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Hydrogen embrittlement susceptibility of over aged 7010 Al-alloy

M. Bobby Kannan · V. S. Raja

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Abstract Slow strain rate testing (SSRT) was carried out on over aged 7010 Al-alloy in laboratory air, glycerin and 3.5 wt.% NaCl solution with and without cathodic charging to study the hydrogen embrittlement susceptibility of the alloy in over aged condition. It was found that the over aged alloy exhibited high resistance to stress corrosion cracking (SCC) than hydrogen embrittlement (HE). The high SCC resistance is due to the modification in the grain boundary precipitate morphology and chemistry due to over aging, however it is suggested that the dislocations in the alloy are not completed annealed during over aging to arrest HE.

Introduction

High strength Al-alloys and in particular 7xxx series alloys suffer from environmentally assisted cracking (EAC). Over aging is a popular heat treatment which provides high EAC resistance to high strength Al-alloys in chloride environment [1–3]. However, our recent study on the stress corrosion cracking (SCC) behavior of 7010 Al-alloy, carried out using slow strain rate testing (SSRT), has shown that the ductility of the alloy in peak aged as well as in over aged conditions decreased as the strain rate was decreased from 10^{-5}/s to 10^{-6}/s even when tested in laboratory air [1]. These results when compared with the fact that in a non-corrosive inert atmosphere the ductility of Al alloys at room temperature remains essentially unchanged with decrease in strain rate [4] have led the authors to suggest that the moisture present in the laboratory air could have reduced the alloy ductility due to hydrogen embrittlement (HE) [1]. In order to examine this proposition, the authors further studied the under aged alloy, as it is more prone to HE than the peak aged and over aged alloys, in a similar condition and confirmed the above proposition [5].

HE studies are generally carried using SSRT under cathodic charged condition [6–8]. However, it is well known that cathodic polarization of Al alloys results in the accumulation of hydroxyl ions at the surface, which dissolve the passive film and then the alloy [9, 10]. Hence, for the first time, glycerin as a non corrosive inert environment was used and the test results of samples were compared to that obtained in just exposed to laboratory air [5]. It was shown that a significant loss in ductility of under aged 7010 Al-alloy occurs when tested in laboratory air containing 50% relative humidity (RH) in comparison with that of in glycerin [5]. The loss in ductility was suggested to be due to only HE for the following reasons: (i) the laboratory atmosphere contained sufficient humidity (RH ~ 50%) to cause HE (ii) the surface of the failed samples in laboratory air and glycerin were unaffected and (iii) the absence of SCC inducing chloride ions in laboratory air. Hence, the ratios of the mechanical parameters obtained from SSRT in 3.5 wt.% NaCl/laboratory air and laboratory air/glycerin represent the SCC and HE susceptibility, respectively. The behavior of the alloy towards SCC and HE is discussed based on these parameters.

Our previous studies though showed the over aged 7010 Al-alloy to exhibit much higher SCC resistance as compared to peak aged and under aged alloys, it also had a tendency of decreasing ductility with the decreasing strain rate, when tested in laboratory air [1]. This indicates a possibility of over aged alloy showing HE. In order to

M. Bobby Kannan · V. S. Raja (✉)
Corrosion Science and Engineering, Indian Institute
of Technology Bombay, Powai, Mumbai 400076, India
e-mail: vsraja@iitb.ac.in

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.

study this proposition, a detailed examination of the over aged 7010 Al-alloy is carried out. An attempt has also been made to delineate the SCC and HE susceptibility of over aged 7010 Al-alloy. For this, slow strain rate testing (SSRT) was carried out on the over aged 7010 Al-alloy in glycerin, laboratory air and with and without cathodic charging in 3.5 wt.% NaCl solution.

Experimental procedure

The chemical composition of 7010 Al-alloy examined in the present work is given in Table 1. 15 mm thick plates produced from ingots of 7010 Al-alloy were heat-treated to over aging (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). The plates were machined down to round tensile samples of dimensions as shown in Fig. 1. The samples were further polished to 1000 grade SiC paper and degreased by acetone before testing. SSRT was carried out at 10^{-6}/s strain rate, using a Universal Calibration Corporation (STM-20) tensile testing machine. The tensile properties were evaluated along the long transverse direction of the sample. Four different environmental conditions namely, laboratory air, glycerin, 3.5 wt.% NaCl solution and cathodic charging at –1500 mV (SCE) in 3.5 wt.% NaCl solution were used for the study. Representative fracture surfaces of the failed samples were examined using scanning electron microscope (SEM) to identify the mode of fracture. Specimens for transmission electron microscope (TEM) were prepared by electrolyte polishing using 30% (by volume) nitric acid and 70% methanol at –35 °C. Thin foils were examined on a PHILIPS CM 200 electron microscope. Energy Dispersive X-ray analysis (EDX) attached to TEM was used to determine the composition of grain boundary precipitates.

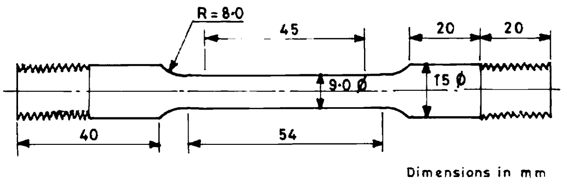

Fig. 1 Schematic diagram of the SSRT tensile sample

Table 2 SSRT data of 7010 over aged Al-alloy obtained in different environments at 10^{-6}/s strain rate

Environment	% Elongation	% Reduction in area	Ultimate tensile strength (MPa)
Laboratory air	12.0	25.0	528
Glycerin	14.0	31.2	515
3.5 wt.% NaCl	11.4	23.5	530
Cathodic charged	9.0	22.7	506

Results and discussion

Various mechanical properties of the over aged 7010 Al-alloy tested at 10^{-6}/s strain rate in laboratory air, glycerin and 3.5 wt.% NaCl solution, with and without cathodic charging, are shown in Table 2. The alloy tested in laboratory air exhibited 12% elongation (E), 25% reduction in area (RA) and 528 MPa ultimate tensile strength (UTS). However, the alloy tested in glycerin showed 14% E, 31.2% RA and 515 MPa UTS. A significant improvement in the ductility of the glycerin-tested sample in comparison with the laboratory air-tested sample is evident. The alloy showed only a marginal decrease in the ductility in 3.5 wt.% NaCl solution from that obtained in laboratory air. Thus the alloy showed 11.4% E and 23.5% RA. However, the ductility of the sample decreased significantly under cathodic charged condition. Thus the alloy exhibited 9% E and 22.7% RA. The UTS of the sample also decreased to 506 MPa under cathodic charged condition.

The SCC susceptibility index (I_{SCC}) and HE susceptibility index (I_{HE}) are determined to quantify the respective susceptibility of an alloy. Generally, they are determined based on the ratio of ductility of the alloy in corrosive environment to that of the alloy in air. For Al-alloys to become susceptible to SCC, chloride ions are necessary to be present in the environment and for HE to occur, H must be formed due to alloy environment interaction. In this study, laboratory air is considered as a corrosive environment for HE, since they contain water vapor, which can decompose and produce H on to the Al-alloy surface. The I_{SCC} and I_{HE} determined from the experimental results are shown in Table 3. The I_{HE} (value obtained laboratory air/value obtained in glycerin) shows 0.86 and 0.8 for E and

Table 3 SCC and HE susceptibility indices for 7010 Al-alloy in over aged condition

I_{SCC} and I_{HE}	Elongation	Reduction in area
I_{HE} (laboratory air/glycerin)	0.86	0.80
I_{HE} (cathodic charged/glycerin)	0.64	0.73
I_{SCC} (3.5 wt.% NaCl/laboratory air)	0.95	0.94

RA, respectively. These values show that the alloy is prone to HE. The I_{HE} calculated from cathodic charged/glycerin ratios show 0.64 and 0.73 for E and RA, respectively. Further decrease in I_{HE} in the latter case can be attributed to high HE susceptibility induced due to high H uptake of the alloy. In order to differentiate HE tendency behavior of 3.5 wt.% NaCl from that of its SCC tendency, I_{SCC} was calculated by comparing the values obtained in laboratory air. By this it is assumed that in 3.5 wt.% NaCl solution the alloy is susceptible to both HE and SCC and the difference in embrittlement tendency of the alloy between laboratory air and 3.5 wt.% NaCl environment is due to SCC. Thus the I_{SCC} values now show 0.95 and 0.94 for E and RA, respectively. It can be noted that I_{HE} value of (laboratory air/glycerin) is lesser than that of I_{SCC} (3.5 wt.% NaCl/ laboratory air). Thus, 3.5 wt.% NaCl induces only a marginal increase in embrittlement tendency further to laboratory air. This could also mean that the alloy is more prone to HE than SCC.

The fractured surfaces of the edge of the failed samples tested in glycerin, laboratory air and in 3.5 wt.% NaCl solution with and without charging are shown in Fig. 2a–d. The following observations could be made:

1. Elongated pancake shaped grains are revealed as a terrace like structure in the sample tested in glycerin environment (Fig. 2a). It should be noted that the fracture was predominantly ductile nature exhibiting intergranular microvoid coalescence (IGMVC). IGMVC of Al-alloy has been reported to be due to preferential deformation of grain boundary area due to the existence of precipitate free zone [11].
2. A mixed mode of failure exhibiting predominant transgranular microvoid coalescence (TGMVC) and

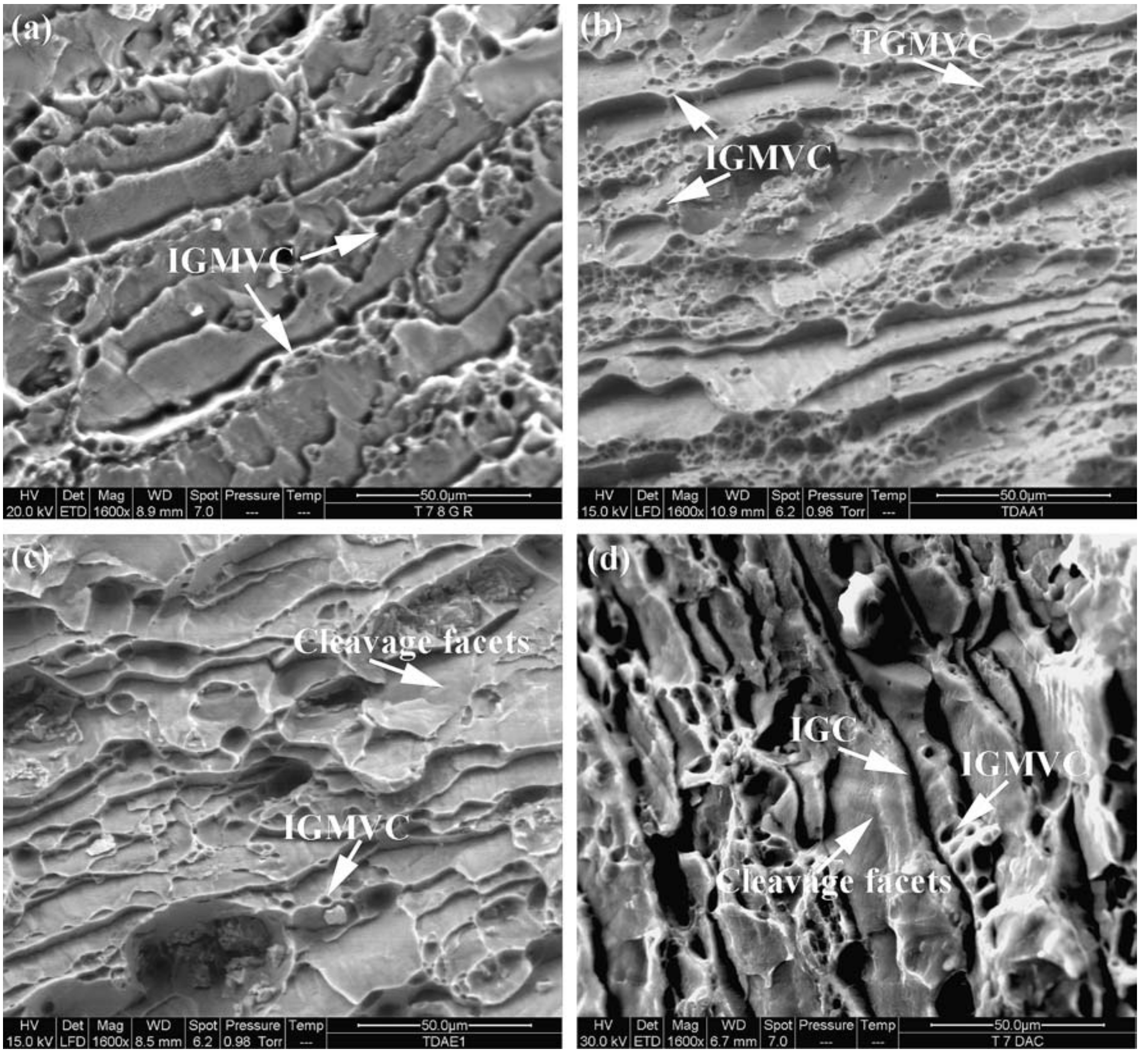

Fig. 2 SEM micrographs of the fractured 7010 over aged Al-alloy tested at 10^{-6}/s strain rate in (**a**) glycerin, (**b**) laboratory air, (**c**) 3.5 wt.% NaCl solution and (**d**) cathodically charged condition. Note: IGMVC, TGMVC and IGC indicate intergranular microvoid coalescence, transgranular microvoid coalescence and intergranular cracking, respectively

Table 4 Comparison of the mode of fracture in the under aged and over aged 7010 Al-alloy in different environments

Environment	Under aged [5]	Over aged
Glycerin	IGMVC	IGMVC
Laboratory Air	IGC + TGMVC	TGMVC + IGMVC
3.5 wt.% NaCl solution	IGC	TGC + IGMVC
Cathodic charging	—	IGC + TGC + IGMVC

Note: TGC indicates transgranular cracking

scattered IGMVC were observed in the sample freely exposed to laboratory air (Fig. 2b). The finer dimples found in this sample than in glycerin tested samples are an indication of HE susceptibility of the alloy [5, 12].

3. Fracture surface of 3.5 wt.% NaCl solution tested sample, showed mix mode of failure, exhibiting cleavage facets and a very few IGMVC (Fig. 2c). Interestingly, the predominant dimples observed in laboratory air tested samples were not evident in the 3.5 wt.% NaCl solution tested samples. It is also possible that the microvoids could have dissolved when exposed to chloride environment.
4. Under cathodic charged condition, a relatively very less IGMVC was observed as compared to the sample tested in glycerin. Instead, cleavage facets and intergranular cracking (IGC) were evident in the fracture surface (Fig. 2d). Higher hydrogen fugacity on the cathodically charged samples than on air tested sample could have caused IGC and faceted crack growth in the sample.

It is also instructive to compare the fracture modes of over aged alloy with that of the highly SCC and HE susceptible under aged alloy published in the literature [5]. Table 4 compares the fractographic features of both the alloys. While both under and over aged alloys exhibited IGMVC features in glycerin, they exhibited different features in air. Thus the former exhibited predominant IGC with a few TGMVC. However, no IGC was evident in the latter, when tested in laboratory air. Similarly, in 3.5 wt.% NaCl solution IGC was found to be prominent in the under aged alloy whereas no such feature was observed in over aged alloy.

Figure 3a, b show the TEM micrographs of 7010 Al-alloy in under aged and over aged conditions, respectively. The major micro-structural features of the over aged alloy, as observed in TEM, are the coarsening of the intra-granular precipitates and the coarsening and discontinuously spaced grain boundary precipitates compared to those in the under aged alloy. The quantitative chemical composition data of the grain boundary precipitates of under aged and over aged alloys are shown in Fig. 4. It can be noticed that the grain boundary precipitates of under aged and over aged alloys contain zinc, magnesium and copper. For the similar alloy, it has been reported that the grain boundary precipitates are $MgZn_2$ precipitates [13]. It is also well known that $MgZn_2$ precipitates are more electrochemically active than the Al matrix. However, the presence of copper in the grain boundary shifts the potential of the grain boundary precipitates towards noble direction since the electrochemical potential of copper is more noble than that of zinc and magnesium [14]. It should be noted that the amount of copper in the grain boundary of over aged alloy is higher than that of under aged alloy, which makes the former grain boundary precipitates more noble than the latter.

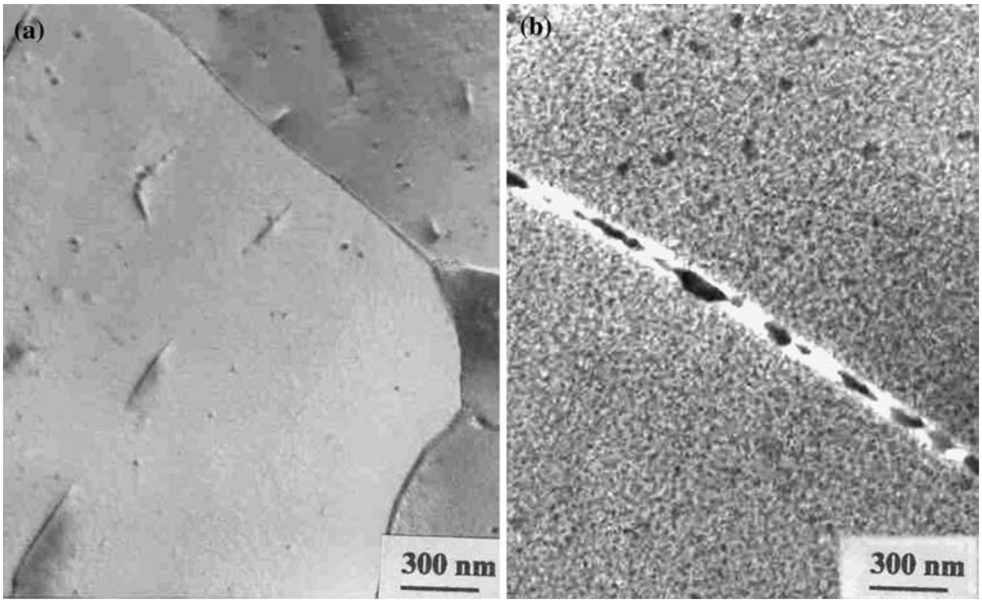

Fig. 3 TEM micrographs of 7010 Al-alloy in (**a**) under aged condition show fine continuous grain boundary precipitates [5], and (**b**) over aged condition shows coarse grain boundary precipitates

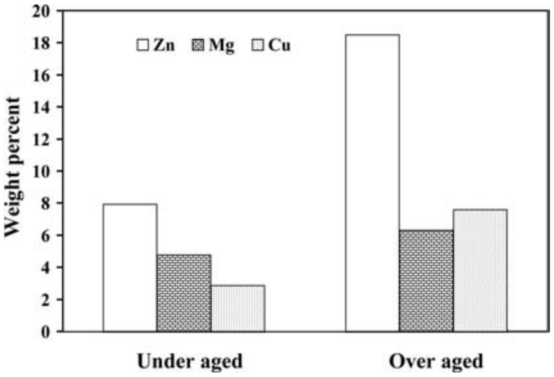

Fig. 4 Quantitative chemical composition data of the grain boundary precipitate of under aged and over aged 7010 Al-alloys

Hence, it is suggested that the continuously populated anodic precipitates observed along the grain boundary in the under aged alloy had been attributed to the occurrence of IGC, while more noble and discontinuously spaced precipitates along the grain boundary opposed IGC of the alloy. Continuously populated anodic precipitates have caused a sharp reduction in the ductility in the former. For example a reduction of 28% E and 38% RA in laboratory air and 74% E and 79% RA in 3.5 wt.% NaCl solution was observed in under aged alloy, as compared to over aged alloy in the respective environment. The precipitates otherwise did not affect the ductility of the alloy in inert atmosphere. The HE susceptibility of the alloy can be discussed as follows. HE susceptibility depends on the presence of dislocations in the alloy. The dislocations can transport hydrogen deep into the alloy and local hydrogen accumulation at the grain boundaries causes brittle failure [6, 15]. It is well known that high temperature aging such as RRA (retrogress at above 200 °C and re-aging) annihilate dislocations [16]. But in this study, it seems that the over aging temperature (172 °C) is not sufficiently enough to effectively anneal the dislocations and hence the HE susceptibility is not completely arrested. A detailed study on the presence of dislocations in the over aged alloy and SSRT experiments at different humidity level can further give an insight on HE susceptibility of the alloy.

Conclusions

Based on the SSRT results of over aged 7010 Al-alloy tested in laboratory air, glycerin and 3.5 wt.% NaCl solution with and without cathodic charging, it was found that the over aged alloy exhibited higher resistance to SCC than HE. The modification in the grain boundary precipitate morphology and chemistry due to over aging has improved the SCC resistance. However, it is suggested that the dislocations present in the alloy are not completed annealed during over aging to arrest HE.

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