Study of β precipitation and layer structure formation in Al 5083: The role of dispersoids and grain boundaries

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Abstract:

Beta (β) phase precipitation and subsequent intergranular corrosion and cracking present some of the main concerns for the usage of Al 5xxx series alloys. In this manuscript, β phase precipitation and changes in grain boundary interfacial structures are presented for Al 5083 samples sensitized at 100°C for 6 months. It was observed that β phase precipitates are formed on/near different type of dispersoids and at high angle grain boundaries. Some precipitates formed directly on the surface of Al₆Mn dispersoids, while some precipitates were detected near Al₆(Mn,Fe) dispersoids and were connected to the β phase precipitate by dislocation bands. This may suggest that dislocation bands existing between the dispersoid and β phase precipitates can act as fast paths for atom diffusion and assist the growth of the β phase. The precipitation of β phase on/near preexisting dispersoids or at boundaries is ascribed to the decrease in nucleation energy needed for heterogeneous nucleation. After sensitization, layer structures containing a high density of dislocations and distortion regions were found at the grain boundaries. The thickness of the grain boundary layer increases at grain boundaries with higher misorientation angles.

Keywords: Transmission electron microscopy; t-EBSD; β precipitation; Grain boundary layer structure; Sensitization; Al 5083 alloy

1. Introduction

5xxx series Al alloys are widely used in marine environments including naval ships, pressure vessels and aquatic hulls due to their favorable combination of strength, formability, weldability and corrosion resistance in atmospheric conditions [1-3]. The relatively high Mg content (>3 wt.%) in 5xxx

Al alloys, including 5083, provides good mechanical strength by solid solution strengthening, dispersion hardening, and/or work hardening [2]. However, this high Mg content can also cause Mg to preferentially diffuse to grain boundaries and form the β phase precipitate (Al_3Mg_2) if the alloy is exposed to elevated temperatures (typically 40-200°C) [4-8]. The β phase corrodes preferentially compared with the Al-Mg matrix in most corrosive environments, which leads to intergranular corrosion and stress corrosion cracking [9-11]. In this case, the sensitization is defined as a microstructure where β phase precipitates on grain boundaries [12]. It is generally thought that β phase precipitates in binary Al-Mg alloys are formed following the reaction [13-19]:

GP zones stand for Guinier-Preston zones; β'' is an L_{12} ordered phase (composition Al_3Mg) [20], β' is a semi-coherent hexagonal intermediate phase [19] and β is the equilibrium phase having a complex FCC structure containing 1168 atoms, space group $Fd3m$ with $a=28.239 \text{ \AA}$ [19, 21, 22].

The sensitization and resulting intergranular corrosion damage in 5xxx series Al alloys have been extensively investigated. Previous reports show that the precipitation of β phase in 5xxx alloys depends on alloy elements [4, 23], elevated temperature exposure [8, 24-26], welding [27], grain size [28], grain orientation [28] and grain boundary characteristics [29, 30]. A wealth of work has demonstrated that β phase precipitate on grain boundaries depends on the grain boundary character. The work by Davenport *et al.* [31] suggests that low angle boundaries ($<20^\circ$) do not facilitate β phase precipitation based on the observation of etched Al 5082 samples with H_3PO_4 acid. Scotto D'Antuono *et al.* [30] reports that the primary initial β phase nucleation sites during in situ Al 5456 sensitization experiments are along low-angle grain boundaries, while larger precipitates were observed at high-angle grain boundaries. Zhao *et al.* [29] has shown that the precipitation of β phase in Al 5456 depends not only on GB misorientation, but also the GB plane orientation. Our recent work has demonstrated that the

degree of β phase precipitation in Al-5.3 wt.% Mg alloy is dependent on the grain boundary misorientation angle, adjacent grain boundary planes and grain boundary types [32]. The corrosion resistance of Al-5.3 wt.% Mg alloy can be improved by optimization of special grain boundaries [32]. For the Al 5083 alloy, it has been shown that β phase precipitation preferentially occurs on grain boundaries. For example, Searles *et al.* [8] showed a continuous film of β phase on a grain boundary in Al 5083 after sensitization at 150 °C for 189 hours, which broke down to a discontinuous film after 333 hours. However, the effect of grain boundary character on the precipitation of β phase in Al 5083 needs further study. Besides the β phase precipitates at grain boundaries, the work by Goswami *et al.* [5, 7] shows that preexisting particles in Al 5083 are also preferential sites for the β phase precipitates. Zhu *et al.* [33] also reports precipitation of β phase along the grain boundaries as well as around and between preexisting particles. It has been shown that different types of dispersoids in 5xxx series Al alloys have a strong influence on the deformation behavior, recrystallization behavior and mechanical properties [12, 34, 35]. Although, it is known that β phase can form on preexisting dispersoids [5, 7, 33], the details about precipitation of β phase on different types of dispersoids and the mechanisms responsible for their formation are still not clear. The work to investigate the precipitation of β phase on different dispersoids in Al 5083 is important for understanding precipitation mechanisms, as well as for understanding the evolution of corrosion in sensitized Al alloys.

In this work, a systematic study about β precipitation on different types of dispersoids and grain boundaries of sensitized Al 5083 is presented. We focus on expanding insight into how β phase formation correlates with the type of dispersoids and with grain boundary characteristics. Changes in grain boundary structures after sensitization are also evaluated. We combine transmission electron microscopy (TEM), high resolution transmission electron microscope (HR-TEM), energy dispersive spectroscopy (EDS) analysis techniques, transmission electron backscatter diffraction (t-EBSD) and

energy loss spectroscopy (EELS) to study precipitation of β phase and changes in interfacial structures in Al 5083 after sensitization.

2. Experimental

The material used in this study was commercial H116 temper Al 5083 with nominal chemical composition (wt.%): Mg 4.5, Mn 0.65, Fe 0.20, Si 0.08, Cr 0.07, Cu 0.03, Ti 0.01 and balanced Al, which were called “as-received (AR) Al 5083.” The sensitization treatment was conducted at a temperature of 100°C for 6 months in air, and the resulting samples were called “sensitized Al 5083.” Each specimen for characterization of AR Al 5083 and sensitized Al 5083 was prepared by focused ion beam (FIB) lift-out technique using a JIB-4500 FIB (JEOL). The element distribution of each specimen was firstly scanned by JSM-7001F-LV SEM (JEOL, Peabody, MA) with EDAX Hikari detector (EDAX, Mahwah, NJ). The TEM and HR-TEM microstructural analysis was obtained using field emission transmission electron microscope (JEOL JEM-2100F) equipment operating at 200kV with imaging detectors. The EELS analysis was conducted with scanning transmission electron microscopy (STEM) mode. The crystallographic orientation of grains was determined by t-EBSD patterns obtained with a JEOL 7001F-LV SEM [36]. The crystallographic orientations of the grains were measured using orientation imaging microscopy (OIMTM), which presented the measured orientation in the form of orientations image maps.

3. Results and discussion

3.1. Element segregation

Fig .1 presents a cross-sectional bright-field TEM image and corresponding EDS elemental mapping of AR Al 5083. There are some rod shaped and equiaxed particles in the Al matrix, as shown in TEM image (**Fig.1a**). Al, Mg, Mn and Fe are detected using EDS, which is consistent with the

primary chemical composition of Al 5083. From the element mapping, it can be further identified that the rod-like and equiaxed particles are rich in Mn-Fe or Mn, which is consistent with the other reports [5]. A cross-sectional bright-field TEM image and EDS element mapping of sensitized Al 5083 are shown in **Fig.2**. It should be noted that the **Fig.1** and **Fig.2** are obtained from different locations using lift-out technique in the Al 5083 material before and after sensitization. Since the Mg concentration in Al 5083 is lower than the solubility limit [22], it is reasonable to assume that the redistribution of alloying elements occur through atom diffusion during the sensitization process. The size of rod shaped and equiaxed preexisting particles in **Fig.2** appear larger compared with **Fig.1**, which may be due to the growth of dispersoids after sensitization [37]. Compared with Mg element distribution in AR Al 5083 (**Fig.1c**), more Mg element segregation is observed. This suggests that the β phase precipitates are formed during the sensitization. A detailed analysis about β phase precipitation will be discussed in the following section.

3.2. β phase precipitation

3.2.1 β phase precipitation on dispersoids

In order to verify the precipitation of β phase on different dispersoids, the microstructure of the sensitized Al 5083 was analyzed by EDS element mapping (**Fig.2**) followed by additional TEM and HRTEM analysis (**Figs. 3 and 4**). **Fig.3** highlights TEM images near a rod shaped dispersoid, which is Mn rich. According to the EDS results and the phase diagram of the Al-Mn system [22], it is known that the Mn-rich dispersoid is Al_6Mn . **Fig.3a,b** show the bright-field TEM images of the rod shaped Al_6Mn dispersoid in Al matrix. The selected area diffraction pattern at the red dashed circle region in **Fig.3b** is indexed as the [111] zone axis of the Al_6Mn phase. A β phase precipitate is found at the end of Al_6Mn dispersoid (**Fig.3a,b**), which is confirmed by the Al-Mg phase diagram and EDS analysis as shown in

Fig.2. The difference of image contrast and diffraction pattern of β phase with the Al matrix in the TEM is also helpful for the phase determination. **Fig.3c** is the dark-field image taken with the (11-2) reflection of rod like dispersoid, which further confirms the existence of an Al_6Mn phase. **Fig.3d** shows the dark-field image obtained by an Al reflection, which corresponds to the adjacent Al matrix grain. **Fig.3e** presents the HR-TEM image of Al_6Mn structure and the corresponding fast Fourier transform (FFT) pattern. It has been reported that the Al_6Mn phase has an orthorhombic crystal structure, with lattice parameters of $a=6.4978\text{\AA}$, $b=7.5518\text{\AA}$, $c=8.8703\text{\AA}$ and space group of *Cmcm* [22, 38]. Inset (**Fig.3e**) shows the simulated atomic arrangements viewed from the [111] zone axis of the Al_6Mn phase using these lattice parameters. **Fig.3f** shows a HR-TEM image and corresponding FFT pattern of β phase precipitated on an Al_6Mn dispersoid.

Besides the Mn-rich dispersoids, there are some dispersoids rich in both Mn and Fe elements. **Fig.4a** presents a bright-field TEM image of a Mn-Fe rich dispersoid. The inset is the diffraction pattern, which is indexed as the [210] zone axis of $\text{Al}_6(\text{Mn,Fe})$ phase. This result is consistent with the other reports, which have shown that $\text{Al}_6(\text{Mn,Fe})$ dispersoids are an important type of intermetallic in 5xxx Al alloys [12, 35]. TEM was used to check the area around the $\text{Al}_6(\text{Mn,Fe})$ particle; no evidence of direct precipitation of β phase on the $\text{Al}_6(\text{Mn,Fe})$ dispersoid was detected. A β phase precipitate is observed near the $\text{Al}_6(\text{Mn,Fe})$ particle, as shown in **Fig.4b**. There are dislocation bands which connect the β phase precipitate and the $\text{Al}_6(\text{Mn,Fe})$ dispersoid. It seems there is a transition region that exists between the dislocations and the precipitate. This could suggest that pipe diffusion through dislocations is contributing to the nucleation and growth of the β phase. **Fig.4c** shows the HR-TEM image at the edge of $\text{Al}_6(\text{Mn,Fe})$ dispersoid which suggest its growth during the sensitization process. In order to clarify the atomic arrangements of the $\text{Al}_6(\text{Mn,Fe})$ dispersoid, a HR-TEM image is shown in **Fig.4d**, which is zoomed in on the white dashed rectangular area of **Fig.4c**. It is thought that $\text{Al}_6(\text{Mn,Fe})$ has an

orthorhombic crystal structure with lattice parameters $a=7.498 \text{ \AA}$, $b=6.495 \text{ \AA}$ and $c=8.837 \text{ \AA}$ [39]. Inset of **Fig.4d** and **Fig.4e** are the simulated atomic arrangements with the parameters viewed from [210] zone axis and the corresponding FFT pattern. **Fig.4f** is the HR-TEM and corresponding FFT of the β precipitate near the $\text{Al}_6(\text{Mn,Fe})$ dispersoid .

These results indicate that β phase precipitates tend to form on Al_6Mn dispersoids, which suggests that the heterogeneous nucleation on Al_6Mn has a lower free energy barrier than homogeneous nucleation. This observation is consistent with the estimated change of the chemical free energy for β precipitation from the supersaturated solid solution of Al-3.5wt% Mg, in which it has been shown that the free energy barrier to nucleation of β precipitation for homogeneous nucleation is higher than that for heterogeneous nucleation [5]. Furthermore, by following nucleation theory [40] , one can observed that the free energy of formation of a static critical nucleus for homogeneous nucleation (ΔG_v^*) is higher than the energy for heterogeneous nucleation (ΔG_v^{**});

$$\Delta G_v^* = 16\pi\gamma^3 / 3\Delta G_v^2 \quad (1)$$

$$\Delta G_v^{**} = 16\pi\gamma^3 f(\theta) / 3\Delta G_v^2 \quad (2)$$

where γ is the surface energies of the nucleus, ΔG_v is volume free energy change, θ is nucleus contact angle, $f(\theta) = (2 - 3\cos\theta + \cos^3\theta) / 4$ and varies in value between 0 and 1. It is also observed that β phase precipitates form near $\text{Al}_6(\text{Mn,Fe})$ dispersoids connected by dislocation bands. This indicates that dislocations can assist in the nucleation and growth of β phase precipitates. The main effect of dislocations on precipitation can be explained by the reduction of the free energy barrier to nucleation by reducing the total strain energy of the embryo [41]. The dislocations can accelerate the growth of the embryo by providing a diffusion pipe, which can enhance the diffusivity at low temperature by several orders of magnitude [42, 43]. The dislocation bands existing between the dispersoid and the β phase can

act as fast paths for diffusing atoms and assist the growth of the β phase, since the disorder in the core region effectively lowers the activation energy for diffusion [44]. This is consistent with other work, which has demonstrated that dislocations can strongly influence precipitation in Al 7075 alloy [45].

3.2.2 β phase precipitation at grain boundaries

Besides the nucleation on/near dispersoids, some β phase precipitates are observed at grain boundaries. **Fig.5a** illustrates a typical TEM image of β phase precipitates at a grain boundary as highlighted by the white arrows. **Fig.5b** is the corresponding t-EBSD image, from which the grain boundary misorientation angles can be obtained. It is shown that the β phase precipitates are only formed at the high angle grain boundaries, while no β phase precipitates are observed at low angle grain boundaries. **Fig.5c,d** are HR-TEM images of the area of **Fig.5a**, which exhibits discrete β -phase at high angle grain boundary. The driving force for precipitation is proportional to the reduction in the Gibbs free energy, ΔG , and can be expressed as follows[46]:

$$\Delta G = \Delta G_s + \Delta G_\varepsilon + \Delta G_\phi \quad (3)$$

where ΔG_s is the surface free energy term, ΔG_ε is the strain energy term, and ΔG_ϕ is the chemical free energy change. It has been reported that the grain boundary energy and mobility of grain boundaries increase as the misorientation angle increases from 2° to 15° , and after this stage the grain boundary energy is almost independent of the misorientation angle in Al alloys [47-49]. It is reasonable to deduce that the β phase tends to form at high angle grain boundaries, which have higher grain boundary energy. This is consistent with previous corrosion studies on Al-Mg5.3wt.% alloy, in which it was found that low angle grain boundaries with misorientation angles ($\leq 15^\circ$) show lower vulnerability to acid attack and high angle grain boundaries with large misorientation angles ($>15^\circ$) are more vulnerable to acid attack [32].

3.3. Layer structures formation in grain boundaries

During our extensive TEM studies, a transition region was observed between grain boundaries in the sensitized Al 5083 as shown in **Fig.6**. This transition region is referred to as a “layer structure” in this paper. To our knowledge, there are no previous published reports about this layer structure formation in Al 5xxx alloys during sensitization. Since grain boundary interfacial structures have strong influence on the mechanical properties, the coarsening process and stress corrosion properties of metals or alloys, we explored this layer structure further [50-52]. **Fig.6** presents typical TEM images showing the layer structure at a low angle grain boundary in sensitized Al 5083. **Fig.6a** is a bright-field image in which the grain B is tilted with a $[110]$ zone axis. The inset shows the diffraction pattern, which exhibits a typical FCC structure. **Fig.6b** is the dark-field image with the grain illuminated using the $[002]$ reflection. **Fig.6c** presents a HR-TEM image of layer structures at a grain boundary with misorientation angle of 7.3° between grain A and grain B. The inset in **Fig.6c** shows the FFT pattern indexed as the FCC structure. **Figs.6d,e** highlight the interface between the layer structure and two adjacent grains (grain A and grain B). **Fig.6f** is the inverse FFT pattern obtained from the highlighted rectangular area of layer structure in **Fig.6c**. It is observed that misfit dislocations are present and the cores of these dislocations are highlighted by the symbol “ $\perp$ ”. Bent atoms were also detected, which are evidence of distortion regions in the layer structure. It is interesting to note that the atoms of the layer structures fit complementarily with those of grain B. While atoms of the layer structures do not fit with atoms of grain A. According to the corresponding FFT pattern in the $[011]$ zone axis, it is shown that the $(1-11)$ atomic plane is parallel to the $(1-11)$ atomic plane of grain B. This phenomenon may be related to the formation mechanism regarding the layer structures. It is thought that a grain boundary represents a deviation from an atomic periodicity and the interfacial phase can be depicted as a transition lattice, which can be envisioned as an array as dislocations [46]. The formation of layer structures containing a high density

of dislocations may be related to the thermal atomic diffusion during grain growth. The growth rate of the adjacent grain is different due to the anisotropy, which may lead to the formation of misfit dislocations and distortion regions in layer structures [46].

In order to verify whether there is element segregation caused by the formation of layer structures, the element distribution across the grain boundary layer structure was analyzed by EELS. **Fig.7a** is an annular dark field (ADF) image showing layer structures near a grain boundary region, and the Mg and Al element maps of the white dashed rectangle area (spectrum image) based on the EELS core-loss spectrum. The regions that are Mg-rich appear dark, whereas regions that are enriched in Al appear white, as shown in the Mg and Al element maps. The relative Mg intensity change is shown in **Fig.7b**, which suggests that there is no difference in the ratio of Mg and Al within the layer structure compared to the interior grain. Within the technique resolution, no element segregation can be observed from the Mg map or Al map, which suggest that there is no chemical difference between the layer region and the interior grain region [29].

To further investigate the relationship between grain boundary character and grain boundary layer structures, TEM (**Fig.8a**) and t-EBSD (**Fig.8b**) analysis are used. Different grain boundaries containing layer structures are labeled from GB1 to GB12. **Table 1** lists these grain boundary characters and corresponding layer thickness. We found that the layer structures can form at both low angle grain boundaries and high angle grain boundaries. No layer structures are observed at the high angle grain boundaries where beta phase precipitates formed. It is interesting that the layer thickness increases as the grain boundary misorientation angle increases from 2° to 25° , as shown in **Fig.8c**. This can be explained by the change of grain boundary energy with changing grain boundary misorientation angles. As previously discussed, the formation of grain boundary layer structures is ascribed to thermal atomic diffusion during the sensitization process. It is expected that the high angle grain boundaries with higher

energy are beneficial for atomic diffusion, which leads to fast growth of the layer structure. Overall, this study shows that β phase precipitates form on/near dispersoids or at the grain boundaries, meanwhile layer structures form in the grain boundaries during sensitization. These changes before and after sensitization of Al 5083 alloy are depicted by a schematic illustration as shown in **Fig.9**.

4. Conclusions

In this study, β phase precipitation and changes in the grain boundary interfacial structure of an Al 5083 alloy during sensitization have been investigated. The β phase precipitates form on/near different types of dispersoids and high angle grain boundaries. β phase precipitates are observed directly on the surface of Al_6Mn dispersoids. Precipitates are also observed near $\text{Al}_6(\text{Mn,Fe})$ dispersoids, which are connected to the β phase by dislocation bands. In addition to β phase precipitates, it was observed that layer structures formed at the grain boundaries of the sensitized Al samples. The layer structures can form at low angle or high angle grain boundaries. However, it is interesting that no layer structures were observed at the high angle grain boundaries where beta phase precipitates were found. The layer structures contain a high density of dislocations and distortion regions. The TEM and t-EBSD results showed that the thickness of layer structures increases with grain boundary misorientation angle. The formation of layer structures may be ascribed to the thermal atomic diffusion during sensitization, which induces dislocations and distortion regions in grain boundaries. The overall results expand our current knowledge of β phase precipitation and the evolution of grain boundary interfaces during sensitization of Al alloys which can allow for future tailored and improved microstructures.

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Table 1 Grain boundary characters and corresponding grain boundary layer thickness

Grain boundary ID	Mis-orientation angle / $^{\circ}$	Misorientation axis	Grain boundary orientations- GB1	Grain boundary orientations- GB2	Layer thickness /nm
GB1	7.3	10 8 9	-7 6 1	1 0 1	16.5
GB2	4.8	14 1 12	-22 -1 22	-16 -1 15	6.8
GB3	20.1	16 6 11	-1 10 -22	1 7 2	23.8
GB4	3.2	1 8 20	-23 21 4	12 1 11	1.7
GB5	3.3	6 12 13	-1 -8 7	13 2 12	4.7
GB6	7.6	19 15 15	-1 -7 6	-1 -6 6	2.9
GB7	12.6	12 13 9	6 1 7	-17 15 2	4.0
GB8	22.9	1 -24 -18	-22 15 3	2 -13 -21	12.2
GB9	4.0	2 17 16	1 -7 -12	2 -11 -18	3.3
GB10	6.0	1 19 23	1 -6 -10	2 -13 22	4.5
GB11	4.0	9 11 26	1 -6 -9	-23 15 1	3.4
GB12	13.8	21 20 0	1 -8 -14	-22 15 1	10.0

Fig.1. (a) Cross-sectional bright-field TEM image and EDS element mapping of AR Al 5083: (b)Al; (c)Mg; (d) Mn; (e)Fe.

Fig.2 (a) Cross-sectional bright-field TEM image and EDS element mapping of sensitized Al5083: (b)Al; (c)Mg; (d)Mn; (e)Fe.

Fig.3. TEM images of the Al_6Mn dispersoid and β phase in sensitized Al 5083. (a),(b) Bright-field TEM images showing the β phase formed on Al_6Mn dispersoid (Inset is the diffraction pattern); (c) Dark-field image of Al_6Mn taken using the (11-2) phase reflection. (d) Dark-field image taken using the Al matrix reflection. (e)HR-TEM image of Al_6Mn dispersoid (insets are FFT pattern and simulated atomic arrangements). (f) HR-TEM image of β phase (inset is FFT pattern).

Fig. 4 TEM images of $\text{Al}_6(\text{Mn,Fe})$ dispersoid and β phase in sensitized Al 5083. (a),(b) Bright-field TEM images showing $\text{Al}_6(\text{Mn,Fe})$ dispersoid and the β phase near $\text{Al}_6(\text{Mn,Fe})$ dispersoid (Inset is the diffraction pattern); (c) HR-TEM at the edge of $\text{Al}_6(\text{Mn,Fe})$ dispersoid. (d) HR-TEM image showing the $\text{Al}_6(\text{Mn,Fe})$ and the simulated atomic arrangements. (e) FFT pattern from image (d); (f) HR-TEM image of β phase (inset is FFT pattern).

Fig.5. TEM images of β phase at a high angle grain boundary: (a) Bright-field TEM and (b) corresponding t-EBSD of sensitized Al 5083, (c),(d) HR-TEM image showing discrete precipitated β phase at high angle grain boundary.

Fig.6. TEM images showing the layer structure formed in the low angle grain boundaries in sensitized Al 5083:(a) Bright-field image with [110] zone axes; (b) dark-field image taken using the [002] Al reflection; (c),(d),(e) HR-TEM image of layer structure and adjacent grains (insets are the corresponding FFT pattern); (f) Inverse FFT image of layer structure marked by the white dashed rectangle area in (c) , the inset is the reflection used to make inverse FFT image.

Fig.7 (a) ADF image showing layer structure near a grain boundary region. Mg and Al composition maps of the dashed rectangle area were obtained by EELS. (b) Relative Mg content (%) calculated using Mg and Al intensity.

Fig.8. (a) Merged bright-field TEM and (b) corresponding t-EBSD image of sensitized Al 5083; (c) Thickness of layer structure with different misorientation angles.

Fig.9 A schematic illustration depicting the formation of precipitates and change of interfacial structures in grain boundaries (a) before and (b) after sensitization of Al 5083 alloy (under the same scale).