Effect of Mg Alloying Addition on Dissolution Behavior of Oxide Films in Al-Si-Mg Alloys

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Cyclic polarization measurements were carried out for Al-10%Si-X%Mg (X: 3%, 6% and 9.5%) alloys in borate solutions with and without additions of 50 mM NaCl. The voltammetric response exhibited some features of oxide film growth consistent with the high field conduction model. However, higher currents and distortions in the voltammetric wave shape compared to those for pure Al were ascribed to a possible incorporation of alloying elements in the oxide film, rendering it more defective, and to the strong electrochemical activity of Mg_2Si particles.

Introduction

The corrosion behavior of aluminum in an aqueous electrolyte is normally governed by the nature and properties of the thin protective aluminum oxide layer on the surface. Although there is enough evidence in the literature that exposure of the passivating layer to sufficiently aggressive solutions (e.g. containing chloride ions) leads to localized breakdown of the protective oxide, an exact description of the mechanism of interaction of the Cl$^-$ ions with the oxide film is still unavailable (1). As discussed in comprehensive reviews by Foley (2) and McCafferty (3) the sequence of steps for the pit initiation process on aluminum (which begins by Cl$^-$ adsorption) may involve chloride ion penetration of the oxide film by a film dissolution mechanism. Some evidence of the importance of such a mechanism has been provided, for instance, by Yu et al. (4) using XPS. A significant contribution which considers the usefulness of cyclic polarization methods for exploring the dynamic balance between oxide growth and oxide dissolution for pure Al was provided by Isaacs and co-workers (5). Their results offered an insight into the interaction of different anions (borate, chromate, phosphate and sulfate) with the oxide film in near neutral solutions: while in borate and chromate solutions the chemical dissolution rate (R_{dis}) was negligibly small compared to the rate of oxide growth, in phosphate and sulfate solutions it was significant. Following Isaacs`s studies, White and co-workers (6) used a similar approach to determine dissolution rates of Al_2O_3 films on pure Al electrodes in neutral borate solutions containing various concentrations of Cl$^-$. The dependence of R_{dis} on Cl$^-$ concentration was found to follow an adsorption type mechanism.

In this study we have investigated the growth and dissolution behavior of oxide films formed on Al-10%Si-X%Mg (X= 3,6, 9.5 wt.%) alloys in borate solution without and with additions of 50 mM NaCl. These alloys have been tailored by our research group for the fabrication of Al/SiC$_p$ composites by the pressureless infiltration method (7, 8). Two of the major problems frequently encountered in processing by the pressureless infiltration method are the presence of considerable levels of residual porosity and the

development of unwanted reaction products (Al_4C_3). Residual porosity is related to inadequate wetting of the silicon carbide by molten aluminum and Al_4C_3 develops by dissolution of the SiC reinforcement by the liquid aluminum. Both problems can be overcome by adequately controlling the processing parameters such as alloy chemistry, temperature, atmosphere, preform porosity, reinforcing particle size, etc. (9). With respect to the effect of alloy chemistry, it is well known that Mg in the system plays an important role in the wetting of the SiC particles by molten aluminum, and that silicon additions help in preventing the development of unwanted aluminum carbide. This explains the unusual levels of Si and Mg compared to those in commercial Al-Si-Mg alloys.

The oxidation process of pure aluminum in aqueous environments has been extensively studied, but the process in aluminum alloys is not as well understood. Claycomb and Sherwood suggest that the process may be complicated by diffusion of alloying elements, and observed that for a 6061 alloy, Mg migrates to the surface as a result of a boiling water treatment (10). Using XPS Baer et al. (11) showed that in a 7 wt% Mg-Al alloy Mg is enhanced at the surface of the air formed oxide, while depleted at the surface of the layer formed at open circuit conditions in a 3.5% NaCl solution. It is expected that for the alloys investigated in this work the possible migration of Mg or Si to the surface might affect the growth and dissolution behavior of oxide films in neutral solutions. Thus, to elucidate the role of Mg on the chemical stability of oxide films in these alloys, the voltammetric method described by Isaacs and co-workers (5) has been applied. The results provide important information which will help in understanding the complex dynamic balance between oxide growth and oxide dissolution in the matrix of the composites reinforced with SiC particles.

Experimental

The three Al-Si-Mg alloys were fabricated in an induction furnace using commercial Al, Si and Mg. The nominal chemical compositions of alloys having increasing amounts of Mg are presented in Table I and the typical microstructure for alloy M2 is shown in Figure 1.

Table I. Chemical compositions (wt. %) of the alloys used in the experiment

Designation	Si	Mg	Total of other elements	Balance
M1	10	3	0.1	Al
M2	10	6	0.1	Al
M3	10	9.5	0.1	Al

For electrochemical measurements small pieces of the alloys were embedded in an epoxy resin leaving an exposed area of approximately 0.5 cm^2. Each specimen was abraded down to a 1200 grit SiC paper, washed ultrasonically in deionized water and dried in air.

Borate buffer pH 8.4 solutions (0.075M $Na_2B_4O_7 \cdot 10H_2O$, 0.3M H_3BO_3) with and without additions of 50 mM NaCl were prepared with analytical grade reagents and deionized water. Bubbling of the unstirred solutions with N_2 started at least 15 min prior to each experiment.

Voltammetric measurements were performed at a scan rate of 1 mV/s using a Gamry CMS 100/PC3 potentiostat. A saturated calomel reference electrode (SCE) and a

platinum foil counter electrode were used throughout. In all cases the electrode potential was held at -1.6 V vs SCE for 5 min prior to recording the voltammetric curves.

Results and Discussion

Figure 2 shows the cyclic polarization behavior of alloy M1 in the borate solution. During the first cycle the current density increases up to ~ 19 $\mu A/cm^2$ at the positive potential limit (-0.6 V) and then, during the reverse scan, it drops significantly. For subsequent cycles the current density at the positive potential limit continues to decrease. This electrochemical behavior is consistent with the high-field conduction mechanism of oxide film growth as described by Issacs and co-workers (5). The voltammetric wave shape for the first cycle in Figure 2 resembles quite closely that reported by White and co-workers (6) for pure Al, using also a neutral borate solution, applying the same scan rate and roughly the same potential range (see Figure 3 in ref. 6). This suggests that oxide film growth for the alloy M1 can still be described by the high-field conduction model, according to which the voltammetric current density due to oxide growth is given by (5, 6)

$$i = \alpha \exp\left(\beta \frac{E - E_{fb}}{\delta} \right) \qquad [1]$$

$$\alpha = \Gamma v q \exp(-W/kT) \qquad [2]$$

$$\beta = qa/kT \qquad [3]$$

$$\delta = \delta_0 + \frac{M}{\rho}\left[(nF)^{-1} \int i\, dt - \int R_{dis}\, dt \right] \qquad [4]$$

where E is the applied potential, E_{fb} the flat band potential, Γ is the surface density of mobile Al^{3+}, v the vibration frequency, q the charge associated with Al^{3+}, W the activation energy, a the activation distance, k the Boltzmann constant, T the temperature, δ the instantaneous oxide film thickness, δ_0 the initial oxide film thickness, M the molecular weight of Al_2O_3, n the number of electrons transferred in producing an Al^{3+} ion, and ρ the density of amorphous Al_2O_3. The units of the chemical dissolution rate are mol s^{-1} cm^{-2}.

The main difference between the voltammetric response for pure Al and alloy M1 is that the current density at the positive potential limit for the alloy M1 is about three times higher compared to the value observed for pure Al in ref. 6. This can be ascribed to a difference in the structure and/or chemical composition of the oxide films due to the incorporation of alloying elements. The possible incorporation of Si into the passive film has been reported recently by S.S. Abdel Rehim et al. (12) for Al-Si alloys (containing 6 and 18 % Si) in neutral sulfate solutions. With regard to Mg, Baer et al. (11) showed a distribution of Mg within the oxide film for an Al-7%Mg alloy in neutral chloride solutions. Based on a simple analysis of equation [1] to [4] (assuming that only one parameter changes while the others remain constant) we can think of three possible

explanations for the higher current densities in the alloy compared to pure Al: a) the initial film thickness in the alloy is smaller compared to that in pure Al, b) the dissolution rate of oxide film in borate solution is several orders of magnitude higher for the alloy compared to that in pure Al and c) incorporation of alloying elements in the oxide films leads to changes in its semiconductive properties (particularly, a shift in the flat-band potential to more negative values for the oxide film in the alloy, compared to that in pure Al). Of these 3 possibilities, the last two are the most likely.

Figure 3b shows the polarization behavior of alloy M1 in a borate solution containing 50 mM NaCl. As observed in the borate solution, current densities on potential reversal are lower than those measured during the forward scan, and also the current for the positive potential limit decreases with consecutive cycles. The presence of chloride ions leads to an increase in the oxide dissolution rate (as evidenced by comparing the first cycle in Figure 3b with that in Figure 3a for borate solution) but not large enough to prevent the increase in oxide film thickness with consecutive cycles.

Fig. 4 shows the polarization behavior for alloy M2 in the absence (Figure 4a) and in the presence (Figure 4b) of 50 mM NaCl. In both solutions the cyclic polarization curves exhibits a decrease in current density upon reversal of potential scan, and also a decrease in the current density at the positive potential limit with consecutive cycles. These characteristics give an indication that film growth still dominates over dissolution and film thickness increases during each cycle. However a detailed observation of the voltammetric response in the borate solution (in the absence of chloride ions) suggests that it is too complicated to be analyzed by equations [1] to [4]: the wave shape is very different compared to that for pure Al (and even compared to that for alloy M1), currents for the whole wave are very high and a sudden rise in current occurs at $\sim$ -0.9 V. This electrochemical behavior is most likely due to an increased role of Mg containing intermetallics (being Mg_2Si the most important in this respect). A recent report by Birbilis and Buchheit (13) on the electrochemical characteristics of intermetallic phases on aluminum alloys showed that Mg_2Si is electrochemically active. Comparing the microstructure of the three alloys we observed that the size of this phase increases as the Mg content in the alloy goes from 3% to 9.5% Mg.

In Figure 5 the polarization behavior for alloy M3 in the absence (Figure 5a) and in the presence (Figure 5b) of 50 mM NaCl is presented. Again, it is observed that the cyclic polarization curves exhibits a decrease in current density upon reversal of potential scan, and also a decrease in the current density at the positive potential limit with consecutive cycles. However the currents are extremely high; film thickness increases during each cycle but large anodic current flows to replace the amount of dissolved oxide. The characteristic feature observed for alloy M2 (the sudden current rise at $\sim$ -0.9V) is even more pronounced in this case. It appears that there are two contributions to the measured current: that from growth/dissolution of the Al_2O_3 film and that from the strong electrochemical activity of Mg_2Si particles. Since the separation of these contributions is difficult, an analysis of the voltammetric response using equations [1] to [4] would be meaningless.

A comparison of the first cycles for the three alloys in the borate solution is presented in Figure 6. As the Mg content increases, the current wave is shifted to higher currents and also a sudden rise in the current at $\sim$ -0.9 V becomes more evident. The

same sequence is also observed for the second and third cycles. The presence of alloying elements in the film renders it very defective. Future studies will involve surface analysis to elucidate the chemical composition of the oxide film and Mott-Shottky analysis to explore differences in semiconductive properties of the film due to incorporation of alloying elements.

Conclusions

The voltammetric response of the three alloys investigated in borate solutions with and without 50 mM NaCl showed some features of oxide film growth/dissolution that are consistent with the high-field conduction model. However the electrochemical behavior is more complicated than that for pure Al. Higher currents and distortions in the voltammetric wave shape were ascribed to possible incorporation of alloying elements in the oxide film rendering it more defective and to the strong electrochemical activity of Mg containing intermetallics (particularly of Mg_2Si). The effect is stronger as the Mg content increases.

Acknowledgments

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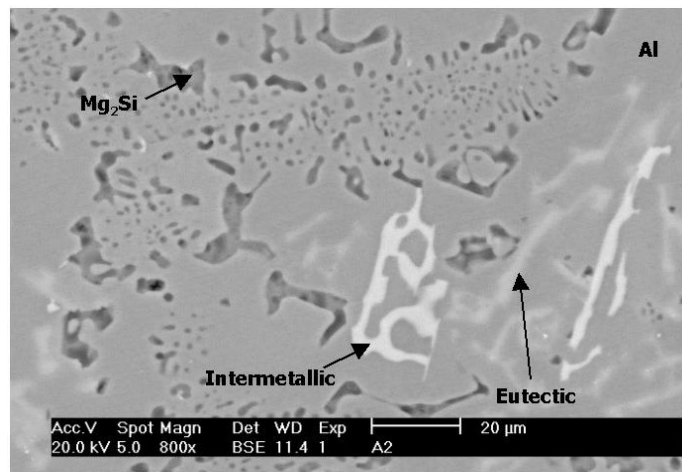13. N. Birbilis and R.G. Buchheit, *J. Electrocfhem. Soc.,* **152**, B140 (2005).

Figure 1. Typical microstructure of alloy M2 (Al-10%Si-6%Mg). The label "intermetallic" refers to $Al_8FeMg_3Si_6$.
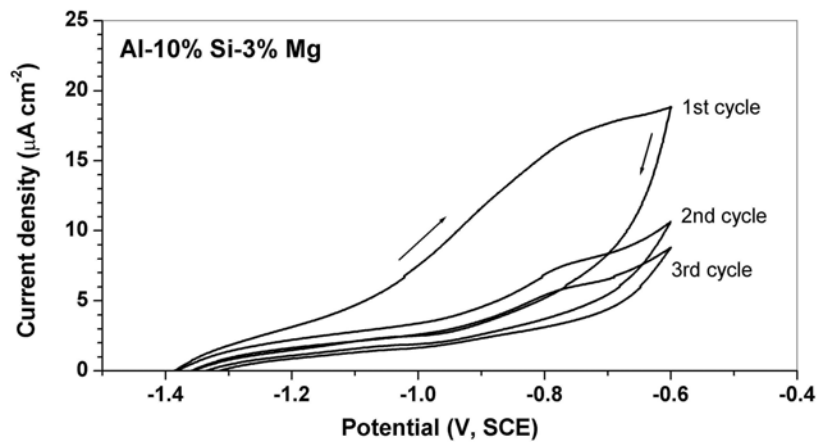

Figure 2. Polarization characteristics of alloy M1 (Al-10%Si-3%Mg) in the borate solution, at 1 mV/s.
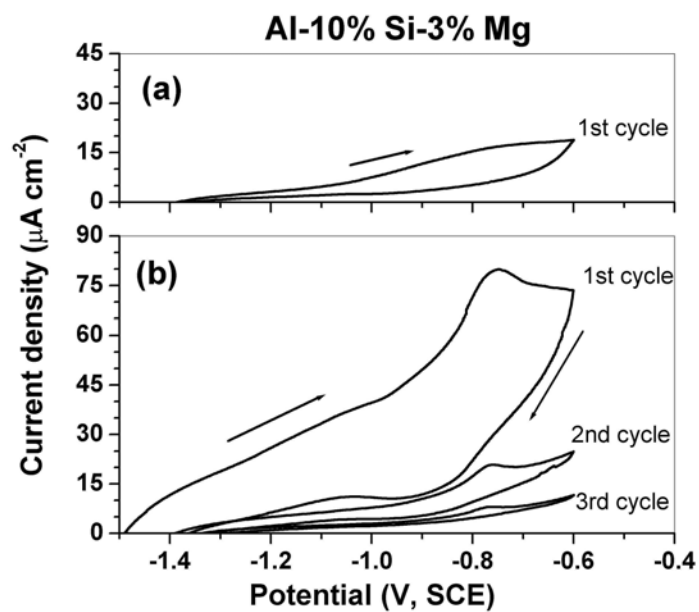
Figure 3. Voltammetric response of alloy M1 in a) borate solution (1st cycle) and b) borate solution + 50 mM NaCl.
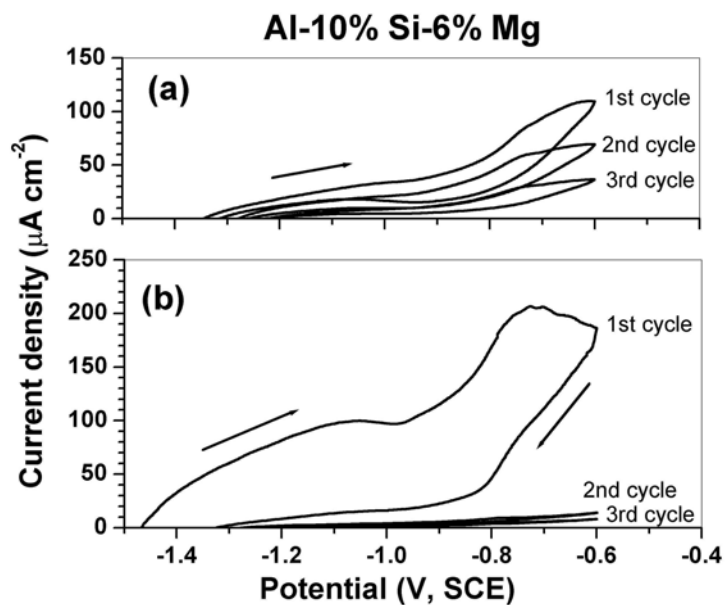

Figure 4. Voltammetric response of alloy M2 in a) borate solution and b) borate solution + 50 mM NaCl.
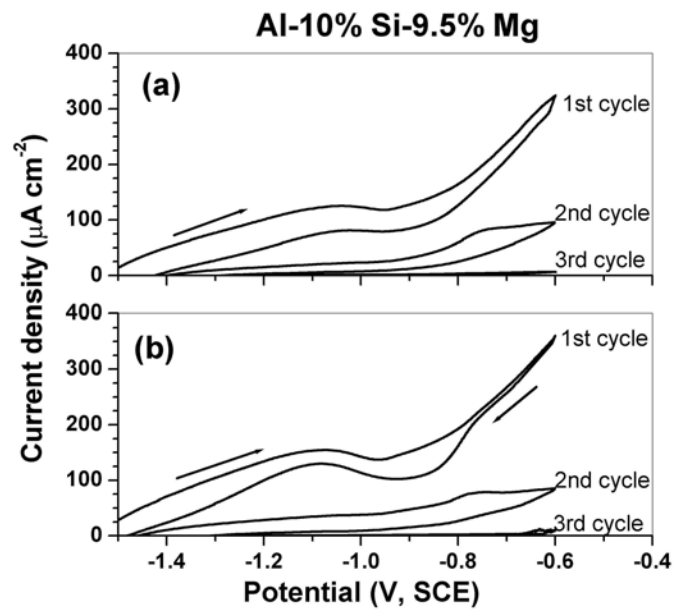
Figure 5. Voltammetric response of alloy M3 in a) borate solution and b) borate solution + 50 mM NaCl.
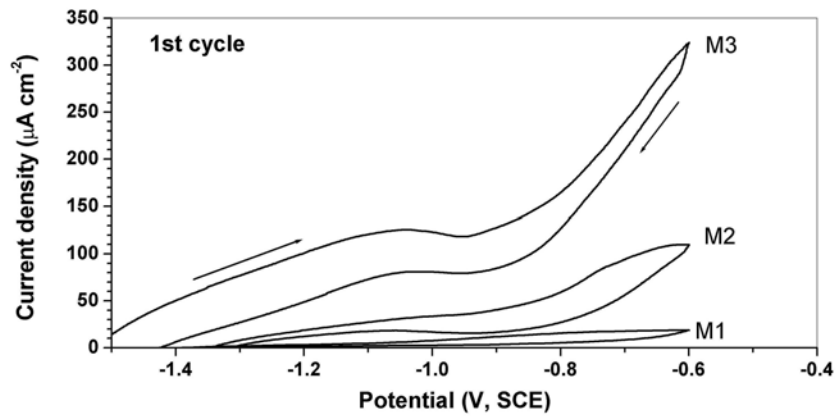

Figure 6. Comparison of the voltammetric response (1st cycle) for the three alloys in borate solution.