Electron beam induced oxidation of Al–Mg alloy surfaces

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Abstract

Electron beam currents of a few nanoamperes, currently used in nanometer scale scanning Auger/electron microscopy, induces severe oxidation of Al–Mg alloy surfaces at room temperature. Auger peak-to-peak oxygen curves for Al–Mg surfaces support the hypothesis that the electron beam creates additional nucleation sites for oxidation. However, the oxygen curves are described with a more complex functional form than that of single element oxidation investigated in the past. The e-beam oxidizes mainly the Al on areas where Mg is in solid solution, while on areas where the Al1Mg2 phase is present a complex oxidation process takes place. In this case, besides Al oxidation also Mg oxidizes on the surface accompanied by Mg segregation through the surface oxide layer. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminium–magnesium (Al–Mg) alloys are potential candidates for a wide variety of applications because they are characterized by excellent corrosion resistance, formability and weldability [1]. Mg is commonly added to increase the strength of light-weight Al-alloys. Moreover, Mg had been shown to improve the wetting properties of liquid metal on solid surfaces [2]. However, enhanced Mg segregation to the alloy surface can diminish such properties since it leads to the formation of relatively thick and friable surface oxides. Such oxides effectively lead to a reduced resistance to corrosion [3], reduced adhesion of organic films due to friability and susceptibility to hydrolysis of the oxide layer [4], and reduced resistance to stress corrosion cracking [5].

A wide variety of studies of Al–Mg alloys have shed light on many aspects of Mg segregation, and its influence on oxidation mechanisms in Al–Mg alloys [6–12]. For a Al–10%Mg alloy [7], Auger electron spectroscopy (AES) analysis showed that the surface oxide layer (grown at 430 °C in an air circulation furnace) was largely Mg-oxide, being an order of magnitude thicker than that formed at room temperature (RT), while at RT the Al-oxide was twice as thick as the Mg-oxide [7]. These findings were in agreement with results on low Mg content alloys (<2.5%) in the temperature range 430–450 °C [10,11]. In an ultra high vacuum study, AES analysis of single crystal Al–Mg alloys (having a low Mg concentration and oxidized at a partial oxygen pressure of ~1 × 10⁻⁶ Pa) showed that the surface was saturated by 30 L (Langmuir) of O and consisted of a mixture of MgO and Al₂O₃.
In general, Mg segregates to both grain boundaries and free surfaces of Al. However, there is some evidence that the amount of surface segregation may be influenced by the quality of the vacuum [13]. Lea and Molinari [14] observed an average enrichment ratio of 12 on the free surface of a polycrystalline material at 200 °C. Esposito et al. [9] measured an enrichment ratio of 31 on the (1 1 0) surface at 227 °C. Vetrano et al. [15,16] observed an enrichment ratio of about 3 at a triple point and 2.5 along a GB at 175 °C. In addition, precipitation of the Al3Mg2 phase was observed to occur initially at triple points and subsequently along the grain boundaries.

Although the previous studies have addressed various aspects of oxidation of Al–Mg alloys and Mg segregation after various annealing treatments, a detailed study of the influence of an electron beam on Al–Mg oxidation and Mg segregation is still absent. This will be the topic of the present work because during AES analysis of segregation phenomena in Al–Mg alloys the incoming e-beam can strongly alter their nature by inducing severe oxide formation.

2. Experimental procedure

The apparatus is described in detail elsewhere [17] and consists of a UHV (base pressure $\sim 4 \times 10^{-8}$ Pa during Auger analysis) scanning Auger/electron microscope (field emission JEOL JAMP7800F). Moreover, under typical imaging conditions (accelerating voltage 10 kV, and electron beam current $I = 2.4$ nA which will be used for the e-beam induced oxidation if not otherwise stated), the attained minimum beam spot size is $\sim 15$ nm. The sample used in the present study is an Al–20 at.% Mg specimen cut from cast ingot (Fig. 1). The sample surface consisted of a rather random distribution of islands termed as ‘dark’ (in SEM images after oxide removal by Ar-ion sputtering), with a ‘bulk’ composition of $15 \pm 1$ at.% Mg (Mg in solid solution in Al: Al/Mg). In between

Fig. 1. SEM topography image of the Al–Mg alloy surface. The bright spots indicate the areas oxidized by the electron beam. The numbers indicate where a depth profile also took place after the oxidation was completed. Position 1: $d = 5$ μm, position 2: $d = 10$ μm, and position 3: $d = 20$ μm ($d$ is the e-beam spot size).
the dark islands (Mg in solid solution), the areas have more than double the Mg content of 38 ± 1 at.% Mg than the dark islands. This is the Al₃Mg₂ or β phase which is termed as the ‘brighter’ areas in the SEM image of Fig. 1.

The AES measurements were performed on polished cross-sections cleaned by Ar sputtering prior to e-beam exposure. Auger depth profile analysis was performed by Ar⁺ sputtering (with ion energy 3 keV) at a low rate 0.18 nm/s calibrated with respect to native SiO₂, and AES data were acquired with 400 ms dwell time (acquisition time/eV). The oxygen was provided by the UHV atmosphere (which typically contains H₂O and CO) to initiate chemisorption and direct oxidation under the influence of the e-beam.

3. Generalized oxidation model

The oxidation of the Al₃Mg₂ areas is described with a more generalized model than that of Li et al. [18] which was used to describe oxidation of Ni [18] and Ni₃Al [19–21]. The basic model of Li et al. is based on the premise that the incident electrons create additional nucleation sites around which oxide islands grow. The oxide nucleation sites are likely to be electron-rich sites, which have also shown evidence of dissociative adsorption of molecular O₂ [18]. In addition, electron impact can also cause dissociation of adsorbed water to form OH groups, which catalyze the oxidation on the surface [18]. In terms of Auger intensities, the model by Li et al. [18] can be written in the form [19–21]

\[
I₀(t) = A - (A - B) \times \exp \left[ -\left( \frac{t}{\tau} \right) - \left( \frac{1}{\tau \varphi_e \sigma} \right) \{ \exp(-\varphi_e \sigma t) - 1 \} \right]
\]

(1)

with A the saturated Auger intensity, and B the intensity at chemisorption. \( \varphi_e \) is the electron beam density flux (cm⁻² s⁻¹), \( \sigma \) the electron cross-section for the creation of oxide nucleation sites, \( t \) the oxidation time, and \( \tau \) an oxidation time constant. Note that Eq. (1) is valid after the onset of O chemisorption, where fast oxide growth proceeds due to the presence of the e-beam that leads to oxide site nucleation around which oxide islands grow [18]. In Eq. (1), the exponential dependence on “\( \varphi_e \sigma t \)” is due to the linear dependence of the rate that the oxide sites change with time on the number of existing nucleation sites [18].

In the case where two or more elements participating in the oxidation process (i.e., Al and Mg in the present case), we have generalized Eq. (1) to the form

\[
I₀(t) = A - \sum_{j=1}^{N} A_j \times \exp \left[ -\left( \frac{t}{\tau_j} \right) - \left( \frac{1}{\tau_j \varphi_{e,j} \sigma_j} \right) \{ \exp(-\varphi_{e,j} \sigma_j t) - 1 \} \right]
\]

(2)

with \( N \geq 1 \). After saturation, we have \( I₀(t \to +\infty) = A \), and at \( t = 0 \), we have \( I₀(t = 0) = A - \sum_{j=1}^{N} A_j \) which corresponds to the chemisorption saturation. For the present experiment (Fig. 2), there are two elements participating in the oxidation process, namely Al and Mg, which means that \( N = 2 \) in Eq. (2) with indices 1: Al and 2: Mg.

4. Results and discussion

Eq. (2) describes adequately the oxidation data for all e-beam spot sizes used in the present experiment \( (d \leq 20 \mu m) \) as Fig. 2 indicates. Moreover, the oxidizing behaviour of Al and Mg is shown subsequently in Figs. 3 and 4. From the fits of the O-curves, we obtain \( A \approx I₀ \) (saturation), while \( I₀(t = 0) = A - (A₁ + A₂) \)

![Fig. 2. Oxidation curves for oxygen on the bright area of Fig. 1 where solid lines are the best fits in terms of Eq. (2).](image-url)
lies within the noise level since the fast oxide growth hinders any O chemisorption (Table 1). For the fits in Fig. 2, we estimated the oxidation constant for Mg initially to have the value $\tau_2 = 285.7$ min as was obtained from similar oxidation experiments on pure Mg (as the fit in Fig. 5a indicates), and further this value was allowed to vary in order to incorporate effects due to the presence of Al. Finally, we considered for simplicity the same oxide nucleation cross-section for both Al and Mg ($\sigma_1 = \sigma_2 = \sigma$).

As Fig. 2 indicates, the oxidation kinetics surpasses the O chemisorption regime and fast oxide growth dominates the oxidation process. Such an oxidation scenario has been observed also on other systems with significant affinity to O such as Ni [18], Ni$_3$Al [19–21], Al (1 1 1) [22], and Mg (0 0 0 1) [23], where oxide nucleation occurs long before the saturation of a chemisorbed coverage is reached.

The fits yield for $\varphi_e \sigma$ values within the range $0.13-0.44$ min$^{-1}$ as Table 1 indicates. The electron flux $\varphi_e$ is estimated as $\varphi_e = I/(\pi d^2/4)$ assuming a circular beam spot size of an area $\approx \pi d^2/4$ (with $d$ the e-beam diameter) for a fixed beam current $I = 2.4$ nA (1 A = $6.25 \times 10^{18}$ e$^-$/s). Therefore, we obtain $\sigma(d = 5 \mu m) = 2.8 \times 10^{-20}$ cm$^2$, $\sigma(d = 10 \mu m) = 37.9 \times 10^{-20}$ cm$^2$, and $\sigma(d = 20 \mu m) = 52.4 \times 10^{-20}$ cm$^2$. These calculations indicate that the cross-section $\sigma$ for oxide nucleation increases with decreasing electron flux $\varphi_e$ (or increasing beam spot size) to account for the similar oxidation behaviour depicted in Fig. 2 for the various e-beam spot sizes in the range $5 \leq d \leq 20 \mu m$.

Moreover, the fits yield for the oxidation time constant $\tau_1$ similar values in the range $\tau_1 = 80–90$ min. However, the oxidation time constant $\tau_2$ further increases from its initial value 285.7 min, which was obtained from the e-beam oxidation of pure Mg (Fig. 5a), to values in the range $\tau_2 \approx 400–600$ min. These values correspond to the onset of saturation of the Mg intensity as can be seen from Figs. 4 and 5b. The latter clearly shows that the presence of Al also affects the oxidation kinetics of Mg on the surface of Al$_3$Mg$_2$.

Al strongly oxidizes upon e-beam exposure of the Al$_3$Mg$_2$ surface (Fig. 3), while the Mg shows an apparently different oxidation behaviour as can be seen in Fig. 4. Indeed, during initial stages of e-beam exposure, the Mg intensity appeared to decrease, and
after reaching a minimum it increases again at longer oxidation times. Previous studies by Wakefield and Sharp [7] indicated a combined contribution of the Mg (oxide) and the Mg (metal) KLL peaks. The Mg (oxide) peak (≈1180 eV) increases as oxidation proceeds, while the Mg (metal) peak (≈1186 eV) decreases [7]. Detectability of both peaks is possible since the Mg KLL Auger peak has a large effective Auger electron escape depth $\lambda_{\text{Mg}}$ from the sample surface of magnitude $\lambda_{\text{Mg}} \sim 2.8$ nm. During the initial oxidation stages, the Mg (metal) peak dominates the contribution to the AES intensity up to the minimum position, having the Mg (oxide) peak dominating at later oxidation stages. However, such a strong enhancement of the Mg intensity can not only be explained by this argument, and Mg diffusion towards the oxide layer with subsequent MgO formation has to be taken into account. This is also strongly supported by e-beam studies on pure Mg samples where the Mg intensity level does not increase as much as that observed in Al$_3$Mg$_2$ (Fig. 5a).

The Mg diffusion during the e-beam induced oxidation of the Al$_3$Mg$_2$ surface is enhanced by the formation of Al-oxide and Mg-oxide upon e-beam
exposure and the high affinity of Mg to O. The activation energy of Mg diffusion in Al₂O₃-MgO is \( Q_{Mg} \sim 369.9 \, \text{kJ/mol} \) which is smaller than that of O diffusion \( Q_O \sim 438.9 \, \text{kJ/mol} \) in the same oxide [24,25]. Furthermore, the diffusion prefactor for Mg is much larger than that of O \( (D_{O}^{Mg} \approx 4.7 \times 10^2 \, \text{cm}^2/\text{s} \gg D_{O}^{O} \approx 8.9 \times 10^{-1} \, \text{cm}^2/\text{s} [24,25]) \). These values indicate that Mg diffusion and thus segregation through the e-beam induced oxide layer towards the surface with further MgO formation. Notably, on the dark areas (Fig. 1, Al/Mg) where Mg is in solid solution only the oxidation of Al occurs without any Mg being participating in the oxidation process and/or segregating towards the surface region.

The depth profile analysis of the oxide spots is depicted in Fig. 6 which clearly indicates that the oxide depth is in all cases approximately 6–7 nm, while that on the surrounding areas (positions 4, 5; due to O chemisorption only) is drastically smaller with a depth <2 nm. The depth profile analysis further
confirms the strong influence the e-beam has on the Al–Mg alloy surfaces leading undoubtedly to severe oxidation of both Al and Mg.

Finally, we should point out that Mg diffusion towards the surface will influence the reduction of the Al peak intensity besides that of the oxidation. However, the Al oxidation remains the dominant factor as comparison with Al oxidation on the dark areas (where Mg is in solid solution and does not diffuse to the surface) indicated. Indeed, as Fig. 7 indicates in comparison with Fig. 5b, the reduction of the Al peak due to e-beam oxidation of the dark area is similar in magnitude with that on the Al$_3$Mg$_2$ area.

5. Conclusions

Electron beam currents of a few nanoamperes, currently used in nanometer scale scanning Auger/electron microscopy, can induce severe oxidation of Al–Mg alloy surfaces at RT. Auger peak-to-peak oxygen curves for Al–Mg surfaces appear to support the hypothesis that the electron beam creates additional nucleation sites for oxidation. However, the oxygen curves are fitted with a more complex functional form than that of single element oxidation which was investigated in the past for Ni and Ni$_3$Al [18–21] surfaces. The e-beam oxidizes mainly the Al on areas where Mg is in solid solution, while on areas where the Al$_3$Mg$_2$ phase is present, a complex oxidation process takes place. In that case, besides Al oxidation also Mg oxidizes on the surface accompanied by Mg diffusion through the surface oxide layer.

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