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ALUMINUM ALLOYS: DEVELOPMENT, CHARACTERIZATION AND APPLICATIONS

Precipitation Behaviors

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EFFECTS OF DIFFERENT TEMPER AND AGING TEMPERATURE ON THE PRECIPITATION BEHAVIOR OF Al 5xxx ALLOY

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Keywords: EBSD, Temper, Al 5xxx alloy, Intergranular precipitates

Abstract

Al 5xxx alloys can become sensitized to intergranular corrosion (IGC) and stress corrosion cracking (SCC) because of the precipitation of intergranular β phase (Al_3Mg_2) when exposed to elevated temperature for sufficient time. In this study, ASTM G67 mass loss tests of Al 5083 H131, H116 and Al 5456 H116 aged at 323 K and 343 K for different times were conducted. The average grain size and grain boundary thickness of the three alloys were obtained from Electron Backscattered Diffraction (EBSD) images, and the classical nucleation theory was used to predict the precipitation behavior. Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDS) were used to characterize Al 5083 H116 aged at different temperature for different times. Scanning Electron Microscopy (SEM) images of Al 5083 H131 etched for different times were used to evaluate the corrosion behavior of different grain boundaries.

Introduction

Al 5xxx alloys are important commercial alloys for their wide application in transportation industries[1] as well as in marine structures[2]. Al 5083 and 5456 alloys are widely used to build ships and offshore structures for their high specific strength, excellent ductility, as well as good corrosion resistance in marine environments[3]. Mg concentration of Al 5083 and 5456 alloys are 4.85 wt.% and 5.25 wt.% respectively [4, 5]. Mg is supersaturated at these levels and will precipitate at dislocations, pre-existing particles, and grain boundaries when exposed to elevated temperature for a relatively long time[4,6]. Precipitates (β' phase, Al_3Mg_2 (hcp), and β phase, Al_3Mg_2 (fcc)) formed at grain boundaries are anodic relative to the grain matrix, and intergranulr corrosion (IGC) and stress corrosion cracking (SCC) will be resulted when exposed to seawater or other corrosive environment[7, 8]. Based on previous research[9 - 11], the precipitation sequence in Al-Mg alloys has been found to be:

Supersaturated solid solution →GP zones→β''→β'→β (Al_3Mg_2)

Recently, a large amount of TEM work has been done to determine the precipitation behavior and mechanism of β phase formation in Al 5xxx alloys. Goswami *et al.*[6] found that, discrete β phase formed at grain boundaries of Al 5083 alloy after aging at 448 K for 1 hour, and β phase became continuous when the aging time increased to 240 hours. Moreover, they showed that pipe diffusion through dislocation networks can be used to explain the rapid thickening rate of β phase at grain boundaries. Yi *et al.* [12] examined intergranular β phase formed in Al 5456 H116 aged at 343 K for 30 months, and in a navy ship sample (Al 5456 H116) exposed to outdoor temperatures for over 10 years using TEM. Their results revealed that continuity of intergranular β phase plays a critical role in the sensitization of Al 5456 alloy. Zhu. *et al.*[4] found that β phase formed at grain boundaries as well as on pre-existing Mn-Fe-Cr particles when Al 5083-H131 alloy was aged at 448 K for 15 days. Based on a collector plate mechanism, capillarity effect and solute mass balance, Yi *et al.* [13] developed a model to predict β phase growth at the grain boundary of Al 5083 alloy.

Although significant research has been done to characterize the precipitation behavior of β phase in Al 5xxx alloy, most of these research are mainly focused on the general response of β phase formation, structure of β' or β phase, as well as nucleation sites of β phase. The aim of this study is to determine the effect of different temper on the precipitation behavior of β phase. In addition, the effect of temperature on β phase precipitation will also be studied.

Experimental Procedures

For this study, the Al 5083 (H131 and H116) and Al 5456 (H116) alloys provided by Alcoa, were cut into cubes and cuboids. Subsequently, these samples were aged at 343 K and 323 K for 1, 1.5, 2, 3, 6, 9, 12, 24 and 30 months. ASTM-G67 mass loss testing was then conducted to evaluate the sensitization degree of the alloy.

TEM was used to characterize the microstructure of 5083-H116 alloys aging at 323 K and 343 K for different times. The characterization was performed using a Hitachi HF 3300 S/TEM (200/300 kV) and JEOL 2200FS (200 kV) TEM. EDS quantification was performed using the Cliff-Lorimer quantification routine built into the Bruker Esprit software package. TEM foils were prepared by ion milling techniques.

SEM images and EBSD results were obtained using a FEI Quanta 600 FEG SEM equipped with an electron backscattered diffraction (EBSD) detector.

Results and Discussion

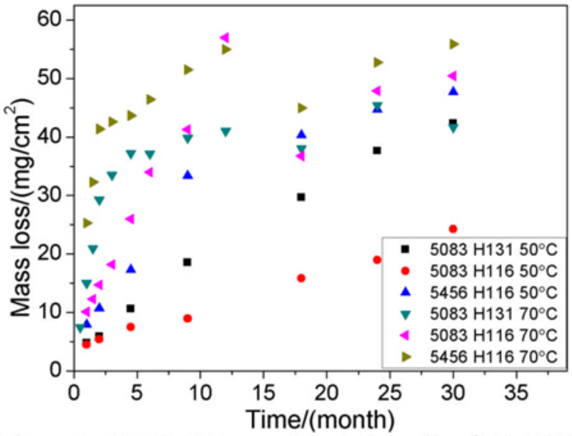

Figure 1. ASTM G67 mass loss test results of Al 5083 H131, H116 and Al 5456 H116 aged at 50℃ (323K) and 70℃ (343 K) for different times.

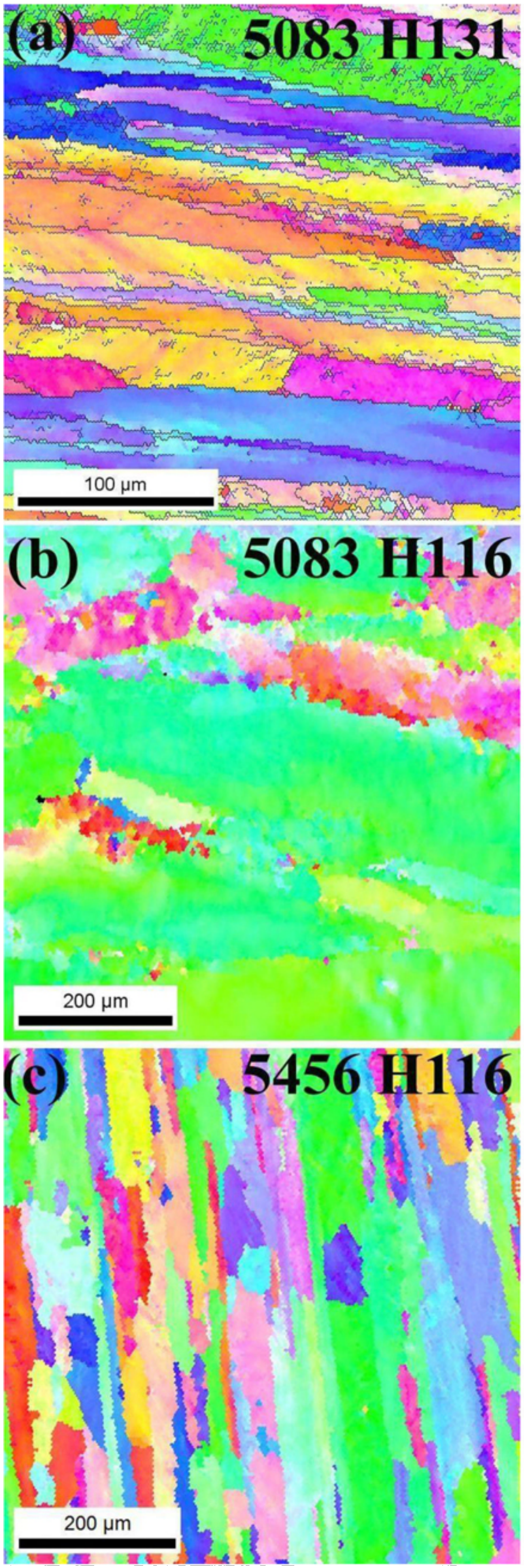

Figure 2. EBSD image of Al 5083 H131 (a), Al 5083 H116 (b) and Al 5456 H116 (c).

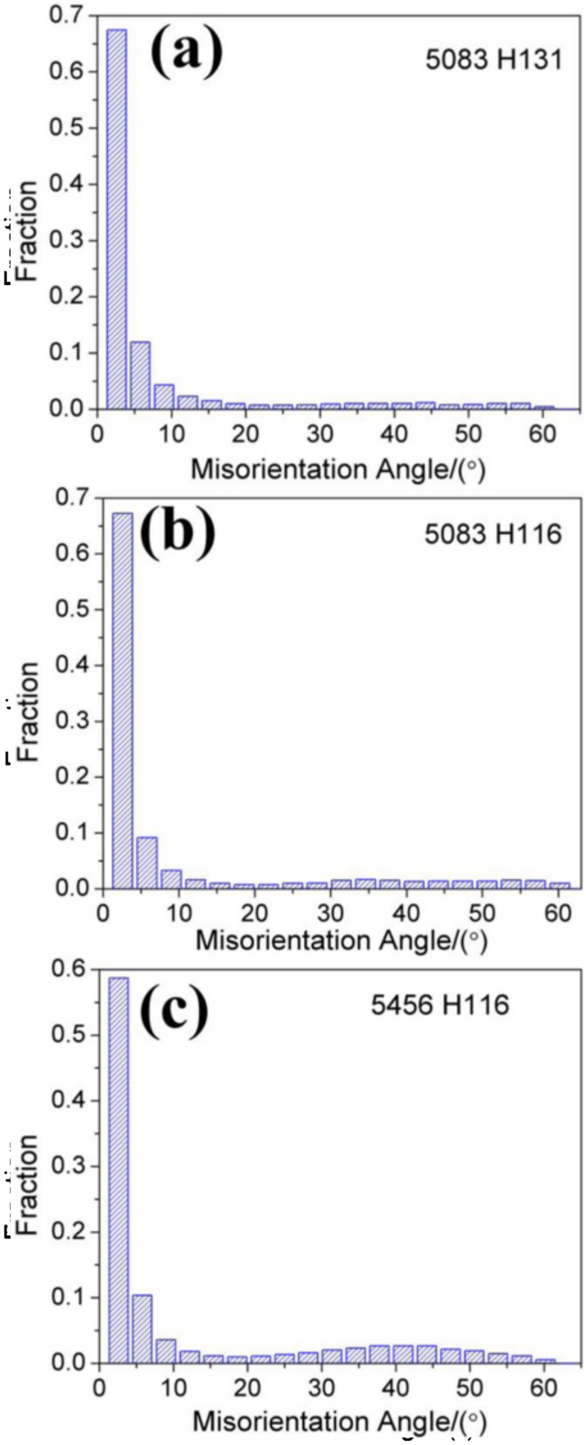

Figure 3. Grain boundary misorientation angle distribution of Al 5083 H131 (a), Al 5083 H116 (b) and Al 5456 H116 (c) obtained from EBSD.

The degree of sensitization for Al 5xxx alloys is usually estimated using ASTM G67 mass loss tests[14]. Fig.1 is the mass loss of Al 5083 H131, H116 and Al 5456 H116 aged at 50℃ (323K) and 70℃ (343 K) for different times. Mass loss of the 3 alloys increased with aging time and temperature. Moreover, when aging temperature is 70℃ (343 K), mass loss of all three alloys will reach a plateau after 12 months, and the value of the plateau is about 45 mg/cm^2. Based on the mass loss, the sensitization degree (from high to low) of the three alloys is given as: Al 5456 H116, Al 5083 H131 and Al 5083 H116. As shown by our previous research, sensitization degree of Al alloy is directly related to the continuity of β phase formed at grain boundary. Based on our β phase growth model, β phase will become continuous more quickly when intergranular β phase nucleation density increased[13].

Classical nucleation theory is based on the changes in Gibbs energy (ΔG_{het}^*) associated with the formation of precipitates at the grain boundary. Russell[15] put forward the nucleation rate at grain boundary as:

$$J_{het} = NZ\beta^* \exp\left(-\frac{\Delta G^*_{het}}{k_B T}\right) \tag{1}$$

where, N is the total number of atoms per unit volume at grain boundaries. Z is the Zeldovich factor, and β^* is a factor involving the diffusion coefficient of solute atoms D, the matrix mean solute atom fraction as well as the lattice parameter. k_B is Boltzmann constant.

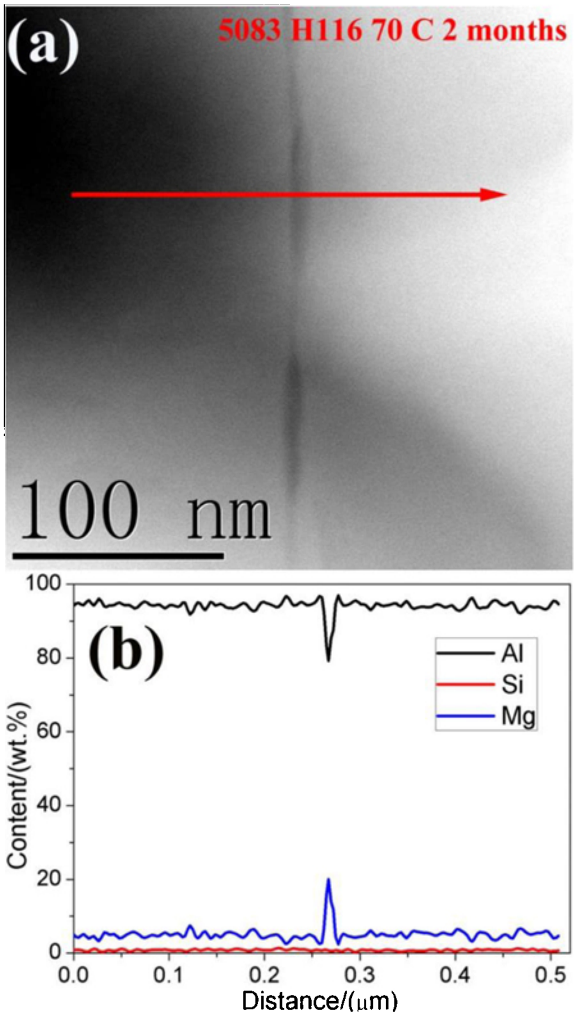

Figure 4. (a) TEM image of Al 5083 H116 aged at 343 K for 2 months, and (b) EDS line scan result across one of the intergranular precipitates as shown in (a).

In fact, N is very hard to determine directly for the complex structure of grain boundary. However, it can estimated from N_0, the number of atoms per unit volume in the grain matrix[16], as:

$$N = N_0 \frac{\delta}{h} \tag{2}$$

where, δ is the average grain boundary thickness, and h is the average grain size.

Fig. 2 (a), (b) and (c) are the EBSD results of Al 5083 H131, H116 and Al 5456 H116 respectively. The largest width for Al 5083 H131 grain is 30 μm, and 70 μm for Al 5456 H116. Whereas, this value increases to over 200 μm for Al 5083 H116. Based on the statistical results of several EBSD images, the average grain size of Al 5083 H131 is 21.3 μm, Al 5083 H116 is 32.5 μm, and 13.8 μm for Al 5456 H116.

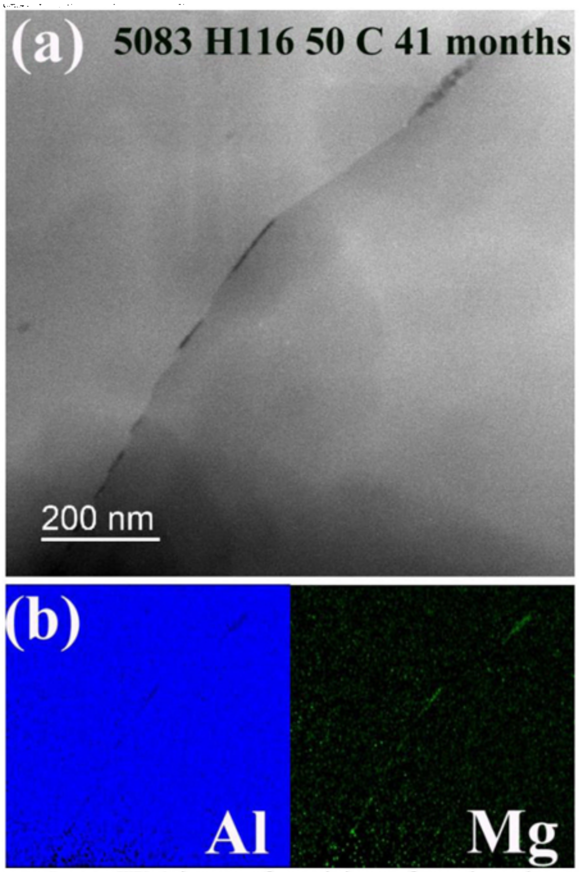

Figure 5. (a) TEM image of precipitates formed at the grain boundary of Al 5083 H116 aged at 323 K for 41 months, and (b) EDS mapping of Al and Mg in (a).

The grain boundary misorientation angle distribution of Al 5083 H131, H116 and Al 5456 H116 is shown in Fig. 3 (a), (b) and (c). Almost 60 percent of the grain boundary misorientation angle is smaller than 5 degrees, which means that the low angle grain boundary is the main grain boundary type in all the three alloys. When misorientation of the grain boundary is larger than 15 degree, the grain boundary is called a high angle grain boundary. The fraction of high angle grain boundary for 5083 H131 is 14%, for 5083 H116 it is 18.7%, and for Al 5456 H116 it is 25.5%. Therefore, Al 5456 H116 has more high-angle grain boundaries than the other two type of alloys.

Hagege *et al.*[17] studied the grain boundary width with the misorientation angle. The typical width of low angle grain boundary is estimated to be 0.25 nm, and width of high angle grain boundary is about 0.6 nm. Combining the grain boundary fraction data obtained from EBSD with the grain boundary width values, the average grain boundary width of Al 5083 H131, H116 and Al 5456 H116 is calculated as 0.3 nm, 0.32 nm and 0.34 nm, which are close to each other.

For Al 5083 H131, H116 and Al 5456 H116, the Zeldovich factor (Z), β^* factor and Gibbs energy change are almost the same. Therefore, the nucleation rate of the three alloys is actually determined by N. Substitution of the average grain boundary width and grain boundary size into equations (1) and (2), the sequence of grain boundary nucleation rate for the three alloys is given as:

$$J_{5456\mathrm{H}116} > J_{5083\mathrm{H}131} > J_{5083\mathrm{H}116}$$

When aging at the same temperature for the same time (during which the grain boundary nucleation is still going on), Al 5456 H116 is likely to obtain the maximum nucleation density, and Al 5083 H116 will have the minimum nucleation density. In other words, Al 5456 H116 is more easily sensitized than Al 5083 H131 and H116, which is consistent with the ASTM G67 mass loss test results. Therefore, grain size difference caused by different temper and different alloy composition plays a critical role in the precipitation and sensitization behavior of the Al 5xxx alloy.

Fig. 4 (a) shows the precipitates formed at the grain boundary of Al 5083 H116 aged at 343 K for 2 months. The length of the precipitates is around 80 nm, and the thickness of the precipitates is about 10 nm. Fig. 4(b) is the EDS line scan result of one intergranular precipitate in Fig. 4(a). Mg concentration of the precipitate is 20 wt.%, which could be β'' phase[18].

Fig. 5 (a) is a TEM image of Al 5083 H116 aged at 323 K for as long as 41 months. EDS mapping shown in Fig. 5 (b) indicates that precipitates formed at the grain boundary are rich in Mg. The length of the precipitate is about 75 nm, and the thickness is 8 nm. Regardless of a shorter aging time, Al 5083 H116 aged at 343 K has an even thicker intergranular precipitate than the sample aged at 323 K for 41 months. According to equation (1), for the same alloy, a higher aging temperature will lead to a higher nucleation rate. In addition, high temperature will also facilitate the diffusion of solute atoms. As a consequence of the two effects, growth rate of β phase formed in Al 5083 H116 aged at 343 K will be significantly faster. As shown in Fig. 1, the higher sensitization speed of Al 5083 H116 aged at 343 K confirms the prediction of the nucleation theory.

In order to explore the IGC behavior, Al 5083 H131 sample aged at 343 K for 12 months was etched using HNO_3 at room temperature for 1, 3 and 5 minutes. Each time, after etching, the sample will be dried and observed under SEM. Fig. 6 (a) is the SEM image of sample etched for 1 minute. Only two grain boundaries can be observed, and the distance between these two grain boundaries is about 40 μm. When etching time increases to 3 minutes, more grain boundaries become apparent, and the smallest distance between two grain boundaries is only 3 μm. Even more grain boundaries can be observed when etching time is as long as 5 minutes, as shown in Fig. 6 (c). And the distance between these boundaries are smaller than 5 μm. Based on the results of the etching experiments, one conclusion can be made that, some grain boundaries are less corrosion resistance than other grain boundaries. Further experiments will be conducted to determine the difference between these two types of grain boundaries.

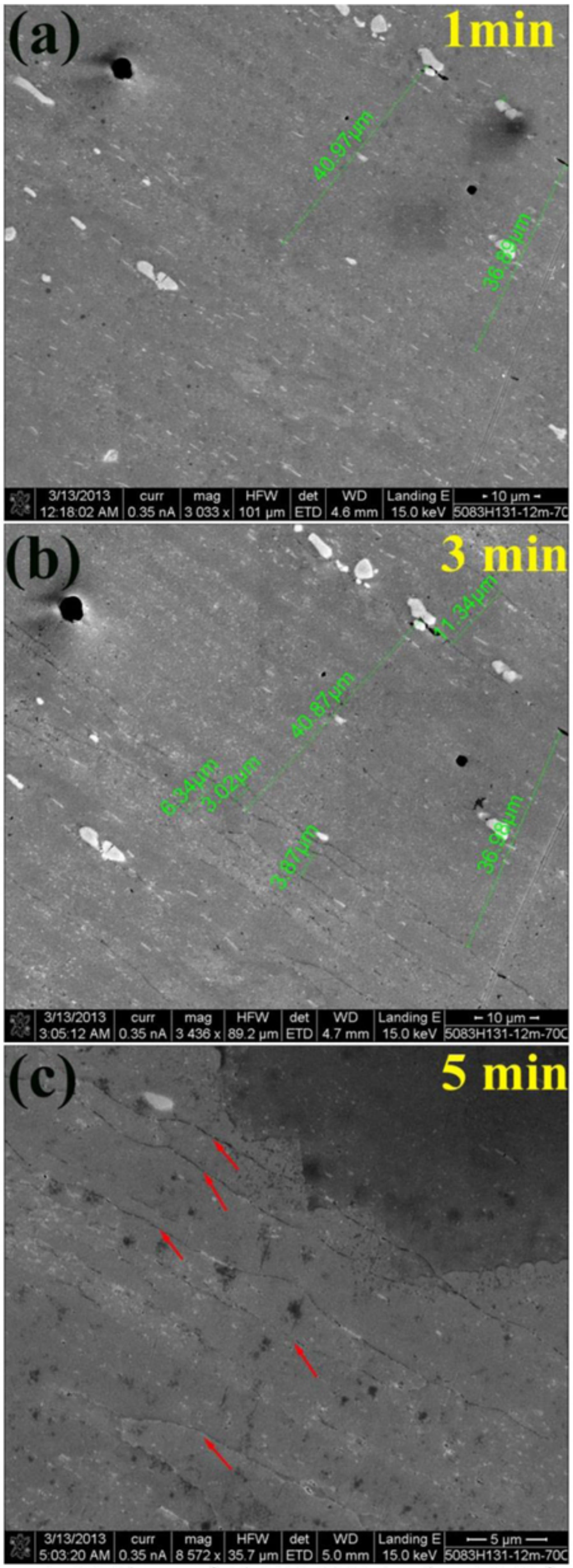

Figure 6. SEM image of Al 5083 H131 (aged at 343 K for 12 months) etched by HNO_3 for (a) 1 min, (b) 3 min, and (c) 5 min.

Conclusions

Al 5083 (H131 and H116) and Al 5456 H116 alloys were aged at 323 K and 343 K for different times. ASTM G67 mass loss test results reveal that the degree of sensitization of the three alloys increased with aging temperature. In addition, Al 5456 H116 is more easily sensitized than Al 5083 H131 and H116. The average grain size and grain boundary thickness of the three alloys were obtained from EBSD results. The classical nucleation theory shows that, average grain size plays a critical role in the sensitization behavior of these alloy. TEM images of Al 5083 H116 aged at 343 K for 2 months and 323 K for 41 months indicates that the higher the aging temperature, the faster the intergranular precipitate growth rate, which is consistent with the ASTM G67 mass loss test results and the classical nucleation theory. Al 5083 H131 sample aged at 343 K for 12 months were etched in HNO_3 for 1, 3, and 5 minutes, and the results reveals that some grain boundaries are less corrosion resistant.

Acknowledgements

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References

1 . European Aluminum Association, *Aluminum in Commercial Vehicles* (Brussels Rev. 1., 2011), 44-49.

2 . R.A. Sielski, "Research Needs in Aluminum Structure," *Ships Offshore Struct.*, 3 (2008), 57-65.

3 . G. C. Blaze, Alcoa Green Letter: *The 5000 Series Alloys Suitable for Welded Structural Applications*, Aluminum Corporation of America, New Kinsington, PA, 1972.

4 . Z. Yakun et al., "Evaluation of Al_3Mg_2 Precipitates and Mn-Rich Phase in Aluminum-Magnesium Alloy Based on Scanning Transmission Electron Microscopy Imaging," *Metallurgical and Materials Transactions A*, 43 (2012), 4933-4939.

5 . N. A. Belov, D. G. Eskin, and A. A. Aksenov, Multicomponent Phase Diagram: Application for Commercial Alloys, 2005, 134.

6 . R. Goswami, "Microstructural Evolution and Stress Corrosion Cracking Behavior of Al-5083," *Metallurgical and Materials Transactions A*, 42 (2011), 348-355.

7 . R.H. Jones, J.S. Vetrano and R. G. Buchheit, "Stress Corrosion Cracking of Al-Mg and Mg-Al Alloys," *Corrosion*, 60 (2004), 1144-1150.

8 . R.H. Jones et al., "Role of Mg in the Stress Corrosion Cracking of an Al-Mg Alloy," *Metallurgical and Materials Transactions A*, 32A (2001), 1699 - 1711.

9 . Starink, M.J. and Zahra, A. M., "Low-temperature Decomposition of Al-Mg Alloys: Guinier-Preston Zones and $L1_2$ Ordered Precipitates," *Philosophical Magazine A*, 76(1997), 701-714.

10 . Eikum, A., and Thomas, G., "Precipitation and Dislocation Nucleation in Quench-aged Al-Mg Qlloys," *Acta Metallurgica*, 12(1964), 537-545.

11 . Bouchear, M., Hamana, D., and Laout, T.," GP Zones and Precipitate Morphology in Aged Al-Mg Alloys," *Philosophical Magazine A*, 73(1996), 1733-1740.

12 . Gaosong. Yi, David Cullen, Yakun Zhu, Alexander T Derrick, and Michael Free, "Characterization of Precipitates Formed in Al 5456," 2014, to be submit.

13 . Gaosong. Yi, Michael Free, Yakun Zhu, and Alexander T Derrick, "Capillarity Effect Controlled Precipitate Growth at the Grain Boundary of Long-Term Aging Al 5083 Alloy," *Metallurgical and Materials Transactions A*, 45(2014), 4851-4862.

14 . L. Tan, and T.R. Allen, "Effect of Thermo-mechanical Treatment on the Corrosion of AA5083," *Corrosion Science*, 52(2010), 548-554.

15 . K.C. Russell, "Grain Boundary Nucleation Kinetics," *Acta Metallurgica*, 17(1969), 1123-1131.

16 . D.A. Porter, K.E. Easterling, and M. Y. Sherif, Phase Transformations in Metals and Alloys, 2008, 275.

17 . S. Hagege et al., "The Variation of Grain Boundary Structural Width with Misorientation Angle and Boundary Plane," *Philosophical Magazine A*, 45(1982), 723-740.

18 . S. Nebti, S. Hamana, and G. Cizeron, "Calorimetric study of pre-precipitation and precipitation in Al-Mg alloy," *Acta Metallurgica et Materialia*, 43(1995), 3583-3588.