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Role of coarse intermetallic particles on the environmentally assisted cracking behavior of peak aged and over aged Al–Zn–Mg–Cu–Zr alloy during slow strain rate testing

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Abstract Coarse intermetallic particles (larger than 1 μm in size) in Al–Zn–Mg–Cu–Zr (7010) alloy were found to significantly influence the crack initiation of the over aged alloy while not affecting the more susceptible peak aged alloy, when subjected to slow strain rate testing (SSRT) in 3.5% NaCl solution. A detailed study was undertaken to examine the causes of such an observation. The study shows that the galvanic action and/or dealloying of the coarse intermetallic particles are responsible for the crack initiation in the over aged alloy. However, this phenomenon is not seen in the peak aged alloy due to its inherent environmentally assisted cracking (EAC) susceptibility and the consequent failure in shorter duration, before the coarse particles can exert an influence.

Introduction

Environmentally assisted cracking (EAC) behavior of 7xxx series Al alloys has been researched extensively. However, most of the work has been directed toward understanding the effect of heat treatment on the EAC behavior of these alloys [1–7]. These studies clearly indicate the following:

1. Peak aging increases the EAC susceptibility of the alloy, whereas over aging improves the EAC resistance with ~10–15% loss in the peak strength [1, 2, 4].
2. Distribution and nature of fine-sized $MgZn_2$ precipitates along the grain boundary also affect EAC. Thus, coarsening and the consequent breaking of the grain boundary precipitates (GBPs) network, due to over aging, enhances the EAC resistance, as opposed to the continuously spaced fine GBPs of the peak aged alloy that promote intergranular cleavage fracture [1, 2, 4].
3. Higher Cu content in the GBPs ($MgZn_2$) of the over aged alloy makes the GBPs not only noble but also lowers their dissolution tendency [8]. Hence, both the factors i.e. coarse GBPs and higher Cu content in them enhance the EAC resistance of over aged alloy, in comparison with that of the peak aged alloy [9].

Nevertheless, in addition to the much required fine $MgZn_2$ strengthening precipitates, 7xxx series alloys also contain coarse (greater than 1 μm size) intermetallic particles. However, there have been a few studies on the role of these coarse intermetallic particles on the EAC behavior of these alloys.

Examination of the published work indicates 7xxx series Al alloys to contain different types of coarse intermetallic particles such as Al_2CuMg, Al_7Cu_2Fe and Mg_2Si [2, 3, 10, 11]. These coarse intermetallic particles with chemistries quite different from that of the matrix are expected to affect the localized corrosion such as pitting and EAC of the alloy. These particles are known to be cathodic to the matrix, hence through galvanic action, the particles can polarize the surrounding matrix and therefore can alter the latter's passive film stability and then the EAC. Not much work has been directed to understand the influence of coarse intermetallic particles on the EAC susceptibility of 7xxx series Al alloy, except by a few authors [2, 12]. Puiggali et al. [2] reported that the coarse Al_7Cu_2Fe intermetallic particles present in 7010 Al alloy suffer brittle

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fracture during slow strain rate testing (SSRT) in both air as well as chloride containing solution, whereas, Mg_2Si intermetallic particles according to them remained stable. They further reported that in chloride containing solution, the peak aged alloy undergoes crack initiation due to either the local dissolution of the alloy or brittle fracture of Al_7Cu_2Fe. Whereas, the over aged alloy undergoes crack initiation either due to brittle fracture of Al_7Cu_2Fe or transgranular cracking of matrix.

On the other hand, Najjar et al. [12] reported that the coarse intermetallic particles, such as Al_7Cu_2Fe and Al_2CuMg induce electrochemical potential gradients between the intermetallic particles and the matrix during SSRT of 7050 Al alloy in chloride containing solution, and thereby initiate crack in over aged alloy matrix. On the other hand, they indicated that the anodic dissolution of GBPs due to galvanic effect between them and the matrix are responsible for intergranular crack growth. However, these authors did not carry out any detailed study on the dissolution kinetics of coarse intermetallic particles to clarify their proposition.

Hence, a detailed study was undertaken to examine the circumstances under which the coarse intermetallic particles influence the EAC behavior in Al–Zn–Mg–Cu–Zr (7010) alloy during SSRT. For this, two different heat treated conditions of the alloy, namely, peak and over aged were chosen.

Experimental procedure

The chemical composition of 7010 Al alloy examined in the present work is shown in Table 1. The material was heat-treated to peak aging (i.e. solution treated at 465 °C, water quenched at room temperature and aged at 100 °C/8 h and 120 °C/8 h) and over aging (i.e. solution treated at 465 °C, water quenched at room temperature and aged at 100 °C/8 h followed by 120 °C/8 h and 170 °C/8 h).

For optical microscopy, samples were mounted using cold cure acrylic compound, polished with various grades of SiC papers (120–1,000 grades) and finally lap-polished with 1 μm diamond paste. Samples were then cleaned with methanol, etched with Keller's reagent (5 mL HNO_3, 3 mL HCl, 2 mL HF and 190 mL distilled water) and examined through an optical microscope. The coarse intermetallic particles were identified using scanning electron microscope (SEM) and the chemical composition was determined using Energy Dispersive X-ray analysis (EDX). SSRT was carried out at 10^{-6}/s strain rate, in 3.5% NaCl solution (continuous immersion) using a United Calibration Corporation (Model STM-20) tensile testing machine. The fracture surfaces of the failed SSRT samples were examined using SEM.

Table 1 Chemical composition (wt.%) of 7010 Al-alloy

Zn	Mg	Cu	Zr	Fe	Si	Al
6.30	2.30	1.55	0.14	0.09	0.06	Bal.

Results and discussion

Optical micrographs shown in Fig. 1a and b bring out the typical coarse intermetallic particles of peak aged and over aged 7010 Al alloy, respectively. SEM micrographs revealed that the coarse intermetallic particles exhibit two different types of morphologies, namely spherical and irregular (Fig. 2a, c). The spherical intermetallic particles were relatively higher in amount than the irregular ones. EDX spectra obtained on these coarse intermetallic particles showed that the spherical shaped particles consisted of Al, Cu, and Mg while the irregular shaped particles had Al, Cu and Fe (Fig. 2b, d). Thus, both are qualitatively different from each other with respect to Mg and Fe. It is necessary to point out the fact that the fine precipitates obtained through solution treatment followed by age

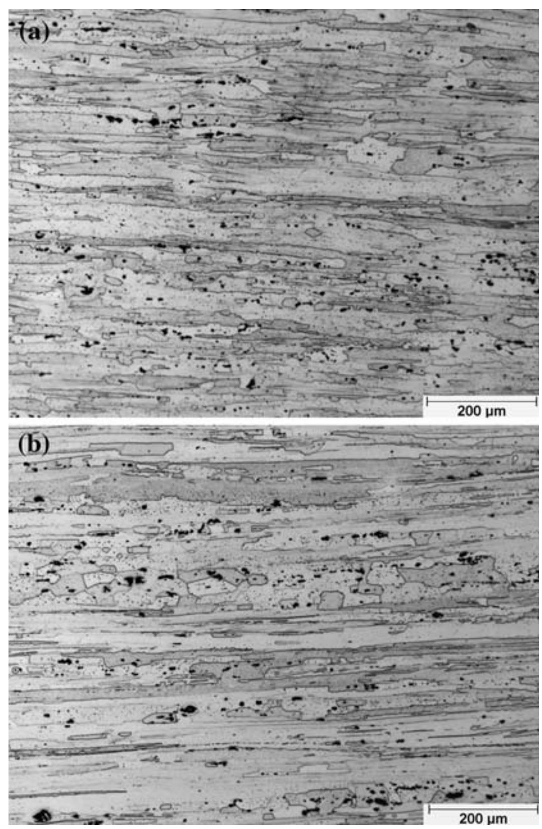

Fig. 1 Optical micrographs of 7010 Al-alloy in: (**a**) peak aged condition (**b**) and over aged condition, in short transverse direction showing coarse intermetallic particles. The dark contrast particles correspond to coarse intermetallic

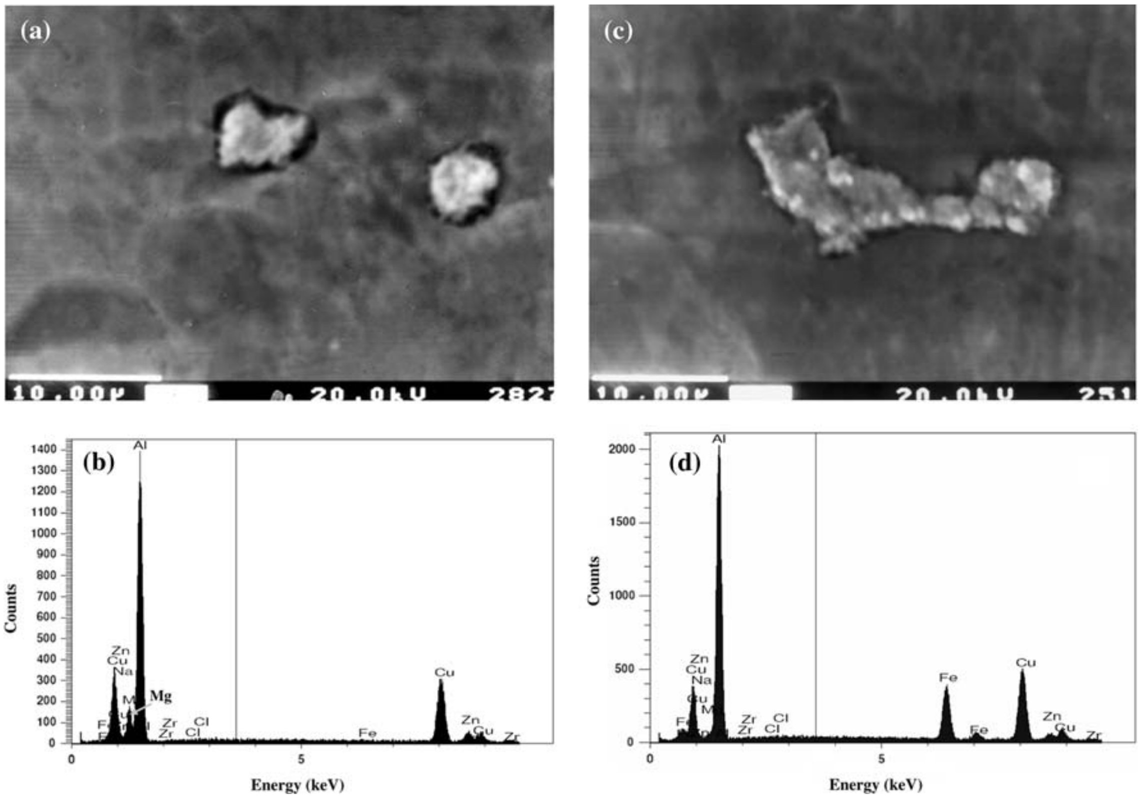

Fig. 2 SEM micrographs and EDX patterns of 7010 Al alloy obtained on spherical and irregular shaped coarse intermetallic particles: (**a**) and (**b**) correspond to SEM micrograph and EDX pattern of spherical shaped intermetallic particles respectively and (**c**) and (**d**) correspond to SEM micrograph and EDX pattern of irregular shaped intermetallic particles respectively

hardening exhibit a different chemistry ($MgZn_2$) as has been reported earlier by the authors [9].

Figure 3a and b shows the SSRT data of peak aged and over aged alloys tested in air and 3.5% NaCl solution at 10^{-6}/s strain rate [4]. As revealed by a significant increase in ductility, the over aged alloy possessed a marked increase in EAC resistance in comparison with the peak aged alloy. Yet, an examination of the fractographs of peak aged (Fig. 4) and over aged alloy (Fig. 5) shows that the spherical shaped coarse intermetallic particles influence the crack initiation of only the over aged alloy and not the peak aged alloy. It should also be noted that the irregular shaped intermetallic particles were not evident in the crack initiation sites of both peak aged and over aged alloys. However, the reason is not clear. Figure 5 shows the crack initiation of the over aged alloy associated with the spherical coarse intermetallic particles. Whereas, in the peak aged alloy, the crack initiation was not associated with coarse intermetallic particles, rather it was a brittle fracture (Fig. 4). Though such an observation was also reported in 7050 Al alloy by Najjar et al. [12] they did not investigate the reasons behind the most resistant alloy being affected by the coarse intermetallic particles. Even though the coarse intermetallic particles in the over aged alloy contributed to the crack initiation during SSRT, these particles do not seem to influence the crack growth rate probably due to the faster crack growth rate than the rate of any localized attack exerted by the coarse intermetallic particles. Hence, the over aged sample fractured predominantly by ductile mode (Fig. 5a). This is in contrast to the brittle fracture exhibited by the peak aged alloy (Fig. 4b).

The reason why coarse intermetallic particles affect crack initiation of over aged alloy and not the peak aged alloy is further examined. For this, both the peak aged and over aged alloys, in un-stretched condition, were immersed in 3.5% NaCl solution for 24 h and then viewed them in a SEM. As expected, the SEM micrographs show the coarse spherical shaped intermetallic particles caused localized attack on the alloy along the grain boundaries in their close vicinity (Fig. 6). Notably, the extent of damage to the matrix surrounding the coarse intermetallic particles seems to be almost the same in both the peak aged and over aged conditions and thus the above observation does not explain why the coarse intermetallic particles assist crack initiation only in over aged alloy.

What distinguishes the over aged alloy from the peak aged alloy is the difference in time taken to complete EAC test (to failure). High EAC resistance of the over aged alloy

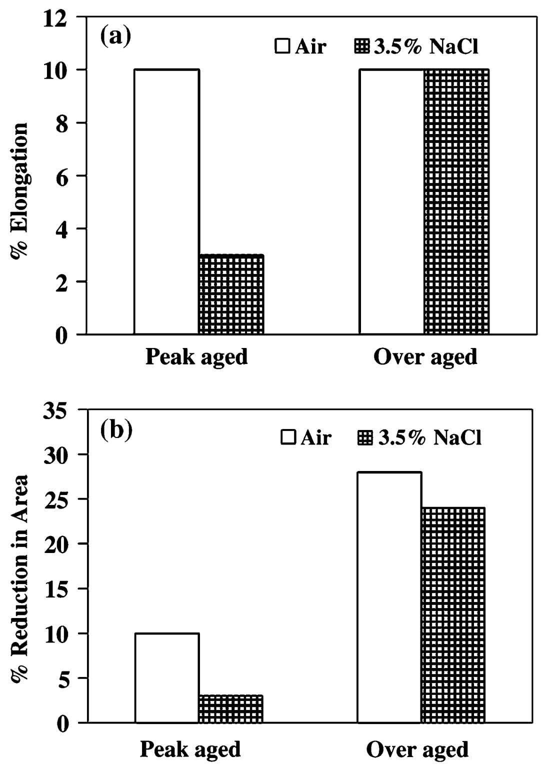

Fig. 3 SSRT data showing: (**a**) % elongation and (**b**) % reduction in area of peak aged and over aged 7010 Al-alloys obtained in air and 3.5% NaCl solution at 10^{-6}/s strain rate [4]

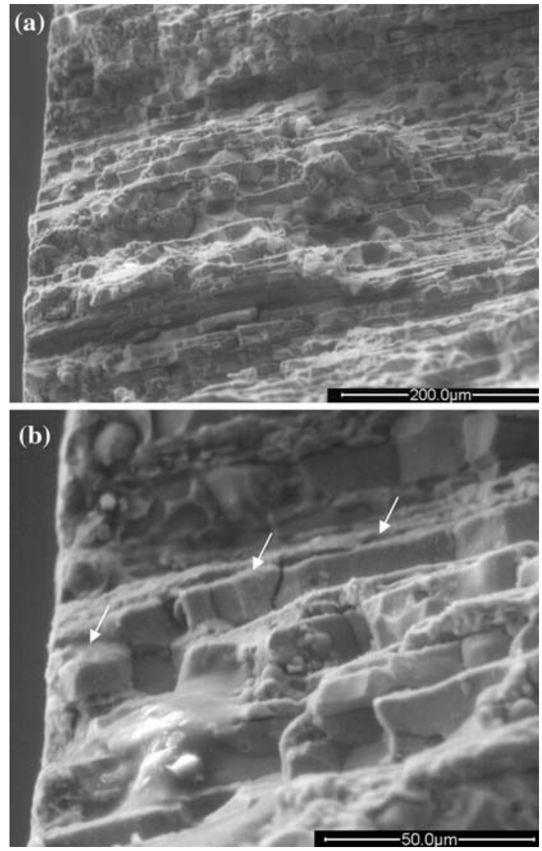

Fig. 4 SEM fractographs of peak aged 7010 Al-alloy tested in 3.5% NaCl solution: (**a**) edge of the fracture surface shows no evidence of crack initiation associated with coarse intermetallic particles and (**b**) higher magnification image reveals that the brittle nature of the fracture surface and the crack propagation to occur intergranularly as indicated by arrow marks

has automatically resulted in a much longer exposure of the sample to the environment than that is possible for the peak aged alloy. Indeed the EAC tests for peak aged alloy get completed within 10 h, while the test for over aged sample takes about 36 h to complete.

In order to examine how the alloy behaves over a shorter interval of immersion, the samples were exposed to 3.5% NaCl solution for 10 h, the duration over which the peak aged sample was exposed during SSRT before it failed. As exhibited by the Fig. 7a and b, 10 h of samples exposure causes much less film break-down than that was observed on 24 h exposed alloys (Fig. 6), though the comparison of the two micrographs shows that peak aged alloy suffered a marginally deeper attack than the over aged alloys. The time dependent processes causing film break-down and EAC are further discussed.

Wavelength Dispersive X-ray analysis (WDX) line scan of the particle and the matrix shows these intermetallic particles to contain higher Cu and undetectable Mg and Al, to those particles that had low Cu and quite detectable Al and Mg before exposure to the corrosive environment. Such a change can happen due to either or both of the following mechanism(s):

(a) Mg and Al were preferentially dissolved leaving behind the Cu [13–15]

$$\mathrm{AlCuMg_{(s)} \rightarrow Cu_{(s)} + Al^{3+}_{(l)} + Mg^{2+}_{(l)}} \tag{1}$$

and/ or

(b) Cu dissolved along with Mg and Al and Cu redeposited back on to the surface of the intermetallic particle by displacement reactions such as

$$\mathrm{3/2Al_{(s)} + Cu^{2+}_{(l)} \rightarrow Cu_{(s)} + 3/2Al^{3+}_{(l)}} \tag{2}$$

and

$$\mathrm{Mg_{(s)} + Cu^{2+}_{(l)} \rightarrow Mg^{2+}_{(l)} + Cu_{(s)}} \tag{3}$$

Coming back to the selective dealloying of spherical shaped particles, Cu enrichment on their surface can affect the following ways.

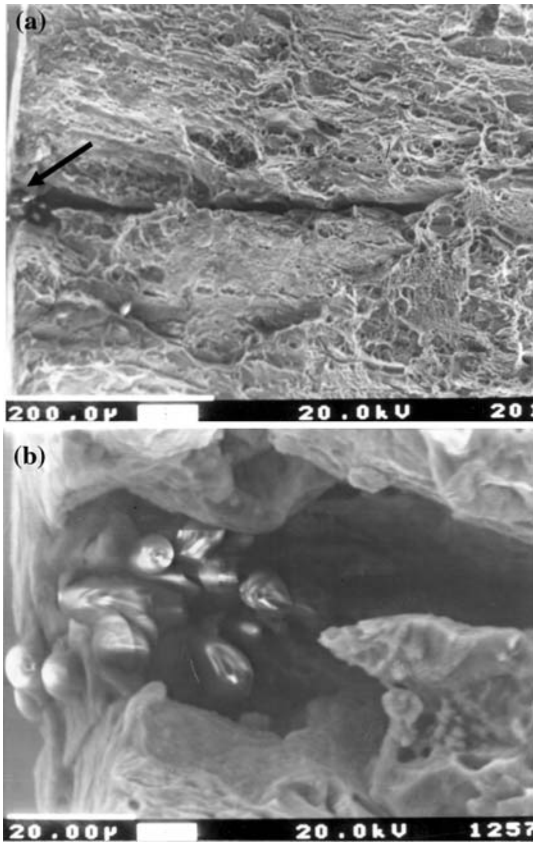

Fig. 5 SEM fractographs of over aged 7010 Al-alloy tested in 3.5% NaCl solution: (**a**) edge of the fractured surface shows crack initiation to be associated with coarse intermetallic particles as indicated by arrow mark and also reveals the ductile mode of failure and (**b**) higher magnification image reveals the presence of broken particle at the crack initiated site

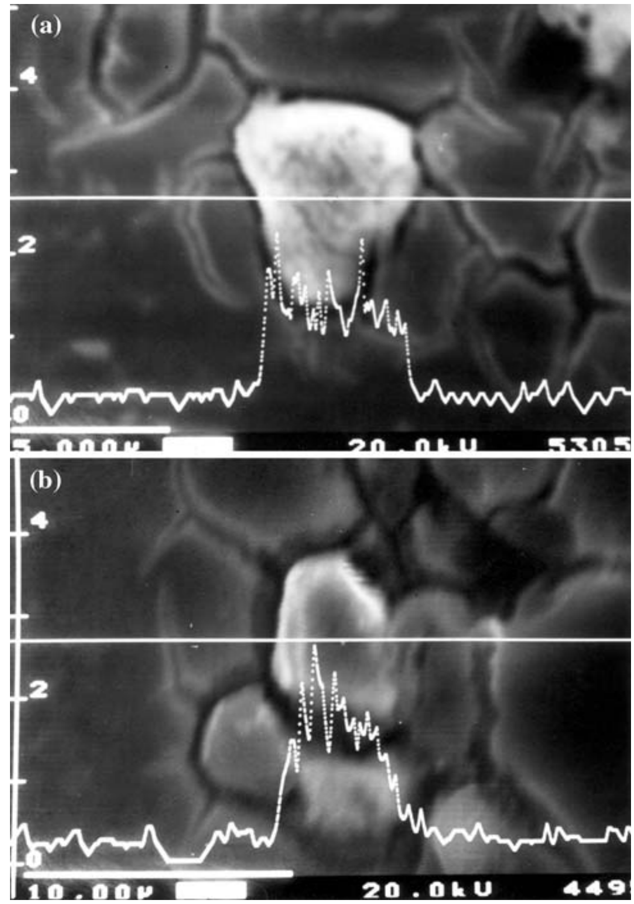

Fig. 6 SEM micrographs of 7010 Al-alloy in: (**a**) peak aged condition (**b**) over aged condition, show film break-down in the vicinity of spherical intermetallic particles, when exposed to 3.5% NaCl solution for 24 h (WDX Cu scans show the spherical intermetallic particles are rich in Cu)

1. As per Newman and his coworker's model of film-induced cleavage crack growth [16], the dealloyed Cu layer can induce a cleavage fracture in the particle itself. This fracture event can be responsible for the crack initiation on the alloy, as has been observed in Fig. 4a.
2. The Cu rich coarse intermetallic particles could also induce galvanic corrosion of the matrix. From the surface area point of view, because of the small size of the coarse intermetallic particles, though cathodic to the matrix, can be less effective in rising the electrochemical potential of the surrounding matrix. However, two factors facilitate the corrosion of the matrix. Firstly the low polarization tendency of the cathodic particle can sustain high polarization of the matrix. Secondly, the corrosion potential of the alloy matrix lies close to the break-down potential and even a small anodic polarization will result in shifting the matrix potential to transpasssive region. Film break-down can then initiate cracking in the matrix. It is necessary to point out the fact that the extent of anodic polarization of the matrix will decrease with the distance from the particles and so the effect will be localized. Also, once the nearby matrix starts dissolving actively, the so called cathodic particles can not sustain polarization of the matrix that lie away from them (due to their smaller surface area than the surrounding matrix and small potential difference between the particle and the matrix) and so even the grains close to particles don't reach their break-down/pitting potential and as a consequence do not suffer pitting.

Though it is not clear as to which of the above mechanisms is operating in the present case (study of which is beyond the scope of this work), the above mechanism(s) should be operable on both the peak aged and over aged alloy. But what makes the difference is that the dealloying is a time dependent process and therefore Cu enrichment on the intermetallic particles is expected to gradually increase with time. So the formation of dealloyed layer, a

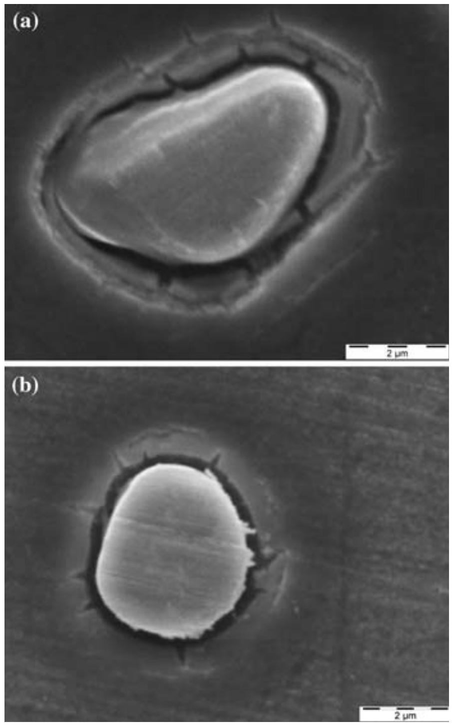

Fig. 7 SEM micrograph of (**a**) peak aged and (**b**) over aged 7010 Al-alloys exposed to 3.5% NaCl solution for 10 h, shows only the initiation of film break-down along the grain boundary

prerequisite for the operation of first mechanism and effectively induce galvanic coupling (due to high Cu content) required to operate the second mechanism is time dependent. The peak aged SSRT sample seems to have escaped from the effect of dealloying and film break-down due to their time for failure of the sample is less than the time required for the dealloying process to occur. The above factors also explain why the coarse intermetallic particles could influence only the crack initiation and not the growth process of over aged alloy. While the ductile features seen in the fractograph of the over aged alloy (Fig. 5a) is an indication of its high resistance to EAC, the absence of even any galvanic effect between the coarse intermetallic particles and the matrix (slightly away from the edge of the fracture surface) suggests that the crack growth occurred at a faster rate than the rate of galvanic coupling exerted by the coarse intermetallic particles.

Based on the above results and analysis it is possible to make a schematic representation of the mechanism(s) that led to differences in the effect of the coarse intermetallic particles on the crack initiation of peak aged and over aged alloy in 3.5% NaCl solution, when subjected to SSR testing (Fig. 8). The figures show that the coarse intermetallic particles are ineffective in influencing crack initiation in the peak aged alloy due to the time taken for failure of the

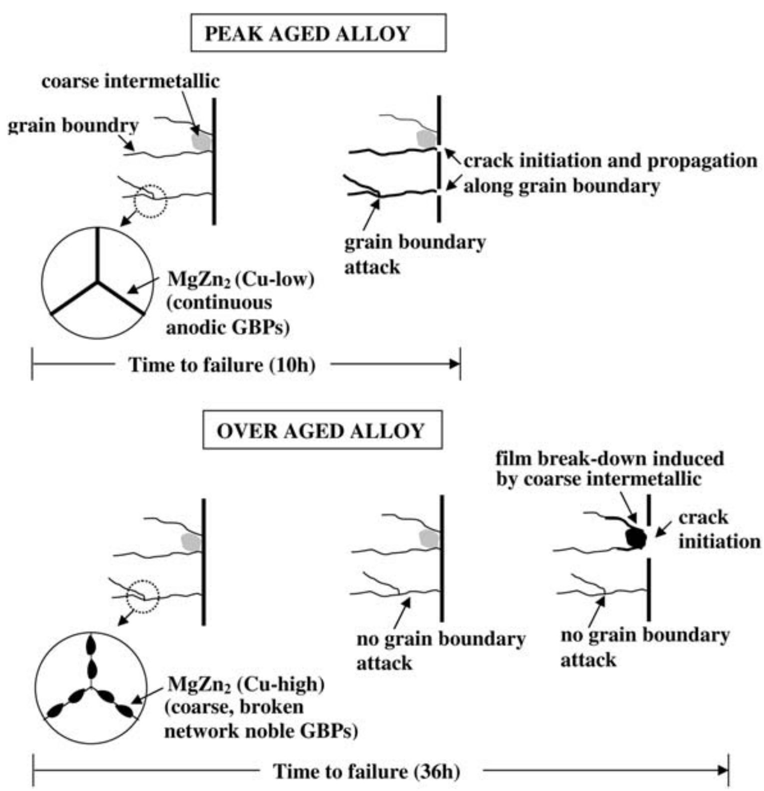

Fig. 8 A schematic diagram illustrating the involved electrochemical process and crack initiation in peak aged and over aged 7010 Al-alloys exposed to 3.5% NaCl solution. The coarse intermetallic particle influences the crack initiation only in the over aged alloy, whereas this phenomenon is not seen in the peak aged alloy due to its fast failure time

sample during SSRT is insufficient for the dealloying process to occur. Moreover, the GBPs of the peak aged alloy is highly active compared to the matrix and hence the crack initiates and propagates along GBPs dissolution path during straining the sample instead of waiting for the coarse intermetallic particles to act. It should be noted that the extent of dealloying and the pitting kinetics become sufficiently high after long intervals of exposure. Hence, the coarse intermetallic particles are able to influence the crack initiation in the over aged alloy (by virtue of its high resistance to EAC).

Conclusions

During SSRT the coarse intermetallic particles induce crack initiation only in over aged 7010 Al-alloy with no effects observed on peak aged 7010 Al-alloy. The study shows that the coarse intermetallic particles of both peak aged and over aged alloys are capable of inducing galvanic coupling and localized attack of the particle matrix interface, as suggested by Najjar et al. [12]. But this alone cannot explain as to why these particles initiate crack only in over aged alloy. The inability of the particles to induce sufficient film break-down and localized attack in the case of peak aged alloy, in spite of it having a more active GBPs than that of over aged alloy is due to the fact that peak aged samples failed much earlier than it could suffer galvanic corrosion and localized attack.

The study enables presentation of a phenomenological model to explain the observation.

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