

Precursor Events in Environmentally Assisted Cracking Behaviour of Light Metals

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Light metal alloys of Mg, Ti, and Al undergo environmentally assisted cracking (EAC). Passive film breakdown and pitting are not only precursor events for stress corrosion, but can accelerate hydrogen evolution that is responsible for hydrogen embrittlement. This is clearly demonstrated in the case of Mg and Ti alloys. The so-called innocuous precipitates, which do not directly participate in either alloy strengthening or EAC can be effective precursors for initiating EAC. This aspect is highlighted using high strength aluminium alloys. Such behaviours lead to a paradigm shift in the design of alloys with resistance to EAC.

Keywords : environmentally assisted cracking, aluminium alloys, titanium alloys and magnesium alloys

1. Introduction

Environmentally assisted cracking (EAC) robs metals and alloys of their ductility and causes failures even when loaded below 20 % of their yield strength. So it poses a serious challenge for designers to build safe, reliable and long lasting structures. Several attempts have been made to understand EAC mechanisms that comprise of stress corrosion cracking¹ and hydrogen embrittlement². It is known that EAC failures occur through initiation and growth processes. However, there seem to be several seemingly unrelated phenomena, called precursor events, which become responsible for EAC initiation. Selective dissolution, pitting and intergranular corrosion are some of them that could greatly influence EAC tendency of alloys. It is imperative to understand various precursor events those are responsible for EAC initiation in order to develop high EAC resistant alloys. This paper brings out some of the precursor events we have observed in some of the light alloys related to Mg, Ti, and Al metals.

2. Precursor Events in Mg-Alloys SCC

SCC of Mg alloys are studied in chlorides³⁻⁹, carbonates¹⁰, sulphates¹¹; and distilled water^{4,6-8}. In all these cases, the EAC mechanism has been attributed to hydrogen embrittlement³⁻⁹. However, not much work has been

carried out on factors that govern the initiation of SCC in Mg-alloys. Since cast alloys are inherently chemically heterogeneous, a wrought alloy (hot rolled alloy that was annealed at 300 - 350 °C for 30 min and then air cooled) the composition Mg-1.75Mn-0.25 Ce-0.3 RE-0.3Zn-0.1Al-0.1Si-(Fe and Cu less than 0.005, Ni is 0.007)³ was undertaken to examine this aspect. Both slow stain rate (SSRT) and constant load tests were carried out in having 0.01 M and 0.1 M NaCl solutions saturated with Mg(OH)₂. Surface examination of the failed specimens showed the SCC cracks to originate from the pits as shown in Fig. 1.

Hence, the role of pitting on SCC was analysed by measuring pit size in each of the failed and unfailed specimens of constant load test. The plot shown in Fig. 2 reveals that the pit depth has a bearing on SCC. Furthermore, the

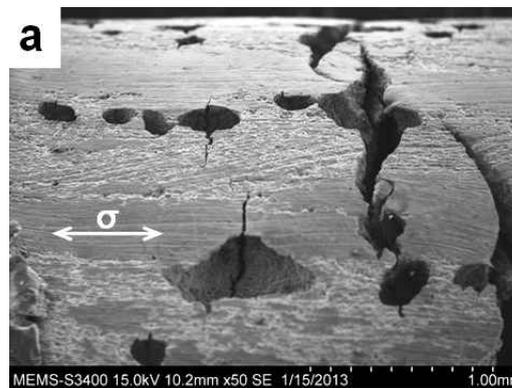


Fig. 1. Pits visible on the surface³.

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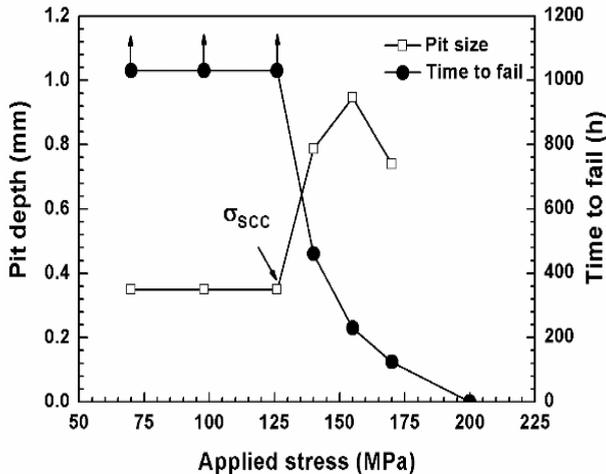


Fig. 2. The plot of pit size vs. applied stress along with time to fail vs. applied stress in CLT specimens tested in 0.1 M NaCl saturated with $Mg(OH)_2$ (Arrow indicates no failure)³.

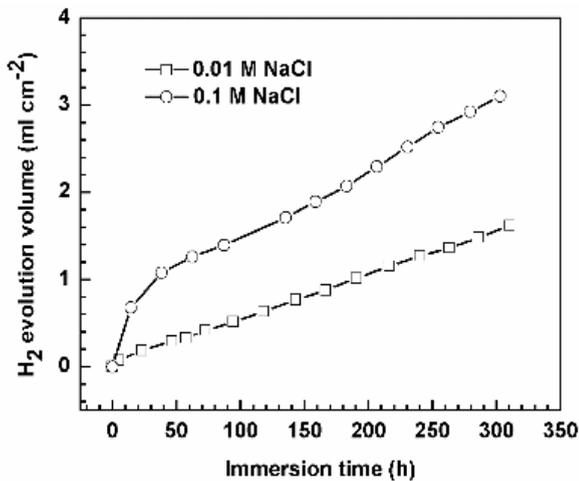


Fig. 3. Hydrogen evolution measurements for Mg-Mn alloy in 0.01 M and 0.1 M NaCl solution saturated with $Mg(OH)_2$ ³.

applied load also seems to influence the pitting tendency of the alloy. However, below the threshold stress, the pit depth remained the same. This is possibly because of the fact that the exposure duration remained the same (maximum test duration of 1000 h) in all the tests, and the pit depth is generally a time dependent phenomena. However, beyond the threshold stress the depth of the pit of the failed specimens increased with applied stress despite the fact that the time taken for failure decreased with the applied stress. An exception however, is found with respect to the last data point of the curve where the pit depth decreased with the applied stress.

The enhanced pitting tendency of the alloy above the threshold stress can be related to stress accelerated pit

growth. Stress can assist lowering repassivation tendency of the alloy, as repassivation can not only lower SCC but also enhance pit growth. The smaller pit depth exhibited by the specimen failed at the highest stress level tested can be attributed by the fact that at such very high stress levels stress concentration at the bottom of the pit can reach sufficiently large value to turn the pit into crack even if it is shorter in depth.

The role of pits in SCC of Mg-alloys in general and Mg-Mn alloys in particular seems to be more than raising the stress concentration required to turn them into cracks. Several authors have reported the influence of chlorides on SCC of Mg-alloys, which is expected to damage passive/oxide films that retard SCC and promote anodic dissolution. This may be true for several passivating alloys including stainless steels. In fact, our work also supports the fact that chlorides retard repassivation kinetics of Mg-Mn alloy³. However, what is not reported, to our knowledge, is the detrimental effect of chloride towards hydrogen embrittlement. Through a systematic study we have shown that chlorides not only accelerate pitting kinetics but also the hydrogen evolution tendency of Mg-Mn alloy. Fig. 3 is a plot of volume of hydrogen collected with time over a Mg-Mn specimen. It is clear from the figure that the hydrogen evolution kinetics is significantly enhanced with chlorides. It is known that the hydrogen evolution kinetics over film covered metallic surface is sluggish even though the thermodynamic tendency for hydrogen ion reduction may be high. Thus the role of pitting in Mg-alloys in general and Mg-Mn alloy in particular seems not only to accelerate anodic dissolution and raise stress concentration, but also make available hydrogen required to embrittle the alloy. This aspect needs to be considered as a factor that influences EAC of alloys.

3. Precursor Events in Hot Salt Stress Corrosion Cracking of IMI 834 Alloy

Most of the titanium alloys are resistant to SCC at ambient temperatures in the absence of surface defects. However, in presence of salts they are prone to hot salt stress corrosion cracking (HSSCC) at moderate temperature range prevailing in gas turbine engines. G. W. Bauer first reported HSSCC of titanium alloys in 1955, when he carried out creep test at 370 °C¹². Despite this observation and its importance in developing reliable gas turbine engines only a few studies have been carried out so far on the HSSCC of titanium alloys¹²⁻²³. As a result, the subject is less understood warranting early replacement of turbine blades. A systematic study has been carried out in our laboratory to understand HSSCC behaviour

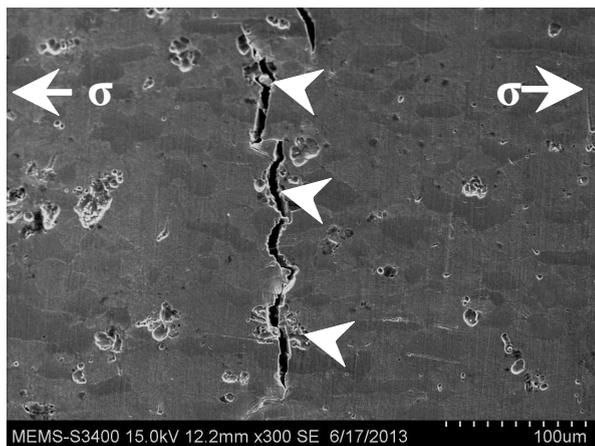


Fig. 4. Pitting beneath the salt deposits and cracking initiation associated with pits²⁴.

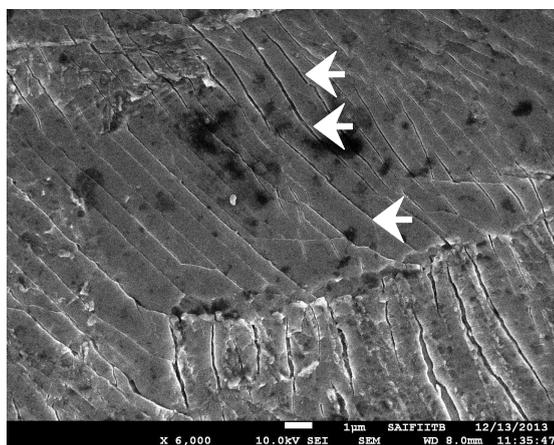


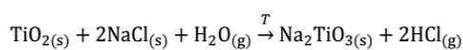
Fig. 5. Preferential attack along the slip lines (attacked slip lines indicated by arrows)²⁴.

of Ti64 (Ti-6Al-4V), Ti6242S (Ti-6Al-2Sn-4Zn-2Mo-0.1Si) and IMI 834 (Ti-5.8Al-4Sn-3.5Zn-0.5Mo-0.7Nb-0.35Si) alloys. Work related to the latter alloy is presented here.

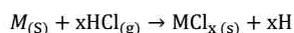
Pitting has been found to be one of the most important precursor events in HSSCC of IMI 834 alloy²⁴. In the presence of sodium chloride, IMI 834 has been found to suffer severe pitting (Fig. 4) in the temperature range of 350 °C where it becomes susceptible to HSSCC. This is in sharp contrast to the behaviour of Ti- alloys at ambient temperatures where they are found immune to pitting even at high anodic potentials; suggesting pitting tendency and SCC are intimately related. The role of chlorides is to damage protective passive/oxide film and accelerate anodic dissolution of Ti-alloys needed for SCC to occur. Pits once formed can become stress raisers and can turn into cracks depending on the pit depth and the applied stress levels.

In addition to pitting, the slip steps are also found to be potential precursor for HSSCC²⁴. From the point of view of passive film damage, slip step formation too is expected to damage the passive film and promote anodic dissolution needed for stress corrosion cracking (Fig. 5). However, it appears that mere slip step formation is not sufficient to cause HSSCC. This suggestion is born out of the fact that in the absence of salts, the alloy did not suffer HSSCC; rather it showed ductile fracture in slow strain rate tensile tests even at the temperature range where it suffered severe HSSCC. So the role of chloride is to accentuate anodic dissolution and retard passivity needed for HSSCC. Chlorides can also enhance slip according to absorption induced dislocation emission (AIDE) mechanism propounded by Lynch².

Film damage, anodic dissolution and pitting are one kind precursor responsible for SCC. However, Ti-alloys are known to be prone to hydrogen embrittlement. In the case of HSSCC of Ti-alloys, film damage and hydrogen embrittlement are seem to be intimately related to each other. Once, film gets damaged as a result of chemical reaction of salt with titanium dioxide that protects the metal, the exposed metal, active in nature, seems to react with hydrochloric acid to form atomic hydrogen. The following reaction is suggested to be damaging the protective oxide film²⁵. Through detecting sodium titanate in pits, Petersen et al. have confirmed the possibility of the occurrence of the following reaction¹².



According to Pustode et al²⁶, the formed HCl gas is expected to react with Ti and its alloying elements to generate atomic hydrogen that is required to cause hydrogen embrittlement.



where, M corresponds to Ti, Al and Sn.

A few authors have indeed showed the presence of hydrogen in Ti-alloys exposed to hot salts. However, what has not been proved is the mechanism through which hydrogen cause embrittlement. Pustode et al²⁶, based on x-ray diffraction studies have shown that hydrogen in the titanium alloys exposed to hot salts exits as titanium hydride which indeed is responsible for transgranular cleavage fracture (Fig. 6). They further showed that the length of the deepest secondary crack in slow strain rate tested specimens depends on the temperature and have reported to increase exponentially with temperature (Fig. 7). The study

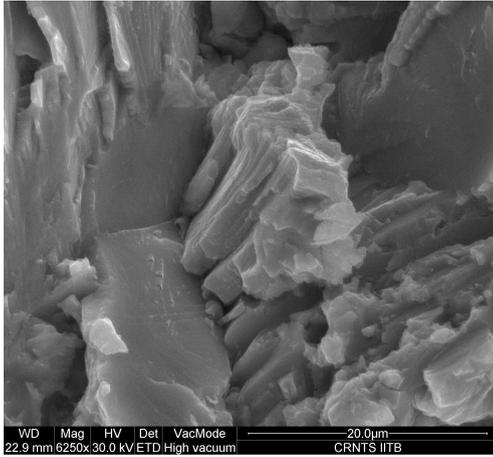


Fig. 6. Fractograph of alloy IMI 834 tested in hot salt environment showing transgranular cracking²⁶⁾.

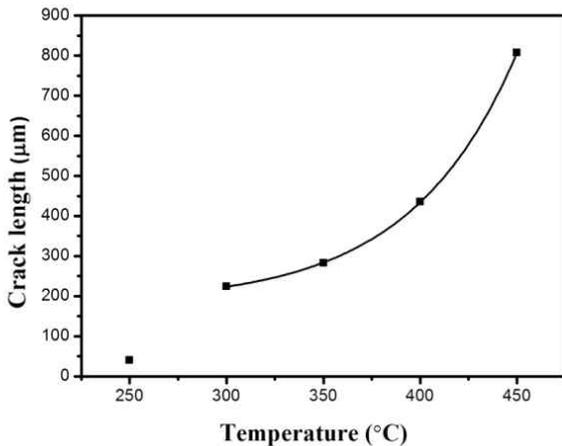


Fig. 7. Variation in the length of the deepest secondary crack of specimens with increase in test temperature in salt-coated condition²⁶⁾.

demonstrates the fact that the strategy to develop HSSCC resistant alloy must take into consideration their resistance to high temperature pitting and hydrogen embrittlement.

4. Precursor Events in EAC of AA 7010

Published literature shows dependency of EAC tendency of high strength aluminium alloys to the state of aging. Peak aging is known to cause EAC of high strength aluminium alloys. Over aging, retrogressive reaging and multistep aging are main aging treatments developed to impart EAC resistance to these alloys. These heat treatments pertain to formation fine intermetallic precipitates through solutionising and subsequent aging treatments. However, there seems to be little recognition about the detrimental role of coarse intermetallics in EAC of aluminium alloys^{27,28)}. Bobby et al²⁸⁾ have carried out a detailed

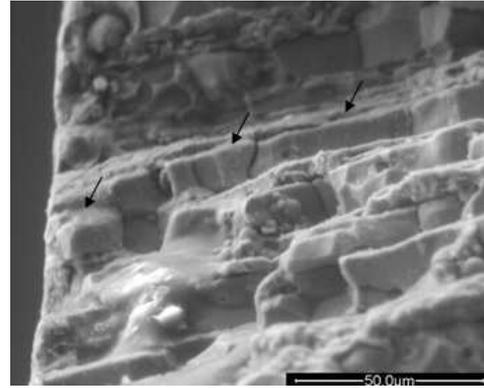


Fig. 8. No evidence of crack initiation associated with coarse intermetallic. Brittle nature of the fracture surface. Crack propagation occurs intergranularly as indicated by arrow marks²⁸⁾.

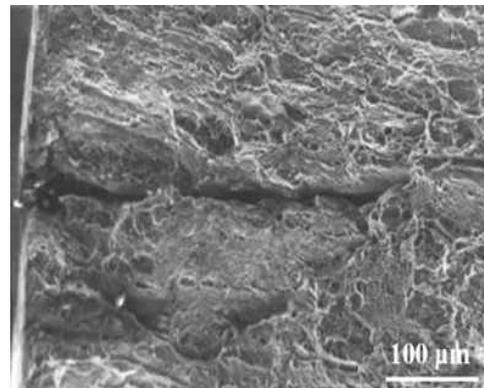


Fig. 9. SEM fractographs of over aged 7010 Al alloy failed in 3.5 % NaCl solution: edge of the fractured surface shows crack initiation to be associated with coarse intermetallic particles as indicated by arrow mark²⁸⁾.

investigation on the role of coarse intermetallics. Notably, these intermetallics did not affect EAC behaviour of AA 7010 in the peak aged condition, when examined through slow strain rate test as shown in Fig. 8.

On the contrary, in multistep aged condition, where AA 7010 has been found to be more resistant to EAC than its peak aged counterpart, the coarse intermetallic particles have been found to be the source of crack initiation as shown in Fig. 9. Possible reason for such a behavior was examined by these authors through immersion study in 3.5 wt.% NaCl solution. The study revealed the existence of galvanic corrosion between the matrix and the coarse intermetallic, the latter being cathodic in nature in relation to the matrix. This might cause film breakdown and SCC. However, there seemed to be not much difference between the two cases in terms of the nature of attack as shown in Fig. 10. Their work suggests that dealloying of spherical shaped particles and Cu enrichment on their surface, as shown by Fig. 11, can affect cracking in the following

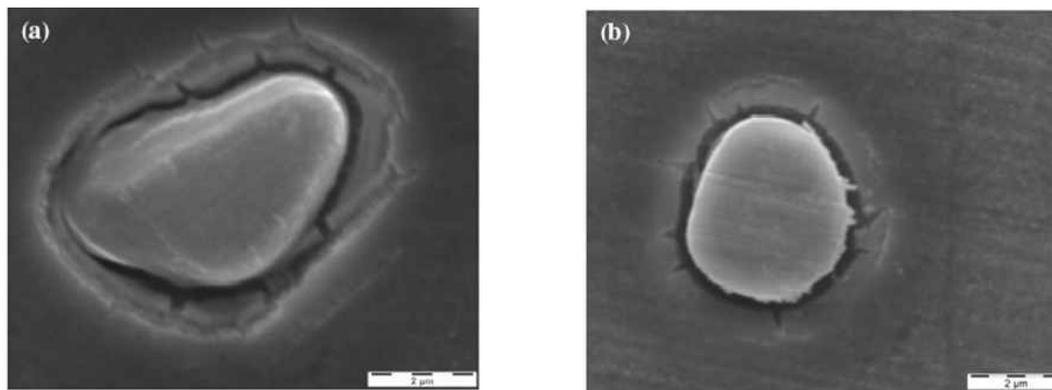


Fig. 10. SEM micrographs of (a) peak aged and (b) over aged AA 7010 specimens exposed to 3.5 wt.% NaCl solution for 10h, shows only the initiation of passive film break-down along the grain boundary²⁸⁾.

ways. The dealloyed Cu layer on the particle can induce a cleavage fracture in the particle itself. This fracture event can be responsible for the crack initiation on the alloy. The Cu rich surface of the coarse intermetallic particles could also develop high galvanic potential difference with the alloy matrix. As Cu being nobler to the precipitate, its enrichment can induce stronger film break-down in the Al-alloy matrix and thus become the cause of crack initiation in the matrix. However, the reason why the coarse intermetallics have affected the multistep-aged specimen and not the peak aged specimen lies in the fact that dealloying and galvanic corrosion are time dependent phenomena and it would take longer to have any significant influence on EAC initiation.

Since, the peak aged alloy specimens, being more prone to EAC, fails much earlier than that of the multistep-aged specimens the extent of dealloying of the coarse intermetallics and its pitting is limited to exert any significant influence

on EAC. On the other hand, the detrimental effect of coarse intermetallic is felt essentially because of the longer exposure duration the specimen in the environment. However, the coarse intermetallic can also affect even the peak aged alloy components in actual applications when the time taken for failure becomes longer.

5. Summary

Stability of passive film against pitting is an important property of light alloys to resist EAC. Pitting can accelerate EAC initiation process as pits are stress raisers. However, pitting also seems to enhance hydrogen evolution kinetics and there by enhance hydrogen embrittlement. Apparently benign phases, not considered to affect mechanical properties and EAC become responsible for EAC initiation due their electrochemical corrosion properties. The above issues need to be considered in designing EAC resistant alloys.

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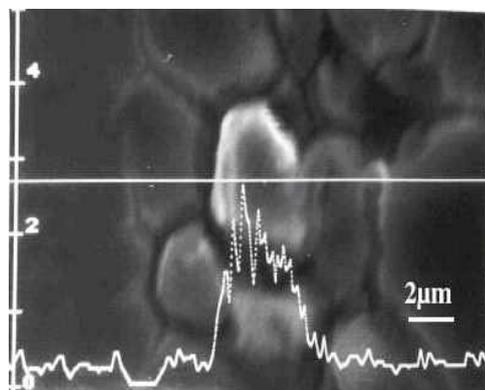


Fig. 11. Passivity break-down in the near vicinity of coarse spherical intermetallic particles of the over aged alloy. The Cu rich coarse intermetallic particles developed high galvanic potential difference with the alloy matrix, causing intergranular attack. The specimen was exposed to 3.5% NaCl solution for 24 h²⁸⁾.

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