Solid Metal Induced Embrittlement of Titanium Alloys

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To my sister and brother
Lina and Jimmy
The work described in this thesis was carried out between October 2009 and May 2012 in the Division of Materials Science at Luleå University of Technology in close collaboration with Volvo Aero Corporation in Trollhättan, Sweden. The project has been funded by the Graduate School of Space Technology, Volvo Aero Corporation and NFFP (the National Aviation Engineering Research Programme).

My devotion to the work comes from people around me and from people who I met along the way, who have encouraged, inspired and believed in me; without those people, friends and strangers, I would not be here today.

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Luleå, May 2012

Pia Åkerfeldt
ABSTRACT

Titanium alloys were for a time believed to be highly resistant to environmentally assisted cracking because of their ability to form a protective oxide film on the surface. Their resistance can still be considered to be high, but when cracking resistance was originally defined to ensure reliable functionality of fracture-critical components, certain conditions that promote cracking were discovered. One of the environmental assisted cracking processes relevant to titanium alloys is solid metal induced embrittlement (SMIE). SMIE refers to the embrittlement that occurs in normally ductile materials under tensile stress in contact with solid metals with a lower melting temperature than titanium. Even though failures resulting from SMIE are rare, they do occur, partly because the industry is not aware of conditions under which SMIE may exist. Titanium alloys are frequently used in the aerospace industry where solid copper contact can be found in for instance, welding electrodes and fixtures in various manufacturing processes. The main scope of the present work has been to clarify the effect of copper in contact with titanium alloys with respect to SMIE and further to increase the understanding of SMIE. Three titanium alloys: Ti-8Al-1V-1Mo, Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V have been evaluated in contact with copper, and in contact with gold for comparison.

In order to be able to evaluate SMIE, a U-bend test method adapted from an aerospace recommended practice for stress-corrosion cracking (ARP SAE 1795A) was modified for SMIE evaluation. The acceptability of the test method was successfully established by using reference specimens that were intended to crack (or not to crack) when in contact with the embrittling environment. The results of the SMIE tests show that both Ti-8Al-1V-1Mo and Ti-6Al-2Sn-4Zr-2Mo are susceptible to SMIE in contact with copper and gold, whilst no SMIE was observed with Ti-6Al-4V. Based on these findings it is suggested that the SMIE susceptibility of titanium alloys is dependent on alloy composition. Furthermore, resistance welded Ti-8Al-1V-1Mo and Ti-6Al-2Sn-4Zr-2Mo were evaluated to investigate whether the presence of copper electrodes, (the welding operation itself) could lead to SMIE. No SMIE was found in the resistance welded specimens, which may be explained by the short time that the copper electrodes were in intimate contact with the titanium alloy, the magnitude of residual stresses after welding, or both, which were too low to initiate SMIE. In order to obtain a better understanding of the crack path characteristics and the mechanisms involved, one U-bent specimen showing SMIE (Ti-8Al-1V-1Mo with copper) was selected for further examination using electron backscatter diffraction (EBSD). The EBSD results indicated a preferable crack propagation path along high angle grain boundaries, which supports the suggested adsorption mechanism of the embrittling species at the crack tip. A tendency for favourable crack growth along grain boundaries adjacent to grains oriented close to [0001] in the crack direction could also be seen, which indicates that there is a connection between the SMIE crack characteristics and the crystallographic orientation.
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1 INTRODUCTION

Titanium was discovered in 1790. It is the ninth most abundant element and the fourth most abundant metal in the Earth’s crust. Even though titanium is plentiful, the use of titanium alloys is limited by its relatively complex and thus expensive production route, which also partly explains why titanium alloys were not widely used until the 1950s. Titanium alloys are known not only for their high strength-to-weight ratio, but also for their excellent corrosion resistance and biocompatibility. These properties make titanium alloys particularly attractive for medical devices such as implants, and for aerospace components, and also for more exclusive sports goods such as golf clubs, climbing gear etc.

Of all the titanium produced in the late 1980s, 70-80% was used in the aerospace industry [1]. In 2009 its use in aerospace was estimated by MetalMiner™ to have fallen to around 50% [2] but this is because of increasing demand from other industries. In commercial aircraft, titanium alloys are found primarily in the jet engine, but also in the airframe. Figure 1 shows a comparison with other commonly used materials in aircraft.

The trend in the aerospace industry is for many traditional metals to be replaced with CFRP (carbon fibre reinforced polymers) [4]. The main reason for this is weight reduction and thereby lower fuel consumption: a reduction of 10% allows the payload of a Boeing 747 to be increased by 10 tons [3]. Consequently the use of traditional structural metals is limited by their poor strength-to-weight ratio. Titanium alloys on
the other hand, which are about half as dense as steel and exhibit high strength and toughness, overcome this limitation and are often used as substitutes for steels and Ni-based super-alloys (lower density) and for aluminium (higher strength). Over the past 50 years the use of titanium alloys in Boeing’s aircraft has increased by 15% [4].

Applications within the aerospace industry demand reliable component functionality. It is of the utmost importance to produce alloys of correct composition, and to avoid environments that might be detrimental to mechanical properties. One important environment to consider is contact with foreign metals, especially those with lower melting temperatures than titanium alloys, since such contact could lead to metal induced embrittlement. There are two types of metal induced embrittlement: liquid metal embrittlement and solid metal induced embrittlement, which depend on the nature of the embrittling metal (solid or liquid) [5-8]. In the aerospace industry, embrittlement is prevented in several ways, and before a process route is decided any risks for embrittlement need to be clarified.

Volvo Aero Corporation initiated this work to evaluate the influence of copper on embrittlement of titanium alloys. Solid copper is used in welding electrodes and fixtures in manufacturing processes in the aerospace industry. During resistance welding titanium alloys are in intimate contact with copper electrodes that resistively heat the titanium alloy work-piece to the required welding temperature under pressure. Furthermore the electrodes degrade during the welding process, resulting in wear debris, which could attach to the surface and lead to embrittlement in service or during subsequent heat treatment.

1.1 Aim and objectives
The aim of the present work is to increase the understanding of solid metal induced embrittlement of titanium alloys, and in particular to study the influence of solid copper on this phenomenon. The objectives of the present project were as follows:

- To adapt or develop a suitable test method to study solid metal induced embrittlement (SMIE) of titanium alloys.
- To investigate the influence of solid copper in contact with Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V on SMIE.
- To evaluate the risk of promoting SMIE when copper resistance welding electrodes are used with titanium alloys.
- To evaluate the crack propagation path of SMIE with respect to grain boundaries and crystallographic orientation.
1.2 Appended papers
This thesis comprises an introduction to and a review of the research field of solid metal induced embrittlement of titanium alloys, and the following appended papers:

**Paper A:** Solid metal induced embrittlement of titanium alloys in contact with copper
Pia Åkerfeldt, Robert Pederson and Marta-Lena Antti

*Proceedings of The 12th World Conference on Titanium (Ti2011), Beijing, China, 19-24 June 2011*

**Paper B:** Investigation of the influence of copper welding electrode on Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo with respect to solid metal induced embrittlement
Pia Åkerfeldt, Robert Pederson and Marta-Lena Antti

*Proceedings of 6th EEIGM International Conference on Advanced Materials Research, Nancy, France, 7-8 November 2011*

**Paper C:** The effect of crystallographic orientation on solid metal induced embrittlement of Ti-8Al-1Mo-1V in contact with copper
Pia Åkerfeldt, Robert Pederson, Marta-Lena Antti, Yiming Yao and Uta Klement

*To be submitted*
2 BACKGROUND

In this chapter background information and the theory underlying the current work is presented. A short introduction to titanium manufacturing, alloy classification, and spot and seam welding is given, as well as a literature review with its main focus on solid metal induced embrittlement.

2.1 Titanium alloys

Among all metals, titanium exhibits the highest strength-to-weight ratio at temperatures up to 550°C. Titanium alloys are distinguished by their low weight (density): about 45% and 50% that of iron and nickel, respectively. The only engineering metals that are lighter than titanium are aluminium, magnesium and beryllium, but with respect to mechanical properties, none of these metals comes close to titanium. On the other hand, titanium alloys are expensive; titanium is about 30 times more expensive than steels and about 6 times more expensive than aluminium [9]. The high price can be explained by the complex manufacturing route and the high reactivity of titanium with oxygen, which means that the production of titanium must be carried out in vacuum or under inert gas. However, the high reactivity with oxygen underlies a beneficial property of titanium, namely its corrosion resistance. A thin protective oxide film will instantly form on a titanium surface when exposed to air, which gives titanium its high corrosion resistance [10]. A comparison of the properties of titanium alloys compared with iron, nickel and aluminium alloys is given in Table 1. Other properties that distinguish titanium are its low thermal and electrical conductivity, high ductility and fracture resistance, and its biocompatibility [9].

Table 1. Basic properties of titanium alloys compared with iron, nickel and aluminium alloys [10].

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
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<tr>
<td>Melting temp.</td>
<td>1670</td>
<td>1538</td>
<td>1455</td>
<td>660</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>4.5</td>
<td>7.9</td>
<td>8.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Yield stress</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Comparable corrosion resistance</td>
<td>Very high</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Comparable reactivity with oxygen</td>
<td>Very high</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Comparable price of metal</td>
<td>Very high</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
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2.1.1 Manufacturing process

The properties of titanium are strongly influenced by the microstructure, which depends on the manufacturing process and several factors that affect the final product, such as alloying additions, impurities, mechanical working and melting processes, heat treatments and fabrication. As a consequence, the condition of each process step must
be carefully adjusted and controlled to achieve the required properties and quality of the final product. The manufacturing process can roughly be divided into the following steps: production of titanium sponge, purification of sponge, melting of sponge together with alloying additions (if required) to an ingot, primary fabrication from ingot to mill products (bar, plate, sheet, strip, wire etc.), see Figure 2.

Figure 2. Overview of the titanium manufacturing process [1].
The raw material is produced from rutile ore (TiO₂) or ilmenite (FeTiO₃), which is chlorinated into titanium tetrachloride (TiCl₄) and then reduced into elemental titanium by magnesium (Kroll’s process) or by sodium (Hunter’s process) [1]. Today Kroll’s process is the most frequently used, mainly because magnesium is more cost competitive [10]. There are several elements that even in small amounts can affect the properties of a titanium alloy and hence it is important to control the types and amount of impurities in the raw material. The presence of brittle titanium oxide could for instance, if retained through the melting processes, promote crack initiation in the final component. The most common residual elements in titanium sponge are nitrogen, oxygen, silicon, carbon and iron. Available melting techniques today remove detrimental residuals efficiently and regardless of the sponge production method used, ingots of high quality can be produced.

Vacuum Arc Remelting (VAR) has been the standard method for ingot production since the commercial introduction of titanium alloys, see “double melting” in Figure 2. The melting process is suitable for environmentally sensitive alloys in which melting and solidification can be carefully controlled and reproduced. In VAR a cylindrical electrode of appropriate composition is melted by an arc in vacuum and subsequently solidified in a water-cooled crucible. The electrodes are compacted aggregates, i.e. briquettes of sponge and alloying elements. In alloy production small pieces of sponge are mixed and blended with alloying material and then pressed into a briquette. The briquettes (which could also be made of carefully chosen reclaimed titanium scrap material) are welded together into a long electrode (up to 4.5 m), which is lowered into the VAR. Traditionally a double consumable-electrode VAR process is used, in which the electrode is melted twice to ensure homogeneity in the resulting ingot. The ingot from the first sequence is used as the electrode in the second melting stage [1].

Another newer melting method is Cold Hearth Melting (CHM), which has advantages over the VAR process when producing high quality titanium. CHM is accomplished by using a water-cooled copper vessel containing molten titanium and a heat source (plasma arc or electron beam) the energy of which is balanced against the heat extracted from the water-cooled copper hearth. Thus a skull (a thin layer of solid titanium) is in contact with the copper hearth, whilst the molten titanium is in contact with the solid titanium alloy, preventing contamination by the hearth. Moreover it allows direct casting to slabs and bars, which are more suitable (cost competitive) than round ingots for conversion into flat mill products.

Primary fabrication from ingot to mill products starts with an initial working operation in which the round ingot is converted to a square or a round cornered square piece in a forging press, as so called the “bloom” in Figure 2. The subsequent fabrication steps depend principally on the shape of the product to be formed, e.g. billet, plate, sheet or bar. The billet is usually used as input material in forging and for ring rolling. Plate and sheet are flat rolled to a thickness greater than or less than 25 mm, respectively. The bar can be shaped into various forms, e.g. round, square or another desired shape.
Electrodes for subsequent casting processes are cut to required lengths and diameters and remelted by a casting producer [10].

### 2.1.2 Alloy classification

Titanium is an allotropic element, which means that it can exist in more than one crystallographic form. At room temperature, commercially pure (CP) titanium has a hexagonal close-packed (hcp) crystal structure, also referred to as the “alpha” phase of titanium. At 882°C the alpha phase transforms into the “beta” phase that has a body centred cubic (bcc) crystal structure. With respect to these two phases, titanium alloys can be grouped into different categories depending on the crystal structure of the alloy composition favoured at room temperature: alpha alloys, near-alpha alloys alpha-beta alloys and beta alloys. Depending on alloy composition, the alpha and the beta phases can be stabilised at high and low temperatures, respectively. The most common alloying elements and their stabilising effects on the alpha and beta phases are shown in Figure 3.

**Figure 3. Alloying elements and their stabilizing effects on the alpha and beta phase [10].**

*Commercially pure (CP) titanium alloys* are the weakest titanium alloys but they exhibit the best general corrosion resistance and are also the most weldable. With small additions of alloying elements, notably interstitial elements such as oxygen and nitrogen, CP titanium alloys can be strengthened by heat-treatment and processing at temperatures at which the alloy exists in two phases (alpha and beta).

*Alpha and near-alpha alloys* have relatively high amounts of alpha stabilisers, usually aluminium, and only small amounts of beta stabilisers. Their high creep resistance in comparison with other titanium alloys characterise alpha and near-alpha alloys, and consequently they are preferred for use in high-temperature applications. Since alpha alloys contain only a single phase (all alpha or almost all alpha), irrespective of temperature, they cannot be heat-treated to improve mechanical properties, which is why near-alpha alloys were developed. In near-alpha alloys small amounts of beta stabilising elements are added to make the alloy heat-treatable to some extent. However, even small amounts of the beta phase present in the microstructure during processing are retained after heating and cooling, giving properties similar to those of...
alpha alloys. As with CP alloys, alpha alloys also possess exceptional weldability, which is explained by their insensitivity to heat-treatment. Their forgeability on the other hand is poor, mainly because of the narrow temperature range that exists for forging below the beta transition temperature, which leads to a higher tendency for surface cracks and centre bursts. Consequently, the forging process involves several reheating steps to avoid such cracking phenomena [1]. Another disadvantage with alpha alloys is their poor resistance to stress-corrosion cracking. It has been shown that alpha stabilisers such as aluminium and oxygen increase susceptibility to stress-corrosion cracking [11].

The alpha-beta alloys contain both alpha and beta stabilizing elements. They are distinguished by their superior combination of strength and ductility. As the alpha-beta alloys are heated, a significant amount of beta phase is formed; the specific amount depending on the amount of beta stabilisers present and the processing conditions. A number of different microstructures can be generated for alpha-beta alloys by adjusting the thermo-mechanical processing parameters. Alpha-beta alloys are often solid solution strengthened: the resulting strength depends on alloy composition, temperature, cooling rate and on the subsequent ageing process. Consequently the conditions and process parameters must be selected carefully to produce the microstructure and thus mechanical properties desired. In order to improve creep properties, certain alpha-beta alloys have been precipitation hardened by adding silica, which precipitates and creates deformation barriers in the structure [1]. The stress-corrosion cracking susceptibility of alpha-beta alloys is dependent on the structure of the alloy (the amount of alpha phase) but is in general lower than that for alpha alloys. This is explained by the presence of the beta phase, which has been shown to increase stress-corrosion cracking resistance [11].

Beta alloys are metastable, which means that they transform into a pseudo equilibrium structure, which has higher free energy than the true equilibrium state. Beta alloys contain a relatively high amount of beta stabilisers and less alpha stabilisers than alpha-beta alloys. Beta alloys are characterised by their hardenability; the major advantages with beta alloys are their forgeability and cold-workability in solid solution treated conditions [1]. Another characteristic of beta alloys is that they do not form martensite upon rapid cooling from the beta phase [10]. The strength of beta alloys comes from the strength of the beta structure itself and from precipitation of alpha or other phases after processing and heat-treatment. The disadvantages with beta alloys are their higher density and lower creep resistance [1]. However, in contrast to alpha alloys, beta alloys are considered to be highly resistant to stress-corrosion cracking. It has been observed that the beta stabilisers reduce or eliminate susceptibility to stress-corrosion cracking, but how is not clear [11].

### 2.1.3 Alpha case formation

One of the limiting properties of titanium alloys is the formation of a brittle surface layer at elevated temperatures. This layer is a result of inward interstitial diffusion of oxygen or nitrogen, which results in solid-solution hardening of the surface. Both
oxygen and nitrogen are alpha stabilisers and therefore this layer is named an “alpha
case” [1]. The brittle alpha case is detrimental to mechanical properties since it
facilitates crack initiation leading to a loss in ductility and fatigue life. Therefore the
alpha case normally is removed by chemical milling, pickling or machining prior to
service. The thickness of the alpha case layer is mainly dependent on temperature and
holding time [12].

2.2 Spot and seam welding
Welding processes are nowadays fundamental in the fabrication of many different
products; a number of joints can be found in components in the aerospace industry.
The particular choice of joining method is related to design criteria, range, payload
and a number of other factors. Among the joining techniques available, welding is the
one most frequently used. Titanium alloys have been welded since the basic nature of
titanium was understood [13].

Spot and seam welding both rely on mechanical pressure and resistance heat generated
by an electric current. In spot welding the electrodes heat the metal to form a nugget
at the electrode site. Seam welding is a type of spot welding in which a series of
nuggets overlap one another forming a continuous seam. The welding operation is
carefully controlled through pressure and duration such that sufficient heat can be
generated to melt the metal, which cools before pressure is released. The spot and
seam welding cycle can be divided into four parts; squeeze time, weld time, hold time
and off time. Squeeze time is defined as the time from time cycle initiation until full
electrode force and contact are achieved. The weld time is the duration of the applied
welding current to make a single impulse weld. During the hold time the force
(pressure) is maintained while the nugget solidifies and is cooled to achieve the
required strength. The time for the electrode to move to the next weld is called the
off time, i.e. the electrodes are removed from the metal. Weld times typically range
from 1/120 of one second for thin sheets to several seconds for thick sheets.

The heat generated in the operation depends on three factors: (a) the current, (b) the
resistance of the conductor (including interface resistance), and (c) the duration of the
current. The heat generated $Q$ (J) is expressed as follows:

$$ Q = I^2 R t $$

where $I$ is the current (A), $R$ is the resistance of the electrode material ($\Omega$) and $t$ is the
duration of the current (s). According to eqn. (1) the welding current is inversely
proportional to the square root of the time for a given energy, which means that to
produce the weld a very high current is needed when the welding time is short. The
combination of a short welding duration and high welding current can result in rapid
electrode deterioration and unwanted heat distribution in the weld zone. The applied
mechanical pressure during welding affects the resistance $R$ in eqn. (1); the pieces to
be spot or seam welded are clamped tightly together such that the current can pass. An
increase in pressure results in a decrease in contact resistance and decreasing reduction in heat generation. On a microscopic level the contact surfaces comprise peaks and valleys, which implies that only a small fraction of the surface will be in metal-to-metal contact and hence experience high contact resistance. As pressure increases, the peaks are depressed and the area of metal-to-metal contact increases, which decreases the contact resistance. If the pressure suddenly drops during welding, the contact surfaces of the welding electrodes may overheat resulting in burning or pitting of the electrode faces. The electrode could also stick to the metal surface, and in some cases the welded surface may vaporise because of the very high energy [14].

2.2.1 Welding electrodes
Seam welding electrodes normally take the form of wheels or discs, see Figure 4, whereas flat electrodes in the form of a rectangular bar are used for spot welding. The welding electrodes perform four functions:

- Conduct current into the metal, determining the current density in the weld zone
- Transmit force to the work piece
- Dissipate part of the heat from the weld zone
- Maintain relative alignment

Required properties of electrodes are: high electrical conductivity, and adequate strength and hardness to resist deformation caused by repeated applied pressure. As the electrode deforms, weld quality decreases, which means that electrodes need to be reshaped or replaced regularly. If the electrodes are incapable of following a sudden change in surface curvature, e.g. because of their deformed shape, the contact pressure will decrease and local heating increases, which can cause overheating and violent ejection of molten metal. This may result in undesirable weld properties and greater wear of the electrodes [14]. In addition, wear debris may influence the properties of the material being welded. However, an alloy with high hardness and wear resistance, normally exhibit lower electrical and thermal conductivity, and consequently the choice of alloy is a compromise between mechanical properties and conductivity. Softer electrode materials are chosen than the material to be welded to increase the contact area. Copper alloys are commonly used as electrode materials; several are available with suitable physical and mechanical properties. In paper B the risk of using copper electrodes is evaluated for two titanium alloys with respect to solid metal induced embrittlement.
Metal induced embrittlement (MIE) is considered to be a type of environmentally assisted cracking material failure. Other examples of environmentally assisted cracking processes are corrosion fatigue cracking, stress-corrosion cracking (SCC) and hydrogen embrittlement (HE). SCC and corrosion fatigue cracking are the most commonly reported in industry, followed by HE - much less frequently reported is MIE [15]. Degradation caused by MIE is characterised by a reduction in ductility [7], which is often undetected until catastrophic failure occurs [16]. MIE is embrittlement that occurs in normally ductile metals subjected to tensile stress that are in contact with metals of lower melting temperature [5]. There are two types of MIE: liquid metal embrittlement (LME) and solid metal induced embrittlement (SMIE), which occur above and below the melting temperature of the embrittling metal, respectively [5-8]. Even though failures caused by MIE are rare in industry, several have been reported. Lynch has documented several failures [15-17] including SMIE of a brass valve caused by internal lead particles [17] and LME of an aircraft brake rotor caused by external copper [15]. The sources of embrittlement can thus be both internal (low-melting temperature inclusions) and external (e.g. surface coatings). Common sources of MIE are listed in Table 2.
Table 2. Common sources of MIE [17].

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<thead>
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<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Coatings, e.g. Cd, Zn on steels, inadvertently exposed to high temperatures</td>
</tr>
<tr>
<td>• Solders, brazes, and galvanising baths (in combination with high applied/residual stresses)</td>
</tr>
<tr>
<td>• Liquid-metal coolants for nuclear reactors, nuclear fission products, neutron spallation targets (Pb-Bi)</td>
</tr>
<tr>
<td>• Overheated bearing materials containing Sn, Cu, Pb</td>
</tr>
<tr>
<td>• Internal sources, e.g. Pb particles in free-machining alloys</td>
</tr>
<tr>
<td>• Na-K impurity phases in Al-Li alloys</td>
</tr>
<tr>
<td>• Mercury from e.g. broken thermometers</td>
</tr>
<tr>
<td>• Molten metal from fires, especially Zn from galvanised steel dripping onto stainless steel</td>
</tr>
<tr>
<td>• Zn-based paint splashes on hot equipment</td>
</tr>
<tr>
<td>• Lubricants containing metals such as Pb</td>
</tr>
<tr>
<td>• Pick-up from contaminated grinding wheels</td>
</tr>
<tr>
<td>• Cu from electrical resistance-heating contacts</td>
</tr>
<tr>
<td>• Deposition from aqueous environments after corrosion/erosion-corrosion of embrittling metals, e.g. Cu, Pb</td>
</tr>
<tr>
<td>• Airborne ZnS (near mining facilities) that reduces to Zn on hot surfaces</td>
</tr>
</tbody>
</table>

2.3.1 Metallurgical characteristics of MIE

The metallurgical factors that influence MIE have not been studied in detail but it has been suggested that they are similar to those responsible for increasing brittleness in metals, i.e. MIE increases with increasing grain size, strain rate, yield strength, solute strengthening, and the presence of notches or other stress raisers [7]. However, there are also factors that have been shown to have a lesser influence on MIE (compared with hydrogen and temper embrittlement), those being the effect of grain boundary impurities such as antimony, phosphorus and tin. Hence a better understanding of MIE would provide valuable information about other environmentally assisted cracking processes e.g. hydrogen embrittlement (HE), since MIE can be studied in a more simple and controlled manner [7, 18].

2.3.2 Fracture characteristics of MIE

Fracture in MIE can be divided into the separate stages of nucleation and propagation [5, 7, 18], but is propagation controlled [7]. Nucleation, i.e. crack initiation in MIE, has been shown to have an incubation time that depends on stress and temperature. Gordon [19] carried out potential drop measurements on a commercial 4140 steel in contact with liquid indium at different temperatures with two stress levels, and confirmed that incubation time increases with reductions in temperature and stress level, see Figure 5.
Crack propagation in normally ductile materials is intercrystalline, cleavage (transcrystalline), or both. Intercrystalline fracture dominates in bcc and fcc materials, whilst cleavage fracture is more common in hcp materials. Fracture paths for LME and SMIE are often similar, but a mixture of intergranular and cleavage fracture is more common for SMIE. Fracture features such as dimples, tear ridges and slip lines are present on the fracture surfaces of most metal induced embrittled materials, but can be difficult to resolve without a high resolution electron microscope. However, the fracture surfaces of MIE are similar to those of SCC and HE, and it is often impossible to distinguish between the different environmentally assisted cracking processes without a knowledge of the service temperature and environment of the sample. In addition, embrittlement can result from several embrittling processes, which means that the crack could be initiated by SMIE and propagated by HE (or SCC, fatigue etc.) [6]. Plane strain fracture toughness in environmentally assisted cracking ($K_{\text{SEAC}}$) is difficult to determine since it depends strongly on the time for which the test is conducted, and can therefore vary between laboratories, depending on test method used. In paper C the SMIE crack characteristics of Ti-8Al-1Mo-1V embrittled by copper is evaluated with respect to grain boundaries and crystallographic orientation.

Figure 5. Initiation (incubation) time plotted against test temperature for two stress levels for commercial 4140 steel in contact with pure indium [19]. Note: LME in this figure is denoted LMIE, which stands for liquid metal induced embrittlement.
When studying the fracture surface, traces of LME can sometimes be seen as a thin metal film, but with SMIE the embrittling species are generally not detected by common fracture surface evaluation techniques since the layer of embrittling metal is too thin [6]. The solid embrittling species can sometimes however be detected at the crack tip by Auger Electron Spectroscopy (AES) analysis [17, 20] or Secondary-Ion Mass Spectroscopy (SIMS) [17].

2.3.3 Solid metal induced embrittlement

For a time it was assumed that no embrittlement could occur below the melting temperature of the embrittling metal and as late as in the 1960s the following could be read in a review of LME:

“Of course, if the temperature falls below the solidus of the wetting agent, no embrittlement is observed” Stoloff (1968) [21]

The doubt in SMIE is probably also the reason why SMIE is not as well-documented in literature as LME; the first case of LME (known to the author) was reported in 1914 [22], while embrittlement recognized as SMIE was first reported in the 1960s [18]. Later, however, for steels it has been suggested that all metals that cause embrittlement in the liquid state also lead to embrittlement in the solid state [7, 23]. In this section a review of previous work on SMIE is given with the focus on the proposed SMIE mechanisms and SMIE reported in titanium alloys.

In general SMIE is considered to be less severe than LME because of the much slower (one or two magnitudes) crack velocity [7]. However, the severity of embrittlement is also dependent on the distance to the source of the embrittling metal. When the embrittling species are present as inclusions the crack growth of SMIE can be extensive, especially when closely spaced, since the distance to the embrittling sources remains short as the crack propagates [17]. In other words, it is agreed that crack propagation will not proceed without a constant supply of embrittling species at the crack tip [5]. The main prerequisite for SMIE to occur is intimate contact between the embrittling metal and the substrate [6, 7, 15, 17, 24]. This means that any existing oxide layer must be removed or ruptured [6, 17]. Other parameters affecting SMIE susceptibility are the temperature and tensile stress; below certain threshold values of these, SMIE is not expected to occur [7, 18, 24, 25]. The severity of SMIE increases with temperature, and is as highest just below the melting temperature of the embrittling species, \( T_m [18] \).

The mechanisms of SMIE are today believed to involve surface self-diffusion from the source to the crack tip and adsorption of the embrittling species at the crack tip, see Figure 6. Surface self-diffusion is assumed to be the transport mechanism since such diffusion rates are fast enough to be consistent with the reported cracking lengths at the temperatures studied [5, 17, 23, 26, 27]. The surface self-diffusion coefficient, \( D_s \), has been estimated by using the standard random-walk equation [23]:

\[ D_s = \frac{k \cdot T}{8 \pi \mu \tau} \]
where $x$ is the projected crack propagation length to failure and $t$ the propagation time. By plotting $D_S$ versus $1/T$, where $T$ is the service temperature (K), it was further shown that the data agreed with an Arrhenius relationship with a particular activation energy. Lynch [26] collected available data for SMIE of titanium alloys, zirconium alloys and steels and plotted the estimated $D_S$ against $T_m$ and concluded that a normalized linear Arrhenius plot could be fitted to most of the data, see Figure 7. However it could further be observed that the $D_S$ values obtained from (2) were one or two orders of magnitude less than the surface self-diffusion coefficient obtained from other studies in which $D_S$ was measured by sintering small particles, scratch decay and grain boundary grooving [28, 29]. The deviation is believed to be an effect of the measured crack propagation length, which is probably underestimated since the measured crack length is the projected length, i.e. not the true diffusion length along the grain boundary, which follows a more serrated path. In Figure 7 it can also be seen that the data deviate from the linear Arrhenius plot at temperatures close to the melting temperature. Based on the estimations of surface self-diffusion coefficients, SMIE is expected to occur at homologous temperatures ($T/T_m$) of >0.5. Furthermore the rate of crack growth is expected to increase with increasing temperature [6, 17], but decrease with increasing crack length since the distance from the embrittling source increases [16]. Anomalous results have been obtained for titanium alloys [20].
where SMIE has been observed at temperatures as low as $0.38 \ T/T_m$ and at higher cracking rates than can be estimated by the previously reported SMIE data. This anomalous behaviour is assumed to be caused by impurities or by a contribution from HE [6]. However, SMIE can occur at temperatures as low as $0.3 \ T/T_m$ when the atoms of the embrittling material are closely spaced [6, 16], especially for internal cracks because of the absence of air, i.e. the crack growth is not be inhibited by an oxide film [17]. Several studies thus support surface self-diffusion as the dominant transport mechanism since the mechanisms proposed earlier (vacancy diffusion and grain boundary diffusion) are associated with diffusion coefficients that are too low [23]. Surface self-diffusion as the dominant transport mechanism is discussed in papers B and C.

Figure 7. Surface self-diffusion coefficient, $D_s$, plotted against $T_m/T$ where $T_m$ is the melting temperature of the embrittling metal and $T$ the service temperature in Kelvin [26].

It is further believed that the embrittling species are adsorbed at the crack tip, which leads to a weakening of the atomic bonds in crack tip region [6, 17, 26]. Adsorption describes a process where a molecule/atom bonds to a surface - it differs from absorption, where the molecules/atoms enter the bulk of the surface. There are two types of adsorption, physisorption and chemisorption, the classification depends on the magnitude of enthalpy of adsorption. The bonding interaction in physisorption is long range but is weak because of its van der Waals nature. The electron density is redistributed within the adsorbate and adsorbent separately, which can lead to an imbalance of electron density on either side of the interface. Chemisorption on the other hand, which is considered to be responsible for SMIE, is distinguished by an
exchange of electrons between the adsorbate and the adsorbent, resulting in interaction resembling covalent-, ionic-, and metallic bonding [30]. The details of how adsorption affects crack propagation are not completely understood, but for LME and SMIE it is suggested that chemisorption influences the crack propagation rate as explained further below (a-c):

**a) Chemisorption reduces the stress required for tensile separation of the atoms at the crack tip**

Westwood and Kamdar [7, 31, 32], and Stoloff and Johnston [33] propose that the cohesion strength of the bond between atoms T1 and T2 (Figure 6) is reduced by adsorption of the metal atom A. The crack propagates by breaking the bonds T1-T2 and later T1-T3. The bonds are described by potential energy separation curves of $U(a)$, see Figure 8, where $a_0$ is the equilibrium distance between atoms in the fracture plane and the stress $\sigma$ acting between T1 and T2 varies as $dU/dA$ from $\sigma = 0$ at $a = a_0$ to $\sigma = \sigma_m$ at potential $U$. A stress of $\sigma_m$ would cause the bond T1-T2 to break. If the atom A is adsorbed, spontaneously or only after the bond of T1-T2 has been strained to $a_C$, the bond becomes weaker and the energy separation curve can be considered to be $U(a)_A$. The stress needed to break the bond T1-T2 is then $\sigma_m(A)$, i.e. much less than $\sigma_m$, and as it breaks the crack propagates by decohesion.

**Figure 8.** Potential energy separation curves showing that chemisorption of atom A reduces the stress $\sigma_m$ needed for separation of the atoms at the crack tip.

**b) Chemisorption hinders the nucleation or egress of dislocations at the crack tip**

Vook [34] studied embrittlement of solid copper caused by liquid bismuth, by using transmission electron microscopy. The aim of the study was to evaluate the influence of dislocations and dislocation interaction on the initiation and propagation of LME. However, the results showed no indications of dislocation pile-ups initiating the embrittlement, suggesting that chemisorption hinders the nucleation or egress of
dislocations at the crack tip because of attractive forces between the dislocations and the adsorbed atoms, resulting in less plastic deformation and brittle fracture.

c) Chemisorption facilitates the nucleation or egress of dislocations at the crack tip

Lynch [26, 35-38] has evaluated fracture surfaces of SMIE and LME, and compared them with the fracture surfaces resulting from overload. It was observed that the plastic zone and the dimples were smaller when SMIE and LME were involved, and shallower than those observed in the fracture surfaces after overload. It was further suggested, based on the observations, that chemisorption facilitates nucleation of dislocations from the crack tip. Lynch also emphasised that the suggested influence of chemisorption as described in a) and b) above are not consistent with the fracture features found in his observations, which indicates slip rather than tensile decohesion, since tensile decohesion would result in an atomically flat fracture surface. In theory, it is suggested that even if chemisorption only influences the surface, it is enough to reduce the amount of plasticity and thus affect nucleation and growth ahead of the crack tip. In ductile fracture, blunting occurs at the crack tip resulting in deep dimples on the fracture surface because crack growth occurs to a large extent through egress of dislocations nucleated ahead of the crack tip. This means that a higher strain will be needed to activate slip and thereby crack growth, only a small portion of the dislocations will intersect the crack tip exactly. The large strain needed results in a large plastic zone around the crack tip before crack growth. In the presence of the chemisorbed atom, according to Lynch, dislocations are more readily injected from the crack tip, causing the crack to grow even at smaller strains. Thus shallow dimples are produced and smaller plastic zones generated. It is assumed that the nucleation of dislocations is more difficult than movement, which means that crack growth occurs as soon as a dislocation is nucleated. A schematic of the proposed crack growth process compared with crack growth in ductile fracture can be seen in Figure 9. Lynch has also emphasized that, in this matter, similarities between MIE, SCC and HE are observed, and that the theory of adsorption-induced localised slip can also be used for some materials and environments involving SCC and HE.

![Figure 9](image-url)

*Figure 9. (a) Dislocation nucleation and void coalescence by adsorption of atom at crack tip and (b) ductile crack growth by dislocation egress and coalescence of voids [39].*
2.3.4 Metal induced embrittlement of titanium alloys

MIE was first reported in titanium alloys in 1965 by Duttweiler et al. [40] who observed SMIE of a compressor wheel made of a titanium alloy in contact with silver. Today metals such as cadmium [20, 25, 41], copper [42, 43], gold [20, 43], mercury [25, 44], silver [20, 40], and zinc [45] are known to cause embrittlement in titanium alloys, see Table 3.

Fager and Spurr [25] concluded in their work on Ti-6Al-4V and Ti-8Al-1Mo-1V that both solid Cd and liquid Hg resulted in intergranular and cleavage cracking. They also observed that cleavage occurred on or near the (0001) plane of the titanium alloy. Meyn [41] reported both intergranular and cleavage fracture in Ti-6Al-4V and Ti-3Al-14V-11Cr when in contact with solid cadmium. Furthermore cleavage cracking in Ti-6Al-4V was observed only in the alpha phase grains. In beta annealed Ti-6Al-4V cracking occurred between the alpha plates in the acicular structure. However, Meyn did not observe any difference in SMIE susceptibility when comparing cracking behaviour of near-alpha (Ti-8Al-1Mo-1V), alpha-beta (Ti-6Al-4V) and beta (Ti-3Al-14V-11Cr) alloys.

Stoltz and Stulen [20] observed SMIE of Ti-6Al-6V-2Sn in contact with cadmium, silver, and gold and reported that fracture primary occurred by an intergranular mechanism with sporadic cleavage through alpha grains. Moreover, they measured crack length and based on these measurements, the elements were ranked in the following order of embrittling power: cadmium (500 μm), silver (250 μm) and gold (50 μm).

Most recently copper contact has been investigated with respect to SMIE. Liu [42] reported SMIE of Ti-6.5Al-3.5Mo-1.5Zr-0.3Si and in the present work (paper A), SMIE was observed in Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V when in contact with solid copper.
Table 3: Titanium alloys and embrittling species reported.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solid embrittling species</th>
<th>Liquid embrittling species</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>Unalloyed Ti (grade 2)</td>
<td>Cd [45]</td>
</tr>
<tr>
<td></td>
<td>Unalloyed Ti (grade 4)</td>
<td>Hg [45]</td>
</tr>
<tr>
<td>α</td>
<td>Ti-5Al-2.5Sn</td>
<td>Ag [40]</td>
</tr>
<tr>
<td>near-α</td>
<td>Ti-6Al-2Sn-4Zr-2Mo</td>
<td>Au, Cu [43]</td>
</tr>
<tr>
<td></td>
<td>Ti-8Al-1Mo-1V</td>
<td>Ag [40, 43], Au [43], Cd [41], Cu [43]</td>
</tr>
<tr>
<td>α−β</td>
<td>Ti-6Al-4V</td>
<td>Cd [25, 41]</td>
</tr>
<tr>
<td></td>
<td>Ti-6Al-6V-2Sn</td>
<td>Ag, Au, Cd [20]</td>
</tr>
<tr>
<td></td>
<td>Ti-6.5Al-3.5Mo-1.5Zr-0.3Si</td>
<td>Cu [42]</td>
</tr>
<tr>
<td></td>
<td>Ti-7Al-4Mo</td>
<td>Ag [40]</td>
</tr>
<tr>
<td></td>
<td>Ti-8Mn</td>
<td>Cd [46], Hg [11]</td>
</tr>
<tr>
<td>β</td>
<td>Ti-3Al-14V-11Cr</td>
<td>Cd [41]</td>
</tr>
<tr>
<td></td>
<td>Ti-13V-11Cr-3Al</td>
<td>Cd, Hg, Zn [45]</td>
</tr>
</tbody>
</table>
3 MATERIALS AND METHODS

In this chapter the materials investigated and the experimental procedures used in the current work are presented in detail. A short introduction to different test methods used to evaluate different cracking processes is also given.

3.1 Materials investigated

Three alloys have been studied in the present work: Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V. The background to why these alloys are of interest is partly explained in the standard test method used for SCC evaluation [47], where Ti-8Al-1Mo-1V and Ti-6Al-4V represent alloys with high and low susceptibility to SCC, respectively. To begin with, in the initial studies, only these two alloys were evaluated. Ti-6Al-2Sn-4Zr-2Mo was added after the first investigation of SMIE, since it is used in the aerospace industry and is, like Ti-8Al-1Mo-1V, a near-alpha alloy. Selected properties of the alloys investigated can be found in Table 4.

| Table 4. Selected properties of the alloys investigated [1, 48, 49]. |
|------------------|------------------|------------------|
|                  | Ti-6Al-4V        | Ti-6Al-2Sn-4Zr-2Mo | Ti-8Al-1Mo-1V     |
| Alloy            | alpha-beta       | near-alpha        | near-alpha        |
| Beta transition temperature [°C] | 1000±20          | 995±15            | 1040±15           |
| Density [g/cm³]  | 4.42             | 4.54              | 4.37              |
| Stress-relief temperature [°C] | 480-650          | 595-705           | 595-705           |
| Stress-relief time [h] | 1-4              | 0.25-4            | 0.25-4            |
| Annealing temperature [°C] | >550             | >650              | >595              |

3.1.1 Ti-6Al-4V

Ti-6Al-4V (Ti-64) is the most widely used titanium alloy and accounts for more than 45% of total titanium production [1] and 80% of the titanium used in the aerospace industry. In addition to aerospace applications, Ti-64 is used in medical prostheses and can be found in the automotive, marine and chemical industries in relatively small amounts [48]. Ti-64 is an alpha–beta alloy with an attractive combination of properties and can be manufactured in all types of mill products. Application of Ti-64 is limited to about 400°C and consequently it is used in low to moderate temperature applications. In the aerospace industry, Ti-64 is extensively used in the jet engine (in the cold section, i.e. fan and compressor sections), as blade, discs and wheels. Although corrosion resistance is not as good as pure titanium, Ti-64 has excellent corrosion resistance compared with other titanium alloys, which is explained by its
ability to form protective oxide layer. The oxidation behaviour of Ti-64 is similar to that of pure titanium [1]. The condition and composition of the Ti-64 sheets used in present work is in accordance with the aerospace material specification AMS 4911L [50].

3.1.2 Ti-6Al-2Sn-4Zr-2Mo
Ti-6Al-2Sn-4Zr-2Mo, or more correctly Ti-6Al-2Sn-4Zr-2Mo-0.08Si (Ti-6242) is a near-alpha alloy developed in the 1960s for high temperature applications. Originally Ti-6242 did not contain any silicon but silicon was added to meet creep requirements in jet engine applications, and now the majority of producers add silicon to the original composition. Today Ti-6242 is mainly used in compressor blades, discs and impellers of gas turbines. It exhibits a good combination of tensile strength, creep strength and toughness. Ti-6242 is one of the most creep resistant titanium alloys and can be used in short-term applications up to 565°C and in long-term applications up to 450°C. Although this alloy is classified as a near-alpha alloy, its microstructure resembles those of alpha-beta alloys. Typically the structure consists of equiaxed alpha in a transformed beta matrix or a fully transformed structure that maximises creep properties. In Ti-6242 sheet the structure consists of about 80-90% alpha phase, the small amounts of beta can be observed between the acicular alpha grains of the transformed phase [48]. The corrosion properties of Ti-6242 are not generally well documented, but it has showed susceptibility to SCC [1]. The condition and composition of the Ti-6242 sheets used in the present work were in accordance with the aerospace material specification AMS 4919F [51].

3.1.3 Ti-8Al-1Mo-1V
Ti-8Al-1Mo-1V (Ti-811) was developed in 1954 for compressor blades and wheels in high temperature gas turbines. Today Ti-811 is widely known in the titanium industry and is produced by most titanium producers. It is characterised by its high elastic modulus, the highest of all commercial titanium alloys, and its good creep resistance up to 455°C. At room temperature, Ti-811 exhibits similar tensile strength to Ti-64, but at elevated temperatures Ti-811 shows much higher tensile strength and better creep properties than other near-alpha and alpha-beta alloys [48]. The corrosion properties on the other hand are poorer, Ti-811 is one of the most susceptible titanium alloys to SCC, which is explained by its high aluminium content and hence its ability to form the low-ductility Ti3Al phase [1]. The condition and composition of the Ti-811 sheets used in the present work was in accordance with the aerospace material specification AMS 4916J [52].

3.2 Test methods
For SMIE evaluation, there is no universal test method, instead there are several different test methods and the method that is applicable depends on the information required and the passivation behaviour of the alloy. However, most of the test methods used have their origin in SCC testing. The following section therefore briefly
MATERIALS AND METHODS

describes the most common test methods used for SCC. The test method used in present work is then presented in detail.

It is generally agreed that SCC test methods do not simulate the service conditions well and consequently cannot be used to predict performance correctly [1]. Consequently it is important to pay attention to parameters that can affect the severity of embrittlement, i.e. relaxation during testing, stress level, testing time etc. The methods applied for SCC can be divided into three categories [11]: smooth specimens under static loads, pre-cracked specimens under static loads, and slow-strain-rate tests, which will be explained further in a-c).

a) Smooth specimens tested under static loading
The characteristic of this type of test is the smooth nature of the specimens that are statically loaded [11, 53]. The test can be accomplished by using a variety of specimen configurations, see Figure 10. Depending on specimen dimensions, a wide range of stresses can be induced in a single test, from zero to beyond the yield strength. If elastic deformation alone is required, it is possible to choose dimensions suitable for elastic stress generation. In this category of test, specimens with a U-bend geometry are most commonly used, made by bending and restraining a metal sheet into a U-shape [53]. In U-bend and C-ring testing the stress varies during testing since relaxation takes place; it is therefore also necessary to consider the differences in relaxation behaviour among the alloys [54]. The U-bend test is normally used for simple go/no-go assessment of SCC and is, compared with the other categories, the least costly. The accuracy of the test is dependent on incubation time, i.e. the test is adequate if the incubation period is not too long in comparison with the length of the test [11]. A slightly different specimen type in this category is the self-stressed specimen, where a Brinell hardness indenter or an Erichsen cup test plunger indents a sheet or plate [53].

Figure 10. Smooth specimens under static loading [53].

b) Pre-cracked specimens under static loading
Testing of pre-cracked specimens under static loading resembles fracture mechanics testing. In this test a notched or pre-cracked specimen is statically (or dynamically) loaded. The various specimen configurations are shown in Figure 11. The cracking behaviour of an alloy changes dramatically if there is a crack-like defect on the surface. Whether the defect develops into e.g. SMIE or not, depends not only on the alloy in
use, the stress level and corrosive environment, but also on the depth of the defect of interest (the notch). This type of test is used to determine $K_{ISCC}$, i.e. the threshold value of stress intensity above which SCC occurs. If $K_{ISCC}$ is known the effect of the combination of a nominal stress level and defect size can be evaluated [53]. This test is preferable if design information is required, i.e. $K_{ISCC}$ or stage I / stage II crack propagation parameters [11]. However, as stated earlier in section 2.2.2 Fracture characteristics of MIE, it is difficult to determine the fracture toughness for environmentally assisted cracking ($K_{IEAC}$) since it strongly depends on the time for which the test is conducted, which may vary between laboratories.

![Figure 11. Examples of pre-cracked specimens under static loading [53].](image)

c) Slow-strain-rate testing
The specimens used in slow-strain-rate testing (SSRT) are smooth or notched tensile specimens that are dynamically loaded under low strain rate conditions. The result - the ductility of the sample - is often given in comparison with rates for reference specimens that are tested in air or in inert gas [11, 53]. SSRT is however considered to be conservative and even unrealistic when design data is desired, because of the accelerated nature of the test, since the film of surface oxide is continuously broken when straining to failure [11].

3.2.1 U-bend test method in present study
The U-bend method used in the present study was adapted from the recommended aerospace practice for SCC evaluation of titanium alloys, namely ARP SAE 1795A [47]. The test method however was modified for SMIE environments.

To start with, 1.25 mm thin sheets of the investigated alloys were initially cut into the specified dimensions of 75 x 19 mm, with the rectangular specimens aligned parallel to the rolling direction as per ARP SAE 1795A. The tolerance of the dimensions was ± 0.25 mm. In order to be able to restrain the specimens after bending, 7 mm holes were drilled in the centre of the specimens, 13 mm from each edge; see Figure 12A. Subsequently each face of the specimen was ground with 240 and 600 silicon carbide papers to remove the oxide layer and residuals from cutting. Although titanium specimens oxidise again shortly after grinding, the thickness of the oxide layer varies less among the specimens, which is desired to achieve reproducibility of the test. After grinding, the specimens were handled with cotton gloves to avoid salt residuals from fingerprints, which can lead to SCC [1].
The bending operation was performed in two steps. First the specimen was bent in a vice (the legs of the U-bend shape were pushed together) until an unrestrained angle of 65° was achieved, see Figure 12B. The bent specimens were then cleaned in a solution of 35 vol% nitric acid, 3 vol% hydrofluoric acid and reagent water. The specimens were immersed in the cleaning solution for 20 s and then rinsed in reagent water and left to dry in air. The second and final U-bending step was performed by bending the free ends, with the help of a vice, until $d=16.5$ mm, see Figure 12C, and then fixed with a clean stainless steel bolt, nut and washers. Thereafter the specimens were restrained to a final diameter of $d=13.5$ mm.

After bending, the specimens were either sputtered with the embrittling species or immersed in the embrittling environment, see Figure 12D. Two types of reference specimen are used in the standard test method for SCC evaluation; one set of specimens is not exposed to any embrittling environment, and the other set immersed in a sodium chloride solution and left to dry prior to heat treatment. The purpose of the reference specimens is to control the acceptability of the test method. A successful test should not show any cracking in the unexposed reference specimens, whilst cracking should be observed for the reference specimens immersed in sodium chloride solution [47], since all titanium alloys have some degree of susceptibility to hot salt stress-corrosion cracking [1]. However, in the present study the two reference specimens were used as extra validation of the test method, even if SMIE and not SCC was of interest. The sodium chloride solution was a mixture of 3 wt% sodium chloride and reagent water. For SMIE evaluation, the specimens were sputtered with solid gold or copper. According to sputtering time, current and type of solid metal, the thickness of the sputtered layer was between 50–100 nm.

Following exposure to the different environments, all specimens were heat treated in an air circulation furnace at 480°C for 8 h; the humidity in the laboratory was 5-10%. In addition, one set of seam-welded specimens, which were heat-treated according to
the process route at Volvo Aero Corporation (593°C for 2 h) were also investigated. Following heat treatment, the specimens were left to air cool before the bolted restraints were removed. Evaluation was carried out along the U-bend section, hence a cross-section was carefully cut according to the arrows indicated in Figure 12E. The two halves of the specimen were then mounted, ground and polished by conventional methods for metallographic evaluation of titanium alloys.

Seam-welded specimens were also evaluated in the present study [55]. However since the aim of that part of the study was to investigate the influence of residual stresses from the seam-welding process itself, those specimens were not U-bent. Consequently the evaluated cross-sections of those specimens were oriented in a different way, see Figure 13, since the stress in those specimens was expected to have a different distribution.

![Figure 13. Evaluated cross-sections of seam-welded specimens.](image)

### 3.2.2 Alpha case evaluation

In order to be able to neglect the effect of alpha case on the SMIE behaviour, a specimen of Ti-6Al-4V was examined for alpha case formation after heat treatment at 480°C for 8 h. The specimen was mounted, ground and polished using conventional methods for titanium alloys. Thereafter the specimen was etched in two steps to reveal the alpha case layer, first by Kroll’s reagent and then by Weck’s tint reagent. If alpha case was present it would appear as a white layer at the surface of the specimen. However, in the present study no alpha case was observed, see Figure 14.

![Figure 14. Ti-6Al-4V etched for alpha case evaluation; no alpha case was observed.](image)
3.3 Evaluation techniques
All specimens were first evaluated in a light optical microscope. If no cracks were observed, the specimen was re-ground and re-polished to a depth of approximately 1 mm below the evaluated cross-section, and thereafter re-evaluated. None of the specimens was etched since this procedure would open the cracks. Instead other evaluations techniques were used, which are described in this section.

3.3.1 Light optical microscopy
The main evaluation was carried out using the light optical microscope (LOM) located in the Division of Materials Science at Luleå University of Technology (Olympus Vanox AH-2 AHBT). The outer surface of the U-bend shape was carefully examined at magnifications up to 1000 times. When cracking was found, the location was noted and the crack documented. The typical appearance of the cracks in the LOM is shown in Figure 15.

![Figure 15. SMIE of Ti-6242 in contact with gold, image captured at 1000 times magnification in the light optical microscope.](image)

3.3.2 Scanning electron microscopy
The specimens showing indications of SMIE where further evaluated in the scanning electron microscope (SEM) located in the Division of Materials Science at Luleå University of Technology (JEOL JSM 6460LV). In order to distinguish between the alpha and beta phase in the titanium alloys, the cracks were evaluated by using the backscattered electron detector in the SEM, which provides atomic number contrast, see Figure 16.
3.3.3 Electron backscatter diffraction analysis

Further analysis was carried out using electron backscatter diffraction (EBSD) equipment in the Department of Materials and Manufacturing Technology at Chalmers University of Technology (LEO 1550 Gemini FEG-SEM equipped with HKL Channel-5 EBSD system and a Nordlys II detector). EBSD is an additional characterisation technique used in the SEM to obtain crystallographic information from a material. A high-energy electron beam scans the area of interest and simultaneously backscattered electrons generate an EBSD (Kikuchi) pattern on a fluorescent screen. The pattern generated is characteristic of the orientation and crystal structure, and can be used to determine individual grain orientations, local texture, phases present, etc.

EBSD equipment comprises three parts: the SEM, a pattern acquisition device, and software. The resolution depends on the interaction volume of the primary electrons in the material, which is characterised by a depth of 20 nm and the projected area of the electron beam. The sample is tilted approximately 70° relative to the incident beam to increase the fraction of backscattered electrons and thereby the contrast in the EBSD pattern, as shown in Figure 17. The phosphor screen connected to the acquisition device is usually located about 2 cm from the specimen, perpendicular to the pole-piece. EBSD software controls the raster grid of the area of interest, pausing the electron beam at each point just long enough to gather the EBSD pattern and to index the orientation. The output of EBSD is normally presented as an image in which different colours correspond to different crystallographic orientations [56]. An orientation map is shown in Figure 18 before (a) and after (b) noise reduction with an average of four neighbours applied.
MATERIALS AND METHODS

Figure 17. EBSD setup in the SEM vacuum chamber showing pole-piece emitting electrons, sample and detector [56].

Figure 18. a) EBSD orientation map, and b) EBSD orientation map after noise reduction with an average of four neighbours applied.
4 SUMMARY OF APPENDED PAPERS

4.1 Paper A

Solid metal induced embrittlement of titanium alloys in contact with copper

Pia Åkerfeldt, Robert Pederson and Marta-Lena Antti

A test method for SMIE evaluation was developed by modifying a U-bend test method normally used to evaluate SCC of titanium alloys in contact with cleaning solutions. By using reference specimens intended to crack or not, depending on the type of environment, the reliability of the test method was established. One of the reference environments evaluated was gold, since it is the subject of another study involving SMIE of a titanium alloy. In the present SMIE study, three titanium alloys: Ti-8Al-1V-1Mo, Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V, representing both near-alpha and alpha-beta alloys, were evaluated. The results showed that the two near-alpha alloys Ti-8Al-1V-1Mo and Ti-6Al-2Sn-4Zr-2Mo were susceptible to SMIE in contact with solid copper (and gold) at 480°C for 8 hours, but no SMIE was found for Ti-6Al-4V. The observations suggest that SMIE susceptibility is dependent on alloy composition.

Contribution of author:
The author planned the experiments, performed the experiments, evaluated the results and wrote the paper after suggestions from the co-authors.

4.2 Paper B

Investigation of the influence of copper welding electrode on Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo with respect to solid metal induced embrittlement

Pia Åkerfeldt, Robert Pederson and Marta-Lena Antti

The risk of using copper electrodes when resistance welding titanium alloys was investigated. Based on the results presented in paper A, resistance welded Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo were evaluated for SMIE. In addition to the welding process itself, the effect of possible wear debris from the copper electrodes on SMIE susceptibility was also evaluated by coating the resistance welded specimens with copper to promote SMIE. No SMIE was found in the resistance welded specimens, which may be explained by the absence of copper in the weld. However,
since no cracks were found on the resistance welded specimens coated with copper neither, it was concluded that the absence of copper was not the reason for the absence of SMIE in the present study. Therefore it was concluded that the residual stresses generated by the welding operation itself are insufficient to induce cracks through SMIE in Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo.

Contribution of author:
The author planned the experiments, performed parts of the experiment (not the resistance welding procedure), evaluated the results and wrote the paper after suggestions from the co-authors.

4.3 Paper C

The effect of crystallographic orientation on solid metal induced embrittlement of Ti-8Al-1Mo-1V in contact with copper

Pia Åkerfeldt, Robert Pederson, Marta-Lena Antti, Yiming Yao and Uta Klement

The crack propagation behaviour of SMIE in relation to the crystallographic orientation of Ti-8Al-1Mo-1V was investigated. Even though SMIE has been evaluated in detail in several studies, no evaluations have been carried out on its dependence on crystallographic orientation. In the present paper the crack propagation path of Ti-8Al-1Mo-1V in contact with copper was evaluated by using electron backscatter diffraction (EBSD). It was generally observed that the crack propagated perpendicular to the surface and the loading direction, presumably towards locations with high stress levels. The EBSD results indicated a favourable crack path along high angle grain boundaries between the alpha phase grains, which supports an adsorption mechanism since adsorption most likely occur on high-energy surfaces. In addition, several grains were oriented close to [0001] in the crack direction, indicating that there is a relationship between the crack characteristics of SMIE and the crystallographic orientation.

Contribution of author:
The author planned the experiments, performed parts of the experiment (not the EBSD analysis), evaluated the results and wrote the paper after suggestions from the co-authors.
5 CONCLUSIONS

Based on the observations presented in Papers A, B, and C the following conclusions can be drawn with regard to the test method, the SMIE susceptibility of titanium alloys, and the SMIE mechanisms in titanium alloys.

Test method
- The modified U-bend test method is valid for SMIE evaluation
- The SMIE susceptibility is highly dependent on testing conditions such as tensile stress, heat treatment temperature and duration of the test
- There are threshold values of temperature and tensile stress below which SMIE does not occur

SMIE susceptibility of titanium alloys
- Ti-8Al-1Mo-1V is susceptible to SMIE in contact with copper or gold at 480°C for 8 hours
- Ti-6Al-2Sn-4Zr-2Mo is susceptible to SMIE in contact with copper or gold at 480°C for 8 hours
- Ti-6Al-4V is not susceptible to SMIE in contact with copper or gold at 480°C for 8 hours
- The tensile stress generated by the seam-welding process itself is not sufficient to generate SMIE of Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo in contact with copper
- SMIE susceptibility is dependent on alloy composition

SMIE mechanisms of titanium alloys
- The SMIE crack propagates principally along high angle grain boundaries between alpha phase grains, which may be explained by the high surface energy and thus the stronger influence of adsorption of embrittling species
- The transportation mechanism of the embrittling species suggested from the source to the crack tip via self-surface-diffusion is consistent with the findings of the present studies
- There is a relationship between crystallographic orientation and SMIE crack path characteristics
- The SMIE crack path tends to follow grains oriented close to [0001] in the crack path direction
6 FUTURE PERSPECTIVES

The nature of solid metal induced embrittlement is complex. One should be careful when generalising phenomena among alloys, predicting the influence of test parameters etc. Even though investigations have been carried out to understand the mechanisms involved in embrittlement, more studies are needed before detailed conclusions regarding its mechanisms and relation to different test and material parameters can be drawn.

6.1 Influence of alloy composition

In the present study, solid copper and gold were found to cause SMIE in two near-alpha alloys (Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo), whilst SMIE was not observed in the alpha-beta alloy (Ti-6Al-4V). Several explanations can be suggested for the observed susceptibility difference. Firstly, SMIE dependence on alloy composition could be explained by the amount of beta phase in the alloys investigated. Seah [57] obtained correlations showing that the extent of adsorption increases with decreasing solubility of the embrittling species in the matrix. Accordingly, species with low solubility in the matrix are more likely to cause embrittlement, which has also been suggested by others studying MIE [6, 17]. However, with titanium alloys one should consider the solubility within both the alpha and beta phases. Elements known to cause MIE in titanium alloys, such as copper, gold, silver, cadmium, and mercury, have limited solubility in both the alpha and beta phases. Moreover, when comparing the solubility of copper and gold, both exhibit lower solubility in the alpha phase (1.6 and 1.7 wt%, respectively), than in the beta phase (14 and 17 wt%, respectively) [58]. This suggests that titanium alloys containing higher amounts of alpha phase will exhibit higher susceptibility to SMIE. Hence, the phase fractions of alpha and beta should be estimated for the alloys investigated, e.g. by x-ray measurements on untested sheet material.

However, the fraction of beta phase in Ti-6Al-4V is rather small, 5-10% [59] at room temperature, and Ti-6Al-4V should contain the highest amount of beta phase, compared with Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V. In other words, since the amount of beta phase is rather small in the alloys studied, combined effects of several parameters probably explain the influence of alloy composition. In the case of SCC, one may explain the observed difference among alloys by the influence of alpha stabilising elements such as aluminium and tin, i.e. the susceptibility increases with an increasing amount of alpha stabilising elements. Furthermore, for aluminium it may be explained by the increasing ability to form the low-ductility Ti₃Al phase with more than 5% aluminium [11]. Therefore, the volume fraction of Ti₃Al present should be examined for the alloys studied to test this theory.
In addition, the test parameters used with different alloys should be reviewed. Ti-6Al-4V appears to be more resistant to SMIE but one should bear in mind that only one test condition has been used so far. Test parameters such as the heat-treatment temperature, holding time and stress level are expected to influence the results to a large extent. Therefore additional tests should be carried out to examine SMIE susceptibility for alloys studied under different test conditions.

6.2 Mechanisms of SMIE

The most important topic for future work with respect to the mechanisms of SMIE is to study the crack propagation path in more detail. This would enable further conclusions regarding mechanisms and the influence of test and material parameters to be drawn.

Concerning the transport mechanism of self-surface diffusion of the embrittling species to the crack tip, additional characterisation of crack propagation should be performed. One suggestion is to open the cracks and evaluate the fracture surface. Previous studies have found traces of the embrittling species on the fracture surface by using Auger Electron Spectroscopy (AES) analysis [17, 20] or Secondary-Ion Mass Spectroscopy (SIMS) [17], techniques that would be of value in the present project for detecting copper or gold on the fracture surfaces. In addition, the fracture surface is interesting with respect to the different theories of how adsorption affects the crack tip. Lynch [26, 35-38] observed plastic zones and dimples on MIE fracture surfaces, supporting his theory of dislocation nucleation at the crack tip because of adsorption. Hence it is suggested that the fracture surfaces should be examined in a high resolution SEM to evaluate if such fracture features are present on the fracture surfaces of the materials investigated. Moreover, complementary studies of fracture surfaces resulting from overload would provide information on the fracture behaviour of the materials investigated, which would be useful information when evaluating the SMIE fracture surfaces.

It would also be interesting to compare the EBSD results for Ti-8Al-1Mo-1V with Ti-6Al-2Sn-4Zr-2Mo and the result of SMIE caused by copper with that for gold. By comparing the results, features and trends for certain alloys, embrittling species may be defined, which will be useful for the understanding of the mechanisms involved.

6.3 Test method

The validity of the test method used requires further evaluation. The test method used in the present work included several reference environments that all suggest that the method is valid for SMIE evaluation. The stress distribution in this kind of test, however, is not controlled, which means that embrittlement cannot be related to a specific value of tensile stress. To enable further conclusions to be drawn on how the stress level affects the SMIE susceptibility, which is important particularly for fracture
critical components in the aerospace industry, one should perform complementary studies using pre-cracked specimens under static and dynamic loading.

Another parameter to consider is the thickness of the coating of embrittling species. By varying the thickness of the layer one could evaluate the amount of embrittling species necessary to assist SMIE. This would be of interest particularly when evaluating the risk of using copper electrodes in the welding process, since the amount of wear debris is probably restricted. Finally additional tests carried out in vacuum are necessary to clarify how air (oxygen) contributes to the SMIE results obtained through oxidation of the copper layer.
REFERENCES


REFERENCES


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Solid Metal Induced Embrittlement of Titanium Alloys in Contact with Copper

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2Department of Materials Technology, Volvo Aero Corporation, S-46181 Trollhättan, Sweden

Solid Metal Induced Embrittlement (SMIE) is caused by a specific combination of a susceptible alloy, tensile stress and a solid metal. Solid copper is commonly used in various manufacturing processes, e.g., in welding electrodes and clamping fixtures, during the manufacturing and handling of titanium alloy parts for the aerospace industry. An initial study indicated that copper in contact with titanium could lead to SMIE and was the reason for initiating the current work. Three titanium alloys; Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V, have been evaluated with respect to SMIE in contact with copper. The evaluation was carried out by using a modified U-bend test method adapted from SAE ARP 1795, a standard used for Stress-Corrosion Cracking (SCC) evaluation of titanium alloys in contact with cleaning solutions. Gold was also investigated in order to validate the reliability of the test method since it has been reported that titanium alloys undergo SMIE in contact with solid gold. The results show that both Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo are susceptible to SMIE in contact with copper whereas SMIE was not observed with Ti-6Al-4V.

Keyword: Solid metal induced embrittlement (SMIE), titanium alloys, copper, gold, Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo

1. Introduction
A specific combination of a susceptible alloy, tensile stress and an environment can lead to cracking of various types. Most frequently discussed are stress-corrosion cracking and hydrogen embrittlement, but as awareness increases, attention has also been given to metal induced embrittlement.

There are two types of metal induced embrittlement: liquid metal embrittlement, which occurs above the melting temperature, \(T_m\), of the embrittling metal and solid metal induced embrittlement (SMIE), which occurs below \(T_m\). In the present study, SMIE is investigated and discussed. Failures within the industry resulting from SMIE are not as frequently reported as liquid metal embrittlement but do occur, for example when an embrittling metal is resistance-heated and in intimate contact with a susceptible alloy. However, the mechanisms behind SMIE are not fully understood but are believed to be a combined action of surface self-diffusion to crack tips and adsorption at crack tips of the embrittling species.

SMIE is highly dependent on service temperature since surface self-diffusion is involved, i.e., the cracking rate increases with increasing temperature. In general, cracking resulting from SMIE is expected to occur at or above a homologous temperature of 0.5 \((T/T_m)\), where \(T\) is the service temperature in degrees Kelvin. However, cracking at lower temperatures has been observed for titanium alloys in contact with silver and gold, at a homologous temperature of 0.38, but the effect of external materials is under debate since the rates are not consistent with surface self-diffusion transport of embrittling species.

Titanium alloys are to a large extent used for parts and components within the aerospace industry where joining of titanium parts can be accomplished by resistance welding. In that case, titanium alloys are in intimate contact with solid copper as the copper electrodes resistively heat the titanium alloy under pressure during the welding process. SMIE of titanium alloys in contact with solid copper has been studied previously. D.N. Meyn and R.E. Stoltz et al. did not observe any cracking after copper contact in Ti-6Al-4V at 148°C and Ti-6Al-6V-2Sn at 287°C. D.-X. Liu et al., on the other hand, observed cracking in Ti-6.5Al-3.5Mo-1.5Zr-0.3Si at 500°C, but not at 300°C or 400°C. SMIE of titanium alloys has been observed in several environments, see Table 1. It has been suggested that environments that lead to liquid metal embrittlement also lead to SMIE, which imply that mercury should be added to the list of SMIE environments.

The risk of using copper for resistance welding electrodes when welding titanium alloys has not been reported in literature. In the present study, an investigation has been carried out in order to survey the influence of copper on different titanium alloys.

Table 1. Reported SMIE environments for different titanium alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>SMIE environments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>Cd(^{10})</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>Cd(^{10})</td>
</tr>
<tr>
<td>Ti-3Al-14V-11Cr</td>
<td>Cd(^{7})</td>
</tr>
<tr>
<td>Ti-6Al-6V-2Sn</td>
<td>Cd(^{7}), Ag(^{5}), Au(^{5})</td>
</tr>
<tr>
<td>Ti-6.5Al-3.5Mo-1.5Zr-0.3Si</td>
<td>Cu(^{5})</td>
</tr>
</tbody>
</table>

2. Experimental Procedure
The SMIE evaluation was accomplished by using a U-bend test method and three batches of specimens were evaluated. The experimental setup for each batch is listed in Table 2. For each combination of alloy and environment, three specimens were examined for cracking.

Table 2. The experimental setup of the evaluated batches with respect to embrittling environment and alloy composition.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Embrittling environment</th>
<th>Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper paste</td>
<td>Ti-6Al-4V, Ti-8Al-1Mo-1V</td>
</tr>
<tr>
<td>2</td>
<td>Copper paste, solid Au, and solid Cu</td>
<td>Ti-6Al-4V, Ti-8Al-1Mo-1V</td>
</tr>
<tr>
<td>3</td>
<td>Solid Au and solid Cu</td>
<td>Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo</td>
</tr>
</tbody>
</table>
In order to evaluate the influence of alloy composition, three alloys were tested. The composition and condition of the sheets investigated were in accordance with AMS4911 (Ti-6Al-4V), AMS4916 (Ti-8Al-1Mo-1V) and AMS4919 (Ti-6Al-2Sn-4Zr-2Mo). In batches 1 and 2, Ti-6Al-4V and Ti-8Al-1Mo-1V were tested to represent an alpha-beta alloy and a near alpha alloy, respectively. In batch 3 an additional near alpha alloy was included, Ti-6Al-2Sn-4Zr-2Mo, which was chosen because of its importance in aerospace industry applications.

2.1 U-bend test method
The method used is a modified standard test method adapted from SAE ARP 1795\(^1\), which is normally used to evaluate stress-corrosion cracking of titanium alloys by aircraft engine cleaning materials.

The specimens were cut parallel to the rolling direction to dimensions of 75x19x1.25 mm. At each side, 13 mm from the edge, in the center as shown in Figure 1A, a 7 mm diameter hole was drilled. To remove surface contaminants and oxides, the two sides of the specimens were mechanically ground with 240 and 600 silicon carbide paper. The specimens were thereafter handled using cotton gloves throughout the experimental procedure.

Bending was performed in two steps separated by a cleaning operation. First, the specimens were preformed in a vise to an unrestrained angle of 65°, see Figure 1B. Thereafter all specimens were cleaned in a cleaning operation. First, the specimens were preformed in a vise to an unrestrained angle of 65°, see Figure 1B. Thereafter all specimens were cleaned in a cleaning solution containing 35vol% nitric acid, 3vol% hydrofluoric acid and reagent water for 20 seconds and finally rinsed in tap water and left to dry in air.

Four environments have been evaluated in this study: (i) untreated control specimens that were not exposed to any environment; (ii) specimens immersed in a sodium chloride solution containing 3wt% sodium chloride and reagent water; (iii) specimens sputtered with solid gold; (iv) solid copper; (v) specimens with copper paste. The acceptability of the test method was established by (i)-(iii). A successful test should not show any cracking in (i), whilst cracking should be observed for (ii) according to the standard and (iii) in order to validate the test method for SMIE examinations. Sputtered gold was chosen as a SMIE reference environment since R.E. Stoltz et al.\(^2\) have reported cracking of Ti-6Al-6V-2Sn in contact with gold at 287°C. To begin with, in batches 1 and 2, the effect of copper was studied by smearing copper paste onto the surface of the specimen. CRC copper paste was used, a high temperature lubricant based on micronized copper powder in a mixture of synergetic anti-oxidant, anti-corrosion and anti-wear additives suspended in a premium grade stable oil\(^3\); the specific ingredients and amounts are unknown.

2.5 Examination of specimens
Metallographic examination of the specimens was carried out in a light optical microscope (LOM) and in a scanning electron microscope (SEM). Cracking was first located and observed in the LOM; the outer radius of the U-bend shape was carefully evaluated, magnifications up to 500x were used. A final examination was performed in the SEM in backscattering mode; the cracks were studied in detail at magnifications up to 2000x. Energy dispersive spectroscopy (EDS) was also used in order to locate copper particles, if visible, in the SEM. The captured SEM images were in some cases combined into a single picture using software in order to obtain an overview image of the cracks.

3. Results
The results from the three batches are summarized in Table 3. Acceptability of the test method was established using environments (i)-(iii), i.e. no cracks were found in the untreated control specimens, whilst cracking was observed for specimens immersed in the sodium chloride solution and sputtered with solid gold. One exception was
Ti-6Al-4V, where no cracking could be observed in contact with solid gold.

The effect of copper was studied in two types of environment; copper paste and solid copper. For both environments, no cracking was observed for Ti-6Al-4V, see typical appearance of surface in contact with solid copper in Figure 2A. Ti-8Al-1Mo-1V, in contrast, showed susceptibility to cracking in contact with both copper paste and solid copper; see Ti-8Al-1Mo-1V in contact with solid copper in Figure 2B and copper paste in Figure 3. EDS studies of the cracking caused by copper paste revealed a copper particle (indicated by arrow in Figure 3) at the crack initiation site. Cracking could also be observed for Ti-6Al-2Sn-4Zr-2Mo in contact with solid copper, see Figure 2C.

For those specimens with a number of cracks, a tendency for crack concentration could be seen in the bending zone of the U-bend. However, cracks were also found in the area between the bending zone and the holes where the bolts were restrained.

Table 3. Result of the SMIE testing

<table>
<thead>
<tr>
<th>Environment</th>
<th>Ti-8Al-1Mo-1V</th>
<th>Ti-6Al-2Sn-4Zr-2Mo</th>
<th>Ti-6Al-4V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>No cracking</td>
<td>No cracking</td>
<td>No cracking</td>
</tr>
<tr>
<td>NaCl-solution</td>
<td>Cracking</td>
<td>Cracking</td>
<td>Cracking</td>
</tr>
<tr>
<td>Solid gold</td>
<td>Cracking</td>
<td>Cracking</td>
<td>No cracking</td>
</tr>
<tr>
<td>Solid copper</td>
<td>Cracking</td>
<td>Cracking</td>
<td>No cracking</td>
</tr>
<tr>
<td>Copper paste</td>
<td>Cracking</td>
<td>N/A</td>
<td>No cracking</td>
</tr>
</tbody>
</table>

Figure 2. Observed effect of copper contact at 480°C for 8 hours; (A) no cracking was observed for Ti-6Al-4V; (B) and (C) shows cracking for Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo respectively.

4. Discussion

In order to evaluate the different titanium alloys with respect to SMIE, a standard test method for stress-corrosion cracking was used. The method was considered as valid for SMIE since cracking was observed for both solid gold and copper, whilst no cracking was observed for the untreated specimens. It should however be noted that the possible embrittlement contribution from hydrogen embrittlement was neglected. S.P. Lynch proposed that crack growth could occur initially by SMIE and continue by hydrogen embrittlement or stress-corrosion cracking, which could also be the case in the present study. However, with respect to the uncertainty in this matter, cracking was evaluated in a yes or no manner.

In the U-bend test, a wide range of stress levels are generated: the highest stresses are found in the bending zone whereas lower stress levels are present at the legs of the U-bend. A tendency for higher crack concentration near the bending zone could be explained by the stress distribution in the U-bend as it has been reported that e.g. stress raisers increase embrittlement. The presence of cracks in the legs indicates that SMIE can occur at quite low stresses, which is important to appreciate when the effect of resistance welding is discussed, concerning residual stresses.

Copper and gold have in this study been shown to embrittle two near alpha titanium alloys, but no alpha-beta alloy. The titanium alloy composition influences the
susceptibility to stress-corrosion cracking and it has been reported that high amounts of alpha stabilizing elements, such as aluminium or tin, increase the cracking susceptibility\textsuperscript{6,13}, which agrees with the current findings. It is believed that the mechanisms of metal induced embrittlement are similar to those of stress-corrosion cracking and hydrogen embrittlement\textsuperscript{2,4}, but since these mechanisms are not well understood further conclusions cannot be drawn. The alloy composition dependence observed however emphasizes the similarities between stress-corrosion cracking and SMIE.

Copper paste was evaluated in batches 1 and 2, in which Ti-8Al-1Mo-1V experienced cracking. Copper was detected on the surface at the initiation site of the crack, which indicates that copper probably was in intimate contact with Ti-8Al-1Mo-1V, a prerequisite for embrittlement to occur\textsuperscript{2,4}. On the other hand, the precise effect of copper in this case is somewhat unclear since it could well stem from the lubricant ingredients, i.e. that stress-corrosion cracking was induced. This was the reason why sputtered solid metal was used in batches 2 and 3, to ensure intimate contact between the embrittling metal and the alloy and no influence from other external matters.

The SMIE susceptibility shown in this study is consistent with the homologous temperature at which SMIE is expected to occur i.e. 0.5. The conditions of solid gold and copper evaluated here correspond to homologous temperatures of 0.56 and 0.55, respectively. Assuming that 0.5 is a reasonable threshold value for SMIE, embrittlement would occur at around 400°C for gold and copper (396°C for gold and 406°C for copper).

Regarding resistance welding with copper electrodes, more tests need to be carried out before the effect can be completely understood.

5. Conclusions
The results indicate that copper in contact with certain titanium alloys can lead to SMIE and that the susceptibility tends to be dependent on alloy composition. The following conclusions can be drawn:

- An adapted test method based on SAE ARP 1795 can be used to evaluate SMIE susceptibility.
- Copper and gold do not result in SMIE in Ti-6Al-4V when exposed to a temperature of 480°C for 8 hours.
- Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo are susceptible to SMIE when in contact with solid gold or solid copper at 480°C for 8 hours.

Acknowledgement
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PAPER B
Investigation of the Influence of Copper Welding Electrodes on Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo with Respect to Solid Metal Induced Embrittlement

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Abstract. Solid Metal Induced Embrittlement (SMIE) is caused by a specific combination of two solid metals in intimate contact. Cadmium, gold, silver and copper are known to cause SMIE in certain titanium alloys. Solid copper is used in welding electrodes and fixtures in various manufacturing processes for titanium parts within the aerospace industry. In the case of resistance welding, titanium alloys are in intimate contact with solid copper, since the electrodes resistively heat the titanium part under pressure during the welding process. No previous published work that investigates the risk of using copper electrodes for welding of titanium alloys is available in the literature, but an initial study using U-bend testing indicates that solid copper in contact with Ti-8Al-1V-1Mo and Ti-6Al-2Sn-4Zr-2Mo could lead to SMIE. Therefore, in the present study, resistance welded Ti-8Al-1V-1Mo and Ti-6Al-2Sn-4Zr-2Mo have been evaluated to investigate the influence of copper electrodes on these alloys. Furthermore, resistance welded specimens sputtered with copper and gold to promote SMIE have also been evaluated. No SMIE was found in the resistance welded specimens, which may be explained by the short interaction time that the copper electrodes are in intimate contact with the titanium alloy, and/or the magnitude of residual stresses after welding, which may be too low to initiate SMIE.

1. Introduction

One of the joining methods that can be used for titanium components within the aerospace industry is seam welding. In seam welding the welding electrodes, commonly made of copper, press overlapping work pieces together and heat them to the welding temperature to form one of the nuggets in a seam weld [1]. However, there are doubts about the influence of the copper electrodes on the titanium work piece; recently the authors found that two near alpha alloys were susceptible to solid metal induced embrittlement (SMIE) in contact with solid copper [2]. For SMIE to occur, two solid metals must be in intimate contact with each other [3-8], which is the case for the copper electrodes and the titanium part during the seam welding process, and which could be the case when the copper electrode degrades if wear debris becomes attached to the titanium part. However, there are other important parameters as well, e.g. the temperature, holding time and surface condition. The mechanism of SMIE is believed to be a combination of surface self-diffusion of the embrittling species to the crack tip and adsorption of the embrittling species at the crack tip [3-5], see figure 1. Surface self-diffusion is assumed to be the
transport mechanism since its diffusion rates are fast enough to be consistent with cracking lengths at the temperatures studied [5,6,9-10] compared with vacancy and grain boundary diffusion. Concerning how the adsorption affects the crack tip, the details are not fully understood but in general it is agreed that the adsorption weakens the crack tip. The two main theories are (1) adsorption reduces the stress required for tensile separation of the atom at the crack tip leading to decohesion [8,11-13] and (2) adsorption facilitates the nucleation or egress of dislocations at crack tip [5, 14-16].

The mechanism of SMIE susceptibility is rather complex to model, but experimental studies indicate that cracking resulting from SMIE is expected to occur above a homologous temperature (T/Tm) of 0.5 [6], where T is the service temperature and T_m the melting temperature of the embrittling species (K). For titanium alloys, SMIE has been observed in contact with the embrittling species listed in table 1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Embrittling species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-3Al-14V-11Cr</td>
<td>Cd [3,17]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Cd [17,18]</td>
</tr>
<tr>
<td>Ti-6Al-6V-2Sn</td>
<td>Ag [19], Au [19], Cd [19]</td>
</tr>
<tr>
<td>Ti-6Al-2Sn-4Zr-2Mo</td>
<td>Au [2], Cu [2]</td>
</tr>
<tr>
<td>Ti-6.5Al-3.5Mo-1.5Zr-0.3Si</td>
<td>Cu [20]</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>Au [2], Cd [17,18], Cu [2]</td>
</tr>
</tbody>
</table>

In the present paper, the influence of copper welding electrodes on two titanium alloys has been evaluated and discussed. Although failures by SMIE are rare in industry, it does occur, partly because of the lack of awareness of SMIE. This study is made in close collaboration with the aerospace industry to increase understanding and knowledge of SMIE.
2. Materials and method

2.1. Materials
Two near alpha alloys were evaluated; Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo, both of which have been shown to be susceptible to SMIE in contact with copper and gold in a previous study [2]. The microstructure of the near alpha alloys investigated mainly consists of alpha grains surrounded by a small amount of beta phase. This kind of microstructure is typical in sheet material of these alloys. The condition and composition of the sheets evaluated here are in accordance with AMS4916J [21] (Ti-8Al-1Mo-1V) and AMS4919F [22] (Ti-6Al-2Sn-4Zr-2Mo).

2.2. Welding procedure
The sheets were seam welded by using resistance welding equipment with wheel-shaped electrodes, made of copper, see figure 2(a). The seam weld can be divided into nuggets that represent one welding cycle, as shown in the cross-section of a seam weld (the nugget) in figure 2(b). A welding cycle comprises the time for which the electrodes are in contact with the work piece, including the set-up time (the time taken to achieve the correct mechanical pressure) and the cooling time. In the present study, one nugget was made using two weld impulses of 160 ms, with a total welding cycle of 2160 ms. The sheets were cut to 75x19x1.25 (±0.25) mm parallel to the rolling direction, and the seam weld was made in the middle of the sheet, see figure 2(c).

2.3. Test procedure
The main parts of the test procedure were adapted from SAE ARP 1795A [23], which is a standard U-bend test method normally used to evaluate stress-corrosion cracking of titanium alloys caused by aircraft cleaning materials. However, the seam welded specimens were not U-bent since the aim was to evaluate the residual stresses from the weld itself. To avoid contamination or embrittlement caused by other sources, the specimens were immersed in a cleaning solution containing 35vol% nitric acid.

Figure 2. (a) Wheel-shaped copper electrodes, (b) cross-section of a seam weld etched with Kroll’s reagent showing the nugget, and (c) typical appearance of seam-welded sheets.
3vol% hydrofluoric acid and reagent water for 20 seconds, then rinsed in reagent water and left to air dry. The specimens were thereafter carefully handled with cotton gloves throughout the experimental procedure. Three conditions were evaluated: seam welded specimens sputtered with either i) copper or ii) gold, and iii) specimens that had only been seam welded. The intention with the sputtered copper and gold was to promote embrittlement by guaranteeing the presence of embrittling species. Both copper and gold have, in previous studies, been shown to embrittle titanium alloys, see table 1. Depending on the sputtering time, current and type of solid metal, the thickness of the sputtered layer was between 50-100 nm.

The subsequent heat treatment was carried out according to two procedures. One batch of specimens was heat treated at 480°C for 8 hours and acid pickled according to SAE ARP 1795A [23]. The other batch was heat treated at 593°C for 2 hours and acid pickled according to a process route used in the aerospace industry. A summary of the alloys evaluated, conditions and heat treatments can be found in table 2.

Following heat treatment and acid pickling, all specimens were carefully cut along and across the seam weld, as indicated by the arrows in figure 3, to produce two cross-sections along the weld length.

Table 2. Alloys tested, conditions and heat treatments.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Condition</th>
<th>Temperature [°C] / Duration [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>Seam welded</td>
<td>480 / 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>593 / 2</td>
</tr>
<tr>
<td></td>
<td>Seam welded + copper</td>
<td>480 / 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>593 / 2</td>
</tr>
<tr>
<td></td>
<td>Seam welded + gold</td>
<td>480 / 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>593 / 2</td>
</tr>
<tr>
<td>Ti-6Al-2Sn-4Zr-2Mo</td>
<td>Seam welded</td>
<td>480 / 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>593 / 2</td>
</tr>
<tr>
<td></td>
<td>Seam welded + copper</td>
<td>480 / 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>593 / 2</td>
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<tr>
<td></td>
<td>Seam welded + gold</td>
<td>480 / 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>593 / 2</td>
</tr>
</tbody>
</table>

The dashed lines and arrows illustrate the locations of the re-ground and re-polished cross sections.

Figure 3. Schematic sketch of the cross-sections evaluated.
and three cross-sections across the weld width. The cross-sections were mounted, ground and polished using conventional methods for titanium alloys. The evaluation of the cross-sections was carried out in a light optical microscope at 500x. If no crack was observed, the mounts were reground and re-polished to a depth of approximately 1 mm, as indicated by the dashed lines and arrows in figure 3.

3. Results and discussion

No indication of SMIE caused by the copper electrodes was observed in seam welded Ti-8Al-1Mo-1V or Ti-6Al-2Sn-4Zr-2Mo, neither was any SMIE observed in the specimens sputtered with copper and gold. All specimens were re-ground, re-polished and re-examined several times without displaying any indication of SMIE.

If one considers the homologous temperature ($T/T_m$) above which SMIE is expected to occur (0.5), SMIE caused by copper has a threshold temperature of 406°C. During seam welding the contact surface of the copper electrodes was heated to approximately 900°C ($T/T_m = 0.86$), i.e. to a much higher temperature than the threshold temperature. However, the electrodes were in contact with the titanium work piece for a very short time (320 ms), resulting in negligible diffusion. During the welding operation, the copper electrodes also degrade, resulting in wear debris, which could attach to the surface of the titanium work piece - this was experimentally studied by sputtering copper onto the surface of the test specimens. After welding, the sheets are normally stress relieved and so the test specimens in the present study were also stress relieved. In this study, the stress relieving treatments were performed at 480°C ($T/T_m=0.55$) for 8 hours or at 593°C ($T/T_m=0.64$) for 2 hours depending on the batch. The diffusion that occurs during heat treatment can be estimated by calculating a characteristic diffusion length. The surface self-diffusion coefficient ($D_s$) for copper depends strongly on the surrounding atmosphere; in an oxygen atmosphere the pre-exponential diffusion coefficient ($D_0$) is 0.15 cm$^2$/s, and the activation energy ($Q$) is 75 kJ/mol [24]. The surface self-diffusion coefficients ($D_s$) at 480°C and 593°C are thus calculated to be 9.4×10$^{-7}$ and 4.5×10$^{-6}$ cm$^2$/s, respectively using a form of the Arrhenius equation [25]:

$$D_s = D_0 \exp(-Q/RT)$$

A characteristic diffusion length may then be calculated using the random-walk diffusion equation [4-5, 18]:

$$\bar{x} = \sqrt{2D_s t}$$

where $t$ is time (s). Assuming that the oxygen atmosphere is a valid approximation for air, the present holding times ($t$) would result in characteristic diffusion lengths of 0.0023 m (480°C, 8h) and 0.0025 m (593°C, 2h), which are sufficient to cause severe embrittlement.

Whilst no cracking was observed in the seam welded specimens, cracking was observed after 480°C for 8 hours in the U-bend test [2] for both Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo that had copper or gold sputtered onto the surfaces. One of the prerequisites for SMIE is tensile stress, which in this study is expected to be generated by the seam welding process itself. Since the work piece is heated to the welding temperature, the material undergoes thermal expansion, which is restrained by cooler adjacent material, resulting in both tensile (in the weld) and compressive (adjacent to the weld) residual stresses. The stress distribution may be different in the seam weld since the weld consists of several small spot welds. In addition, the distribution and size of the residual stresses are also dependent on the alloy in question, phase transformations that occur, cooling rate, peak temperature, and grain size [26] and are therefore difficult to predict. In the present study, the seam welded specimens were evaluated in two orientations to cover at least two possible crack growth directions -
along and across the seam weld - see figure 3. However, even if the residual stresses induced by welding attain the yield stress in some cases, it is supposed that the stress levels in the present study were less than those observed in previous U-bend tests [2] since the sheets in the U-bend tests experience plastic deformation as they are bent. It should on the other hand be noted that in the U-bend test, severe cracking was observed in the low stress region at the legs of the U-bend in Ti-6Al-2Sn-4Zr-2Mo in contact with copper, see figure 4, indicating that SMIE may also occur at stress levels lower than the yield stress.

Titanium alloys are known for their ability to form a stable protective oxide surface layer when exposed to air [27]. In this study, the oxide layer was largely removed by acid pickling prior to sputtering and/or heat treatment, but since titanium alloys are highly reactive a new oxide layer is instantly formed when exposed to air. Thus, during intimate contact between the two solid metals, for crack initiation to occur the oxide must be ruptured either mechanically or chemically. This also emphasises the role of tensile stress, which can tear apart the oxide film and maintain intimate contact of the embrittling species with the exposed titanium at the crack tip. The inhibition of transport and adsorption processes of the embrittling species because of the oxide layer has been observed by Fager and Spurr [18], who studied SMIE of titanium alloys in contact with cadmium. The oxide layer could explain why no embrittlement was observed for the seam welded specimen, i.e. the tensile stresses were too low. Further, SMIE in the U-bend specimens may be explained by a higher stress level, even when compared with the low stress region in the legs of U-bend samples. In addition to the threshold temperature, a threshold stress level above which SMIE is more likely to occur is believed to exist.

Concerning the applicability of seam welding of titanium alloys in the aerospace industry, there are additional parameters to consider before establishing the influence of copper electrodes or copper debris on SMIE in titanium alloys. First, one must consider the influence of additional forces that could increase the tensile stress and thereby increase the susceptibility to SMIE. Secondly, cyclic forces must be considered; tests have so far only been carried out with static forces.

4. Conclusions

No cracks were found in the seam welded specimens, which could be explained by the absence of copper in the weld. However, since no cracks were found neither in the seam welded specimens sputtered with copper or gold, it can be concluded that the absence of copper was not the reason for the absence of embrittlement in the present study. Therefore, it can be concluded that the residual stresses generated by the seam welding operation itself are insufficient to induce cracks through SMIE in Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo.
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The Effect of Crystallographic Orientation on Solid Metal Induced Embrittlement of Ti-8Al-1Mo-1V in Contact with Copper

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Abstract
Solid metal induced embrittlement (SMIE) occurs when a metal experiences tensile stress and is in contact with another solid metal with a lower melting temperature. SMIE is believed to be a combined action of surface self-diffusion of the embrittling species to the crack tip and adsorption of the embrittling species at the crack tip, which weakens the crack tip region. In the present study, both SMIE of the near alpha alloy Ti-8Al-1Mo-1V in contact with copper and its influence on crystallographic orientation have been studied. U-bend specimens coated with copper were heat treated at 480°C for 8 hours. One of the cracks was examined in detail using electron backscatter diffraction technique. A preferable crack path was found along high angle grain boundaries with grains oriented close to [0001] in the crack direction; this indicates that there is a connection between the SMIE crack characteristics and the crystallographic orientation.

1. Introduction
Metal induced embrittlement (MIE) can occur when a metal experiences tensile stress and is in contact with a metal of lower melting temperature. What distinguishes MIE is that normally ductile metals become brittle in contact with metals under certain conditions [1] and that the degradation is often undetected until the catastrophic failure occurs [2]. There are two types of MIE: embrittlement that occurs above the melting temperature of the embrittling metal ($T_m$), referred to as liquid metal embrittlement, and embrittlement that occurs below $T_m$, known as solid metal induced embrittlement (SMIE) [1, 3, 4]. SMIE has been investigated in the present study.

The essential condition for SMIE to occur is intimate contact between the embrittling metal and the metal substrate [2, 4-8]. In order to promote SMIE, any oxides present must first be removed either chemically or mechanically. The service temperature and the amount of tensile stress present are also influencing parameters; below certain threshold values, SMIE is not expected to take place [1, 5, 9, 10]. The crack propagation rate of SMIE increases with increasing temperature, and is highest just below $T_m$ [4, 6, 9]. However, the severity of SMIE is also dependent on the distance between the source of the embrittling species and the crack tip. If embrittling species are present as inclusions the crack propagation rate has been found to be high [4, 7], whilst severity is expected to decrease with increasing crack length when embrittling species are present as thin films on the surface [7]. The mechanism of SMIE is believed to be a combination of surface self-diffusion of the embrittling species to the crack tip [3, 7, 11, 12] and adsorption of the embrittling species at crack tip [4, 5, 7, 11]. It is generally agreed that adsorption of the embrittling metal leads to a weakening of the crack tip, but exactly how adsorption affects the crack propagation is not fully understood. Two principal theories are: (1) chemisorption reduces the stress required for tensile separation of
the atoms at the crack tip leading to decohesion [1, 13-15], and (2) chemisorption facilitates the nucleation or egress of dislocations at the crack tip [11, 16-19].

SMIE of titanium alloys in contact with the following solid materials has been observed: silver, gold, copper and cadmium, see Table 1. In 1965 Duttweiler et al. [20] concluded that the failure of titanium compressor discs resulted from SMIE caused by silver chloride. Additional studies showed that Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V and Ti-7Al-4Mo alloys all exhibited SMIE when in contact with solid silver. Embrittlement caused by solid silver has also been studied by Stoltz and Stulen [21], who observed SMIE of Ti-6Al-6V-2Sn in contact with solid silver, gold and cadmium. Meyn [22], and Fager and Spurr [10] have reported SMIE caused by cadmium in contact with Ti-8Al-1Mo-1V, Ti-6Al-4V and Ti-3Al-14V-11Cr. Most recently however, the influence of solid copper has been studied; Liu [23] reported in 2006 that solid copper caused SMIE of Ti-6.5Al-3.5Mo-1.5Zr-0.3Si. The present work is a continuation of a previous study of SMIE in Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V in contact with copper and gold [24]. Although SMIE has been observed in previous studies, crack propagation behaviour in relation to crystallographic orientation has not been evaluated; this is the aim of the present study.

Table 1. Previous investigations of titanium alloys and embrittling species.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solid embrittling species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-5Al-2.5Sn</td>
<td>Ag [20]</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>Ag [20], Au [24] Cd [22], Cu [24]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Cd [22]</td>
</tr>
<tr>
<td>Ti-6Al-6V-2Sn</td>
<td>Ag [21], Au [21], Cd [21]</td>
</tr>
<tr>
<td>Ti-6Al-2Sn-4Zr-2Mo</td>
<td>Au [24], Cu [24]</td>
</tr>
<tr>
<td>Ti-6.5Al-3.5Mo-1.5Zr-0.3Si</td>
<td>Cu [23]</td>
</tr>
<tr>
<td>Ti-7Al-4Mo</td>
<td>Ag [20]</td>
</tr>
<tr>
<td>Ti-3Al-14V-11Cr</td>
<td>Cd [22]</td>
</tr>
</tbody>
</table>

2. Materials and Methods

A U-bend test was used to evaluate SMIE of Ti-8Al-1Mo-1V in contact with copper. The sheet material, condition and composition were in accordance with AMS4916J [25] and were statically loaded by U-bending, and then coated with 0.05-0.1 μm solid copper using sputtering technique. Specimens were subsequently heat treated at 480°C for 8 hours; details of the test method can be found in previous work [24]. Principal metallographic examination was performed in a light optical microscope at 500x magnification. The outer surface of the cross-section of the U-bend shape was examined for cracking and the locations of the observed cracks noted.

Specimens exhibiting cracking were further examined in a scanning electron microscope (SEM, LEO 1550 Gemini FEG-SEM). The cracks were studied by using backscattered electron imaging (BSE) with high contrast, which allowed the alpha and beta phases to be discriminated by compositional contrast without etching. Electron backscatter diffraction (EBSD), a characterisation technique employed in the SEM, was used to determine the local crystallographic orientation and the texture of the area of interest along the crack propagation path in a specimen. For EBSD mapping an HKL Channel-5 EBSD system with a Nordlys II detector was used. Two orientation maps were acquired at 5000x magnification with an accelerating voltage of 20 kV and a step size of 200 nm. An average noise reduction of four neighbours was applied.
3. Results
In Figure 1 a), the BSE image of a typical crack path is shown. Alpha and beta phase can clearly be discriminated by the compositional contrast as grey and white, respectively. For a better understanding of the crack propagation characteristics, EBSD measurements were performed along the crack path. To the right in Figure 1, band contrast images are shown obtained at area A and B, which clearly shows that the crack is mainly propagating along the grain boundaries.

![Figure 1. a) The typical appearance of the SMIE of Ti-8Al-1Mo-1V in contact with copper and b) the band contrast images of area A and B indicating how the crack is propagating along the grain boundaries.](image)

Two orientation maps were acquired along the crack path and in the respective inverse pole figures in Y-direction, the orientations of the grains along the crack were found to be close to [0001]. In Figure 2 a), the orientation maps given in inverse pole figure scheme are stitched together to create a map including the whole crack path. According to the inverse pole figure colour scheme given in Figure 3, the grains with the orientation close to [0001] are coloured red. In the phase map (Figure 2 b)), the alpha and the beta phases are coloured blue and red, respectively, and the orientations of the grains along the crack path represented by the unit
cell. The grain boundaries in the orientation map in Figure 2 a) are defined by the degree of misorientation ($\theta$) between two neighbouring pixels. The high-angle grain boundaries ($\theta>10^\circ$) are given as black lines while the low-angle boundaries ($3^\circ<\theta<10^\circ$) by white lines. The EBSD results indicate that the crack path is following high-angle grain boundaries and there is a tendency of the crack to propagate along [0001]-oriented grains (along Y-direction).

Figure 2. a) Orientation map in inverse pole figure colour code and b) phase map with grain orientations along the crack path represented by their respective unit cells.
4. Discussion

Metals with hcp (hexagonal close-packed) crystallographic structure such as alpha titanium (see grey phase in Figure 1), normally fracture by cleavage fracture [26]. In this study the crack growth path was found to be intergranular, which itself is a clear indication that there is an influence of an embrittling environment. The crack propagates along grain boundaries, perpendicular to the surface and loading direction, i.e. in a direction towards high stress levels. The embrittling environment in the present study was solid copper. During heat treatment in air at 480°C however, the copper layer oxidises and consequently the embrittling species closest to the titanium surface are in the form of CuO, Cu₂O, and Cu, see Figure 4. Because of the strong reducing properties of titanium, the copper oxide closest to the titanium surface is probably reduced to form titanium oxide and copper:

\[
2Cu_2O(s) + Ti(s) \rightarrow 4Cu(s) + TiO_2(s) \quad (1)
\]

Once the crack is initiated, the embrittling species is believed to be transported by surface self-diffusion to the crack tip and adsorption of the embrittling species at the crack tip weakens the crack tip region. In previous work the characteristic diffusion length of copper for 8 hours at 480°C, has been calculated to be 2300 μm [27]. Hence, the diffusion length is longer than the crack length observed in the experimental study. When comparing the
characteristic diffusion length with the experimental crack length however, one should also consider the incubation time and the fact that the experimental crack is following a serrated path making the crack much longer than what it first appears as. In addition the amount of copper available for surface self-diffusion needs to be taken into account since the presence of copper at the crack tip is crucial for crack growth to occur. The relationship between crack length and amount of copper available can be estimated using the following simple stoichiometric calculation. Assume that the crack is two-dimensional and that the copper atoms originate from a layer of copper atoms 10 μm wide (w) and 0.05 μm thick (t) at the surface. Moreover, assume that the crack wall are covered with at least five atom layers of copper, this to sustain the SMIE crack propagation rate Thus, at least ten atom layers (N) are required along our two-dimensional crack. The estimated crack length, $L_{\text{crack}}$, can then be calculated:

$$L_{\text{crack}} = \frac{wt}{Nd} = \frac{10 \times 0.05}{10 \times 0.00256} \approx 200 \mu m$$

where the diameter of a copper atom ($d$) being 0.00256 μm. Thus, with an estimated thickness of sputtered copper layer of 0.05 – 0.1 μm, the calculated stoichiometric crack length lies between 200 and 400 μm. Taking the diffusion rate and availability of copper atoms into consideration, the transport mechanism of surface self-diffusion appears to be applicable for the present results.

The mechanism of adsorption at the crack tip is complex. It is generally agreed that chemisorption of the embrittling species weakens the crack tip region, but exactly how is debatable [1, 17]. The result of this EBSD study shows that the crack propagates principally along high-angle grain boundaries, which is in agreement with theories of adsorption: the thermodynamic driving force for adsorption is the reduction in surface free energy, which is larger for high-angle grain boundaries [28]. However, when the orientation of grains along the crack path is considered, a favourable crack growth is observed along grains oriented close to [0001] in Y-direction (see Figure 2). A possible reason may be the coordination number of the bulk atoms, which influences surface energy. Along the crack there is a layer of copper and copper oxides, see Figure 5, and at the interface of the crack tip both oxygen and copper atoms bond to the titanium lattice. In the present study, several grains along the crack are oriented with (01\overline{1}0) parallel to the local crack path direction. When comparing the coordination number of bulk atoms in (0001) with (01\overline{1}0), the surface free energy of (0001) is lower because it is more densely packed. Hence, adsorption of copper is more likely to occur on (01\overline{1}0), since the driving force (potential reduction in energy) is higher. In addition, oxygen atoms are attracted to octahedral interstices in the hcp crystallographic structure, which are available in the crystallographic structure oriented (01\overline{1}0). Thus by considering the atomic configuration in (01\overline{1}0), adsorption of both copper and oxygen atoms is more likely to occur in that plane than in others such as (0001).
Figure 5. *a) Schematic illustration of the crack wall and b) the crack tip. Copper (and oxygen) enters the crack by surface self-diffusion and at the crack tip the copper atom “A” is adsorbed. The crack growth occurs under the tensile stress $\sigma$.*

Another contributing reason to favourable crack growth along grains oriented close to [0001] in the crack direction (Y) could originate in the crystallography of titanium (alpha) and copper having hcp and fcc (face-centred cubic) structure, respectively. Studies of grain boundary segregation report that some grain boundaries are more prone to the segregation than others. Partly that is explained by the orientation relationship, that grain boundaries with preferable crystallography in relation to the segregate may be able to accommodate more segregates [29]. However, the work carried out in this area is limited, and no previous work has been done in this respect regard to SMIE of titanium. When studying hcp and fcc systems, four principal orientation relationships can be predicted [30], see Figure 6, corresponding to the directions and planes in the hcp unit cell as given in Figure 7.

\[
\begin{align*}
A: & \quad [1120]_{\text{hcp}} || [110]_{\text{fcc}}, \quad (0002)_{\text{hcp}} / (111)_{\text{fcc}} \\
B: & \quad [1120]_{\text{hcp}} || [110]_{\text{fcc}}, \quad (1\bar{1}01)_{\text{hcp}} / (1\bar{1}1)_{\text{fcc}} \\
C: & \quad [10\bar{1}0]_{\text{hcp}} || [112]_{\text{fcc}}, \quad (1\bar{2}10)_{\text{hcp}} / (\bar{2}20)_{\text{fcc}} \\
D: & \quad [10\bar{1}0]_{\text{hcp}} || [112]_{\text{fcc}}, \quad (0002)_{\text{hcp}} / (1\bar{1}1)_{\text{fcc}}
\end{align*}
\]

*Figure 6. Four predicted orientation relationships between the hcp (alpha titanium) and fcc (copper) systems.*
With regard to SMIE, the orientation relationship could influence the crack path by attracting copper atoms to sites where they can adopt a structure similar to fcc. In Figure 2 b), the crack path can be found along grains oriented in the directions $[1\bar{1}0\bar{1}]$ or $[1\bar{1}20]$ relative to the crack path, with one exception in the middle of the orientation map where the crack has propagated through a low angle boundary and across another grain, both oriented with (0001) parallel to the crack direction. However, the tendency of a favourable crack growth along grains orientated in the directions $[1\bar{1}0\bar{1}]$ and $[1\bar{1}20]$ relative to the crack path corresponds well with the hcp directions listed in the orientation relationships in Figure 6. For instance, when $[1\bar{1}0\bar{1}]$ is parallel to $[112]$ and $(0002)$ is aligned with $(\overline{1}1\overline{1})$ there is an orientation relationship between the hcp and the fcc crystallographic structure. Accordingly, for that specific crystallographic orientation, the atomic misfit between hcp and fcc is low, which enables the copper atoms may adopt a structure similar to fcc. Hence, as with segregation, a certain grain boundary orientation could attract and accommodate more copper, than another resulting in a heterogeneous distribution of copper atoms and thereby the crack growth might be preferable in certain directions.

However, it is important to realise the complexity of adsorption; there are several theories that describe how the embrittling species weakens the crack tip region. The influence of adsorption on the crack tip will depend on the strength of adsorption, which in turn is dependent on several parameters, such as the surface energy and the solubility of the embrittling species in the matrix. Moreover, one should also keep in mind that the atomic bonds at the crack tip in the vicinity of atom “A” in Figure 5 b), are strained by the tensile stress $\sigma$. Therefore, when the crack advances, crack growth is a result of both local stress and weakening of atomic bonds because of adsorption; depending on their magnitudes, the crack tip may experience either decohesion or dislocation emission.
5. Conclusions
The results of the present study agree with theories of surface self-diffusion and adsorption. Based on the observations of crack propagation path in relation to crystallographic orientation, the following conclusions can be drawn:
- Cracking in SMIE propagates principally along high-angle boundaries.
- Cracks propagate preferably along [0001] oriented grains in the crack direction, indicating that additional parameters influence the SMIE crack characteristics.

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