$$

and cathodic reaction

$$\text{H}^+ + \text{e}^- \rightarrow \text{H} \quad (I)$$

because a cathodic current is required to decrease the halide concentration in the crack to a low enough level to stop propagation.

3. Linear relationship of current and potential: It is predicted that the current flowing into the crack under potentiostatic conditions is linearly related to velocity. As velocity is linear with potential (from (2) above) current is linear with potential. The zero current potential is the
Independence of velocity from cation: The velocity is limited by halide ion concentration together with formation and reduction of hydrogen ions, this is relatively independent of cations present under potentiostatic conditions.

Non-linear relationship of velocity to halide ion concentration: The model includes provision for the local recycling of halide in the tip region due to halide displacement by oxide in the monolayer zone, this local recirculation results in a non linear relationship of tip halide concentration to bulk halide concentration and so a non linear relationship of velocity to bulk halide concentration.

An activation energy of approximately 3.5 kcal mole$^{-1}$ for velocity. Considerably higher activation energies are normal for electrochemical reactions however the activation energy for diffusion of ionic species in aqueous solutions is about 3.5 kcal mole$^{-1}$ [65]. An activation energy of 3.5 kcal mole$^{-1}$ for velocity is there strong evidence that mass transport rather than electrochemical reaction is the controlling effect.

Open circuit transient effects: These are partly explicable by the model in that it predicts the IR drop in the crack to be small, thus the initial open circuit potential would be expected to be similar to the control potential. Also the transient time to reach -800mV (SCE) is consistent with the time required for diffusion down the crack predicted from mass transport considerations, the final potential reached is the mixed potential of (I) and (II).

Although the model is qualitatively and in some respect quantitatively in agreement with experimental results Beck has pointed out several serious limitations. Firstly, some important parameters such as crack tip angle and electrochemical kinetic data are imprecisely known and it will be difficult to obtain their values with any accuracy. Secondly, the continuum treatment becomes doubtful near the crack tip because of the magnitude of the potential gradients involved. Also the model is not applicable to the actual cracking mechanism which occurs on the atomic level. Thirdly, the formation and transport of the soluble Titanium ions Ti$^{2+}$ and Ti$^{3+}$ has not been included because of the lack of kinetic data on the formation of these ions in the conditions pertaining at the crack tip. It became clear during the development of the model and from subsequent experimentation that these soluble Titanium ions must be formed. In addition thermodynamic considerations [66] indicate that these ions should be present.

Beck's electrochemical model has been considered in some detail here because in spite of its shortcomings it is one of the few attempts to give a quantitative understanding of the cracking mechanism. In part it is easier to criticise than some other models because of the detail of its postulated mechanism and the unequivocal nature of its experimental predictions. Models giving a more qualitative explanation may be open to less criticism because their mechanism is less detailed and the nature of their predictions incomplete.

The third major variant of the electrochemical theory of SCC proposed for Titanium alloys has been developed by Krafft [67]. Krafft had previously developed a theory to correlate fracture toughness with strain hardening exponent where ligamental cell instability was a critical concept, in this theory the strain hardening rate balanced the reduction in area of the ligament until a critical ligamental cell size was reached when instability and tensile rupture occurred [68]. This theory was extended to cover fracture toughness in stress corrosion environments (K$_{SCE}$) by simply adding a dissolution term to the rate of reduction in area of the unit ligamental cell. Thus the idea of rapid anodic dissolution of highly strained metal developed by Hoar and his co-workers [69-71] for other systems was put on a quantitative mathematical basis for Titanium alloys.
of Titanium alloys in an effort to predict SCC behaviour. They found good agreement for $K_I$ values above $K_{Isc}$ but that the level of $K_{Isc}$ was not well predicted. They postulated that some factor which predicts whether SCC will occur and therefore whether the model is applicable needed to be added to the analysis. A major criticism of the Krafft model is that it postulates crack propagation by tensile ligament rupture which would give a dimpled fracture surface. Fracture is known to occur by cleavage on the $\{10\overline{7}\}$ and $\{10\overline{1}8\}$ planes. Crack propagation however does occur by dimpling through the $\beta$ phase, also an increasing amount of dimpling occurs as $K_I$ approaches $K_{IC}$ in stress corrosion environments, this may be a reason why Krafft's model works better at high $K_I$ values.

The importance of electrochemical considerations in SCC of Titanium alloys has been widely demonstrated: the dependence of cracking on potential $\{25, 34, 37, 38\}$, the effect of inhibitors $\{20, 34\}$ and existence of a limiting crack velocity independent of stress intensity $\{42\}$ all is evidence for the importance of electrochemical effects. These observations however should not be taken as evidence that anodic dissolution is necessarily the cracking mechanism, the Hydrogen Embrittlement mechanism discussed next is also dependent on electrochemical factors and experimental observations of the type discussed above can often be interpreted as supporting either type of mechanism.

2:3:4 Hydrogen Embrittlement Mechanism of Cracking

The Hydrogen Embrittlement effects which may be important in Titanium alloys have been listed by Kolachev and Livanov $\{76\}$ as:

(i) Hydride Brittleness occurring at high strain rates by cracking at the hydride metal interface.

(ii) Cold shortness. An effect similar to that obtained with high Oxygen or Nitrogen contents due to the blocking of dislocation movement by Cottrell atmospheres observed at high strain rates.

(iii) Supersaturated solid solution of Hydrogen in Titanium decomposing at low deformation rates to precipitate hydride.

(iv) Directed diffusion of Hydrogen (by stress fields, thermal gradients etc) leading to a localised increased concentration.

(v) Attachment of Hydrogen atoms to moving dislocations, slowing them, and increasing the stress for glide. A low strain rate phenomenon.

Effects due to high pressure molecular Hydrogen or Hydrogen compounds in discontinuities in the structure which occur in other metals are not possible in Titanium because the equilibrium pressure of Hydrogen gas on Titanium is too low.

Of the factors outlined by Kolachev and Livanov hydride brittleness is probably not important in a Stress Corrosion situation because hydride forms on the $\{10\overline{7}0\}$ and $\{10\overline{7}1\}$ slip planes $\{52\}$ whereas cracking is observed on the $\{1077\}$ and $\{1078\}$ planes. Effects (ii) and (v) due to Hydrogen in solid solution may be significant but are probably less important than hydride precipitation effects. Directed diffusion of Hydrogen in the intense stress field at the crack tip and precipitation of hydride from a supersaturated solid solution are probably the most important factors in Stress Corrosion.
The experimental work performed on investigating the role of Hydrogen in the SCC of Titanium alloys falls into two main groups.

(1) Control of Hydrogen content by thermal means

(2) Control of Hydrogen content by electrochemical means.

5.1 Control of Hydrogen Content by Thermal Means

Several authors have investigated the influence of Hydrogen content on $K_{IC}$ and $K_{ISCC}$ values for Titanium alloys, the Ti-8Al-1Mo-1V material being most widely investigated. The pertinent results are summarised below:

(1) Removing Hydrogen by vacuum annealing raises $K_{ISCC}$ values [77, 78]. Howe and Goode [77] have shown that annealing in an inert gas atmosphere does not remove Hydrogen and does not raise $K_{ISCC}$ values thus providing strong evidence for a connection between Hydrogen content and SCC susceptibility. Mackay and Tiner [79] found that variations in Hydrogen content from 10 to 110 ppm had no effect on SCC susceptibility of Ti-8Al-1Mo-1V but the material had a martensitic structure which would be expected to render it virtually immune from SCC whatever its Hydrogen content. A more serious disagreement is that of Sandoz and Newbegin [26, 80] who found that Hydrogen content of Ti-8Al-1Mo-1V had no effect on $K_{ISCC}$ values. Although there are some differences in heat treatment conditions, specimen thickness etc no systematic explanation of the discrepancy between the results of Sandoz and Newbegin and other authors is immediately obvious.

(2) Removing Hydrogen raises the inherent fracture toughness. The data of Orman and Picton [78] and Sandoz and Newbegin [26] show that this is particularly significant at very low Hydrogen content (<15 ppm) where $K_{IC}$ rises steeply with falling Hydrogen content. ($K_{IC}$ is the fracture toughness under non plane strain conditions.)

(3) The Kinetics of Hydrogen absorption are affected by microstructure, Aluminium having a particularly important effect. This has been commented on earlier when considering microstructural effects. The "c" and "a" Titanium lattice parameters and hence the size of the octahedral and tetrahedral interstitial positions decrease with increasing Aluminium content. Since Hydrogen is thought to enter these interstitial positions and expand the lattice [81, 82] the rate of Hydrogen absorption may be expected to decrease with increasing Aluminium content. However, the structure of Ti3Al is such that the octahedral site size increases and the tetrahedral decreases; the increase in octahedral position size is thought to account for the rapid Hydrogen absorption rates in ordered Ti-Al alloys. Thus material containing Ti3Al through ageing at 600°C or mill annealing may be expected to absorb Hydrogen more rapidly than quenched or duplex annealed material.

(4) There is a nucleation barrier for the formation of hydrides in Ti-Al alloys [36, 42]. This barrier may be overcome by a large supersaturation of Hydrogen in the matrix eg 800 ppm. The hydrides nucleate randomly and grow rapidly on [1010] planes until they impinge, all of the available Hydrogen is consumed in the formation of the hydride, the equilibrium solubility of Hydrogen in the matrix being negligible [42]. The nucleation barrier may also be overcome by small amounts of plastic strain, Boyd et al [42] found that Ti-8Al-1Mo-1V containing 200 ppm of Hydrogen precipitated hydrides on the [1010] slip planes after 2% plastic strain. These hydrides grew rapidly to consume all of the available Hydrogen.

Control of Hydrogen Content by Electrochemical Means

A large amount of work particularly by Scully and his co-workers [23, 51, 52, 56, 83-86] has been performed on the effect of hydrides on SCC and the production of these hydrides by electrochemical reaction. The important results are
(1) Hydrides can be formed on polishing electron microscope foils of Titanium Alloys. Scully and Sanderson \[52\] have shown that γ hydride laths form readily during chemical polishing of dilute Ti-Al alloys. Hydrogen absorption under these conditions was found to occur rapidly to a considerable depth. The absorption of Hydrogen by Titanium Alloys from aqueous solutions is not confined to this situation, it has been reported in a variety of environments \[52\]. In general any mechanical or chemical situation which produces an area of bare unpasivated Titanium may be expected to allow the entry of Hydrogen into the metal. Titanium is thermodynamically unstable in water \[87\] and some of the Hydrogen produced from the resulting reaction may be expected to be absorbed.

(2) Increased amounts of Aluminium in Ti-Al alloys make hydride formation easier. Sanderson and Scully \[52\] when examining the effect of chemical polishing on a range of Ti-Al alloy found that the hydride lath length increased with increased Aluminium content. This may be due to easier absorption of Hydrogen as the Aluminium content is raised, an effect which has been commented on earlier. In aqueous environments increased Aluminium widens slip steps and raises the critical current density for repassivation \[50\], this will also serve to make the entry of Hydrogen into the material easier. There is a possibility that Aluminium may have a direct microstructural influence on hydride formation, Smith \[57\] has observed that the stacking fault structure arising from the dissociation of the \{10\overline{1}0\} slip plane dislocation requires only small additional movements to attain the Titanium Hydride structure. Areas of stacking fault have been observed in the Ti-6Al-4V alloy \[88\] but there is no direct evidence that Aluminium affects the Stacking Fault Energy, the co-planar dislocation arrays formed in Ti-Al alloys are more probably due to Short Range Order.

Whatever the reason, the easier formation of hydride at higher Aluminium contents fits in well with the increased SCC susceptibility.

(3) Hydride formation has been demonstrated in a susceptible alloy when deformed in a SCC environment but not in an environment which does not cause cracking. Similarly hydrides are not induced in non-susceptible material. Sanderson and Scully \[84\] have bent foils of Ti-5Al-2.5Sn in acidified sodium chloride solution. This ruptured the protective oxide film and hydrides grew along the bend. No hydrides appeared when this was repeated with pure Titanium foils neither did they appear when Ti-5Al-2.5Sn was bent in acidified sodium sulphate solution. These critical experiments are strong evidence for the importance of hydrides in SCC of Titanium Alloys.

(4) Cathodic protection against SCC is ineffective in non-film forming conditions. A criticism of the importance of Hydrogen in SCC of Titanium Alloys has been that cracking can be inhibited by the application of a cathodic current. A cathodic current which generates Hydrogen may, from simple theory, be expected to enhance cracking if this was due to any type of Hydrogen Embrittlement mechanism. This effect is in fact observed in some other stress corrosion systems. Powell and Scully \[89\] have observed that cathodic polarisation does not prevent cracking in 10N HCl, they consider that in neutral solutions the effect of cathodic polarisation is to increase the OH\(^{-}\) concentration at the crack tip and promote the formation of a passive layer. Hydrogen entry is reduced and cracking stops. Thus the ratio of activating to passivating species \(\frac{\text{Cl}^-}{\text{OH}^-}\) is critically important in determining whether or not a passive film forms at the crack tip, slowing Hydrogen ingress. The critical \(\frac{\text{OH}^-}{\text{Cl}^-}\) ratio for passivation cannot be achieved in 10N HCl and so cathodic polarisation is ineffective in preventing SCC. It is interesting to note that cracking is severe in other non-film forming environments, eg methanol-HCl.
Stress is important in the formation of hydride. Sanderson, Powell and Scully postulated that the role of stress is to rupture the passive film so that hydride growth from the bared surface may begin. The relative rates of rupturing and repassivation are important here, if too much of the surface is unpassivated general attack occurs, if the surface repassivates too quickly no attack occurs. The localisation of stress seems important, a pre-existing hydride, crack or notch is necessary to provide the stress concentration required for the large local exposure of bare metal needed. In support of these views Sanderson, Powell and Scully have observed that Ti-5Al-2.5Sn will only crack in dynamic strain stress corrosion tests at cross head speeds of 0.05-0.2 cm/min for unnotched specimens and 0.005-0.05 cm/min for notched specimens.

Although these repassivation ideas seem reasonable when discussing cracking in dilute chloride solutions the fact that cracking will occur in environments where a passive film (at least of the classical type) does not exist makes their more general application doubtful.

Discussion of the Hydrogen Embrittlement Mechanism

The results outlined in 5.1 and 5.2 provide considerable evidence that Hydrogen and hydride formation are important in the SCC of Titanium alloys. In particular Scully and his co-workers have qualitatively explained many of the phenomenological features of cracking on a Hydrogen Embrittlement basis. In spite of this there are several objections to the Hydrogen Embrittlement mechanism. Firstly, cracking has been observed in dinitrogen tetroxide and carbon tetrachloride environments containing no source of Hydrogen. It is possible that water contamination may be the source but it seems more likely that cracking does not occur by a Hydrogen Embrittlement in these situations. Although Hydrogen Embrittlement may not therefore be of general applicability this does not detract from its relevance to aqueous environments. The effect of cathodic polarisation on cracking and the answer of Scully and his co-workers to this criticism of the mechanism has already been mentioned. It is worth noting however that in recent years the simple idea that anodic polarisation stimulates anodic dissolution type SCC and cathodic polarisation stimulates Hydrogen Embrittlement has been increasingly questioned. This is because the potential and environment at the metal surface may be very different from that at the bottom of a pit or crack (eg see Wilde on cracking in martensitic steels). The effect of polarisation on cracking in Titanium Alloys and other materials may therefore be more complicated than previously thought.

Beck, on the basis of his electrochemical model considered Hydrogen effects to be of little importance because the low rate of Hydrogen discharge coupled with the high crack velocity made the crack "outrun" the cathodic Hydrogen producing reaction. This meant that the Hydrogen concentration a short way from the crack tip was virtually unchanged. Boyd et al however following Beck's procedure have calculated a Hydrogen concentration of 20 ppm at 10 nm from the crack tip and 200 ppm at 1 nm from the crack tip. Assuming a pre-existing Hydrogen content of 80 ppm this gives a total content of 100 ppm at 10 nm and 280 ppm at 1 nm. They argue that the Hydrogen content in this thin layer adjacent to the crack tip is sufficient to form strain induced hydrides. The application of electrochemical calculations based on bulk thermodynamic data over atomic distances is questionable but the fact remains that the mechanism of cracking may operate over these short distances and a high concentration of Hydrogen some way from the crack tip may not be necessary. In addition once hydride has nucleated at the crack tip rates of cathodic Hydrogen discharge on TiH and diffusion rates of Hydrogen in TiH may be more pertinent than rates applicable to Titanium metal. The overpotential for Hydrogen discharge is much lower for TiH than Ti, so data on H diffusion rates in TiH seems available but the localisation of Hydrogen discharge and diffusion along hydride laths may be an important effect. The size, shape and orientation of hydride may also be important, Loutham has found that hydrides tend to orientate at right angles to an applied tensile stress.
Effects due to pre-existing interstitial Hydrogen in the material seem to be important. This has been demonstrated by the work of Orman and Picton \[\text{78}\]. It is unlikely that the effects of pre-existing Hydrogen and Hydrogen generated from electrochemical reaction at the crack tip are simply additive i.e. giving a concentration of Hydrogen above a threshold needed for cracking. The variation in \(K_c\) values in air with Hydrogen content indicates a strong dependence of crack tip mechanical properties on pre-existing Hydrogen content. These mechanical properties may be expected to strongly influence the rate of Hydrogen absorption in any subsequent stress corrosion situation. Thus the effects of pre-existing Hydrogen and Hydrogen generated during stress corrosion may be synergistic rather than simply additive.

In spite of the amount of work done the actual mechanism of cracking on an atomistic level is still unclear, perhaps the slip inhibition ideas of Mauney and Starke \[\text{54}\] are the most attractive in that they take into account the effects of Aluminium content and hydride formation while accounting for the peculiar crack path.

As in all stress corrosion situations the mechanical and chemical environment at the crack tip may be very different from bulk metal in bulk environment. Aggressive ions may affect notch (or crack) plasticity \[\text{93}\], strain induced electric fields may aid the kinetics of Hydrogen absorption \[\text{94}\] and low pH has been measured at crack tips \[\text{95}\]. It seems that to further advance stress corrosion understanding, work aimed at investigating the environment at the crack tip must be performed so that the important parameters can be better defined. Only then can possible mechanisms of cracking be tested and developed on a quantitative basis. It also seems possible that mechanisms are too rigidly delineated as "Electrochemical Dissolution", Hydrogen Embrittlement", etc, interaction of effects such as anodic dissolution \(\rightarrow\) hydrolysis \(\rightarrow\) low pH \(\rightarrow\) enhanced Hydrogen discharge \(\rightarrow\) Hydride formation are perhaps more likely. Cognizance of such possibilities will be necessary to achieve a basic understanding of the cracking mechanism.


Stress Corrosion Testing Using a Potentiostatic Dynamic Strain Technique.
J. Brettle and S. Orman. AWRE Report 022/73.


G Sanderson and J C Scully. Unpublished Work reported in Ref 52.


Private Communication. R Otuska to G Sanderson, D T Powell and J C Scully, Reported in Ref 56.


Table 1: Typical SCC Data for Titanium Alloys
(From Peterson et al. 1987)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Yield Strength (ksi)</th>
<th>Fracture Toughness Index (ksi√in)</th>
<th>$K_{ISCC}$ (ksi√in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-7Al-2Nb-1Ta</td>
<td>102</td>
<td>110</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>105</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>105-110</td>
<td>100</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>106</td>
<td>106</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>113</td>
<td>41</td>
<td>40</td>
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<td></td>
<td>131</td>
<td>130</td>
<td>88</td>
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<td>Ti-8Al-1Mo-1V</td>
<td>108</td>
<td>112</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>90</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>54</td>
<td>18</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>116</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>115</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>64</td>
<td>55</td>
</tr>
<tr>
<td>Ti-5Al-2.55n</td>
<td>111</td>
<td>130</td>
<td>72</td>
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<td>114</td>
<td>112</td>
<td>39</td>
</tr>
<tr>
<td>Ti-6Al-4V-15n</td>
<td>131</td>
<td>112</td>
<td>42</td>
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<td>Ti-6Al-6V-2.55n</td>
<td>186</td>
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<td>Ti-6Al-2Mo</td>
<td>126</td>
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<td></td>
<td>127</td>
<td>123</td>
<td>103</td>
</tr>
<tr>
<td>Ti-7Al-3Mo</td>
<td>104</td>
<td>128</td>
<td>45</td>
</tr>
<tr>
<td>Medium</td>
<td>Temp., F</td>
<td>Susceptible Titanium Materials</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>----------</td>
<td>------------------------------------------------------------------------------------------------</td>
<td></td>
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<tr>
<td>Cadmium</td>
<td>&gt; 610</td>
<td>Ti-4Al-4Mn</td>
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</tr>
<tr>
<td></td>
<td>625-750</td>
<td>Ti-8Mn</td>
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<tr>
<td>Mercury</td>
<td>RT</td>
<td>Ti-75A, Ti-6Al-4V</td>
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<tr>
<td></td>
<td>700</td>
<td>Ti-13V-11Cr-3Al</td>
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<td>Silver</td>
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<tr>
<td>Ag plate</td>
<td>875</td>
<td>Ti-7Al-4Mo, Ti-5Al-2.5Sn</td>
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<td>AgCl</td>
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<td>Ti-7Al-4Mo, Ti-5Al-2.5Sn</td>
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<td>Ag-5Al-2.5Mn</td>
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<td>Ti-6Al-4V, Ti-8Al-1Mo-1V</td>
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<td>Chlorine</td>
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<tr>
<td>Hydrochloric Acid</td>
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<td>10%</td>
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<tr>
<td>10%</td>
<td>95</td>
<td>Ti-5Al-2.5Sn</td>
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<tr>
<td></td>
<td>650</td>
<td>Ti-8Al-1Mo-1V</td>
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<td>Nitric Acid</td>
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<td>RFNA</td>
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<td>Ti, Ti-8Mn, Ti-6Al-4V, Ti-5Al-2.5Sn, Ti-2Fe-2Cr-2Mo</td>
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<td>Sulfuric Acid</td>
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<td>7-60%</td>
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<tr>
<td>Chloride Salts</td>
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<tr>
<td>various, residues</td>
<td>550-800</td>
<td>All commercial alloys</td>
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<tr>
<td>Nitrogen tetroxide</td>
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<tr>
<td>(no xs NO)</td>
<td>85-165</td>
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<tr>
<td>Methyl alcohol</td>
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<td>Ti-6Al-4V</td>
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<td></td>
<td></td>
<td>Ti-6Al-4V, Ti-8Al-1Mo-1V</td>
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<td></td>
<td>Ti-75A, Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn, Ti-4Al-3Mo-1V</td>
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<tr>
<td>Methyl chloroform,</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>inhibited</td>
<td>700</td>
<td>Ti-8Al-1Mo-1V, Ti-6Al-4V, Ti-5Al-2.5Sn, Ti-13V-11Cr-3Al</td>
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<tr>
<td>Ethyl alcohol</td>
<td>RT</td>
<td>Ti-8Al-1Mo-1V</td>
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<td></td>
<td></td>
<td>Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn</td>
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<td>Ethylene glycol</td>
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<td>Trichloroethylene</td>
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<td>1150, 1500</td>
<td>Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn</td>
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<td>Trichlorofluoro-</td>
<td>1450</td>
<td>Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn</td>
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<tr>
<td>ethane (&quot;Freon PCA&quot;)</td>
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<td>Ti-6Al-4V, Ti-13V-11Cr-3Al</td>
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<td>Chlorinated diphenyl</td>
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<tr>
<td>(&quot;Aeroclor 1262&quot;)</td>
<td>600-700</td>
<td>Ti-5Al-2.5Sn</td>
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<tr>
<td>Sea Water</td>
<td>ambient</td>
<td>Unalloyed Ti (with high oxygen content, i.e., 0.317 percent)</td>
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<td>Ti-8Mn</td>
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<td>Ti-2.25Al-1Mo-11Sn-5Zr-0.2Sc (IMI-679)</td>
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<td>Ti-3Al-11Cr-13V</td>
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<td></td>
<td>Ti-4Al-4Mn</td>
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<td></td>
<td></td>
<td>Ti-5Al-2.5Sn</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti-6Al-2.5Sn</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Ti-6Al-4V</td>
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<td>Ti-6Al-4V-2Co</td>
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<td></td>
<td>Ti-6Al-6V-2.5Sn</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti-7Al-2Cb-1Ta</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Ti-7Al-3Cb (as received and beta annealed)</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>Ti-7Al-3Cb-2Sn</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Ti-8Al-1Mo-1V</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti-8Al-3Cb-2Sn</td>
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</tr>
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</table>
### Table 1. Titanium - Aluminium Equilibrium Diagram

(From Crossley (19))

<table>
<thead>
<tr>
<th>Aluminum Content, Weight Per Cent</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single Phase</td>
</tr>
<tr>
<td></td>
<td>Two Phase</td>
</tr>
<tr>
<td>O</td>
<td>Optical and Electron Microscope</td>
</tr>
<tr>
<td>o</td>
<td>Quench Transformation Structures</td>
</tr>
<tr>
<td>◯</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>△</td>
<td>Electron Diffraction</td>
</tr>
</tbody>
</table>

Note: ◯ Denotes Pseudo Two-Phase Alloys

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![Diagram](image-url)
Diagram 2. Fracture of Titanium Alloy Oxide Films by Slip Step

(from Feige and Murphy [33])
2.4 A Survey of the Literature on SCC of Cobalt Based Alloys

2.4.1 Introduction

Since the 1940's cobalt based alloys have received much attention because of their high temperature applications in gas turbine and jet engines. The work has concentrated on the oxidation/sulphidation resistance and mechanical properties at very high temperatures. Although the alloys have been used for a similar period of time for orthopaedic and dental applications a search of the medical literature has not revealed any work on the stress corrosion of these alloys in these fields.

Titanium based and iron based alloys have been widely used in chemical, marine and aerospace technology in conditions comparable to those found in the body i.e. a dilute chloride environment at ambient temperature. Therefore there is a wealth of literature on the SCC of these materials from non-medical sources. This is not the case with cobalt based alloys, their non-medical use has been almost entirely in service situations not relevant to surgical implants. The literature on the stress corrosion properties of these materials is therefore extremely sparse.

2.4.2 Stress Corrosion of Co-Cr-Mo alloys (vitallium type alloys)

No information concerning the incidence of SCC susceptibility or research on SCC of these alloys has been found.

2.4.3 Stress Corrosion of Co-Cr-Ni-W alloys (wrought vitallium, WR125, HS25 alloy)

No report of research on stress corrosion of these alloys has been found but there are some suggestions that a SCC problem may exist. Cracking of cold worked Co-Cr-Ni-W hip nails has been attributed to SCC, this has been subsequently avoided by using hot worked rather than cold worked material for nails (1). Also Devine et al (2) have reported crevice corrosion leading to corrosion fatigue in this alloy. This predisposition to forms of localised electrochemical attack suggests that stress corrosion may be possible in this material.

2.4.4 Stress Corrosion of Co-Cr-Ni-Mo alloys (Multiphase alloys MP20N and MP35N)

The multiphase alloys MP20N and MP35N are recent developments and are atypical of cobalt based alloys in general in that they have not been developed for aeroengine use but for high strength, corrosion resistant fastener applications. Although these fasteners may be used at high temperatures their ambient and cryogenic temperature properties are also important. The stress corrosion, hydrogen embrittlement, corrosion fatigue and impact properties of these materials at ambient temperature have therefore received some attention.

Two alloys have been developed MP20N, 50\% Co - 20\% Ni - 20\% Cr - 10\% Mo and MP35N, 35\% Co - 35\% Ni - 20\% Cr - 10\% Mo. Very high strengths may be achieved by cold working which produces strain induced hcp platelets in the fcc matrix, additional strengthening may be achieved by subsequent ageing due to precipitation of a phase tentatively identified as Co,Mo \(3\). The majority of work has been done on the MP35N material.
Early tests on the stress corrosion properties of MP35N were conducted by the producers, the Latrobe Steel Company. Cold worked and coupons were stamped with indentations to produce areas of high local strain and immersed in boiling 42% MgCl$_2$ solution for 192 hrs. No cracking was observed (3). Similar tests were performed in 10% FeCl$_3$, 10% NaCl with the acidity adjusted to pH2 and 10% HCl + FeCl$_3$. The test temperature was not reported but no cracking was observed after 1000 hrs exposure (3, 4). Simple U bend specimens were immersed in sea water at a marine exposure site and no cracking was observed after two years (5).

More sophisticated tests were performed by Montano (6) for NASA. Cold worked and aged bar was tested at stresses up to 0.2% Proof Stress alternate immersion test in 3.5% NaCl solution. C-ring and tensile specimens were used to test the transverse and longitudinal direction of the bar. No cracks were observed after 180 days exposure.

Less work has been done on MP20N than MP35N and no published data stress corrosion testing can be found. However Smith and Yates (7) that the crevice and stress corrosion properties of MP20N are inferior to MP35N in halide solutions but quote no results to support their statement.

Conclusions

There has been very little published on stress corrosion of cobalt based alloys. This is due largely to the fact that they are mainly used at very high temperatures where stress corrosion is unimportant. While stress corrosion failures have not been reported in the aedic or dental literature should not be taken to mean that stress corrosion does not necessarily occur in the body environment. These lines have until recently been metallurgically unsophisticated with failures simply attributed to "overstressing". A comprehensive study of failure modes of cobalt based alloys in the body has not been previously undertaken.

Some stress corrosion testing has been performed on MP35N. Tests indicate that MP35N should be immune to SCC in the conditions tested in the human body.

References

Private communication, Dr Keys, University of New South Wales, Australia to Mr A N Hughes, AWRE


A Mechanical Property and Stress Corrosion Evaluation of MP35N Multiphase Alloy, J W Montano NASA Technical Memorandum NASA TM X-64591

High Strength, Ductility, Corrosion Resistance, Multiphase Alloys Have all Three. G D Smith, D H Yates. Metal Progress, 93 3 pp100-102 (March 1968)
3: EXPERIMENTAL METHODS USED IN STRESS CORROSION TESTING

3.1 INTRODUCTION

Reviewed below are the techniques commonly employed in stress corrosion testing.

As a general rule laboratories undertake accelerated testing for the following principal reasons:

(i) to produce an order of merit within a group of materials;
(ii) to estimate the life of a given material under specified environmental conditions;
(iii) to investigate a mechanism of failure.

Ideally a test method should not be so severe that it leads to the condemnation of a material that would prove adequate for a particular service condition, nor so trifling as to permit the usage of a material in circumstances where rapid failure would ensue.

Although SCC is a result of the conjoint effect of stress and corrosion it is convenient to classify the tests according to the method used for stressing the specimen; the provision of the corrosive environment being considered separately. The methods of stressing a smooth test piece involves either:-

(i) a constant total strain;
(ii) a constant stress

or

(iii) a constant strain rate

while other methods use precracked specimens.

3.2 CONSTANT STRAIN TESTS

This type of test is widely used because the specimens and jigs are cheap and simple. Examples of this type of test are described below.

Plastically deformed specimens

In this test the surface of a metal coupon is deformed by stamping, cupping, bending or welding; plastic strain exists in the deformed areas and elastic strains at the junction with the undeformed areas. The coupon is immersed in the environment of interest and monitored for cracks. This test has the advantage that the stress generating mechanisms are similar to those often encountered in service. It is useful as a preliminary sorting test but only supplies a crude qualitative measure of susceptibility.
Bend Specimens

These are commonly used to test sheet materials, a coupon from the sheet is bent elastically and held in a restraining jig (figs 1 and 2). The specimens are small and cheap which makes them suitable for multiple long term exposure tests or exposure in restricted conditions, eg in a process stream in a chemical plant.

The method of manufacturing the specimen is important as cracks may propagate more easily from "broken edges" than machined ones\(^1\). For immersion conditions jigs have to be made from an insulating material to prevent galvanic action, but insulation is not normally required for atmospheric exposure tests. There are problems with creep allowing specimen relaxation in this type of test\(^2\). For small deflections of the specimen the stress may be calculated easily\(^3\), whereas a more complicated analysis is required for larger deflections\(^4\). Such calculations have been found to agree with measured stresses to within 5%\(^4\). This is sufficiently good for many applications although much larger edge to centre variations in the stress have been reported\(^5\). Where a better defined stress distribution is required four point loading may be used. This of course complicates the experimental procedures and makes the test more expensive. Three point loading is not advised as it introduces a crevice in the area of maximum stress.

C Ring specimens (Fig 3)

These have the advantage of compactness and are therefore useful in testing specimens taken from tube, extrusions and forgings. The strain is applied by tightening the nut and bolt and the outer fibre stress is calculated from a standard equation\(^6\). If the specimens are immersed in the corrosive environment the nut and bolt must be of the same material as the C ring, or alternatively insulating bushes should be used to prevent galvanic corrosion.

Tuning Fork Specimens (Fig 4)

These specimens are similar to the C ring in that they are compact and useful for testing the directionality of scc properties in plates and forgings. This feature is important for some materials, eg aluminium alloys are often much more susceptible to scc when stressed in the short transverse direction of the parent plate. Tuning fork specimens with tapered tongs may be used to give a uniform stress distribution. Stresses can be calculated using a formula derived from the bending of a cantilever beam\(^6\).
Other types of specimen deriving strain from interference fits or rigid stressing jigs have been used but these are more expensive and complex. They have therefore found only limited use.

Constant strain tests of the type described above have found wide use as technological tests because of cheapness, compactness and convenience, in addition constant strain is more representative of many service situations than constant stress. Care has to be taken to avoid galvanic coupling and effects due to specimen manufacture have to be considered. Orientation with respect to parent stock material and method of cutting and preparing specimen surfaces are particularly important.

A disadvantage of constant strain tests is that stresses are not known accurately and are difficult to reproduce from specimen to specimen. A further disadvantage is that stress relaxation due to crack growth may slow further growth or even stop propagation depending on the system studied. Where fracture of the specimen does not occur a parameter such as "time for the first crack to appear" must be used as a criterion of failure. This requires frequent interruption of the test for tedious specimen examination and an arbitrary decision of how large a defect has to be before it is classified as a crack.

Stress relaxation effects mean that in general constant strain tests are less accelerated than those at constant stress.

### 3.3 Constant Stress Tests

Constant stress tests may be used with tensile or bend specimens, some common experimental arrangements are shown in Fig. 5. Such tests use more complex apparatus than the previous tests described but have the advantage that the stress state within the specimen is well defined and can be measured easily. Loads may be applied by springs, weights or hydraulically. Springs are simple and cheap but can apply only a limited load and allow stress relaxation on extension of the specimen due to cracking. Because of their load limitations they are often restricted to the testing of wires. Weights with lever systems may be used to apply higher loads but for high strength materials, particularly in thick sections, hydraulic loading must be used. Such systems are obviously more expensive than the simple rigs described earlier.

Tensile specimens for constant stress tests are normally cylindrical if taken from wire or bar. Rectangular section specimens
taken from plate may fail more rapidly because of easier crack initiation from sharp edges. Deliberate notching of the specimens may also be used to accelerate failure\(^7\).

An advantage of constant stress tests compared to constant strain tests is that crack propagation decreases the net section and so accelerates the cracking process until failure of the remaining ligament occurs by mechanical rupture.

Methods of statistically treating SCC data from constant stress and constant strain tests are given in Appendix 1.

### 3.4 PRECRACKED TESTS

Tests using precracked specimens and a fracture mechanics analysis of the results have come into increased use in recent years. These tests are particularly relevant to high strength materials with a limited ductility and restricted tolerance to defects where a small SCC crack may initiate catastrophic brittle failure. The whole process may be treated in an integrated manner using fracture mechanics.

A simple type of widely used precracked test was first introduced by Brown\(^8\). In essence the test consists of stressing a notched and fatigue cracked rectangular beam under cantilever loading conditions (Fig 6), weights being added to the loading arm until catastrophic failure occurs. The stress intensity at the crack tip required to produce this failure, \(K_{ic}\), can be calculated from the load and specimen geometry (Appendix II). With sufficiently large specimens plane strain conditions are obtained and minimum values of \(K_{ic}\) known as \(K'_{ic}\) (the fracture toughness of the material) can be obtained. Repeating this procedure in a stress corrosion environment results in lower values of \(K_I\) causing failure over a period of time. A threshold value \(K_{isc}\) may be defined by analogy with \(K_{ic}\). Stress corrosion does not lower the inherent fracture toughness of the material, but \(K_{isc}\) is a threshold stress intensity for subcritical crack propagation. When the crack has grown to a critical length the stress intensity \(K_{ic}\) is exceeded and fast fracture ensues.

The normal experimental procedure is to test specimens over a range of \(K\) values in a stress corrosion environment and measure time to failure. On plotting \(K_I\) against time to failure a threshold below which a crack will not propagate, may be measured \(K_{isc}\). Since the original work of Brown a variety of specimen types, borrowed from fracture toughness testing technology, have been used for stress corrosion testing (Fig 7). As with constant stress and strain tests, various specimens
are available to simulate particular loading conditions in the relevant directions of the parent material. Information on specimen types and calculation of $K_I$ values is contained in Appendix II. The major advantages of precracked testing are:

(1) $K_I$ uniquely defines stress conditions at the crack tip. Effects of specimen type, size etc do not need to be considered.

(2) Meaningful design data, eg safe geometries, working loads and inspection periods may be derived from these tests.

(3) Crack propagation only is studied. This is useful in materials which are resistant to SCC initiation but susceptible to propagation. Tests on smooth specimens may lead to erroneous conclusions as to the susceptibility of these materials when used in structures containing initiating defects.

(4) No test acceleration is required, overall acceleration is achieved by omitting the initiation stage. The crack propagation data obtained is directly comparable to service conditions. No dubious extrapolation of laboratory results is required.

In spite of these advantages there are certain drawbacks:

(i) Initiation, which is the rate controlling step in many systems, is not studied. The efficacy of surface treatments etc in preventing SCC cannot therefore be investigated.

(ii) This method of testing is well developed only for relatively low toughness materials. Its relevance to tough ductile materials has not yet been established.

(iii) Not all materials have a definite $K_{I_{SCC}}$ limit, slow crack growth occurs over long periods\(^9\). Arbitrary criteria for nil crack growth, such as the highest value of $K_I$ which will not cause failure in 360 minutes, $K_{II}(360)$, has been used in these circumstances.

(iv) Pre-cracked testing may not be relevant to systems where environmental effects are dominant, eg Freedman\(^{10}\) has
reported that in precracked tests on sensitised AISI 304 stainless steel fresh cracks initiate from the smooth specimen surface.

3.5 CONSTANT STRAIN RATE TESTS
Tests employing smooth specimens strained at a constant rate rather than under conditions of constant stress or strain have been used mainly in work on stress corrosion mechanisms. In these tests susceptibility has been indicated by the presence of cracks in the deformed specimen or by a reduction in mechanical properties when compared to those obtained in air. The advantages for this type of test are that results can be obtained in a short time and there is less need for acceleration by high temperature or aggressive chemical environment because the dynamic strain acts as an accelerant. Environmental conditions closer to those in service can therefore be employed. The test may be strain rate sensitive making it possible to extrapolate results to the strain rates experienced in service (creep rates), although the possibility of a threshold strain rate for susceptibility must be borne in mind.

The application of potentiostatic control is a further refinement to the dynamic strain test. The advantages of this are dealt with in some detail in the section on "Environmental Control and Acceleration".

The dynamic strain test has been suggested as a rapid sorting test and good correlation has been obtained with more conventional long term tests on a limited number of alloys (11). Once the validity of the test has been established for a particular system it can be used to evaluate rapidly the effect of compositional changes, heat treatments, environmental variations etc on SCC. If the theory of the effect of dynamic strain on SCC can be refined it may be possible to use the data directly without recourse to correlation with the results of more conventional tests.

A particular advantage of the dynamic strain test is that it accelerates the initiation phase of cracking rather than omits it as does the precracked test. Therefore it is particularly useful in the many systems which are initiation controlled.

3.6 ENVIRONMENTAL CONTROL AND ACCELERATION
Stress corrosion cracking is the conjoint effect of stress and corrosion on an alloy. The earlier sections dealt with methods of applying mechanical stress to specimens without considering the corrosive
environment. It is incorrect, however, to describe an alloy as being susceptible to SCC since it is the alloy/environment combination which determines the susceptibility. The specification and control of the environment is therefore an important aspect of SCC testing.

Most SCC tests are accelerated to enable a programme of laboratory tests to be completed in a reasonable length of time. The four main types of test described previously are accelerated in different ways. Overall acceleration is achieved in precracked tests by omitting the initiation stage, acceleration in constant strain rate tests is normally mechanical, i.e., by the strain, although simultaneous environmental acceleration is also possible. Constant stress and strain tests usually rely entirely on environmental acceleration. This is achieved normally by using a more aggressive environment than that encountered in service. Although this technique has found wide use it is purely empirical and the validity of the application of test results to service conditions is questionable. The use of boiling, saturated magnesium chloride in testing stainless steels is a good example of this approach. The occurrence of SCC in such laboratory tests is of little assistance in predicting behaviour in service under conditions of much lower temperatures and chloride concentrations. The different methods of environmental acceleration of SCC are described below.

### 3.6.1 Temperature

Increased temperature is a common accelerant; solution conductivity, diffusion rates and chemical reaction rates are increased giving decreased time to failure. The degree of acceleration varies from system to system depending on the SCC mechanism operative. Two points require caution however: firstly high temperature results cannot be reliably extrapolated to lower temperatures in all systems as a temperature threshold for cracking may exist, secondly if the temperature is too high the mechanism and mode of cracking may change and give results which are not relevant to low temperature conditions.

### 3.6.2 Concentration

Increasing the concentration of chemical species known to be important to SCC is another common acceleration method. Again it is not possible to generalise, cracking in some systems is more concentration dependent than in others. An added difficulty is that too great a concentration of aggressive ions may cause general corrosion rather than stress corrosion.
3.6.3 pH

In many systems low pH accelerates SCC and as a corollary high pH may inhibit cracking. Examination of the particular system under test is required and care must be taken because too low a pH may give general corrosion.

3.6.4 Oxygen

Oxygen, as a cathodic reactant, often accelerates SCC and removal of oxygen may inhibit cracking. Other oxidising agents may be used, eg potassium dichromate has been used in testing some non-ferrous alloys(12).

Much of the scatter observed in SCC test results is due to insufficient control of the environmental variables, eg small amounts of impurities in MgCl₂ greatly influence cracking times in stainless steels(13). Corrosion prior to SCC may be important, this is known to be so in cracking of a brasses(14). Where corrosion produced species are important, pre-exposure to environment, reuse of test solution, volume of test solution etc will exert an influence on failure times. Closely specified standard test procedures are required in these circumstances to make the comparison of results from different laboratories meaningful.

Atmospheric exposure tests are an important type of SCC test where environment cannot be controlled. Results vary according to rainfall, hours of sun, etc. A statistical treatment of data obtained over several years is necessary to mitigate this disadvantage. To some extent atmospheric exposure can be simulated in the laboratory by using an alternate wetting and drying immersion test. Close control of drying time, temperature and humidity is required to give reproducible results(2).

A direct approach to control and acceleration of environmental conditions which has come into increasing use in recent years is electrochemical control. In this technique the specimen is held at a constant potential (potentiostatic) or a constant current is impressed (galvanostatic) by means of external electronic control equipment. Electrochemically controlled tests have been used widely in basic studies of stress corrosion mechanisms. By eliminating the variable cathodic reaction results are made more reproducible and a judicious choice of potential or current density can accelerate failure. Tests performed over a range of potentials can give valuable information on the mechanism of cracking. Basic work such as this is required before electrochemically
accelerated tests can be used reliably for technological testing. Although control equipment is expensive these tests will probably find increased use. The possibility of close direct control of corrosion conditions, together with the ease with which conditions may be varied, makes this technique powerful in the controlled acceleration of tests and analysis of subsequent data.

3.7 CONCLUSIONS

The features of each type of SCC test (Table 1) means that each is suited to particular practical requirements. The simpler tests will continue to be used in technological testing with precracked and constant strain rate tests finding wider use in stress corrosion research.
REFERENCES


| 1. Test method | 2. Chemical | 3. Physical
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<td>Elastic strain tests.</td>
<td>As for constant strain test</td>
<td>Some tests may be more expensive than the comparator, but loading apparatus can be better than comparator. Normally some means.</td>
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<td>Soft test</td>
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<td>Weakly used.</td>
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<td>Mechanism.</td>
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<td>Relatively cheap and easy to use</td>
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**Table 1. Resume of test characteristics**
<table>
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<th>Tests</th>
<th>Commentary</th>
<th>Material</th>
<th>Machine</th>
<th>Conclusion</th>
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<td>Tensile strain and has advantages as for rapid, relatively simple equipment.</td>
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Table 1 continued.
Fig 1. Bend specimen in jig

Fig 2. Loading device for bend specimens
Fig 5. Constant load stress corrosion tests
Fig 6. Typical pre-cracked stress corrosion test
Fig 7. Types of specimen and recommended proportions for pre-cracked stress corrosion testing (18)
Fig 8. Stress/endurance curves for a mild steel immersed in boiling LiNO$_3$ solutions

Fig 9. Stress/log endurance curves for various steels
Fig 10. Distribution of stress corrosion results for USS 12 MoV stainless steel
APPENDIX I. TREATMENT OF SCC DATA

To establish unequivocally a material's susceptibility to SCC both stressed and unstressed specimens should be exposed to the corrosive environment. Thus failure due to stress corrosion can be distinguished from failure due to a reduction of load supporting area by corrosion. This is particularly important in corrodible materials such as aluminium alloys in constant stress tests. Booth et al(15) have taken account of this by using a stress corrosion index (SCI) where:

$$\text{SCI} = \frac{T_{Su} - \sigma}{T_S - \sigma}$$

$T_{Su} =$ tensile strength (based on original cross sectional area) of unstressed specimen exposed for the time-to-failure of the stressed specimen.
$T_S =$ tensile strength of unexposed specimen.
$\sigma =$ stress at which failure occurs on exposure.

High SCI values indicate greater SCC susceptibility. The SCI is very dependent on test conditions and is not therefore very useful for comparing materials.

Stress corrosion data often has a wide scatter and a representative value of specimen life has to be chosen. The arithmetic mean is often used because of its suitability for standard statistical manipulation. It is affected however by extremely large or extremely small values which render it atypical of the average distribution. The median is often a better representative value and has the advantage that only half the specimens have to fail for its determination. It has the further advantage that it requires no assumption about the population distribution. It is often the case that not enough specimens are tested to allow the type of statistical distribution to be determined. The use of an unrepresentative mean value in these situations can result in an incorrect interpretation of the results.

More information on stress corrosion susceptibility is obtained by testing specimens over a range of stresses. Stress versus specimen-life curves can then be plotted which are hyperbolic for a large number of systems. If the specimen lives are plotted on a logarithmic scale the
curve is transformed into two straight line branches, the one parallel to the time axis being the threshold stress for these particular conditions (see figures 8 and 9). The determination of stress thresholds is of obvious practical importance. Strain versus specimen life can be similarly plotted to give strain thresholds which may be more applicable to certain service situations.

To overcome the problem of "run-out" specimens, ie specimens which do not fail in the duration of the test, per cent failure of a group of specimens versus stress is often plotted. The presentation of data may be further refined by plotting per cent survival values versus log cracking time on normal probability paper (Fig 10). The results often lie on a straight line. Confidence limits can be computed and also plotted on the graph.
APPENDIX II. FRACTURE MECHANICS

The elastic stress field at the tip of a crack in a plate of metal under uniform tensile stress may be characterised by the single parameter, $K$, the stress intensity. $K$ is proportional to the product of the nominal stress and the square of the crack size, the dimensions of $K$ being stress/length. At a sufficiently high value of $K$ designated $K_c$, the fracture toughness of the material, unstable fast fracture occurs.

No metal is totally brittle, ie a plastic zone forms at the crack tip. This means that calculations based on linear elastic fracture mechanics are not strictly applicable to real situations. In practice however provided the size of the plastic zone is small compared with the specimen dimensions linear elastic results are a close approximation to the actual $K$ value at the crack tip. Such conditions are known as plane strain condition and the stress intensity is labelled $K_I$, the "I" indicating plane strain and opening mode crack propagation. Figure 7 shows dimensions and $K_I$ calculations for commonly used fracture toughness specimens. If specimen thickness is less than the minimum required for plane strain the $K$ values calculated by linear elastic mechanics will be higher than the actual crack tip $K$ value. Such values are often labelled $K_{IC}$ and $K_{ISC}$ are called 'invalid' as they are not fundamental to the material but are dependent on specimen configuration. They may however be useful for comparison purposes. In the limiting case of sufficiently thin specimens plane stress conditions prevail and $K_I$ values are a maximum.

It is presently recommended that to achieve plane strain conditions for the measurement of valid $K_I$ values,

$$B < 2.5 \left( \frac{K_I}{\sigma_y} \right)^2$$

where $B$ is the specimen thickness and $\sigma_y$ the yield stress.

A great advantage of pre-cracked scc testing is that $K_{ISC}$ data may be applied directly to a service situation. A member containing a surface flaw under uniaxial tension is often encountered in service (see Fig. 7 (e)). The value of $K_{ISC}$ for the material limits the various combinations of stress ($\sigma$), flaw depth ($a_o$) and flaw shape ($\gamma$) allowable. It is useful when comparing the stress corrosion susceptibility of various materials to compare the depth of a long surface crack which would be sufficient to cause stress corrosion crack propagation at yield point stress levels. For this situation the equation of Fig. 7 (e) reduces to:
\[ a_{cr} = 0.2 \left( \frac{K_{I_{SCC}}}{\sigma_y} \right) \]

where \( a_{cr} \) is the critical crack depth.

Thus for a particular \( K_{I_{SCC}}/\sigma_y \) ratio a minimum allowable crack depth can be calculated. Alternatively by estimating the minimum \( a_{cr} \) value detectable by non-destructive testing methods a limiting value of \( K_{I_{SCC}}/\sigma_y \) may be obtained. A material is then chosen with a \( K_{I_{SCC}}/\sigma_y \) ratio within this limit.
Two types of stress corrosion test were used:
(a) constant stress tests on smooth and notched specimens,
(b) dynamic strain tests.

Constant stress tests were performed because of the need to use a well-developed accepted technique which would generate basic susceptibility data for a wide range of materials. Constant stress was used in preference to constant strain because accurately known stresses were difficult to reproduce from specimen to specimen in constant strain tests and stress relaxation during crack propagation made the results of these tests less amenable to interpretation.

Originally tests were performed on smooth specimens but later notched specimens with much larger cross-sectional areas were tested to investigate the possible accelerating effects of a multiaxial state of stress.

Dynamic strain stress corrosion tests were performed because such tests under potentiostatic control made it possible to study phenomena which were of mechanistic importance in the stress corrosion process, e.g. passive film rupture, slip step dissolution, hydrogen embrittlement, etc. Also dynamic strain acted as an accelerant to cracking so that tests could be performed in environmental conditions closer to those in service, i.e. near ambient temperature.

4.1 Static load tests on smooth and notched specimens
Specimens were uniaxially loaded to their 0.2% proof stress in an environment designed to simulate that of the body. Elevated temperature (100°C) was used as an accelerating factor and test times of up to 10,000 hours (approximately 60 weeks) were employed.

4.1.1 Environment
Elevated temperature was chosen as the accelerating variable for these stress corrosion tests because:
(a) it was easily varied and controlled,
(b) it held the promise that extrapolation of results to lower temperatures may have been possible to predict stress corrosion lives under service conditions,
(c) it had been widely used and studied in a variety of stress corrosion systems.

The alternative accelerating variables were: increased concentration of environmentally active species, increased stress or the
use of special environments known to cause cracking in the alloy systems of interest. Increased concentration was rejected because this was not greatly accelerating and as the body environment had a relatively high concentration of the active species of interest (the chloride ion) this approach was limited. Stresses higher than the 0.2% proof stress could not be used without yielding in the specimens. The use of special environments known to cause cracking would certainly have produced positive results quickly and may have been useful in comparing the stress corrosion susceptibilities of alloys of a similar type, however comparison between alloys of different types would have been impossible and the results irrelevant to the problem of predicting the importance of stress corrosion failure in the body.

Biological fluids and physiological salt solutions designed to chemically simulate the body environment could not be used because they decomposed below 100°C.

At this time Hoar and Mears [1] reported electrochemical corrosion studies on surgical implant materials. They found that results in a 0.17M sodium chloride solution with its pH adjusted to 7.4 (that of the body) were the same as those in more complicated physiological salt solutions or serum. On this basis 0.17M NaCl solution was chosen as the stress corrosion environment. Laboratory air was bubbled through the solution during test to maximise the cathodic oxygen reduction reaction and thereby the aggressiveness of the medium. Trials showed that the pH of the aerated hot solution could be controlled reproducibly between 7.35 and 7.45 by the addition of 0.034 g l⁻¹ of sodium carbonate, the additive used by Hoar and Mears.

Temperatures above 100°C could not be employed because the solution boiled at 102-103°C and this could not easily be accommodated in the pumped system used to circulate the corrodent.

4.1.2 Materials

The materials may be classified as:

Iron based alloys: three steels to the American specification AISI 316, 316L and 317 were tested. These fell within the then current British Standard, En 58J, and correspond to the now current British Standards 316S16, 316S12 and 317S16 [2]. A 316S16 steel with the addition of 0.2 w/o nitrogen to improve mechanical properties was also tested.

Two further iron based alloys were studied: IN-748-X, an experimental high nickel austenitic alloy and ferralium, a duplex stainless steel of approximately 50% ferrite 50% austenite. These alloys were studied.
because their mechanical and corrosion properties were claimed to be superior to the more conventional stainless steels.

Titanium based alloys: Commercially pure titanium and a number of $\alpha + \beta$ titanium alloys were tested.

Cobalt based alloys: Vitallium was tested in the form of "as-cast" test specimens. The Co-Cr-Ni-W alloy which had found some limited use in the implant field was obtained in three forms
(a) as machined, solution treated test specimens from one manufacturer;
(b) solution treated bar from the same manufacturer (material designated WR125);
(c) solution treated bar from a second manufacturer (material designated HS25). This was tested in the solution treated and the cold worked and aged conditions. Very high strengths could be obtained from this material by a combination of cold working and ageing (3).

Finally the recently developed Co-Cr-Ni-Mo alloy MP35N was tested in its high strength, solution treated, cold worked and aged condition.

Details of the chemical analysis and thermomechanical treatment afforded to each of these materials is given in tables 2 and 3.
The intention in each case was to test a commercially available material in the condition likely to be used in service. Mechanical properties were determined for each alloy (tables 4, 5 and 6) primarily to obtain a 0.2% proof stress for the stress corrosion tests but also to see if any potentially useful material had undesirable properties, eg low ductility. The 0.2% proof stresses obtained at room temperature were corrected to 100°C values using published data.

4.1.3 Apparatus

Two types of equipment were available for the static load tests:
(1) a sixteen position creep frame which could apply loads of up to 1000 kg via a 5:1 ratio lever arm system. This equipment, known as the A48 rig, was used to test smooth specimens of the type shown in figure 1a;
(2) a four position hydraulic stress corrosion testing machine which could apply loads of up to 10,000 kg. This equipment, known as the T66 machine, was used to test notched specimens of the type shown in figure 1b.
A single loading position of the A48 rig is shown in figure 2. Loads could be applied smoothly by the screw jack and axiality of loading was ensured by universal joints. Specimen failure was recorded automatically by a microswitch and timer clock.

The T66 machine, figure 3, applied load hydraulically, provisions for failure recording were similar to the A48 rig.

The means of providing the environment and environmental control were similar for both pieces of equipment. The major experimental variables to be considered were:

1. Electrochemical potential;
2. Temperature;
3. Environment composition, i.e., oxygen, chloride ion and hydrogen ion concentrations.

Absolute control of electrochemical potential could not be achieved without the use of costly electronic potentiostatic equipment. The more limited approach followed therefore was to allow the specimens to assume the potential characteristic of the particular metal/environment system, i.e., the isolated corrosion potential. To achieve this it was essential to prevent galvanic coupling between the specimen and its grips. The work done on the prevention of galvanic coupling has been described in detail previously [4, 5] but briefly, three lines of approach were attempted:

1. Coating the threads of the specimens to produce an insulating layer between the specimen and grips;
2. Making the grips of an electrically insulating material;
3. Confining the corrosive environment to the gauge length of the specimen thus avoiding the problem.

Coating the threads proved unsuccessful; even with the hardest coating material used, an acrylic thermosetting plastic, electrical insulation was lost after a short period under load. Electrically insulating grips were more successful, after testing a variety of material a fabric reinforced epoxy resin known as 6F/45 (Tufnol Ltd) was used. A grip for the A48 specimens made from this material is shown in figure 4. The stainless steel ring reinforced the grip but did not come in contact with the specimen. The environment which surrounded the string of three specimens was contained in a stainless steel chamber externally heated by an armoured cable heater. The whole assembly was wrapped in asbestos tape to help maintain a constant temperature.

The insulated grip system proved successful for early testing on the A48 rig but could not fulfil the requirement to test high strength
titanium and cobalt based alloys. The 0.2% proof stresses of these alloys were so high that loads in excess of those supportable by the insulating grips would be required to test them. For this situation it was necessary to develop environment-containing cells.

It was essential to continuously circulate the corrodent liquid through the cell rather than have the cell closed because:

(a) in the small volume of a closed cell large changes in the composition of the solution could occur due to corrosion of the specimen;
(b) boiling in a cell due to unforeseen temperature excursions might cause bursting in a closed system;
(c) variation in environment from cell to cell might occur if there were no connection to a common reservoir.

The system finally adopted for some units of the A48 rig and also for the T66 machine is shown in figure 5. Each stress corrosion unit had three cells. The pump used had a 24 channel capacity so that eight units could run simultaneously with each of 24 cells having an independent corrodent supply from the common reservoir.

The cell used for the A48 rig is shown in figure 6 and for the T66 machine in figure 7. They were made of high density polyethylene or PTFE.

The environmental circulation arrangement for the A48 rig is shown in figure 8. The reservoir, a round bottomed flask, was heated in a mantle, the corrodent was boiled and aerated in this flask before being sucked up one of 24 tubes to pass to a stress corrosion cell. The tubes used were of narrow bore silicone rubber and were sealed with araldite through a ground glass joint before passing to the exterior. The pump sucked solution rather than pumped it because if there were leaks in any of the cells air would be drawn into the system rather than corrodent pumped out. If corrodent was allowed to leak out, eg, along the threads of the specimen, there was a chance that a conducting path between specimen and grip may have occurred thus allowing galvanic coupling. Having the system under suction obviated this risk. The solution was kept heated in three ways: firstly the solution was boiled in the reservoir, secondly it was heated by heating tapes wrapped around the tubing just before each unit. Finally a heating tape was wrapped around each unit to maintain a uniform temperature throughout. The temperature was monitored by three thermocouples. The arrangement can be seen in figure 9.

The experimental arrangement for the T66 system was very similar slight differences in cell design etc being necessary because of the
larger specimens and the restrictions in space caused by the loading shackles. However, in this case a properly sealed furnace was available to closely control the temperature.

The facilities for temperature control on the A48 rig were relatively crude, the electrical current to the flexible tape or armoured cable heaters could be controlled by variac controllers but there was no automatic thermostatic control. In spite of this, because the ambient laboratory temperature was reasonably constant, the chamber temperatures could normally be controlled to ± 2°C. The temperature gradient in each chamber was monitored by three thermocouples, thus although automatic control was absent manual monitoring of the temperatures throughout the various chambers was possible.

The temperature control and monitoring system of the T66 machine was considerably more sophisticated, the string of three specimens was surrounded by a tubular furnace. Temperature control was achieved by a platinum resistance thermometer built into the furnace windings driving a Mayes RPSI Resistance Thermometer temperature controller. Using this system a constant temperature could be achieved throughout the length of the furnace to ± 0.5°C. Clamped to the exterior of each stress corrosion cell was a thermocouple. The twelve thermocouples were constantly monitored using a Honeywell twelve point recorder. Once the original setting up and adjustment of the equipment had been achieved, however, the Mayes controllers controlled the furnace temperatures so accurately and constantly that routine temperature monitoring was discontinued.

The three environmental factors which merited close control were dissolved oxygen concentration, chloride ion and hydrogen ion concentration. Filtered laboratory air from a compressor was bubbled through the solution during testing. As any oxygen consumed would be slight the solution was saturated with oxygen at that particular temperature.

The chloride ion concentration was less easily controllable: it was not automatically controlled at a saturation level by means of an excess (cf oxygen) but was present at a fixed amount at the beginning of a test and may have been slowly consumed by reaction or lost by leakage during the test. To obviate this the solution was changed weekly.

Monitoring of the pH revealed that it stayed relatively constant from 7.2 to 7.5.
4.1.4 Method
The test method was as follows:
(1) specimens were mounted and the environment control system put into operation at room temperature.
(2) load was gradually applied to give a stress equivalent to the 0.2% proof stress on the particular material under test;
(3) the temperature was raised to 100°C;
(4) the test was continued until failure or for 10,000 hrs (A48 rig) or 5000 hrs (T66 machine);
(5) the specimens were demounted and examined for cracks.

It was not possible with either equipment to operate continuously for the full test period, occasional short shut downs were required because of failure of cooling water, electricity etc. In these circumstances the specimens were left loaded in cold stagnant NaCl solution for the period of shut down and this time omitted from the total test time recorded.

Removed specimens were washed and scrubbed in hot detergent solution, rinsed, air dried and examined under a stereomicroscope at magnifications of up to x40. Any signs of surface attack were examined in more detail as metallographic sections on a Reichart microscope.

4.2 Dynamic strain stress corrosion test
In the work reported below the dynamic strain tests were performed under potentiostatic control and the corrosion current flowing during the tests monitored. Control of the important variables of strain and electrochemical potential, together with measurements of corrosion current, meant that much more basic information could be obtained from this type of test. This led to a better understanding of the mechanism of cracking.

4.2.1 Environment
The same 0.17M NaCl solution, pH 7.4, as that used in the static loading tests was employed. There were two differences however; firstly the tests were performed at ambient laboratory temperature, usually 22-25°C, and secondly the solution was saturated with argon instead of air. An elevated temperature was not used because straining was being used as an accelerant and the use of two accelerating factors together may have complicated the interpretation of the results. In addition potentiostatic control would have been more difficult experimentally at elevated temperatures. The solution was saturated with argon by constant bubbling.
to reduce the dissolved oxygen concentration to a constant low level. Oxygen was not required as a cathodic reductant, the role it fulfilled in the static loading tests, because the electrochemistry of the system was potentiostatically controlled. Cathodic oxygen reduction in fact would have complicated the interpretation of the net corrosion currents measured during the test.

4.2.2 Materials

The test was performed on:

(1) 316S16 stainless steel 15% cold worked;
(2) cast vitallium
(3) the titanium alloy Ti-8Al-1Mo-1V. Annealed,
(4) the titanium alloy Ti-6Al-4V. Annealed.
(5) Co-Cr-Ni-W alloy in the cold worked and aged condition.

Although Ti-8Al-1Mo-1V had not been considered earlier as a possible implant material it was examined because it had previously received much attention, particularly in the USA, as a SCC susceptible Ti-Al based alloy. As most commercially available α + β titanium alloys are based on the Ti-Al system, a study of this "typical" susceptible alloy could give information applicable to all α + β titanium alloys.

4.2.3 Apparatus

A photograph of the apparatus is shown in figure 10 and a schematic representation of the electrochemical control equipment in figure 11. The constant strain rate was provided by a standard Hounsfield tensometer equipped for autographic recording of approximate engineering stress/strain curves by a hot pen system. Cross head speeds from $5 \times 10^{-6}$ to 1 mm sec$^{-1}$ could be obtained from the 1380 rpm motor using various combinations of reduction pulleys, together with a 15,000:1 reduction gearbox for the lower speeds. The maximum stress available was 20 kN. It is emphasised that this tensile machine was a soft beam instrument, ie flexing of the crosshead and slack in the grips meant that crosshead displacement was only approximately related to strain in the gauge length of the specimen. Thus the stress/strain curve obtained from the autographic recorder could be used only qualitatively.

Four types of specimen have been used with this equipment, originally A48 static loading specimens (figure 1) and standard Hounsfield No. 5 flat specimens (figure 12) were used but these were later superseded by specially designed round and flat specimens (figures 13 and 14). The requirements for the corrosion cells which surrounded the specimens and the gripping arrangements were:
(a) avoidance of galvanic coupling between specimens and grips;
(b) prevention of oxygen ingress into the cell;
(c) provisions for calomel (reference) electrode, counter electrode and electrical connection to the specimen (working electrode);
(d) electrical insulation of the specimen and its immediate grips from the mass of the tensometer to avoid instabilities in the potential control circuitry.

The same type of cell as that used for the static loading tests was originally used and electrical insulation achieved at bolts which screwed into the specimen threaded grip. The bolt heads were wrapped in PTFE tape and seated on fibre washers in a split collet grip. Thus on loading the stress was taken in compression on the fibre washers and the bolt was electrically insulated from the loading arm. Electrical contact to the specimen was obtained via a wire brazed to a brass washer held in place on the exposed threaded portion of the bolt by two lock nuts.

A simple cell used with Hounsfield No. 5 flat specimens is shown in figure 15. The method of electrical insulation was the same as above but the specimen shoulders were gripped in tapered collets. The cell itself was a polythene specimen tube with a small slit at either side to allow the specimen to be pushed through; the slits were subsequently closed with sealing compound or PTFE tape. The tube was used upsidedown with the platinum (auxiliary) electrode and argon supply a push fit through holes drilled in the top closure.

The problem with both of these cells was that they were tedious to set up and seal, in addition on occasion they leaked during a test allowing escape of electrolyte or admission of oxygen rendering the test result invalid. In the light of this experience two types of specimen and cell were designed to be easily assembled and efficiently sealed, these have been used in the majority of tests. Fig 14 shows the cylindrical specimen developed from the A48 specimen and figure 16 its PTFE corrosion cell. The elongated specimen shoulders allowed positive sealing on silicone rubber 'O' ring seals at the exits of the cell. Threaded connections in other parts of the cell ensured a leakproof container. The Hounsfield No. 5 flat specimen was similarly developed by elongating its shoulders (figure 13). It was used with a perspex corrosion cell (figure 17) which allowed observation of the specimen during the test. Sealing was achieved by passing the rectangular section shoulders through
slits in rubber stoppers lubricated with silicone grease. The gripping and insulating arrangement with this particular type of cell and specimen was different to that previously described because at this stage a load cell was incorporated in series with the specimen to give a more accurate record of stress which could be more directly correlated with variations in corrosion current. Electrical insulation was achieved by having the loading pins supported in Tufnol bushes.

The electrochemical potential of the specimen was controlled throughout a test by a Witton T6 potentiostat. This electronic device sensed the potential difference between the specimen and the calomel electrode and compared it with the desired potential set on a ten turn precision helical potentiometer fed by Mallory mercury cells. By means of operational amplifier circuits a current was passed between the platinum electrode and specimen, this changed the potential of the specimen with respect to the calomel electrode until it was equal to the desired potential. A varying corrosion current therefore was provided by the potentiostat to control the specimen potential at the preselected value throughout the test.

The selected potential could be read from the helical potentiometer control or more accurately could be measured directly by a high impedance Vibret millivoltmeter. On occasion tests at uncontrolled potential were performed and the variation in potential during the test monitored. The Vibret millivoltmeter had output facilities so that using a suitable shunt the potential could be monitored on a high impedance pen recorder. More normally tests were performed at constant potential and the corrosion current monitored. The current was taken from the external ammeter socket of the potentiostat and passed through a suitable shunt, the potential developed across this shunt was then recorded on a Servoscribe flat bed high impedance pen recorder. By Ohm's law a linear relationship existed between corrosion current and shunt potential thus pen deflection was a direct measure of corrosion current. As the recorder chart speed and the crosshead speed of the tensometer were both constant a trace of corrosion current versus crosshead position was obtained during a test, this could be approximated to corrosion current versus strain. In early tests features on the trace were correlated with features on the Hounsfield autographic recording of the stress/strain curve by eye. In later tests a load cell was introduced in series with the specimen. The signal from this load cell was fed to a solid state amplifier which gave
an output of 1.10 mV·kg⁻¹. At the same time the single pen recorder used previously was replaced by a two pen recorder thus corrosion current could be recorded on one pen and load on the other. In this way a closer correlation of effect in the approximate corrosion current/strain and stress/strain curves could be obtained.

To avoid damage to the electronic equipment by current surges caused by open circuit potentials at specimen failure a fracture trip was devised. This consisted of a microswitch, mounted just below the corrosion cell, which controlled the mains supply to the equipment via a relay. At specimen failure the cell sagged, tripped the microswitch and cut off the mains supply. Details of the limitations, accuracy and sensitivity of various parts of the system are given in Appendix I.

4.2.4 Method

Before the test a gauge length was marked on the specimen using a pair of preset punches to produce small "pop marks". The gauge length and cross-sectional area of the specimen were then measured. The specimen was inserted in the corrosion cell, the NaCl solution introduced and deaerated with argon. The isolated corrosion potential (ICP) of the specimen fell during this deaeration due to the reduced polarisibility of the oxygen cathodic reduction reaction. De-aeration was continued for some time after the ICP had reached a minimum value thus ensuring that the oxygen concentration has reached a constant low level. The ICP was recorded, the potentiostat switched on and the required potential achieved by polarising the specimen at a slow rate from its ICP to the required set potential (SP). The corrosion current provided by the potentiostat to achieve the SP was monitored on the flat bed recorder and allowed to settle to a steady value before proceeding with the test.

Once the initial setting up of the electrochemical equipment had been performed and the system allowed to reach equilibrium the tensometer motor was switched on and the straining begun. In the tests where the load cell was not available the occurrence of significant features in the stress strain curve on the Hounsfield autographic recorder ie, start of strain, transition from elastic to plastic strain, necking etc were marked on the corrosion current/strain trace.

The maximum load achieved during the test could be read from the Hounsfield mercury capillary load cell or the strain gauge load cell. The cross-sectional area of the specimen at fracture was measured by taking an average of the areas of the two fracture faces. The gauge
length of the fractured specimen was also measured with the two fractured ends held lightly together. The mechanical properties of the material could then be calculated using the expressions in Appendix II.

Using this method points could be plotted of mechanical property versus potential plots and regions of stress corrosion susceptibility identified.
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<th>15% Pal</th>
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**TABLE 2. DETAILS OF TITANIUM BASED ALLOYS**
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ST Solution Treatment
CW Cold Worked
A Ageing treatment
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Specimen 12A (H12A) or 48 mm gauge length specimens to BS18 (BS 18.2) were taken from bar used to produce A48 or T66 specimens or both, according to the bar diameter. The thermomechanical treatment afforded to this bar is recorded in Table 1.
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<td>13.0</td>
<td>40.0</td>
<td>1044</td>
<td>1142</td>
<td>395</td>
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</tr>
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<td>1263</td>
<td>397</td>
<td>A48 and T66</td>
</tr>
<tr>
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<td>46.0</td>
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<td>1267</td>
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<tr>
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<td>14.0</td>
<td>45.0</td>
<td>1206</td>
<td>1260</td>
<td>397</td>
<td>A48 and T66</td>
</tr>
</tbody>
</table>

Notes 0.1% Proof Stress

Mechanical treatment in Table 2.
### TABLE 6. MECHANICAL PROPERTIES OF COBALT-BASED ALLOYS

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Elongation R %</th>
<th>R of A %</th>
<th>0.2% PS MPa</th>
<th>UTS MPa</th>
<th>Hardness VPN</th>
<th>Relevant SCC Specimens</th>
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</thead>
<tbody>
<tr>
<td>A48</td>
<td>0.2</td>
<td>0.1</td>
<td>829</td>
<td>829</td>
<td>388</td>
<td>A48</td>
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<tr>
<td>A48</td>
<td>11.6</td>
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<td>471</td>
<td>812</td>
<td>-</td>
<td>A48</td>
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<tr>
<td>A48</td>
<td>12.2</td>
<td>11.7</td>
<td>500</td>
<td>770</td>
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</tr>
<tr>
<td>T66U</td>
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<td>20.8</td>
<td>521</td>
<td>788</td>
<td>386</td>
<td>T66</td>
</tr>
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<td>261</td>
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<td>1005</td>
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<td>T66</td>
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<td>945</td>
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<tr>
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<td>44</td>
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<td>1622</td>
<td>508</td>
<td>A48</td>
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<td>10</td>
<td>43</td>
<td>1592</td>
<td>1617</td>
<td>508</td>
<td>and</td>
</tr>
<tr>
<td>H12A</td>
<td>14</td>
<td>42</td>
<td>1580</td>
<td>1622</td>
<td>519</td>
<td>T66</td>
</tr>
</tbody>
</table>

Type and un-notched T66 specimens (T66U) were used as tensile specimens in some of the tests.

Post-mechanical treatments in Table 3.
Figure 1a  Smooth specimen used on M48 Rig.

Figure 1b  Notched specimen used on T66 Machine.
Figure 2 Diagram of a loading position on the AH8 Rig.
Fig 3. T66 stress corrosion machine
Figure 4  Static loading grip in 6F/45 Tufnol with stainless steel tube surround (x2)

Figure 5  Corrodent circulating system for the A48 Rig
Fig 6a. A48 cell open

Fig 6b. A48 cell closed

Fig 7a. T66 cell open

Fig 7b. T66 cell closed
Fig 8. Heated corrosive reservoir and pump used for the environment circulating system

Fig 9. Internal arrangement of A48 stress corrosion unit
Figure 10  Equipment for RMP test.
Figure 12  Hounsfield No. 5 flat tensile specimen.

Figure 13  Flat tensile specimen.

Figure 14  Cylindrical tensile specimen.
APPENDIX I

Details of Equipment used in Dynamic Strain Tests

MECHANICAL

The tensometer crosshead speeds used in this work were checked and found to be accurate and reproducible to 2%. The load cell was not checked during the work against any absolute standard. This was not thought necessary as all mechanical properties calculated were used for comparative purposes only as an indication of SCC susceptibility. The zero and internal reference voltage of the load cell amplifier was constant throughout a test to 0.5%.

POTENTIOSTAT

A T6 type potentiostat (Witton Electronics Ltd) was used with the following relevant characteristics:

- Maximum output: ± 20V at ± 0.5A
- Absolute maximum output current: ± 0.75A
- Internal reference: + 5V to 0 to - 5V
- Sensitivity: > 1 mV
- Control current: < 10 nA

The corrosion currents were measured by recording the voltage developed across shunts fed by current from the external ammeter socket of the potentiostat. This in effect placed the shunt resistance in the current supply line to the working electrode. Shunt values were chosen so that voltages of no more than 10 mV would be generated across them thus minimising disturbance to the control loop circuit. The recorder full scale current deflections for various shunt values are given below.

<table>
<thead>
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<th>Shunt Resistance</th>
<th>Recorder fsd</th>
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<tbody>
<tr>
<td>0.1 Ω</td>
<td>100 mA</td>
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<tr>
<td>1 Ω</td>
<td>10 mA</td>
</tr>
<tr>
<td>10 Ω</td>
<td>1 mA</td>
</tr>
<tr>
<td>100 Ω</td>
<td>100 μA</td>
</tr>
<tr>
<td>1 kΩ</td>
<td>10 μA</td>
</tr>
<tr>
<td>10 kΩ</td>
<td>1 μA</td>
</tr>
</tbody>
</table>

Precision resistors to 0.1% were used as shunts.

MILLIVOLTMETER

A model 3920 Vibret pH meter used on its voltmeter recording mode was used. The following characteristics were relevant:
Accuracy  + 0.5 mV
Range      + 1400 mV
Input resistance 1000 MΩ
Recorder output  1.4 mA fsd into any resistance up to 5000 Ω

When it was desired to monitor corrosion potential during an uncontrolled test the recorder output was shunted with 100 Ω giving 1 mV input at the recorder terminals per 10 mV deflection on the millivoltmeter scale.

**RECORDERS**

Early in the work a servoscribe type RE511.20 flatbed single pen potentiometric recorder was used. Later a similar two pen recorder type RE520.20 was used. The following characteristics are relevant to both types.

- Fixed input ranges: 2, 5, 10, 20, 50, 100, 200, 500 mV; 1, 5, 20 V fsd on a 200 mm writing width.
- Accuracy: + 0.5% of range or + 20 μV whichever is greater
- Response time: 1.5 sec for fsd
- Chart speeds: 30, 120, 600 mm/h and 30, 120, 600 mm/min

Platinum was used as an auxiliary electrode and a Radiometer Type K401 combination calomel electrode and saturated KCl salt bridge used as a reference.
APPENDIX II

Expressions used to calculate Mechanical Properties.

(a) Ultimate Tensile Strength (UTS)

\[
\text{Engineering UTS} = \frac{\text{Maximum load}}{\text{Original cross-section area}}
\]

True UTS = \[
\frac{\text{Engineering UTS}}{100 - \% \text{ Reduction of area}}
\]

or \[
\frac{\text{Maximum load}}{\text{Final cross-section area}}
\]

(b) Percentage Elongation

The percentage elongation was calculated over a gauge length of 12.70 mm:

\[
\% \text{ Elongation} = \frac{\text{Final length} - \text{Original length}}{\text{Original length}} \times 100
\]

(c) Percentage Reduction of Area

\[
\% \text{ Reduction of Area} = \frac{\text{Original Cross-sectional area} - \text{Final cross-sectional Area}}{\text{Original cross-sectional Area}} \times 100
\]
5. RESULTS OF TESTS

5.1.1 Static Load Test Results on Iron based Alloys

Tests on smooth and notched specimens of the iron based alloys did not produce any cracking. Pitting was observed on some specimens however and cracking occurred in stainless steel items of ancillary equipment. The incidence of pitting was about equal on specimens of 316S16, 316S12 and 316N steel and ferralium; pitting was less severe on specimens of 317S16 steel and IN-748-X. An example of pitting on the shoulder of a 316N T66 specimen is shown in figure 1. In addition to the pitting slight crevice corrosion was observed under "O" ring seals on several specimens.

In spite of the absence of cracking in the test materials SCC was observed in items of ancillary equipment.

Figure 2 is a metallographic section through stress corrosion cracks which developed in the constraining rings of some grips used on the A48 equipment. The material was niobium stabilised 18Cr-9Ni type AISI 347 steel. Similar cracking was observed in a 18Cr-9Ni titanium stabilised type AISI 321 steel thermocouple sheath used in preliminary tests to check temperature gradients on the furnaces of the T66 machine. This is shown in figure 3.

The absence of stress corrosion in the iron based alloys under test in conditions of high stress for long periods of time at an elevated temperature gives basic confidence in the ability of these materials to resist SCC. This statement must be qualified by the observation of a similar form of localised corrosion attack, ie pitting corrosion, in many materials and the observation of severe cracking in stainless steels with compositions close to those tested.

Stress corrosion can probably be discounted as a mechanism of failure in iron based alloy implants which have a short period of use, eg fracture plates which are removed after healing of the fracture. The results give no support to the view that SCC is important in long term behaviour either, but the difficulty of deciding how accelerative the elevated temperature had been makes it impossible to predict a minimum safe SCC life from this data.

5.1.2 Static Load Test Results on Titanium based Alloys

No failures attributable to stress corrosion were observed in any of the titanium alloys tested in the smooth or notched condition.

Failures attributable to room temperature creep were observed in commercial pure titanium and brittle failure, on initial loading, due
to inherently low ductility was observed in specimens of T700 alloy. These effects have been discussed elsewhere (1) but are not directly relevant to the stress corrosion problem and will not be considered here. No corrosion was observed but a slight darkening of the original polished surface could be seen on several specimens. This was probably due to thickening of the oxide film after long exposure to the environment.

These results discount the importance of SCC as a means of failure in titanium alloy implants of smooth and notched section. The same difficulty exists as for the iron-based alloys however, ie the problem of prediction of SCC behaviour for very long service exposures. An additional problem is that of SCC crack propagation from a pre-existing crack: implants may reasonably be expected to enter service without cracks but may crack in service due to corrosion fatigue. It is widely recognised that SCC may occur in precracked titanium alloy specimens yet be absent in smooth or notched specimens. The present results give no information on this phenomenon.

5.1.3 Static Load Test Results on Cobalt Based Alloys

No failures have been observed in smooth specimens of any cobalt based alloy tested. Some cracking has been observed however in notched specimens of cast vitallium and solution treated Co-Cr-Ni-W alloy, WR 125. These failures are reported in detail in table 1.

Two cast vitallium specimens failed during testing. Initially a string of three specimens SC/18, SC/19 and SC/20 were loaded to 2200 kg, ie equivalent to the 0.2% Proof Stress of the material. The load was removed for a short period after 1036 hours to rectify a fault in the corroden circulating system. When slowly reloading, SC/18 fractured at the notch as the load reached 2100 kg. On reloading the remaining two specimens with care at a very slow rate SC/19 fractured at a load of 1500 kg. SC/20 was successfully reloaded and the two broken specimens replaced with SC/35 and SC/36. SC/20 was removed after the normal 5000 hr exposure time and found to be circumferentially cracked at the base of the notch. This specimen was replaced by SC/37. Testing was continued until SC/35 and 36 completed a total of 10,000 hr exposure and SC/37 8000 hrs.

Scanning electron microscopy of SC/18 showed an intergranular fracture with little ductility; subsidiary cracks, probably following grain boundaries, could be seen emerging from the fracture surface Fig 4. Grain boundaries were often delineated by lines of shattered carbides (Fig 5). Low power optical microscopy (figs 6 and 7) revealed striations,
the orientation of the striations varying from area to area. A dark brown patch (Fig 7) was present at the edge of the fracture, this may have been corrosion product from pitting attack at the root of the notch which initiated the failure. Optical metallography (figs 8 and 9) showed a structure containing carbide particle arrays within the grains and segregation of carbides and non-metallic inclusions to the grain boundaries. The striations referred to earlier were due to these arrays breaking through the fracture surface, changes in orientation occurring from grain to grain. The general appearance and microstructure of SC/19 was similar to SC/18 although surface striations were better developed and small areas of ductile dimpling were occasionally observed. Fig 9 shows in section the fracture of a carbide particle, an effect often observed on the stereoscan photographs. The initiation point of the failure could not be seen on this specimen.

The circumferential crack in SC20 is shown in figure 10. Figure 11 is an unetched metallographic section through the specimen. The "V" notch and crack on one side of the specimen can be clearly seen, the "V" notch on the other side of the specimen has been distorted by burring over during rough machining of the specimen to give a flat surface prior to polishing. The crack from this notch was shorter and less distinct. The penetration of the longest crack in this section was 0.8 mm in a sectional width of 2.35 mm. A simple geometrical calculation showed this to be equivalent to a radial penetration of 0.13 mm, ie about 2.5% of the 4.76 mm specimen radius. Figures 12 and 13 are a metallographic section through the larger crack in more detail. Cracking generally followed intergranular carbides but occasionally the crack branched out and propagated a short distance through interdendritic carbides.

In spite of these failures, when specimens SC/35-37 were removed after up to 10,000 hrs exposure no cracking at the notch roots was observed. Because of the equivocal nature of the first observation of failures (ie, when reloading after shutdown) and the absence of cracking in extended tests, stress corrosion has not been demonstrated in vitallium with total certainty. It does seem likely however that a slight susceptibility to SCC may exist which is strongly dependent on the plastic yielding at the notch tip. This means that cracking would be closely dependent on load and means of load application. A closer investigation of the material is justified on the basis of these early results.

Similar cracking to that observed in vitallium was seen in specimens of solution treated Co-Cr-Ni-W alloy, WR 125. No failures
occurred during the test but cracking was observed in each of the three specimens removed after 5000 hr exposure. These specimens were replaced by a further three and a 5000 hr duration test repeated. No cracking was observed in the second batch of specimens. These results are summarised in table 1. Figure 14 shows the cracking which had occurred in specimen WR125/ST/4; the cracking in specimens 5 and 6 was very similar to this. Multiple cracks often initiated at the root of the notch and followed a zig-zag path a short distance into the material. This is shown in the unetched metallographic section in figure 15. It seemed possible that the crack path followed a metallurgical feature but it was found impossible to etch the specimen without destroying the crack because of its closeness to the specimen surface. The depth of crack penetration was small, typically 0.02-0.04 mm radially.

The comments made on the cracking of vitallium specimens apply equally to Co-Cr-Ni-W alloy. SCC has not been demonstrated unequivocally but there seems a need for further investigation. An additional piece of information was that surgical reports had been received reporting cracking in cold worked Co-Cr-Ni-W implants. The material had been tested so far in the solution treated condition. The only area where cold work had occurred to a significant extent was locally at the root of notches in the T66 specimens on loading to the 0.2% proof stress.

5.1.4 References


153
<table>
<thead>
<tr>
<th>Specimen Serial Number</th>
<th>Test Time elapsed (h)</th>
<th>Time to failure (h)</th>
<th>Load at failure (kg)</th>
<th>Comments</th>
</tr>
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<td>-</td>
<td>1036</td>
<td>2100</td>
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<td>-</td>
<td>1036</td>
<td>1500</td>
<td>&quot; &quot; &quot;</td>
</tr>
<tr>
<td>SC/20</td>
<td>5000</td>
<td>-</td>
<td>-</td>
<td>Removed, found to be cracked</td>
</tr>
<tr>
<td>SC/35</td>
<td>10000</td>
<td>-</td>
<td>-</td>
<td>Replaced SC/18</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
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</tr>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>WR125/ST/9</td>
<td>5000</td>
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<td>-</td>
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</table>
Figure 1  Pitting on shoulder of 316N T66 specimen. x25

Figure 2  Stress corrosion crack in constraining ring. x330 (OM)

Figure 3  Cracks in thermocouple sheath. x100 (OM)
Figure 4  SC/18 Fracture. x200 (SEM)

Figure 5  SC/18 Fracture. x600 (SEM)

Figure 6  SC/18 Fracture. x25

Figure 7  SC/18 Fracture. x25

Figure 8  SC/18 Section through fracture. x100 (OM)

Figure 9  SC/19 Fracture through a carbide particle. x700 (OM)
Figure 10 Crack in SC/20. x25

Figure 11 Polished but unetched section through SC/20. x20

Figure 12 SC/20. x60 (OM)

Figure 13 SC/20. x100 (OM)

Figure 14 Crack in WR125/ST/4. x25

Figure 15 Polished but unetched section through WR125/ST/6. x385
316S16 is the only iron based alloy tested so far by the REMP test. It was of major interest because of the uncertainty in the literature over the existence of a temperature limit for SCC in this material.

Figures 1-3 show the variation of mechanical properties with potential for 316S16 at a cross head speed of 0.004 mm sec⁻¹. The changes in properties were quite small compared with the errors expected in their measurement, in particular the small scatter in results on the reduction of area curve may have been fortuitous. In spite of this, four regions of the curve could be confidently delineated:

1. Cathodic to -200 mV properties were essentially the same as in air.
2. Anodic to -200 mV there was a dip in properties with a minimum near 0 mV.
3. At more anodic potentials properties recovered to be equal to or higher than air properties.
4. At sufficiently high anodic potentials (above +300 mV) properties again fell rapidly when large pits were observed on the specimen surface.

Figures 4-7 show typical net corrosion current versus crosshead displacement traces for specimens tested in the potential regions described above. There was no sharp change in type of trace from one potential to another but rather a gradual transition. Specimen to specimen variations in current of up to 50% were also observed. In spite of these differences in the magnitudes of the currents the characteristic shape of the curves were reproducible from test to test and the important features were one to two orders of magnitude larger than the specimen to specimen variation.

Scanning electron microscopy was performed on the fracture surfaces and optical metallography on sections through the fractures.

Widespread ductile dimpling was observed on specimens tested at all potentials, the initiation points for the dimples being particles in the troughs of the dimpled structure. Optical metallography (fig 8) revealed these particles to be non-metallic stringers lying parallel to the parent bar rolling direction and at right angles to the fracture surface. The only difference between specimens tested at different potentials was the occurrence of holes in the troughs of the dimples. These holes were present in all
specimens to a degree and may be expected from simple mechanical tearing around the inclusion particle, the particles remaining in the other half of the fracture surface or "falling out" on fracture. It was found however, that specimens tested at more anodic potentials showed a larger number of more pronounced holes. This can be seen by comparing figures 9-11. This effect was presumably due to dissolution of highly deformed material around the inclusion after failure, little dissolution occurring at −400 mV, some dissolution at 0 mV and considerable dissolution at +600 mV. Although this was visual evidence of the preferential dissolution of highly strained material the effect was not directly relevant to the failure mechanism because it occurred after fracture. Features important to the mechanistic interpretation of results eg localised dissolution or cracking could not be observed. Any defect propagating at a rate lower than the strain rate would be "yielded out" by the straining, in particular a defect initiating local necking prior to fracture would be lost in the deformation in the neck region. Thus the absence of visible defects is to be expected; these ideas will be expressed in a more quantitative manner later.

Figure 12 shows an anodic polarisation curve for 316Si6 steel. A number of curves were obtained on several specimens of 316Si6 to determine the electrochemical reactions likely (Table 1). The important potentials for the interpretation of the test results are:

(1) Hydrogen evolution potential. Below this potential there was a sharp increase in cathodic current and hydrogen bubbles could be seen to evolve from the solution.

(2) Pitting potential. Above this potential anodic current increased rapidly due to the formation of pits. There is some controversy over the theoretical significance of this potential as over long periods pits may initiate at potentials cathodic to the pitting potential. In the short period of these tests however the pitting potential was a valid measurement to divide pitting from non pitting behaviour [1].

(3) Repassivation potential. This is the potential below which it was necessary to cathodically polarise the specimen to reform the passive film after it had been ruptured by pitting.
The potential region between the pitting and repassivation potential may be considered as a region of unstable passivity where once the passive film is broken by chemical or mechanical means it has difficulty in reforming. In particular at potentials near the repassivation potential it is expected that the majority of the surface would remain passive but small unpassivated areas would suffer anodic dissolution.

The results described above are consistent with a slip step dissolution model for stress corrosion. This type of model as developed by Staehle and independently by Scully has been outlined in 2.1. In the particular case of these results, yielding is too rapid to allow the formation of a crack like defect morphology but it is postulated that the observed lowering of properties is due to the presence of slip step dissolution defects. These ideas are developed below for each potential region of the mechanical property/potential curve and extrapolations made to more realistic service situations.

**Region I, -400 mV to -200 mV**

The isolated corrosion potentials of the specimens measured before each test typically were around -200 mV. Small cathodic currents due to reduction of the residual oxygen were normally observed during the test although these sometimes changed to small anodic currents as the test progressed. The emergent slip steps were cathodically protected, their dissolution reduced and therefore a low susceptibility to SCC predicted on the slip step dissolution model. This is in accordance with the observations i.e mechanical properties were "high".

**Region II, -200 mV to +200 mV**

According to the general model suggested by Staehle [2] SCC will occur in regions of "unstable passivity" if other requirements of dislocation structure etc are met. Parkin et al [3] have experimentally confirmed these ideas for the carbon steel/nitrate system. In such potential regions emergent slip steps are anodically dissolved while the rest of the surface remains passive. The dissolved slip step is the initiation of a stress corrosion crack.

Propagation of this embryo crack occurs by further slip step emergence into the original dissolved slip step which has become a stress concentrator at the end of an active slip plane. These secondary slip steps dissolve and further propagate the crack. For this mechanism to work there has to be a critical balance between dissolution and repassivation to maintain the sharp profile.
of the embryo crack. If repassivation is too rapid the slip step is covered by a passive film before dissolution can occur (as in region I). If repassivation is too slow a large amount of dissolution occurs resulting in a shallow pit rather than a sharp intrusion. These ideas are shown schematically in fig 13. The corrosion current/strain characteristics observed in Region II give support to the application of these ideas in this case. A very small constant current is observed during elastic deformation of the specimen indicating either that the passive oxide film is ductile at least up to the elastic limit of the underlying metal or that any rupture of the film which does occur is small, scattered and easily repaired. An elastically strained specimen cannot in fact be distinguished from a static specimen with respect to corrosion current characteristics.

Once a transition from elastic to plastic behaviour begins a sharp rise in corrosion current occurs, increases of \( X_{30} \) are typical. Coplanar dislocation arrays leading to a relatively small number of large slip steps are known to predominate in this type of steel \([4]\). The large current increase is due to anodic attack of these steps which emerge when large scale dislocation movement begins in the material. The slip steps are sufficiently large to overcome any residual ductility in the passive film by shear rupture and expose a large localised area of unpassivated metal to the environment. The dissolution of these steps is the critical event in the mechanism of SCC in this material.

Once the sharp rise in corrosion current has occurred the current/strain trace flattens off and the value of the current stays approximately constant with strain until localised necking occurs just before specimen fracture. Current again rises sharply here typically by a factor of \( x \) 4. Behaviour during necking may be regarded as a localised increase in strain rate. Tests have been performed at higher strain rates and larger currents have been observed in these tests.

The constant current seen during the majority of the test implies, in accordance with the slip step dissolution model, that some repassivation must be occurring. If this were not so the corrosion current would rise throughout the test. In the widely investigated environment, \( \text{MgCl}_2 \) at 154°C, Hoar and Hines \([5]\) originally have posulatated repassivation by an oxide film whereas Stashele\([4]\) has presented evidence for an ennobled nickel surface film mechanism. Repassivation by an oxide film seems most likely in diluted saline solution at ambient temperature because:
The formation of an oxide film on stainless steel in aqueous solutions is well established.

Active dissolution, which would be required to remove Fe and Cr to leave an enriched Ni surface is not observed in polarisation scans in this environment.

Maximum susceptibility correlates with the potential at which the oxide film is unstable ie repassivation potential.

Region III and IV + 200 mV -> + 600 mV

Two types of behaviour are seen in these regions:

1. "High" properties for specimens which showed little anodic attack.

2. "Low" properties for specimens which showed deep corrosion pits.

Type (1) behaviour is in agreement with the postulated model which predicts that if repassivation is rapid sufficient slip step attack does not have time to occur. Repassivation becomes increasingly rapid until pitting occurs. These massive defects result in type (2) behaviour.

This interpretation of the results is supported by the fact that the pitting potential was about + 400 mV and that large, relatively constant, corrosion currents in the mA range were observed before and during the test. An interesting effect was noticed for the deeply pitted specimens which showed particularly large corrosion currents. Small (10–20%) reductions in current were noticed at the transition from elastic to plastic behaviour, during the test. This can be explained by considering the mechanism of pitting. It is generally accepted that autocatalytic effects which cause a low pH to exist within the pit are important. For further rapid growth of the pit it is necessary to retain localisation of this highly corrosive environment. This localisation is hindered on plastic deformation by yielding around the pit and flow of fresh electrolyte into the pit area.

A Quantitative Consideration of Region II

Described below are calculations based on simplified assumptions, performed to quantify the qualitative statements made earlier.

Calculation of Defect Propagation Rate

It was not possible to calculate exactly the fresh area exposed by emergent slip steps as this depended on factors such as passive film thickness, slip step height etc which were not readily available. It was possible to get some measure of the fresh area exposed however by considering the gauge length of the specimen as a cylinder which upon longitudinal straining increased its length but decreased its diameter because of conservation of volume.

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basis an elongation of \(x/2\%\) gave an increase in macroscopic surface area of 
\(x/2\%\) - - - (1) (Appendix IA).

Defining an event time, \(T\) sec, as the average time between rupture of the passive film by a slip step and repassivation of that step i.e. the time in which anodic dissolution of the step can occur and using the relationship, between elongation and increase in macroscopic surface area it is possible to express the number of slip steps emerging in the event time \(T\) as:

\[
\frac{\pi d T S}{2A \sin 45^\circ} = - - - (2) \text{ Appendix (B))}
\]

The amount of dissolution occurring in time \(T\) may be expressed as:

\[
\frac{L_p T E}{F \rho} \text{ mm}^3 = - - - (3) \text{ Appendix (C))}
\]

Combining (2) and (3) gives the amount of dissolution per step per event as:

\[
\frac{2L_p E A \sin 45^\circ}{\pi d F S \rho}
\]

Dividing this by the average step surface area, \(A\), gives the depth of dissolution per step per event:

\[
\frac{2L_p E \sin 45^\circ}{F H d S \rho} \ldots (4)
\]

This equation is important in that if the slip step dissolution model of SCC is broadly correct equation (4) gives the rate of propagation during a discrete crack propagation step. Visible cracks will only be present however if the rate of macroscopic crack propagation is greater than the rate of specimen extension. The rate of macroscopic crack propagation depends on:

(i) Rate of step dissolution i.e. depth of dissolution per step per event/event time

(ii) Rate of reoccurrence of events i.e. rate at which slip steps emerge into the embryo crack tip.

The specimen extension rate depends only on the cross head speed.

These ideas are presented diagrammatically in Fig 14 where a penetration/extension ratio is defined for the penetrating defect such that:

\(R>1\) penetration occurs faster than yielding, the defect root angle decreases and a sharp crack results i.e. SCC

\(R<1\) yielding occurs faster than penetration. Cracks yield-out, are not observed i.e. classical SCC symptoms absent.
Effects of Defects on Mechanical Properties

The mechanical properties as derived from this test were not a measure of any basic material property as obtained in a normal tensile test. The basis of the test was the detection of defects in the gauge length of the specimen as reflected in these parameters. Three mechanisms by which the presence of defects may have reduced the measured mechanical properties are:

(1) A simple reduction in the cross sectional area of the specimen by the presence of the defect.

(2) Initiation of brittle failure in notch sensitive materials.

(3) Enhancement of dislocation movement by the provision of a dislocation sink. A defect of the type under consideration here may act as a sink in that it would be at the end of an active slip plane with any dislocation pile-up at the free surface being removed by dissolution.

For austenitic stainless steel postulate (2) is unlikely. Postulate (1) is very likely and postulate (3) is possible but does not seem to have been reported in the literature as being observed in practice and does not seem easy to express in any quantitative manner.

To further develop the slip step dissolution model it will be assumed that the reduction in mechanical properties observed is totally attributable to postulate (1) i.e. a simple reduction of effective cross-sectional area.

Proceeding on this basis the failures of specimens tested in air and in saline solution can be pictured schematically as in Fig 15. For case A, as tensile ductility becomes exhausted the specimen locally necks from a uniform diameter and fractures at a final cross-sectional area $F_{A\text{, air}}$. For case B, as tensile ductility is exhausted the specimen locally necks across an area where the presence of defects reduces the effective cross-sectional area. It should be noted the cross-sectional area reduction produced by these defects is independent of any yielding-out effects as the direction of yielding is perpendicular to the section being considered. The situation at fracture is shown in an exaggerated form in Fig 15. The true final area at fracture is the same as for the specimen tested in air because the inherent ductility of the material is unchanged. However the measured final area is larger (giving a reduced reduction of area) because of the presence of intrusive defects at points around the fracture circumference.

Some estimate of the size of defect required to produce the observed lowering of reduction of area values can be made:

With reference to Fig 15,
FA\textsubscript{s} - DA = FA\textsubscript{A} where DA is the "dissolution area"

\[
DA = FA\textsubscript{s} - FA\textsubscript{A}
\]

\[
DA = \left( \frac{1 - RA\textsubscript{s}}{100} \right) OA - \left( \frac{1 - RA\textsubscript{A}}{100} \right) OA
\]

\[
DA = OA \left( \frac{RA\textsubscript{A}}{100} - \frac{RA\textsubscript{s}}{100} \right)
\]

Using fig 1, it can be seen that representative values are RA\textsubscript{A} = 71\% and RA\textsubscript{s} = 67\%.

\[\therefore DA = 0.04 OA\]

The dissolution depth, DD is the depth to which defects have propagated from the surface due to dissolution and is related to the dissolution area in a complex unknown manner, being dependent on dissolution area geometry and number of defect sites. However it is possible to obtain some measure of average defect depth by considering the depth required for a uniform continuous annulus of defect area around the specimen circumference (see Fig 44)

\[\therefore DD < \frac{0.04 OA}{\pi d\textsubscript{F}} \quad d\textsubscript{F} = \text{final specimen diameter}\]

\[DD < \frac{0.04 \frac{\pi}{4} d\textsubscript{o}^2}{\pi d\textsubscript{F}} \quad d\textsubscript{o} = \text{original diameter}\]

\[DD < 0.042 \text{ mm} \] ....(5)

The reason for the lowering of elongation values observed in saline solution tests is that the cross-sectional area was locally narrowed by intrusive defects plastic deformation concentrated in this area and necking occurred earlier than it would have in a specimen of uniform cross-sectional area thus producing "premature" failure and a reduced test time. The lowered UTS may be explained on a similar basis. As defined in this work the UTS is the maximum load measured during the test divided by the final specimen area, this final area is increased as explained above, lowering UTS values. In addition the maximum load measured is reduced because of the reduced area available for its sustenance further contributing to a lowering of UTS.

**Estimation of Macroscopic Defect Propagation Rate**

Earlier it was established that the macroscopic defect propagation rate would depend on rate of step dissolution and rate of event reoccurrence.
If reoccurrence does not occur at a previous rupture site but at a fresh site dissolution will be evenly spread over the surface, the acuity and localisation of attack required for SCC being absent. There are three reasons why a previously attacked step will be re-attacked however.

1. It is at the end of an active slip plane so that further step emergence is likely.
2. The reformed oxide film is probably mechanically and chemically weaker than the original.
3. The previous attack may have produced a localised aggressive environment by hydrolysis of corrosion products.

Equation (5) can be used to test the hypothesis that attack is concentrated at a previously attacked step giving the small number of localised intrusive defects required for SCC.

From (4):

\[
\text{Depth of dissolution/step/event} = \frac{2IP\sin 45^\circ}{P/\pi d_1 S}
\]

Substituting values: \( F = 96,500 \text{ coulombs/chemical \cdot equivalent} \). Assuming dissolution in the divalent state of material with an effective atomic weight 56 (Fe = 55.85, Ni = 58.69, Cr = 52.01) one chemical equivalent = \( 56/2 = 28 \text{ g} \).

\[
E = 28 \text{ g} \quad \sin 45^\circ = 0.7071
\]

\[
\rho = 0.008 \text{ g mm}^{-3}
\]

\[
d_1 = 2.4 \text{ mm}
\]

\[
\text{Depth of dissolution/step/event} = 0.0068 \times \frac{I_p}{S}
\]

Total depth of defect = Depth of dissolution/step/event \( \times \) number of events, \( N \), at that step

\[
\text{from (5)} \quad 0.042 > 0.0068 \times \frac{I_p}{S}, \quad N,
\]

\[
N \times \frac{0.042}{0.0068} \times \frac{0.004}{30 \times 10^{-6}}
\]

substituting \( I_p = 30 \times 10^{-6} \) at \( S = 0.004 \text{ mm sec}^{-1} \) (See Table 2)

\[
N < 825 \quad \ldots \ldots (6)
\]

The time during which plastic deformation occurs in the test is approximately 900 sec which from (6) implies the occurrence of about one event per second.
Thus the corrosion current and reduction in mechanical properties observed for specimens tested at 0.004 mm sec\(^{-1}\) is consistent with a defect propagation rate per event as expressed in equation (4) with an event rate of approximately one per second. Although the mechanism of SCC was present and productive of intrusive defects which lowered measured mechanical properties the classical symptoms of SCC ie cracks were absent because R values were below one.

Results at Different Cross Head Speeds

A series of tests at different cross head speeds were performed:

(i) To investigate the possibility of obtaining R > 1 ie tests with cracks.

(ii) To enable an extrapolation of results to very low cross head speeds equivalent to strain rates likely in service.

The potential was held constant for every test at +100 mV and speeds of 0.4, 0.04, 0.004, 0.0004, 0.00004 mm sec\(^{-1}\) employed. Unfortunately over the long periods of time required for the very slow cross head speeds random breakdown and recovery of the specimen oxide film occurred producing erratic and large corrosion currents. This masked the corrosion currents-strain effects of interest and by generating random numbers of small pits produced erratic mechanical property data. Because of these difficulties only results from 0.4, 0.04 and 0.004 mm sec\(^{-1}\) tests could be used (Table 2).

Little information is available on the strain rates to be expected in service but some estimate may be made from the results of Voyer and Weil (6) who found that a 25 Cr-20 Ni steel at 0\(^{\circ}\)C and at a stress of 520 MPa crept at a rate of approximately 5 x 10\(^{-6}\) mm min\(^{-1}\). Taking this as a representative figure it is equivalent to a cross head velocity on a 12 mm gauge length of:

\[
\frac{12 \times 5 \times 10^{-6}}{60} \times 12 \text{ mm sec}^{-1}
\]

\[= 10^{-6} \text{ mm sec}^{-1}\]

By making certain assumptions it is possible to calculate the crack propagation rate at this cross head speed.

Depth of dissolution/step/event = 0.0068 x \(\frac{T_p}{3}\)

The actual defect propagation rate/second is depth of dissolution/step/event x number of rerupturing events/second.

The number of rerupturing events per second for tests at 0.04 and 0.4 mm sec\(^{-1}\) could not be calculated in the same way as the 0.004 mm sec\(^{-1}\) test because reductions in mechanical properties were too small to be reliably measured. If, however, it is assumed that the number of rerupturing events
per second, \( N \) is a simple linear function of cross head speed \( S \) then: 
\[
N = kS
\]
where \( k \) is a constant.

Substituting the results obtained at \( 0.004 \text{ mm sec}^{-1} \):
\[
1 = k \cdot 0.004,
\]
\( k = 250 \)

The macroscopic defect propagation rate is then
\[
0.0068 \times \frac{10^5}{0.004} \times 250S = 1.7 \text{ Ip}
\]

This macroscopic defect propagation rate is plotted as a function of cross head speed in Fig 16. Also plotted is a time joining point of equal cross head speed and macroscopic defect propagation rate. To the right of this line macroscopic defects are yielded out and no cracks are produced to the left of this line a crack like morphology is possible. The lines do not intersect until \( S = 10^{-8} \text{ mm sec}^{-1} \). This is considerably lower than the probable operative creep rate indicating that incipient macroscopic cracks will be yielded out. If conditions are optimum for crack propagation and the cross head velocity is constant at \( 3 \times 10^{-8} \text{ mm sec}^{-1} \) then the maximum rate of macroscopic crack propagation is \( 3 \times 10^{-8} \text{ mm sec}^{-1} \) which is just below 1 \text{ mm yr}^{-1}.

A major defect in this analysis of results was the large extrapolation required to reach cross head speeds representative of deformation rates in service. To overcome this a second batch of specimens were tested at OmV with cross head speeds from \( 4 \times 10^{-1} \) to \( 4 \times 10^{-5} \text{ mm sec}^{-1} \). The problem of pitting over long periods did not occur at OmV and valid results were obtained down to \( 4 \times 10^{-5} \text{ mm sec}^{-1} \). Also the constancy of "\( k \)" with cross head speed assumed in the earlier analysis could be investigated.

The variation of reduction of area with cross head speed for tests at OmV is shown in Figure 17. For cross head speeds from \( 4 \times 10^{-3} \) to \( 4 \times 10^{-5} \text{ mm sec}^{-1} \) values of "\( k \)" and macroscopic propagation rate could be calculated in the same manner as previously described for tests at +100mV. Changes in Reduction of Area for tests at 0.04 and 0.4 mm Sec\(^{-1}\) were again too small to be significant so that \( k \) values could not be calculated. A value of 150 was assumed for these tests as reasonable in comparison to values obtained at lower cross head speeds. The results are shown in Table 3. The plastic deformation time fell with decreasing cross head speed because of the "premature failure" effect described earlier. Plateau currents were generally too small to be measured accurately at \( 4 \times 10^{-5} \text{ mm sec}^{-1} \) but were of the order of 1-2\( \mu A \). The macroscopic defect propagation rate is plotted against cross head speed in figure 18, the dotted line represents the results obtained at +100mV.

The newer results support the tentative extrapolation of the earlier results. The dependence of propagation rate on cross head speed is logarithmically
A major difference between results at +100mV and 0mV was that for any particular cross head speed the propagation rate was approximately 2.5 x lower at 0mV than +100mV, this is due to the lower plateau currents observed at the more cathodic potential and hence the slower rate of attack at emergent slip steps. A second difference between the two sets of results was the value of "k". Relatively good agreement was obtained between "k" values at 4 x 10^-3, 4 x 10^-4 and 4 x 10^-5 mm sec^-1 for the 0mV tests, this supported the assumption made in the earlier tests that k was constant with cross head speed. It also allowed the reasonable assumption of k values of 150 for the 4 x 10^-1 and 4 x 10^-2 mm sec^-1 tests at 0mV. The discrepancy of k value between 0mV and +100mV tests (150 as opposed to 250) cannot be explained by the difference in potentials, "k" is essentially dependent on metal physics rather than electrochemistry. The two batches of specimens came from different stock sheets and although attempts were made to cold roll both sheets to the same degree there were inevitably small differences in composition and cold work. These differences through their effects on dislocation structure and density may have affected "k".

A limitation of the analysis is that an expression for the slip step dissolution rate can be derived relatively rigorously but no easily derived expression exists for the repopulating rate which is required to translate the slip step rates into macroscopic propagation rates. The assumption of the expression N = kS overcomes this difficulty but means that the correlation of observed reductions in area to slip step dissolution rates results in k values which are repositories not only of real differences in behaviour but of all the defects, inaccuracies and omissions in the data and analysis. On this basis the variation from 150 to 250 in k value between the two batches of specimens is not excessive.

5.2.1.2 CONCLUSION

The dynamic strain stress corrosion test described is a unique SCC test in that it does not necessarily produce the classical symptoms of susceptibility ie cracks. This is a direct result of the fact that the accelerating factor in the test, dynamic strain, destroys the profile of any but the most rapidly propagating cracks. Such cracks are produced only in very susceptible systems. The test has provided evidence for the importance of the slip step dissolution model in the stainless steel/chloride system. The results are interpretable in a quantitative manner using this model and may be used to predict the occurrence and propagation rate of cracks. For the system studied SCC is extremely unlikely in the conditions encountered in service and even under the most unfavourable conditions of potential and deformation rate the possible rate of crack propagation is very low.
References


### Table 1

**Anodic Polarisation Data for 316 Stainless Steel in 0.17M NaCl Solution**

**Conditions**

- Specimen surface Area: $700 \text{ mm}^2$
- Solution deaerated with argon
- Scan Rate: 10 steps min$^{-1}$
- Step Size: 10 mV

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Hydrogen Evolution Potential mV (SCE)</th>
<th>Repassivation Potential mV (SCE)</th>
<th>Pitting Potential mV (SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1040</td>
<td>+100</td>
<td>+380</td>
</tr>
<tr>
<td>2</td>
<td>-1020</td>
<td>-40</td>
<td>+420</td>
</tr>
<tr>
<td>3</td>
<td>-1020</td>
<td>-60</td>
<td>+420</td>
</tr>
<tr>
<td>4</td>
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<td>0</td>
<td>+360</td>
</tr>
<tr>
<td>6</td>
<td>-1040</td>
<td>-20</td>
<td>+380</td>
</tr>
</tbody>
</table>
Table 2

Current Changes on Plastic Deformation for 316S16 Specimens Tested at +100mV (SCE).

<table>
<thead>
<tr>
<th>Cross Head Speed mm sec⁻¹</th>
<th>&quot;Plateau&quot; Corrosion Current A</th>
<th>Macroscopic Propagation Rate mm sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>483</td>
<td>8.21 x 10⁻⁴</td>
</tr>
<tr>
<td>0.4</td>
<td>530</td>
<td>9.02 x 10⁻⁴</td>
</tr>
<tr>
<td>0.4</td>
<td>490</td>
<td>8.34 x 10⁻⁴</td>
</tr>
<tr>
<td>0.04</td>
<td>115</td>
<td>1.96 x 10⁻⁴</td>
</tr>
<tr>
<td>0.04</td>
<td>92</td>
<td>1.56 x 10⁻⁴</td>
</tr>
<tr>
<td>0.04</td>
<td>97</td>
<td>1.65 x 10⁻⁴</td>
</tr>
<tr>
<td>0.004</td>
<td>23</td>
<td>3.91 x 10⁻⁵</td>
</tr>
<tr>
<td>0.004</td>
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<td>5.10 x 10⁻⁵</td>
</tr>
<tr>
<td>0.004</td>
<td>35</td>
<td>5.95 x 10⁻⁵</td>
</tr>
</tbody>
</table>
### Table 3

Data from REMP tests on 316S16 Specimens

Tested at OmV

<table>
<thead>
<tr>
<th>(Mean R of A in Air) - (Mean R of A in NaCl)</th>
<th>Cross Head Speed mm sec</th>
<th>Plastic Deformation Time mm sec</th>
<th>&quot;k&quot; value</th>
<th>Plateau Current µA</th>
<th>Macropscopic Propagation Rate mm sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 0.25</td>
<td>4 x 10^-1</td>
<td>-</td>
<td>(150)</td>
<td>300</td>
<td>3.1 x 10^-4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>3.1 x 10^-4</td>
</tr>
<tr>
<td>0.8</td>
<td>4 x 10^-2</td>
<td>-</td>
<td>(150)</td>
<td>80</td>
<td>8.2 x 10^-5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>85</td>
<td>8.7 x 10^-5</td>
</tr>
<tr>
<td>1.95</td>
<td>4 x 10^-3</td>
<td>11.7 x 10^2</td>
<td>144</td>
<td>17</td>
<td>1.7 x 10^-5</td>
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<td></td>
<td></td>
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<td></td>
<td>20</td>
<td>2.0 x 10^-5</td>
</tr>
<tr>
<td>5.8</td>
<td>4 x 10^-4</td>
<td>11.1 x 10^3</td>
<td>167</td>
<td>6</td>
<td>6.8 x 10^-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>5.7 x 10^-6</td>
</tr>
<tr>
<td>8.2</td>
<td>4 x 10^-5</td>
<td>9.6 x 10^4</td>
<td>132</td>
<td>1</td>
<td>9 x 10^-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>18 x 10^-7</td>
</tr>
</tbody>
</table>
FIGURE 1. REDUCTION OF AREA / POTENTIAL FOR 316®16 STEEL
FIGURE 2. FRACTURE STRESS POTENTIAL FOR STEEL
FIGURE 4. TYPICAL CORROSION CURRENT TRACE FOR SPECIMENS STRAINED AT POTENTIALS BELOW $-200 \text{ mV (SCE)}$.
FIGURE 5. TYPICAL CORROSION CURRENT TRACE FOR SPECIMENS STRAINED AT POTENTIALS -200 to +200 mV (SCE)
FIGURE 6. TYPICAL CORROSION CURRENT TRACE FOR SPECIMENS STRAINED AT POTENTIALS +200 +400mV (SCE)
Figure 7. Typical corrosion current trace for specimens strained at +600 mV (SCE) (heavily pitted)
Figure 8  Section through fracture surface of specimen tested at 0 mV. x 400 (OK)

Figure 9  Fracture surface of specimen tested at -400 mV. x 1000 (SEM)

Figure 10  Fracture surface of specimen tested at 0 mV. x 1000 (SEM)

Figure 11  Fracture surface of specimen tested at +600 mV. x 1000 (SEM)
Anodic polarisation curve for 316S16 stainless steel in 0.17K NaCl solution.
FIGURE 13. SCHEMATIC REPRESENTATION OF EFFECT OF REPASSIVATION RATE ON SLIP STEP DISSOLUTION
FIGURE 14: EFFECT OF DISSOLUTION RATE/STRAIN RATE RATIO, R, ON PROPAGATION OF EMBRYO DEFECT
FIGURE 15. SCHEMATIC COMPARISON OF SPECIMENS TESTED IN AIR AND SALINE SOLUTION
Figure 16: Macroscopic defect propagation rate/crosshead speed for 316L SS stainless steel at +100 mV.
Figure 17 Variation of Reduction of Area with crosshead speed for 316L at 0.17 M NaCl solution
Figure 18  Macroscopic defect propagation rate / crosshead speed for 316L at OmV.
Appendix I Derivation of Expressions

Used in Interpretation of Region II Behaviour

(A) Relationship between elongation and change in macroscopic surface area

Considering the gauge length of the specimen as a cylinder:

\[ A_1 = \pi d_1 l_1 \]  \hspace{1cm} \text{..... (1)}

\( d_1 = \) initial diameter

\( l_1 = \) initial length

\( A_1 = \) initial area

Straining by an increment \( \delta l \) to \( l_2 \) gave an area \( A_2 = \pi d_2 l_2 \)

with a macroscopic change of area \( \delta A = A_2 - A_1 \)

\( \therefore \delta A = \pi d_2 l_2 - \pi d_1 l_1 \)  \hspace{1cm} \text{..... (2)}

By conservation of volume

\[ \frac{\pi}{4} d_1^2 l_1 = \frac{\pi}{4} d_2^2 l_2 \]  \text{ie}  \( d_2 = d_1 \sqrt{\frac{l_1}{l_2}} \)

Substituting in (2) gives:

\[ \delta A = \pi d_1 l_1 \left( \sqrt{\frac{l_1}{l_2}} - 1 \right) \]

\[ \delta A = \pi d_1 l_1 \left( \sqrt{\frac{l_1}{l_2}} \cdot \frac{l_2}{l_1} - 1 \right) \]

\[ \delta A = A_1 \left( \sqrt{\frac{l_2}{l_1}} - 1 \right) \]

Putting \( l_2 = l_1 + \delta l \)

\[ \delta A = A_1 \sqrt{\frac{l_1 + \delta l}{l_1}} - A_1 \]

\[ \delta A = A_1 (1 + \frac{\delta l}{l_1})^{\frac{1}{2}} - A_1 \]

Expanding binomially, neglecting \( \delta l^2 \) terms and higher for \( \delta l \) small

(valid for \( \delta l \leq 30\% \))

\[ \delta A = A_1 \left( 1 + \frac{\delta l}{2l_1} \right) - A_1 \]

\[ \delta A = \frac{A_1 \delta l}{2l_1} \]

\[ \frac{\delta A}{A_1} = \frac{\delta l}{2l_1} \]  \hspace{1cm} \text{..... (3)}
Thus for the elongations encountered in this work an elongation of X% gave an increase in macroscopic surface area of X/2%.

(B) **Number of slip steps emerging in time, T.**

From derivation (A):

\[ \delta A = \frac{\delta l A_1}{2 l_1} \]

The macroscopic surface area exposed per event is therefore:

\[ \frac{A_1 TS}{2 l_1} \]

\( S = \) cross head speed

\[ A_1 = \pi l_1 d_1 \]

Thus macroscopic fresh surface area exposed per event = \( \frac{\pi d_1 TS}{2} \)

This macroscopic surface area is composed of a number of slip steps emerging at varying angles to the specimen surface. If the average true area evolved by a slip step is \( \bar{A} \) and the step emerges from the surface at an angle \( \theta \) the contribution to the macroscopic area increase measured in the plane of the specimen surface is \( \bar{A} \sin \theta \). Taking \( \theta = 45^\circ \) as an average emergent angle, the number of steps emerging per event is

\[ \frac{\pi d_1 TS}{2 \bar{A} \sin 45^\circ} \]

Number of steps/event = \( \frac{\pi d_1 TS}{2 \bar{A} \sin 45^\circ} \)

(C) **Amount of dissolution occurring in event time, T**

If \( I_p \) is the "plateau" current flowing during the plastic deformation of the specimen and, according to the theory previously discussed, this current is generated by the dissolution of the fresh area exposed, then during one dissolution event \( I_p T/F \) chemical equivalents of metal are removed where \( F \) is Faraday's constant.

This is equivalent to \( \frac{I_p T F}{P p} \) mm

\( E = \) equivalent weight of dissolved material, \( p = \) density.
Some limited testing was performed on the Co-Cr-Mo cast alloy because notched static SCC tests had indicated slight SCC susceptibility. It was thought that cracks could be initiated at grain boundaries in the deformed material at the root of a notch and that little crack growth would be required before catastrophic brittle failure ensued. Corrosion fatigue studies had also shown that the presence of a corrosive environment lowered the fatigue properties of Co-Cr-Mo much more than other implant materials.

The tests were performed at 0.004 mm/sec⁻¹ cross head speed in the same manner and under the same conditions as those described for 316S16 stainless steel. The mechanical properties versus potential plots obtained are shown in figures 1-3. There was a large scatter in the results, particularly the elongation and reduction of area measurements. As explained earlier, the large and variable grain size of cast vitallium results in an inherently large variation in properties from specimen to specimen. Elongation and reduction of area values were unaffected by applied potential but the UTS/potential graph could be divided into two sections:

(a) for potentials cathodic to the isolated corrosion potential (ICP) the UTS was constant with increasingly cathodic potentials;
(b) for potentials anodic to the ICP UTS values were initially high but fell with increasingly anodic potentials.

The corrosion current traces obtained in these tests are shown in figures 4-6. The change from elastic to plastic behaviour was much less marked in Co-Cr-Mo than in cold worked stainless steel but the estimated position of the first deviation from linear elastic behaviour is marked on each trace. Necking was absent or very slight in this material. Low corrosion currents were observed at potentials cathodic to the isolated corrosion potential until ~1000 mV when a larger corrosion current was generated; this indicates a high overpotential for hydrogen evolution. At the isolated corrosion potential there was a sharp transition in the type of trace. Cathodic to the ICP currents steadily rose to ~5 μA. Anodic to the ICP the trace was more S shaped with currents rising to 10-35 μA. This transition correlated with the transition observed in the mechanical property/potential graphs. Behaviour was different to that observed with 316S16 in that a flat plateau anodic
current was not present and the initiation of current rise did not correlate with the beginning of plastic deformation. This suggests that the oxide on Co-Cr-Mo (identified as hydrated Cr₂O₃ by Hughes and Lane[1]) was considerably more brittle than that on 316S16 stainless steel and ruptured while the underlying metal is still deforming elastically.

Coplanar dislocations arrays have not been reported in Co-Cr-Mo alloys although there are theoretical reasons for expecting that they may occur [2,3]. Even if they are present their importance in SCC is diminished by the fact that the hydrated Cr₂O₃ is sufficiently brittle at the grain boundaries to rupture and allow localised attack before plastic deformation of the underlying metal and shear rupture of the oxide by slip steps can occur; this will be discussed more fully later. In addition the absence of any changes in the corrosion current/crosshead displacement traces at the transition from elastic to plastic behaviour supports the view that such slip steps are absent or not sufficiently large to cause the current transients of the type seen in 316S16 steel. Therefore the slip step dissolution model developed for 316S16 steel was not applicable to Co-Cr-Mo.

Figure 7 shows the type of microstructure observed in all specimens. The grain size was large, grain diameters of 1-2 mm being typical with non-metallic inclusions and mixed metal carbides segregated at the grain boundaries. Regular lamellar arrays of carbides also occurred within the grains. Fracture of all specimens, including those in air, was by intergranular failure. Subsidiary intergranular cracks were seen close to the fracture but these were few in number for specimens tested in air or at potentials cathodic to the ICP. A small subsidiary crack in a specimen tested at -400 mV (SCE) is shown in figure 8. At increasingly anodic potentials more and deeper subsidiary cracks were observed (figure 9). At very anodic potentials, i.e. above +800 mV (SCE), grain boundaries were preferentially attacked resulting in a grain boundary etching effect. A secondary preferential attack occurred at the carbide particles within the matrix revealing the lamellar microstructure. Figure 10 is a section through such a specimen, localised grain boundary and carbide attack can be seen.

Mechanism of failure at potentials cathodic to the ICP

The mechanical properties measured at potentials cathodic to the ICP were essentially the same as those obtained in air. Small corrosion currents were generated by dissolved oxygen reduction and no anodic dissolution of the specimen grain boundary or interior was observed. At very
cathodic potentials (-1000 mV (SCE)) where hydrogen evolution occurred there was no reduction in properties indicating that hydrogen embrittle-
ment was not a mechanism of failure in this material.

**Mechanism of failure at potentials anodic to the ICP**

Large anodic currents were observed at potentials increasingly anodic to the ICP, dissolution being primarily concentrated at the grain boundaries. Two reasons may be postulated for this:—

(a) the oxide film covering the boundary was structurally less perfect than the oxide on the grain interior because of gross physical and chemical inhomogeneities at the boundary. Thus the boundary oxide was more easily ruptured.

(b) the inhomogeneities referred to above would have made the exposed boundary more anodic than the grain interior.

In a freely corroding situation the relatively low grain boundary length resulting from the large grain size would be important. The low anode (grain boundary) to cathode (grain interior) ratio would result in an increased intensity of attack.

The events leading to fracture are postulated to be:—

1. plastic deformation of the specimen occurs mainly in the grain interior as the stress is raised. The grain boundaries are relatively strong and are not destroyed or deranged by this plastic deformation. This can be seen by referring to the microfractographs. As the grain interiors are strengthened by strain hardening the stress rises to a level where limited yielding occurs at the grain boundaries. Rupture of the relatively brittle boundary material follows.

The increasing amount of grain boundary dissolution observed at potentials anodic to the ICP serves to notch the brittle boundary and allows rupture at lower stresses than an un-notched boundary, thus lowering the measured UTS. The macroscopic ductility is unaffected by this grain boundary notching because it is largely dependent on the grain interior deformation. Grain boundary deformation is prematurely terminated by the notched failure but this contributes little to the measured ductility. Calculations have been made to predict the depth of grain boundary grooving expected from the corrosion currents measured during the test (Appendix 1 ). A corrosion current of 20 μA produces a dissolution rate of
3.6 x 10^{-6} \text{ mm sec}^{-1} \text{ giving a radial penetration of 0.1\% of the specimen diameter. Penetrations of this order were observed in notched static loading tests on Co-Cr-Mo specimens some of which subsequently failed. Thus small penetration can be expected to lower the load carrying capacity of the material without affecting measured reduction of area properties.}

The value of 0.1\% was obtained assuming a uniform dissolution rate at all points along all exposed boundaries, in fact probably dissolution was more concentrated at carbides and inclusions giving deeper local intrusions than the 0.1\% indicated.

For potentials from +800 mV to +1000 mV where much higher corrosion currents were measured (10 mA) a penetration rate of 1.8 x 10^{-3} \text{ mm sec}^{-1} \text{ giving a radial penetration of 1.1 mm (60\%) was obtained. This value was much higher than the grain boundary grooving depths typically of 0.1 mm measured on metallographic sections of specimens tested at these potentials. There are two main reasons for this discrepancy: firstly, the assumption made in the calculations that all of the dissolution was concentrated at the grain boundaries was invalid because intragranular attack could clearly be seen for tests at these potentials; secondly, examination of metallographic sections revealed that boundary dissolution was not confined to a 0.001 mm boundary width but that dissolution could break out from the boundary into the structures segregated at the boundary. Both of these phenomena reduce the effective current available for grain boundary penetration.}

5.2.2.2 Conclusions

The reduction in mechanical properties observed in Co-Cr-Mo at potentials anodic to the ICP is consistent with a grain boundary grooving mechanism. The occurrence of "high" mechanical properties within the data band spread at potentials slightly anodic to the ICP cannot be explained on this model however.

Previous work on failed implants [4-5] and impact studies [6] has shown that Co-Cr-Mo is notch sensitive. Corrosion fatigue [7-8] and static stress corrosion tests (reported earlier) revealed that a synergistic effect occurs between a notch and a corrosive environment. The REMP test has shown that this effect proceeds by a mechanism of localised dissolution at the grain boundaries resulting in notching of
the brittle boundary and subsequent fast fracture. The oxide rupture required to expose the boundary to anodic dissolution is provided by the local high strain rate at the root of a notch in a loaded specimen.

The reduction in properties measured in the REMP test for potentials likely in service (typically 0 - +100 mV (SCE)) is small but calculations based on the observed corrosion currents indicate the existence of grain boundary grooving rates high enough to effectively notch the grain boundaries. Although this is not stress corrosion in the classical sense the effect is an important initiator of brittle fracture.

The theory predicts that the stress corrosion and corrosion fatigue properties of Co-Cr-Mo could be improved by:

(i) a smaller grain size to decrease the localisation of attack,
(ii) a solution heat treatment to reduce the heterogeneity of the grain boundary,
(iii) vacuum casting to reduce the non-metallic inclusion content of the boundary.

Further work to evaluate the effect of these treatments on susceptibility would be useful.
REFERENCES

1. The Identification of the Protective Oxide Film Formed on a Co-Cr-Mo Alloy. A N Hughes and R A Lane. AWRE Report 018/70.


FIGURE I. REDUCTION OF AREA/POTENTIAL FOR VITALLIUM IN 0.17 M NaCl
FIGURE 2. ELONGATION / POTENTIAL FOR VITALLIUM IN 0.17M NaCl
FIGURE 3. TRUE UTS / POTENTIAL FOR VITALLIUM IN 0.17M NaCl
FIGURE 4: CORROSION CURRENT STRAIN CHARACTERISTIC FOR Co-Cr-Mo - 1000 mV → -400 mV (SCE)
FIGURE 5. CORROSION CURRENT / STRAIN CHARACTERISTIC FOR Co-Cr-Mo. -200→+400 mV (SCE)
FIGURE 6. CORROSION CURRENT/STRAIN CHARACTERISTIC FOR Co-Cr-Mo +600 mV—+1000 mV (SCE)
Figure 7  Typical microstructure.  
*100 (OM)

Figure 8  Subsidiary crack near fracture of specimen tested at -400 mV (SCE).  *100 (OM)

Figure 9  Subsidiary cracks in specimen tested at 0 mV (SCE).  *100 (OM)

Figure 10  Grain boundary and carbide particle attack in specimen tested at +1000 mV (SCE).  *100 (OM)
APPENDIX I DEPTH OF GRAIN BOUNDARY
ATTACK IN Co-Cr-Mo

If the average grain boundary area exposed at a surface is $A_g$ and the average boundary length is $l_g$, the number of grains exposed on a specimen surface is:

$$\frac{\pi d s l s}{A_g}$$

$ds$ specimen diameter

$$l_s$$ gauge length

and total grain boundary length is:

$$\frac{\pi d s l s}{A_g} \cdot \frac{l_g}{2}$$

N.B. A grain boundary is shared by two grains.

Area over which dissolution occurs $= \frac{\pi d s l s l_g w}{2A_g}$  

$$w = \text{width of dissolution at boundary}$$

Rate of dissolution $= \frac{I}{F}$

$I$ = corrosion current

$F$ = Faraday's constant

It is assumed that material dissolved with an effective atomic weight of 56 (Co = 58.9, Cr = 52.0) in the divalent state. Molybdenum, atomic weight 95.9 dissolving as $\text{MoO}_4^2-$, $z = +6$ is ignored because of its low concentration in the alloys. Therefore 1 chemical equivalent of material $= 28g$. Assuming the density of dissolving material is $0.008g\ mm^{-3}$ (Co $= 0.0089$, Cr $= 0.0071$).

$$\text{Volume dissolved sec}^{-1} = \frac{I}{F} \times \frac{28}{0.008} \ mm^3$$

$$= \frac{\pi d s l s l_g w}{2A_g}$$

If all of this dissolution is concentrated on grain boundaries it is equivalent to a uniform boundary dissolution rate of:

$$\frac{I}{F} \times \frac{28}{0.008} \ mm sec^{-1}$$

by combining (1) and (2).
Uniform boundary dissolution rate = \( \frac{56 \, I_{Ag}}{0.008 \, F \, d_s \, d_g \, w} \) mm sec\(^{-1}\)

\[ F = 96,500 \text{ coulombs mole}^{-1} \]
\[ d_s = 3.58 \text{ mm} \]
\[ l_s = 12.7 \text{ mm} \]
\[ Ag = 3.6 \text{ mm}^2 \]
\[ l_g = 10 \text{ mm} \]
\[ w = 0.007 \text{ mm} \]

Estimated from measurements on polished and etched metallographic specimens

Taking I = 20 μA for a typical corrosion current at potentials slightly anodic to the ICP:

Uniform boundary dissolution rate = \( 3.6 \times 10^{-6} \) mm sec\(^{-1}\)

For a test time of 600 sec this gives a radial penetration of \( \sim 2 \times 10^{-3} \) mm or

\[ \frac{2 \times 10^{-3} \times 2}{3.58} \times 100 \text{ per cent} \]

of the specimen diameter, ie \( \sim 0.1\% \).

Repeating the calculation for a current of 10 mA, ie the magnitude of currents observed at more anodic potentials a uniform dissolution rate of \( 1.8 \times 10^{-3} \) mm sec\(^{-1}\) and a radial penetration of 1.1 mm (\( \sim 60\% \)) are obtained.
The long term stress corrosion resistance of titanium alloys is important because of their possible use for artificial hip joints. High loads on thick sections for very long periods (up to 50 years) are possible in these circumstances. Most of the SCC testing on these materials has been done using precracked specimens but dynamic strain testing was used here to investigate economically a range of experimental variables.

Because little work has been done on applying this test to titanium alloys the first tests were performed on Ti-8Al-1Mo-1V, an alloy whose stress corrosion properties has been widely studied. By examining this material the test method could be evaluated. The majority of commercially available titanium alloys have an $\alpha + \beta$ structure. Therefore information gained on Ti-8Al-1Mo-1V had relevance to other $\alpha + \beta$ titanium alloys. Further work was performed on Ti-6Al-4V, the commercial alloy likely to find the widest use in orthopaedic surgery.

5.2.3.1 REMP Test Results and Discussion on Ti-8Al-1Mo-1V with Various Hydrogen Contents

Results on Ti-8AL-1Mo-1V Hydrogen Content 65 ppm

Specimens of the modified Hounsfield No. 5 Flat type were taken from duplex annealed 2 mm sheet. The hydrogen content was determined by a vacuum extraction technique (1). Tests were initially performed at a cross head speed of 0.004 mm sec$^{-1}$ over a range of potentials from -3000 to +5000 mV (SCE). The method and conditions of test were as described previously.

Figures 1, 2 and 3 show the variation of reduction of area with potential obtained. Plots of UTS/potential and elongation/potential were exactly similar. Properties obtained in air and in saline solution at an uncontrolled potential are also plotted. The corrosion potential in these uncontrolled tests remained constant at approximately -350 mV (SCE) during elastic deformation but at the onset of plastic deformation the potential fell steadily to a value of -700 $\rightarrow$ -300 mV at fracture.

The mechanical property/potential graphs may be divided into three regions:

1 A region of protection cathodic to -2000 mV.

2 A region of susceptibility between -2000 and +500 mV, the maximum susceptibility being between -500 and 0 mV.

3 An anodic protection peak at +500 to +1000 mV.

4 Increasing susceptibility at potentials anodic to +1000 mV.

These findings correlate well with those of Beck (2) and Chen et al (3) on Ti-8Al-1Mo-1V and Feige and Murphy (4) and Leckie (5) on Ti-7Al-2Nb-1Ta. This correlation is shown in figure 2.
Because of the good correlation between the REMP test results and e of more conventional, lengthier tests the REMP test was used to stigate the effect of particular variables on the SCC of Ti-8Al-1Mo-1V.

Recent work at AWRE (1) had revealed the importance of alloy content on stress corrosion susceptibility. This had practical e for the specification of maximum allowable hydrogen content alloy compositions and theoretical importance in its bearing on a hydrogen embrittlement mechanism for SCC. For these reasons the effect hydrogen content of the SCC of Ti-8Al-1Mo-1V was investigated.

Effect of Hydrogen content on SCC of Ti-8Al-1Mo-1V

Figure 3 shows the effect of potential on reduction of area over restricted range of potentials for Ti-8Al-1Mo-1V with a hydrogen content 5 ppm and figure 4 for Ti-8Al-1Mo-1V with a hydrogen content of ppm. Exactly similar results were obtained with other mechanical rities as before. These materials were prepared by controlled hydrogen removal or addition to the as received 65 ppm material. The ique is described in appendix I. Blank runs, subjecting specimens his heat treatment without hydrogen removal, had only a slight effect CC susceptibility (1).

Results on the 15 ppm material showed that reducing the hydrogen ent narrowed the zone of susceptibility greatly, the minimum in rities occurring at -100 -> -200 mV. A secondary effect was to extend anodic protection region at least up to +2000 mV.

The stress corrosion behaviour of the material was changed rely by the addition of 300 ppm hydrogen. A much greater scatter rerties was observed but a band could be drawn which delineated areas:

1. At potentials cathodic to -500 mV the material was relatively immune to SCC.
2. At potentials anodic to -500 mV behaviour ranged from relative immunity to severe susceptibility.

Fractography and Microstructure

The microstructure of "as received" Ti-8Al-1Mo-1V is shown in e 5. The matrix was phase with approximately 10% of phase ntrated mainly at the poorly defined α grain boundaries. The ogen removal heat treatment resulted in a microstructure such as shown in figure 6, growth and regularisation of the α grains occured coalescence of the β particles to form more massive grain boundary pitates. In addition structures within some grains other than ional β particles were observed. These were not positively iden-d by may have been martensitic phases resulting from the rapid cool. e 7 shows the effect of hydrogen addition during the same heat ment. Grain growth and coalescence of α phase had again occured but areas of the specimen developed an acicular type of microstructure families of parallel β platelets forming islands in the otherwise
homogeneous microstructure. This type of structure had been observed before in as-received material and seemed to occur randomly in a few specimens. Needles, tentatively identified as titanium hydride, were also seen in specimens with 300ppm hydrogen (figure 8).

Optical microscopy of the fracture surfaces of 15 and 65ppm Ti-8Al-1Mo-1V showed little difference from each other and from the fracture mode in air, this was by ductile dimpling. An exception to this was for tests of 65ppm material at very anodic potentials where cracks could be seen in an area adjacent to the fracture surface which had been eroded by massive pitting (figures 9 and 10).

**Corrosion Current/Strain Traces**

Typical corrosion current versus nominal strain traces are shown in figures 11-20 for material with various hydrogen contents. For the "as received" material large cathodic currents due to copious hydrogen evolution were generated below -2000 mV. At -1000 mV a much smaller cathodic current was observed indicating a considerable over-potential for hydrogen evolution on the oxide covered metal. At 0 and 500 mV small anodic currents flowed, rising throughout the test. No current surge occurred at the transition from elastic to plastic behaviour with the current recording sensitivity used in these tests. (About one microamp was the smallest current which could be reliably measured.) At +1000 mV currents two orders of magnitude larger flowed with still larger currents at more anodic potentials as pitting attack became increasingly severe.

The 15ppm hydrogen extracted material showed a similar high overpotential for hydrogen evolution and a barely detectable current between the potentials of -500 and +1500 mV. This is much smaller than the currents observed on the 65ppm material. In addition currents were low up to +2000 mV (the most anodic potential tested) indicating that pitting had not yet begun.

A third type of behaviour was shown by material with 300ppm hydrogen content. Hydrogen evolution was again not appreciable until the potential was more cathodic than -1000 mV. The transition from small cathodic to small anodic currents occurred at more cathodic potentials (~-500 mV) compared with the 65 and 15ppm material (~0 mV). These anodic currents were again small until +1500 mV where pitting began.

**Discussion of Results on Ti-8Al-1Mo-1V 65ppm H₂**

The validity of the dependence of SCC susceptibility on potential is amply supported by comparison with the results of other authors.

It is important to note that the results obtained on smooth specimens under constant strain rate conditions were essentially the same as those obtained using precracked or notched specimens in a fracture toughness type test. Much of the work on SCC of titanium alloys had emphasised the importance of critical crack tip stress intensities and crack tip solution chemistry for susceptibility. The present work however suggests that strain is the important mechanical parameter and that a specific crack...
p chemistry is not necessary for SCC. The earlier work can then be interpreted on the basis that $K_{ISC}$ is equivalent to a critical strain or strain in the crack tip plastic zone. The crack tip chemistry while being a product of the cracking process and the occluded conditions is not a necessary condition for cracking although, as will be seen later, it may be an accelerating factor.

The dependence of SCC susceptibility on potential is best explained by a slip step dissolution model modified to take account of titanium halide hydrolysis. The model is similar to that previously described for 316S16 steel with important differences resulting from the titanium/halide electrochemistry.

Considering each region of the susceptibility/potential graphs in mn:

1. **Cathodic Protection Region**

From the corrosion current/nominal strain plots it can be seen that cathodic protection is at a maximum when massive hydrogen evolution is occurring at the specimen surface. The lack of susceptibility under these hydrogen charging conditions is a strong argument against any hydrogen embrittlement theory of SCC in this material. Scully (6) has explained the apparently anomalous immunity of titanium alloys under hydrogen charging conditions as being due to the more rapid repassivation of an emergent slip step and pedeance of hydrogen ingress into the underlying metal by the passive film. Millips (7) has found experimentally that the rate of hydrogen absorption can lowered by two orders of magnitude by a surface film on titanium. In the present work however in the cathodic protection region the oxide is being nrimally ruptured by plastic deformation cathodic to -1500mV (SCE), the oxide is not thermodynamically stable and the Pourbaix Diagram for the titanium water system (8) predicts the titanium hydride, TiH$_2$, should be formed. Cause of the slow kinetics of the reaction, it is not expected in the test me that the unruptured oxide would be transformed to the hydride, however when the oxide is ruptured by straining at potentials below -1500mV either titanium hydride would be the stable solid phase at slip step rupture sites coring to the rate of titanium hydride formation. Repassivation by oxide uld not occur. These conditions are ideal for hydrogen diffusion into the derlying metal or hydride growth from the surface. Immunity to SCC at these tentials is evidence against a hydrogen embrittlement mechanism of SCC in tinanium alloys.

2. **Susceptibility Region**

The mechanism of susceptibility most consistent with the data is one slip step dissolution; an important extension to the theory in the case of tinanium alloys is titanium halide formation and hydrolysis.

Coplanar dislocation arrays giving massive oxide rupture on straining known to exist in Ti-8Al-1Mo-1V (9). In an aqueous environment not containing halide ion, repassivation of an emergent step is extremely rapid and immunity is predicted. Susceptibility is only observed in the presence of halide ions. These species have the ability to slow repassivation of a step by formation and subsequent hydrolysis of a titanium halide complex. Chen et (3) have postulated the following reactions for halogen ion attack on a bare tinanium surface:

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The net result is that oxide is formed remote from rather than immediately on the metal surface, chloride ion is recycled and the pH of the solution drops sharply. The absence of rapid repassivation combined with low pH means that titanium dissolution can also occur directly by

$$\text{Ti} \rightarrow \text{Ti}^{+++} + 3e^-$$

These effects can be observed macroscopically on corrosion specimens polarised anodic to the pitting potential. Discolouration of the solution near to the specimen surface can be seen due to $\text{Ti}^{+++}$ (titanium ion, violet) formation. White deposits, identified as $\text{TiO}_2$, also form on the specimen holder.

On the microscopic scale at an emergent step recycling and anodic attack occurs within the diffusion layer. Examination of the corrosion current flowing during the test can not therefore be expected to give information on processes within the halide recycling region.

The effects described above are transient; titanium surfaces artificially bared e.g by abrasion are observed to repassivate within $\sim 100$ ms in the conditions used here once abrasion stops (10). The rate of attack in a stress corrosion situation will depend on the rate of emergence of bare surface which is a combination of slip step height and step emergence rate.

The beginning of protection at potentials cathodic to approximately $-500$ mV is due to two reasons, firstly:

$$\text{Ti} + 4\text{Cl}^- \leftrightarrow \text{TiCl}_4 + 4e^-$$

$$E_{eq(SHE)} = -0.39 - 0.059 \log a_{\text{Cl}^-} - (3)$$

Putting $a_{\text{Cl}^-} = 0.1M$ and assuming activity coefficients of unity

$$E_{eq(SCE)} \simeq -700\text{mV}$$

Thus the hydrolysable titanium halide will not form at potentials cathodic to $-700$ mV. At the higher local chloride concentrations probable at the emerging step the equilibrium potential is somewhat more anodic ($-640$ mV for $1M$ and $-580$ mV for $10M$).
Secondly hydrogen evolution occurs cathodic to \(-650\ \text{mV (SCE)}\) at pH 7 and at correspondingly more anodic potentials at lower pH (\(\sim 60\ \text{mV change per pH unit}\)). The result of this is to raise the pH of the solution and inhibit the direct dissolution of titanium which occurs only at low pH.

3 Anodic Protection Region

The existence of an anodic protection region is predicted in a slip step dissolution model because of the increasing thickness of the oxide film with increasing potential. The equilibrium film thickness at 0 mV is 80Å and at 1.5V (approximately the top of the anodic protection peak) 140Å (11). Boyd (12) has recently reported an average slip step height in Ti – 8Al – 1Mo – 1V of \(\sim 120\ \text{Å}\). Thus at 0 mV, 120 – 80 = 40Å "height" of bare metal would be exposed whereas at 1.5V slip is insufficiently high to expose any bare metal at all.

4 Susceptibility of high anodic potentials

The susceptibility observed anodic to +1500 mV (SCE) correlated with the observation of very much larger corrosion currents during the test. Separate anodic polarisation experiments on Ti–8Al–1Mo–1V gave values of pitting potential close to +1500 mV. The results of these ancillary experiments will be discussed more fully later.

In the absence of any film breakdown once the oxide had thickened sufficiently to stifle slip step emergence an anodic protection plateau would exist. This plateau is interrupted shortly after its formation by pitting of the oxide film which allows the environment access to emergent steps again and also develops a low pH anolyte by hydrolysis in the pit. The reduction of properties at these potentials is partly due to pitting and partly to cracks growing within these pits. It is difficult to distinguish practically in these circumstances between rapidly growing pits, fissures and yawning cracks within the pits. Mechanistically these phenomena are a spectrum of increasingly acute forms of localized attack.

The thesis that the anodic protection peak is a plateau interrupted by pitting attack is supported by the observations of Beck (2) that the anodic peak is narrower in KBr than in KCl and is entirely absent in the case of KI. The aggressiveness of halide ions as pitting agents for Ti alloys increase in the order \(\text{Cl}^- < \text{Br}^- < \text{I}^-\).

Discussion of Results on Ti – 8Al – 1Mo – 1V 12 ppm H₂

It was not immediately obvious how small changes in hydrogen content of the material could affect any of the parameters critical in the slip step dissolution model of SCC, in addition the work of Orman and Ickon (1) had also shown that the effect of hydrogen content on Ti – 8Al – 1Mo – 1V in precracked SCC tests was not consistent with predictions based on a hydrogen embrittlement theory either. It may be suggested that the hydrogen content effects were secondary, the important actor being the microstructural changes brought about by the heat treatments necessary to achieve different hydrogen contents. Microstructure is known to be important in SCC susceptibility of titanium alloys. This view is untenable however because:
(1) Orman and Picton (1) in "blank-run" heat treatment without hydrogen removal found only negligible changes from as-received SCC properties.

(2) 12ppm and 300ppm H₂ content Ti - 8Al - 1Mo - 1V had exactly the same heat-treatment. In one case with vacuum extraction of hydrogen, in the other with controlled additions of hydrogen.

As-received material vacuum extracted to a low hydrogen level with a subsequent controlled readdition of hydrogen back to the as-received level behaved in a similar manner to specimens which had had no heat treatment at all.

Thus differences in stress corrosion behaviour could only be attributed to hydrogen content, microstructural or other differences brought about by hydrogen content and not to heat treatment effects alone.

The fact that differences were observed in the corrosion current/strain characteristics of different hydrogen content Ti - 8Al - 1Mo - 1V led to the effect of hydrogen content on corrosion properties being investigated more systematically using a conventional anodic polarisation technique. The experimental conditions are described briefly in Appendix II. Table 1 gives values of repassivation, pitting and hydrogen evolution potentials obtained with a number of specimens, and figures 21-23 present this data in graphical form. The date indicate that at low hydrogen contents pitting, repassivation and hydrogen evolution occur easily; at intermediate hydrogen contents with more difficulty and at higher hydrogen contents (100 ppm) again more easily. At very high hydrogen content (300 ppm) the material contains a discrete hydride phase and the data is not directly comparable with that for lower hydrogen contents. The dependence of the electrochemical data on hydrogen content rather than thermally produced microstructural changes has recently been verified by vacuum extracting hydrogen and reintroducing it into a specimen to the as-received level. Electrochemical data similar to that for untreated specimens is obtained after this extraction-reintroduction cycle.(13)

It is probable that the repassivation results are not independently significant but are dependent on their respective pitting results: the experimental procedure followed was to reverse the direction of potential scan once pitting had occurred, if pitting did not occur until very anodic potentials attack was extremely rapid, once pitting had initiated resulting in a large deep pit which was difficult to repassivate; lower pitting potentials gave smaller more easily repassivated pits. Thus the mirror image relationship observed between the pitting potential/hydrogen content and repassivation potential/hydrogen content plots is probably experimentally induced.

The data for pitting potential and hydrogen evolution potential indicate that the metal hydrogen content has an effect on the properties of the passive film. It seems reasonable to suppose that a free exchange of hydrogen between the passive film and underlying metal is likely. Without detailed knowledge of how hydrogen enters into the molecular and electronic structure of the oxide it is difficult to be specific as to how it affects the film's properties, however three possibilities are apparent:
1 Hydrogen segregates to defect sites in the oxide to give reas with characteristics more typical of hydroxide than oxide. These ess stable areas may act as centres for pit initiation and hydrogen volvation reaction.

2 Hydrogen as H⁺ in the film moves under the influence of he electric field caused by adsorbed Cl⁻ ions on the passive film surace to neutralise the Cl⁻ ion charge. By preventing the build-up of a harged layer this would aid Cl⁻ ion adsorption thus making the first tage of pit initiation easier.

3 Hydrogen can act as an impurity doping element to make he oxide n-type semiconducting. Bianchi et al (14) have recently shown hat thermal treatments to 304S16 stainless steel which make the film oxygen defective (n-type conductivity) markedly increase the pitting susceptibility. The effect is reversed in oxygen rich p-type films. Hydrogen extraction from Ti -8Al - 1Mo - 1V may therefore be expected to make the film more p-type and less susceptible to pitting. The electro-defect structure of the film also has been reported to be important n determining the corrosion potential (15) and cathodic reactions (14, 5) at the film surface. The anomalous behaviour at higher hydrogen contents y be due to hydride precipitation effects. A major problem is locating the over level of hydrogen content where hydride precipitation will occur. Slow train rate hydrogen embrittlement is observed in a range of titanium alloys ith hydrogen contents of 100 ppm and below. This embrittlement has the lassical features of a strain induced hydride precipitation mechanism although ery often these hydrides are not observed metallographically, possibly due to heir highly localised precipitation and the small amounts necessary to induce racture (16). The equilibrium concentration of interstitial hydrogen in i - Al alloys is only a few ppm (17). Hydride precipitation is initiation controlled and precipitation has been reported at a bulk hydrogen content of 00 ppm for commercially pure titanium (16) although no data specifically for i - Al - 1Mo - 1V seems to be available. Once precipitation has initiated ydrides grow quickly, essentially denuding the matrix of interstitial hydrogen 17). Thus a hydride precipitated material is similar to a low hydrogen material with respect to mobile hydrogen content. At still higher hydrogen ontents the hydrides become massive (they can be observed metallographically 300ppm in Ti - Al - Mo - V, figure 8). The presence of such large scale ructural effects would have a deleterious effect on the stability of e overlying oxide. This is in fact observed, figures 21-23 show the oxide ability peaking at ~150ppm H₂ before falling at 300ppm H₂.

Although it has been established that hydrogen has effects on the ssive film, the explanation of these effects is not easy. The importance of e data is that it has revealed another possible role of hydrogen in SCC: evious work has largely been concentrated on physical metallurgical effects, g hydride precipitation in a stress field, segregation of hydrogen to dis-cations etc. The present work suggests that the presence of hydrogen may rt primarily an electrochemical effect in reducing the stability of the cide film. Aladjem et al (19) have recently investigated the effect of a ne of environmental and metallurgical variables on the passivity of Ti - 1 - 6V - 2.5Sn using passive current density as a measure of passivity. ey found that factors which decreased passivity increased SCC susceptibility ile factors which increased passivity decreased SCC susceptibility. Thus e effects of hydrogen on film stability and SCC susceptibility observed in is work are part of a wider generalisation.
The stress corrosion data for 12 ppm H$_2$ material (figures 5 -7) shows an extension of the anodic protection peak to more anodic values. This is a manifestation of the more anodic pitting potential of the low hydrogen material. A close examination of the narrowing of the susceptibility zone shows that nearly all the narrowing occurs from the cathodic side, within the scatter of data points anodic protection occurs from the same potential for 65 and 15 ppm H$_2$ material. This is to be expected from the slip step dissolution model which predicts the onset of anodic protection to be dependent only on the oxide film thickness/slip step height ratios. The restriction of susceptibility at more cathodic potentials for the low hydrogen material may be qualitatively explained on the basis that the potential boundaries of the susceptibility zone in 'as received' Ti - 8Al - 1Mo - 1V were limitations on the possibility of slip step dissolution. Within these boundaries the rate of attack would be dependent on the balance between rate of oxide rupture, rate of dissolution and rate of repair. The restriction of susceptibility to a narrow range within the theoretically possible zone implies that the reduction in hydrogen content of the material affects either the repassivation or anodic dissolution kinetics although the mechanism of the process is unclear.

**Discussion of Results on Ti - 8Al - 1Mo - 1V 300ppm**

From an examination of the microstructures of failed specimens, three types of behaviour may be listed

1. Cathodic to -500mV, the material was immune to SCC
2. Anodic to -500 mV, the material was relatively immune to SCC if it had a regular equiaxed grain structure
3. Anodic to -500 mV the material containing areas of acicular microstructure showed severe susceptibility with cracking following acicular areas.

This data is very different from that obtained on lower hydrogen material and is not explicable on the slip step dissolution model. It is however consistent with the hydride dissolution model described below.

Hydride precipitates readily at 300ppm bulk hydrogen content in Ti - 8Al - 1Mo - 1V. The islands of acicular microstructure observed in an otherwise regular structure have been reported by other authors (1, 20), differences in structure for material which has received nominally the same thermomechanical treatment are common in Ti - 8Al - 1Mo - 1V, the production of an homogeneous structure being difficult in Ti - Al alloys particularly after working or annealing in the $\alpha + $ $\beta$ region (21). Titanium hydride is known to precipitate preferentially at $\alpha / \beta$ boundaries (22, 23), the semicontinuous orientated boundaries observed in the islands of acicular structure therefore provide a 'hydride path' into the interior of the material. Cracks observed in severely susceptible specimens are observed to follow this 'hydride path' and are very similar to the cracks observed in hot salt (27) and hydrogen gas embrittlement (24) of the material: two phenomena where a hydride cracking mechanism of failure is well established.

It is difficult in this case to decide the relative importance of hydride cracking and hydride dissolution. The large scatter in mechanical
properties observed in tests in air indicate that a purely mechanical effect exists, the scatter in data being due to the variation in orientation and occurrence of the required acicular islands. The fact that no susceptibility occurs cathodic to -500mV emphasises the importance of hydride dissolution. It is postulated that as hydride needles are exposed to the environment by the rupture of overlying oxide the oxide reformed by attack of the exposed hydride is less coherent than the oxide formed over eutectic titanium and allows intrusive attack of the hydride 'active path' by direct dissolution. Sanderson and Scully (25) have observed preferential attack of hydride laths in titanium alloys in saturated magnesium chloride solution at 154°C, the attack being initially concentrated at the hydride/matrix interface.

The value of -500mV is significant in that it is the zero current potential for straining electrodes of 300ppm H₂Ti - 8Al - 1Mo - 1V. Considerably higher zero current potentials were observed for material with lower hydrogen contents. This is evidence that the electrochemical behaviour is significantly influenced by the presence of titanium hydride which may be ejected from dissolution at potentials cathodic to -500mV.

The study of the effect of hydrogen content on stress corrosion susceptibility of Ti - 8Al - 1Mo - 1V described above has shown that hydrogen has a marked effect over the range of contents likely to be encountered in commercial products. Stress corrosion resistance can be greatly improved by vacuum extraction heat treatments although a narrow range of susceptibility persists at the lowest hydrogen content studied in this work (12 ppm). Such a heat treatment may be advisable as 'insurance' for devices required to have a long life in critical situations. Increasing the hydrogen content have beneficial effects also if a uniform correct microstructure can be obtained. This approach however is probably less commercially attractive.

The mechanism of cracking in the presence of visible hydrides is fairly clear but the mechanism by which the susceptibility range is narrowed in 12ppm material is obscure. The anodic polarisation curves have emphasised the portance of hydrogen in the electrochemistry of the passive film rather than physical metallurgical terms.

2.3.2 Effect of Cross Head Speed on Stress Corrosion Susceptibility of Ti - 8Al - 1Mo - 1V, 65ppm Hydrogen Content

To investigate further the importance of slip step emergence and the applicability of a slip step dissolution model in SCC of titanium alloys a series of tests were performed at cross head speeds from 4 x 10⁻⁵ to x 10⁻³ mm sec⁻¹ giving nominal strain rates of 3 x 10⁻⁴ to 3 x 10⁻⁶. For a particular cross head speed, tests were performed in duplicate, or sometimes triplicate in air and in 0.17M NaCl solution at OmV (SCE). By subtracting the arithmetic mean measured mechanical property in salt solution from the arithmetic mean measured mechanical property in air an index of stress corrosion susceptibility could be obtained which was free from any influence of cross head speed on true mechanical properties.
The specimens used for this series of tests were taken from a different sheet of stock material than that used for the hydrogen content tests. Blackburn and Williams (26) had earlier reported an irreproducibility of data from sheet to sheet in SCC tests on Ti-8Al-1Mo-1V which could not be fully explained by differences in heat treatment, grain size, distribution of phases, preferred orientation etc. This effect occurred in the present work to a small extent, susceptibility as measured by the lowering of mechanical properties at OinV in salt solution was less than half that measured in the corresponding earlier tests on the first sheet. The comparison of results at different strain rates were not however invalidated by this sheet to sheet variation.

Figures 24 and 25 show the effect of cross head speed on susceptibility as measured by different mechanical property criteria. A peak in susceptibility occurs at 0.004 mm sec\(^{-1}\) for the Reduction of Area graph; the UTS/cross head speed plot is very similar to this. A smoother profile curve peaking at slightly higher cross head speeds is obtained for elongation/cross head speed; within the accuracy of the data this difference is not considered significant.

Typical corrosion current/cross head displacement traces for the tests performed at OinV are shown in figure 26. A current monitoring system of increased sensitivity was used in these tests enabling currents down to 10 nA to be recorded.

Powell and Scully (6, 27) had observed a similar optimum strain rate for susceptibility in Ti-5Al-2.5Sn, of 0.0005 in saline solution and 0.00025 - 0.001 in methanolic solutions (cf 0.0003 in the present work). It is clear that at the higher cross head speeds failure occurs too rapidly by mechanical rupture for any stress corrosion effects to occur. As the cross head speed decreases the test time becomes longer and allows stress corrosion cracks to develop inspite of the fact that the accelerative effect of dynamic strain decreases. At too low cross head speeds oxide rupture occurs too slowly and no SCC is observed inspite of the long time available for crack propagation. The dependence of measured susceptibility upon cross head speed is therefore due to the interaction of two competing effects: SCC propagation rate and test time. At high cross head speeds ie 4 \(\times\) 10\(^{-3}\) mm sec\(^{-1}\) the data gives no information on the SCC propagation rate (except to say that it is not extremely high) because of the short test time. At low cross head speeds ie <4 \(\times\) 10\(^{-3}\) mm sec\(^{-1}\), the SCC propagation rate must be very low compared to that at 4 \(\times\) 10\(^{-3}\) mm sec\(^{-1}\) to produce no susceptibility in the long test time available. Thus 4 \(\times\) 10\(^{-3}\) mm sec\(^{-1}\) is a critical cross head speed for susceptibility. This implies that a specific minimum rate of oxide film rupture is required to maintain anodic attack and crack propagation. At lower rates the repassivation reaction occurs.

The corrosion current/nominal strain traces (fig 26) at various cross head speeds are unfortunately of no use in investigating the dependence of anodic attack on oxide rupturing rate. This is because of the impossibility of deciding how the externally provided current is partitioned between repassivation and anodic dissolution and also the contribution of local anodic/cathodic cells discussed earlier.

The susceptibility/strain rate data although supporting the concept that slip step emergence is important in the stress corrosion mechanism provides no mean of judging the subsequent applicability of a dissolution or slow strain rate hydrogen embrittlement (SSRHE) model. At room temperature SSRHE does not vanish until strain rates somewhat higher than those used in these tests (16). SSRHE is therefore a possible mechanism over the range of cross head speeds tested although for the reasons previously discussed the dissolution mechanism is thought more likely.
In titanium alloys the great majority of testing and presentation of 
analytical data has heen done using a fracture mechanics approach. Although this has been 
fulfilling in the quantitative engineering application of the data the approach has 
ated the titanium alloy work from much previous work on other SCC systems 
hes inhibited comparison from one system to another.

The concepts used in fracture mechanics as applied to SCC are strictly 
ly relevant to linear elastic situations, they provide a useful phenomeno-
celestial description of fracture criteria in real (plastic) materials however 
hin certain limitations. These concepts are not useful in characterising 
ical parameters of SCC at a mechanistic level. Plastic strain is of 
cical importance here and plastic strain enters fracture mechanics theory 
plied to SCC only as a semi-empirical extension of essentially elastic 
ory. For these reasons KISCC has not generally been used to describe 
titatively the mechanical parameters in theories of SCC, an exception to 
s generality being Krafft's Ligamental Cell Model discussed earlier.

From the present work it seems that the division between the study 
 SCC in titanium alloy and other systems has arisen because of the much 
her strain rates required to counterbalance the rapid repassivation 
erved in titanium alloys. The concepts used to characterise the SCC 
anism need not be any different from those used in other systems. To 
extent fracture mechanics are irrelevant to a consideration of the SCC 
anism.

The origin of the observed KISCC values is suggested to be as 
ows: if a precracked specimen is loaded in air the rate of plastic defor- 
nation at the crack tip will depend initially on the instantaneous stress 
ensity at the crack tip when the load is applied. This deformation 
atal produces a plastic zone at the crack tip the rate of 
donation decreasing as the hardening occurs until equilibrium is reached. 
higher loads higher rates of deformation and larger plastic zones occur. 
at large enough loads the limit of the ability of the crack tip material 
work harden is reached and fracture occurs. A KIC value may be then cal-
ated from load and specimen geometry. In a stress corrosion environment 
the stress intensity is such as to produce a crack tip deformation rate below 
critical value (approximately $3 \times 10^{-4}$ sec$^{-1}$) as determined in the present 
k for Ti-6Al-4V) the same sequence of deformation, work hardening and 
ilibrium as that for air occurs. If however deformation proceeds at greater 
the critical rate dissolution at the crack tip occurs and the crack is 
anced into a less work hardened region, deformation is therefore not arrested 
utes in this less work hardened region to allow further dissolution. 
process continuously advances the crack by a combination of yielding 
and dissolution.

The theory as set out above not only requires that the crack tip 
dformation rate should be within a certain range for the anodic dissolution 
anism to be operative but the deformation rate must persist within this 
elong enough for the crack to grow into a less work hardened region. 
simplicity an instantaneously applied load giving a crack tip deformation 
creasing with time has been considered above but the "persistence" 
rement described predicts that susceptibility as measured in precracked 	s should be sensitive to loading rates. Feeney and Blackburn in their 
2(28) reported that this is in fact commonly observed and gave an example 
de the measured KISCC value of Ti-6Al-4V could be increased by 30% by 
esting the rate of loading.
The volume of material deforming within the critical strain rate range may also be critical. The rate of anodic dissolution (in terms of mass or volume per second) is limited by electrochemical factors in the small volume of crack tip solution. For a maximum rate of crack advancement to result from this limited dissolution the deformed volume must be concentrated at the crack tip. This is the situation in conditions of plane strain. Where conditions are closer to plane stress, deformation becomes much more diffuse with crack tip yawning and allows a much larger deformed volume to "absorb" the available anodic dissolution. The importance of plastic zone volume in this model explains the dependence of SCC susceptibility on the crack tip stress state.

5.2.3.3 Effect of Environmental Variations on Stress Corrosion Susceptibility of Ti—8Al—1Mo—1V, 65 ppm Hydrogen Content

In the previous section the function of the precrack in SCC of titanium alloys has been explained in terms of a critical strain rate for susceptibility. It has been observed however that the occluded corrosion cell formed by such a crack produces a crack tip environment different from the bulk solution and it is commonly speculated that this environment plays an important role in the stress corrosion mechanism.

To investigate this possibility a series of tests were performed in three environments:

1. 0.17M NaCl solution pH 7.4. A small number of tests were performed in this solution to correlate results on this new batch of specimens with the previous work.

2. 0.17M NaCl solution pH 1.7. The pH of 0.17M NaCl was adjusted from neutral with sulphuric acid. This solution was used because Brown et al (29) had studied the solution chemistry within advancing stress corrosion cracks and had observed a minimum crack tip pH of 1.7 for Ti—8Al—1Mo—1V.

3. Hydrochloric acid pH<0 with Ti$$^{4+}$$ and TiO$$^{2+}$$ ions present. It had been suggested that extremely low pHs may exist at crack tips (8) and a solution was developed in an attempt to simulate the result of this process by exposing a relatively small volume of low pH high Cl-concentration electrolyte to a large surface area of titanium. The solution was prepared by stirring a thick suspension of titanium powder in concentrated (60M) hydrochloric acid. Effervescence due to hydrogen evolution occurred initially; after three days, obvious reaction had ceased and the suspension was filtered to yield a violet solution with a pH<0. Pourbaix (30) has reported that titanium dissolves in concentrated strong acids to yield titanous, Ti$$^{4+}$$ (violet) ions and titanyl, TiO$$^{2+}$$ (colourless) ions. The results obtained with these environments are shown in figure 27. Similar plots were obtained with elongation and UTS versus potential. The pH 1.7 solution gave a slightly deeper susceptibility dip between the anodic and cathodic protection regions previously observed. The slip step dissolution model predicts that the anodic protection zone should persist in this solution because its existence depends on the slip step height/oxide thickness ratio which is not strongly dependent on pH.

Cathodic protection is observed for the same reasons as those proposed for neutral solutions.

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The slightly increased depth of the susceptibility dip may be explained by the easier achievement of a local low pH at the slip step. The diffusion of H\(^+\) ions from the slip step to the bulk solution will be less for pH 1.7 than for pH 7.4 therefore it will be easier to maintain the environmental conditions required for dissolution in the low pH solution. The bulk of the face will remain passive because the pH is not low enough to cause general dissolution. This absence of general dissolution is seen from the corrosion current/cross head/displacement traces (figure 28) where the currents are low, as were those observed in pH 7.4 solution.

A very different susceptibility/potential behaviour was observed with very low pH solution. A cathodic protection zone still existed even down to potentials where the Pourbaix diagram indicates that the oxide was no longer stable. Large cathodic currents from hydrogen evolution were evolved at these potentials (figure 29) but no susceptibility due to a hydrogen embrittlement anisom was observed. Susceptibility was observed at more anodic potentials than the highest potential tested, no anodic protection zone being present. Anodic currents were observed in this region (figure 29) and specimens showed sharp pits particularly at the more anodic potentials. This behaviour is analogous to that observed by Beck (2) for Ti-6Al-1Mo-1V in iodide solutions. The pitting potential was too low to allow an anodic protection peak. The present work the corrosion currents shown that the passive film is easily unstable and allows a reduction in measured mechanical properties by development of sharp pits.

The effects of environmental variables on susceptibility described above can be interpreted in two ways:

The cracking process itself generates the low pH environment, the crack tip being the rapid diffusion of this localised environment and accelerating subsequent cracking. Cracking is therefore not dependent on the pre-existence of special environmental conditions but generates them as a by-product of its anisom, the retention of this localised environment by the occluded cell entry may aid subsequent propagation in an autocatalytic manner.

A low pH is developed in the precrack before SCC crack propagation. This low pH makes crack initiation easier; once this has occurred autocatalytic mechanism referred to above can take place.

The important difference between the two theories is the crack tip environment at the initiation of crack propagation: neutral for (1) and acidic (2). It should be possible to distinguish between the two possibilities by measuring the crack tip pH of a precrack (a fatigue crack or other defect of initiating an SCC crack) and a propagated SCC crack. In the absence of this definitive experiment theory (1) seems the more likely because susceptibility is still present in pH 7.4 solution, and crevice corrosion which be expected if low pH conditions developed in nonpropagating cracks is not observed in titanium alloys in dilute saline environments.

The results obtained in pH<0 solution indicate that such low pH es are not achieved in practice. If the pH was low enough to destroy the crack tip oxide then the anodic protection peak observed in bulk pH 7.4 solution be absent. It was not possible to distinguish between the effects of TiO\(^{4+}\) ions and the low pH because such low pH conditions rapidly generate ions in the presence of titanium and these ions are not stable in higher conditions.
5.2.3.4 RECP Test Results and Discussion on Ti-6Al-4V

An alloy, Ti-6Al-4V, has recently found use in the place of pure titanium in implants which require higher strength and it seems likely to be the most widely used titanium alloy in the immediate future. For these reasons some additional work was performed on Ti-6Al-4V, the general features of SCC in α/β titanium alloys having already been established by the work on Ti-8Al-1Mo-1V.

Figure 30 shows the variation of R of A with potential for as-received Ti-6Al-4V at potentials from -2000 to +5000V. The results are similar to those obtained on Ti-8Al-1Mo-1V, showing regions of cathodic protection, susceptibility, anodic protection and pitting attack. Similar corrosion current/cross head displacement traces were also obtained. The following differences were observed however:

(a) Only a small dip in properties was observed in the susceptibility zone.

(b) A sharp fall in UTS but not in elongation or reduction of area was observed at potentials from -1500 to -2000 mV (SCE).

The small dip in properties observed indicates that susceptibility in Ti-6Al-4V is less than that in Ti-8Al-1Mo-1V. This is in agreement with the results of other workers using precracked tests (31). The fall in UTS at cathodic potentials may be explained by solution heating effects. Currents of up to 700 mA were generated at these cathodic potentials and caused resistive heating of the small volume of electrolyte. A solution temperature of ~80°C was measured for tests at -2000 mV. The UTS of Ti-6Al-4V is reduced by about 8% for a temperature rise from 20°C to 80°C whereas reduction of area and elongation are relatively unaffected (32). It was concluded therefore that the apparent susceptibility in the UTS plot at cathodic potentials was an experimental artifact due to solution heating and not a true indication of susceptibility.

The above work established the general applicability of the theory developed for Ti-8Al-1Mo-1V to Ti-6Al-4V. This theory was used to predict heat treatment conditions which may cause susceptibility and which should be avoided in implant fabrication.

5.2.3.5 Effect of Heat Treatment Conditions on SCC Susceptibility of Ti-6Al-4V

The conditions investigated were:

(1) A thermal ageing treatment which may cause ordering.

(2) Heat treatment atmospheres which may affect the hydrogen, oxygen and nitrogen content of the alloy.

As discussed earlier a major reason for the reduced SCC susceptibility of Ti-6Al-4V compared with Ti-8Al-1Mo-1V was the lower aluminium content of Ti-6Al-4V which made ordering and the resulting planar dislocation arrays less likely. It is difficult to be definitive about the aluminium level in Ti-Al-V alloys which is required for the ordering reaction for the following reasons:
Homogenisation of Ti-Al alloys is difficult even with very long solution treatments (33). Local variations in Al content are therefore possible.

A considerable amount of work has been done on the Ti-Al system but there is still dispute over the exact position of the Ti/Ti₃Al phase boundary (33).

The Ti/Ti₃Al boundary is probably not sharp but a transition through structures of increasing order occurs and merges with the observation of isosceles Ti₃Al particles which become larger with increasing aluminium content.

Little work has been done on the Ti-Al-V system. It is normally assumed that the ordering reaction is similar to the Ti-Al system, the only effect of the 4 w/o vanadium being to shift the Ti/Ti₃Al boundary to slightly lower aluminium levels.

As a result of these problems the critical aluminium content for ordering in Ti-Al-4V can only be located at about 6 w/o making Ti-6Al-4V "borderline" or ordering. It has been shown (26) in pre-cracked and dynamic strain stress corrosion tests that ageing treatments which lead to ordering in Ti-8Al-1Mo-1V give greatly increased SCC susceptibility. This is in agreement with the slip restriction requirement of the slip step dissolution model. Fopiano et al (34) have identified a thermal ageing treatment for Ti-6Al-4V leading to strengthening which they associate with the precipitation of Ti₃Al. This treatment (solution treat 950°C, 1 hr, quench; age 540°C, 1 hr, quench) was therefore investigated to see what effect it had on the SCC susceptibility of Ti-6Al-4V.

The other major variable to be examined was the heat treatment atmosphere, this had two effects:

1. Hydrogen content. Solution treatment in vacuum would tend to extract the hydrogen from the alloy. Heat treatment in certain reducing atmospheres would have the opposite effect.

2. Oxygen and nitrogen content. These elements are readily absorbed during heat treatment as interstitial solutes. By impeding dislocation movement they lead to higher strength and lower ductility. In high enough concentrations they severely embrittle the material. Oxygen is of particular interest because it has been shown that at a concentration of 0.38 w/o in commercially pure titanium it results in planar dislocation arrays and SCC susceptibility (35). Commercially pure titanium normally has tangled dislocation arrays and is immune to SCC. Oxygen therefore has a similar effect to aluminium and a high oxygen concentration in Ti-6Al-4V may be expected to further enhance SCC susceptibility.

Experimental details of the heat treatment conditions used are contained in Appendix III and Table 2. Dynamic strain stress corrosion tests were performed at OCP (SCE) or at uncontrolled potential; elongation was used as a susceptibility parameter although similar results were obtained with reduction of area or UTS values.

The results are shown in Table 2. The data for specimens 1 - 6 shows that severe stress corrosion susceptibility can be induced by heat treating in an air vacuum. In these conditions the hydrogen content remains near the optimum
level for susceptibility and a combination of oxygen ingress and ordering promotes the formation of planar dislocations. Figures 31 and 32 are optical macrographs of subsidiary cracks in specimens 5 and 6. The cracks generally follow slight residual milling marks on the specimen surface, these markings are particularly distinct in figure 32 because of the oblique lighting used. Figures 33 and 34 are sections through subsidiary cracks. Rounding of the specimen edges occurred during metallographic polishing so not all parts of the photographs are in focus, however crack branching can be seen in Figure 34 and crack propagation through a β phase particle in Figure 33. Although the cracks are short and indistinct examination of these and other micrographs suggests that the cracks propagate transgranularly and through both α and β phases. The results for specimens 7 – 12 show that susceptibility is reduced, probably through reduced oxygen ingress, when heat treated in a better vacuum. These specimens were lightly abraded with 600 grit SiC paper to remove milling marks prior to testing so that any cracks would be more easily seen. Examples of SCC cracks observed in these specimens are shown in Figures 35 and 36. Heat treatment in a good vacuum (specimens 13 – 18) which extracted hydrogen and prevented oxygen ingress, reduced susceptibility still further. At the opposite extreme heat treatment in open air (specimens 19 – 21) resulted in severe mechanical embrittlement of the specimens when tested in air. Some subsidiary cracks were seen in these specimens (figures 37 and 38) but the morphology of cracking was of a much more brittle, regular nature than that observed earlier in the stress corrosion cracks. Finally a series of specimens (22 – 27) was heat treated in argon. Previous work (1) had shown that this prevented hydrogen extraction, thus this treatment retained hydrogen while inhibiting oxygen ingress. Slight susceptibility consistent with the rest of the data and the predictions of the slip step dissolution model was observed in these tests.

No attempts were made to examine specimens by electron microscopic techniques to verify the presence or otherwise of planar dislocation arrays, but the effects of heat treatment and oxygen content has been established by other authors and a limited amount of work on the effect of hydrogen extraction on the SCC characteristics of Ti-6Al-4V (1) has shown a close similarity to the more detailed work performed earlier on Ti-6Al-1Mo-1V. On this basis the work on Ti-6Al-4V has provided support for the slip step dissolution model of SCC in titanium alloys by fulfilling predictions made using this model concerning the effects of metallurgical changes on susceptibility.

The work has also provided a basis for manufacturing recommendations to minimise any susceptibility to SCC. Heat treatment to aerospace specifications would normally require a solution treatment and fast cool in an inert atmosphere; from the data this would give good SCC resistance. Unfortunately not all implant manufacturers are accustomed to working to high metallurgical standards. Particularly deleterious practices are slow cooling of hot forged components in a pile and heating in a gas flame to bend a device to a surgeon's particular requirement. These would lead to inferior SCC resistance. It is recommended therefore that:

1. Rapid cooling of titanium alloy components from annealing or solution treatment temperatures is preferred to minimise the possibility of ordering.

2. Heat treatment should be performed in the absence of oxygen. Industrially this is probably most easily achieved using an inert atmosphere. Embrittlement due to heating in air is already a well recognised problem and has been observed in
this work. However, the possible long term deleterious effect on SCC resistance of heat treating in a poor vacuum is a new finding.

(3) The best SCC resistance can be achieved by heat treatment in a good vacuum.

2.3.6 REFERENCES


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TABLE 2

EFFECT OF HEAT TREATMENT CONDITIONS ON STRESS CORROSION SUSCEPTIBILITY OF Ti-6Al-4V.

<table>
<thead>
<tr>
<th>Specimen Number</th>
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<th>Heat Treatment Atmosphere</th>
<th>Elongation</th>
<th>Comments</th>
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<td>H₂ extraction, no O₂ ingress, ordering</td>
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<td>No O₂ ingress but 'as received' H₂ content and ordering</td>
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<td>Argon</td>
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Figure 1. Reduction of area / potential for Ti-BaL-1Mo-IV hydrogen content 65 ppm
FIGURE 2. CORRELATION OF ELECTROCHEMICAL SCCR TEST RESULTS
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As-received duplex annealed microstructure. x 385

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Hydrogen content 300 ppm. x 385
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H₂ Ti-8Al-1Mo-1.6V SPECIMENS TESTED AT 
POTENTIALS FROM -1500mV TO +2000mV
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Hydrogen evolution potential
mV (SCM)

Direction of Increasing
Oxide Stability

Hydrogen content ppm

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Cross head speed: mm/sec.

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APPENDIX I

Heat Treatment to Control Hydrogen Content

Heat treatments were carried out in an all glass vacuum system giving a dynamic vacuum of $1 \times 10^{-4}$ torr. Vacuum was achieved by a mercury diffusion pump fitted with a liquid nitrogen cold trap backed by an oil filled rotary pump. The specimens were pumped via a Toepler pump and a second mercury vapour diffusion pump again fitted with a liquid nitrogen cold trap. The backing side of the second diffusion pump was fed to the Toepler pump to which was attached a non-return mercury valve. Gas pumped through this valve was passed into a calibrated volume. The pressure of gas in the calibrated volume could be measured. Converting to NTP, volumes of gas as low as 0.05 ml could be measured.

Using this system specimens could be heat treated and any gas evolved could be measured and analysed by mass spectrometry.

To obtain 15 ppm hydrogen (i.e. removal of hydrogen from the as-received condition of 65 ppm) the specimens were first heated to 200°C for 2 hour to remove absorbed moisture. Hydrogen removal is most efficient at 550 - 650°C so the specimens were heated to 650°C and allowed to cool to 550°C during which time the hydrogen was removed into the calibrated volumes. The specimens were then heated to 970°C to remove residual hydrogen and a final sample of the gas collected in the calibrated volumes was collected for analysis. Compressed air was then passed down the furnace to cool the specimens.

To obtain a hydrogen content of 300 ppm the specimens were initially treated as before, i.e. the hydrogen was removed, but instead of cooling from 970°C a measured amount of hydrogen was admitted at this temperature. The specimens were then cooled as before.
APPENDIX II

Experimental Details of Anodic Polarisation Curves

Specimens were ground on 600 grit SiC paper and mounted in a screwed polythene holder sealed against solution ingress with a PTFE gasket. Polarisation curves were determined in a cell constructed totally of glass and polythene with facilities for magnetic stirring, de-aeration with argon and temperature control at 37 ± 0.1°C. The environment used was 0.17M NaCl solution pH 7.4.

The potentiostat was capable of controlling currents down to 1nA; the potential being scanned by a potentiometer in steps of 10mV at 3 steps/minute. Polarisation curves were automatically recorded on an X-Y recorder.

The curves reported in this work were constructed by scanning cathodically from the ICP, reversing the scan back to the ICP, scanning anodically and reversing the scan again. Because of the possibility of electrolytically discharged hydrogen penetrating the film during cathodic polarisation and confusing the interpretation of pitting and repassivation potential in terms of alloy bulk hydrogen content some later work was done omitting the cathodic branch of the scan. This later work revealed no differences between pitting and repassivation potentials obtained with or without a prior cathodic sweep.
APPENDIX III

Experimental Conditions Used in the Heat Treatment of Ti-6Al-4V

Heat treatment was performed in an all glass vacuum system which could achieve a dynamic vacuum of 0.0001 torr by means of a rotary pump backing a water cooled mercury diffusion pump fitted with a liquid nitrogen cold trap.

The specimens were contained in a silica tube housed in a tubular furnace. Temperature control to $\pm 3^\circ$C was achieved by a Varian solid state controller driven by a Pt/PtRh thermocouple. By sliding back the furnace and rotating a ground glass joint specimens could be quenched directly into vacuum-outgassed silicone oil without leaving vacuum.

For heat treatment in argon the line was evacuated before heat treatment and backfilled with "white spot" purity argon admitted through a cold trap. Argon was maintained at a positive pressure of 380 torr by slowly bleeding argon in and venting the excess through a mercury trap.
6. CONCLUSIONS

The results of failed implant examination and static stress corrosion tests have shown that stress corrosion is not a major cause of failure in currently used implant materials.

The problem of predicting the likelihood of SCC failure in presently used and potentially useful implant materials for very long term implantation has been investigated using a dynamic strain SCC test.

The test has been applied to 316 stainless steel and a critical range of electrochemical potential has been shown to be necessary for susceptibility. This critical potential range is one of metastability of the oxide passive film; the majority of the surface remaining passive while ruptured areas are not repassivated. This observation is strong evidence for a slip-step dissolution model for stress corrosion and the use of this model has allowed a semi-quantitative extrapolation of test data to conditions likely in service.

The observation of a critical susceptibility potential in an environment of practical utility, rather than the high temperature aggressive environments conventionally used in testing is important. It suggests that the effect on SCC susceptibility of environmental changes e.g. inhibitors, temperature, galvanic coupling, or material composition is predicted by the effect the changes have on moving the open circuit potential into or out of the range of susceptibility. Investigation of these effects should prove a useful area of future work. In addition the whole concept of applying the slip-step dissolution model in a semiquantitative prediction of long term susceptibility should be verified in other systems where the model is thought to apply; particularly where long term susceptibility data is available so that a comparison of observation and prediction can be made.

Application of the dynamic strain test to Co-Cr-Mo alloy has shown a completely different mechanism of attack. Straining of the
material allows attack of the anodic grain boundaries. The depth of grooving produced by this attack has been calculated, and although small in situations encountered in service, is sufficient to initiate premature failure in this notch sensitive material. This effect has in fact been observed in static stress corrosion tests. It is predicted that heat treatment to produce a more homogeneous microstructure or a finer grain size would minimise susceptibility. It is now commercial practice to use a homogenising heat treatment which raises ductility and renders the material less notch sensitive as well as improving the stress corrosion properties.

The dynamic strain test has proved useful in investigating the effect of a wide range of variables on the SCC susceptibility of titanium alloys. It has been shown to reproduce the results obtained with the more conventional fracture toughness type of testing while generating data significant to a mechanistic interpretation of susceptibility. The mechanism of failure is thought to be by slip-step dissolution as for 316S16 steel but modified to take account of TiCl$_4$ hydrolysis. This prevents a quantitative treatment of the corrosion current data being performed. The importance of alloy hydrogen content has been studied and its effect is not consistent with any mechanism of cracking based on slow strain rate hydrogen embrittlement; rather it seems to exert an influence via oxide film stability. Work on the effects of environment and strain rate on susceptibility show that pre-existing cracks are important for initiating SCC in service because of the locally high strain rate at their tip. Crack tip stress intensity is neither a useful nor necessary approach to discussing the mechanism of cracking and the particular environment at the crack tip is of secondary importance. The findings discussed above have been applied to a titanium alloy of particular importance in the implant field, Ti-6Al-4V. Critical experiments have been performed to test
predictions based on the theory of cracking: these predictions have been validated and as a result recommendations for the heat treatment and heat treatment conditions used to minimise susceptibility in Ti-6Al-4V made.

In general the use of a dynamic strain test to investigate the SCC susceptibility of iron, cobalt and titanium based alloys has allowed a deeper insight into the mechanism of cracking than the constant strain, constant stress or fracture toughness type of test widely used previously. It is thought that much future testing will employ this technique which allows a close integration with basic research. This basic research into areas of passive film structure and rupture behaviour and the electrochemical kinetics of newly bared surfaces will be required to make further advances in the knowledge of the SCC process.

As discussed in the introduction the work described above on SCC was conducted in parallel with a number of other programmes on different aspects of the implant problem. It was found that simple mechanical failure through overstressing was only important in highly stressed components such as surgical screws. This may be overcome by correct design and the use of high strength alloys. Impact fracture was a possible cause of failure in Co-Cr-Mo alloy but the major cause was corrosion fatigue. Testing showed that titanium and its alloys were particularly good in this respect and certain cobalt based alloys particularly poor. To complete tests in a reasonable period of time it was necessary to perform tests at a relatively high frequency (~100Hz). The frequency in a service application is low (~1-2Hz). The problem of correlating high frequency results to service is a general one, in this case it is difficult at low frequency to apportion crack propagation between stress corrosion and corrosion fatigue. At the moment, good high frequency corrosion fatigue and good SCC resistance are taken to indicate good low cycle corrosion fatigue behaviour. However the problem
of low cycle corrosion fatigue is worthy of study in its own right because of its long term importance for hip joint materials which may be subjected to many millions of stress reversals during their lifetime. The problem is probably best studied using a crack propagation technique which allows a unified approach to the interaction of conventional fatigue and stress corrosion crack propagation.

Electrochemical work designed to characterise the corrosion properties of implant materials has shown that iron based alloys are not suitable for long term use. Titanium and its alloys should resist attack indefinitely in the body environment. For long term use such as joint replacement, titanium or cobalt based alloys are preferable; for short term use such as fracture fixation, high strength cobalt based alloys would be a useful replacement for stainless steel. Future work will have to concentrate on the problems brought about by the increasing use of joint replacement in young people where the joint is expected to function for decades without replacement. Studies of the wear characteristics of under loading conditions and in environments closely simulating those in service are required here together with an investigation of the effect of ions released from the implant into the tissues. A close collaboration between physical and biological scientists will be required to achieve the goal of reliable long term implantation.
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