

V. Riveros · M. Gulppi · M. Páez · J. H. Zagal
C. M. Rangel · D. Huerta · P. Skeldon · G. E. Thompson

Influence of surface treatments in the initial stages of anodizing Al–Ag alloys in neutral electrolytes

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Abstract Using voltage-time responses and cyclic voltammetry, the initial stages of anodizing of Al–2.1 at.% Ag and Al–4 at.% Ag alloys are shown to depend upon the heat treatment of the alloys and the pre-treatment of the alloy surfaces. Chemical polishing of solution-treated alloys leads to relatively uniform anodic oxidation on a relatively smooth alloy surface, in the absence of significant effects of coarse, silver-rich intermetallics. In contrast, losses of current to oxygen generation arise for the roughened alloy surface from mechanical polishing. With ageing, secondary reactions at the relatively silver-rich intermetallics are more prevalent, although the effects on the voltage-time response depend upon the balance between processes occurring on the matrix and intermetallic regions, including film growth, oxygen generation within the anodic film, film damage due to release of oxygen, dissolution of silver species and re-growth of damaged film.

Keywords: Anodic films · Aluminium alloys · Surface treatments

Introduction

The composition and structure of the surface regions of aluminium alloys are influenced strongly by chemical or electrochemical pre-treatments [1–6]. For example, alkaline etching or acid pickling can deplete or enrich the surface of particular phases and constituents relative to the bulk alloy. In turn, the modified surface influences the response of the alloy in any subsequently applied surface treatments, such as conversion treatments. While the importance of local chemistry is widely recognized as a major influence in surface treatment of aluminium, the details of the local effects are often less certain and remain of relevance to understanding of surface performance and durability.

Some of these are considered here using Al–Ag alloys, containing 2.1 and 4 at.% Ag, with surfaces either mechanically or chemically polished and then anodised: the influence of the pre-treatment on the anodizing response is of primary interest. Solution treatment, with or without subsequent ageing produced differing amounts of silver in solid solution, in fine Guinier Preston (GP) zones and in coarser Ag_3Al_2 . Notably, silver in solid solution can enrich beneath amorphous alumina films of the types generated during air-oxidation, chemical polishing and anodizing, the development of the enrichment layer, about 2 nm thick, being a pre-requisite of incorporation of silver species into the oxide [7]. For alloys of the present compositions, the required enrichment corresponds to about 6×10^{15} Ag atoms cm^{-2} [7]. The requirement for enrichment of silver reflects the general behaviour of alloying elements more noble than aluminium [1, 4, 7]. After sufficient enrichment, silver is oxidized and silver species migrate outward in the alumina film faster than Al^{3+} ions, correlating with the $\text{Ag}^+ - \text{O}$ bond being weaker than that of the $\text{Al}^{3+} - \text{O}$ bond, a common observation for relative migration rates of species in amorphous anodic alumina [7].

V. Riveros · M. Gulppi · M. Páez (✉) · J. H. Zagal
Departamento de Química de los Materiales,
Facultad de Química y Biología,
Universidad de Santiago de Chile,
Casilla 40, Correo 33, Santiago, Chile
E-mail: mpaez@lauca.usach.cl
Tel.: +56-2-6812575
Fax: +56-2-6812108

C. M. Rangel
INETI, Electrochemistry of Materials Unit, DMTP, Paço do
Lumiar, 22, 1649-038 Lisboa, Portugal

D. Huerta
Universidade de São Paulo, Instituto de Química de São Carlos,
C.P. 780, Sao carlos, 13560-970, Brasil

P. Skeldon · G. E. Thompson
Corrosion and Protection Centre, School of Materials, University
of Manchester, P.O. Box 88, M60 1QD, Manchester, UK

Experimental details

Binary Al–Ag alloys, containing 2.1 and 4 at.% Ag, were prepared by melting high purity aluminium and silver. The alloys were cast and hot-rolled at 623 K to produce sheet of 1 mm thickness. Subsequently, the alloys were solution heat-treated (773 K for 2 h and water-quenched) or solution heat-treated and aged (773 K for 2 h and water-quenched, and then aged at 613 K for 48 h and water-quenched). The heat treatments thus provide alloys with silver present in solid solution in GP zones or, largely, as the equilibrium γ phase. After heat treatment, specimens, of 5×2 cm dimensions were mechanically polished to 800 grit paper. Selected mechanically polished specimens were chemically polished in a mixture of 0.5 M acetic acid, 12 M phosphoric acid and 0.5 M nitric acid for 3 min at 373 K, followed by immersion in 1 M nitric acid for 15 s, to remove silver re-deposited, and then rinsed in distilled water. The specimens were then examined in a JEOL 5410 scanning electron microscope, with energy dispersive X-rays (EDX) facilities. Anodizing of the alloys was undertaken at a constant current density of 5 mA cm^{-2} to various voltages in 0.01 M ammonium pentaborate electrolyte at 293 K, using a two electrode system, with a cathode of Al 99.99 wt% and an anode of the corresponding Al–Ag alloy. Further, cyclic voltammetry was undertaken in 0.01 M ammonium pentaborate solution at 293 K in a three-compartment glass cell, using a platinum counterelectrode, a saturated calomel electrode (SCE) and a working electrode made from the Al–Ag alloy in study. Comparisons were made with high purity aluminium and silver. The anodic potential limit was increased after each potential cycle, while keeping the electrode in the solution, in order to reveal the potentials of electrochemical processes associated with silver in the alloy. The potentiodynamic measurements were carried out with a microprocessor-controlled potentiostat (AUTOLAB).

Results

Electronoptical examination

Scanning electron micrographs of the Al–2.1 at.% Ag alloy, for both heat treatments, reveal similar appearances after mechanical polishing (Fig. 1a, c) with polishing marks present on the surface. However, for the aged alloy, grain boundaries and local light regions, of the order micron size and containing about 18–25 at.% Ag by EDX analysis, are evident (Fig. 1c). Chemical polishing reduces markedly the features of mechanical polishing, leaving an irregularly textured surface, with silver-rich regions being distributed as previously. Similarly for the Al–4 at.% Ag alloy, chemical polishing eliminates the topography of the mechanically polished surface (Fig. 2), developing texture of relatively fine

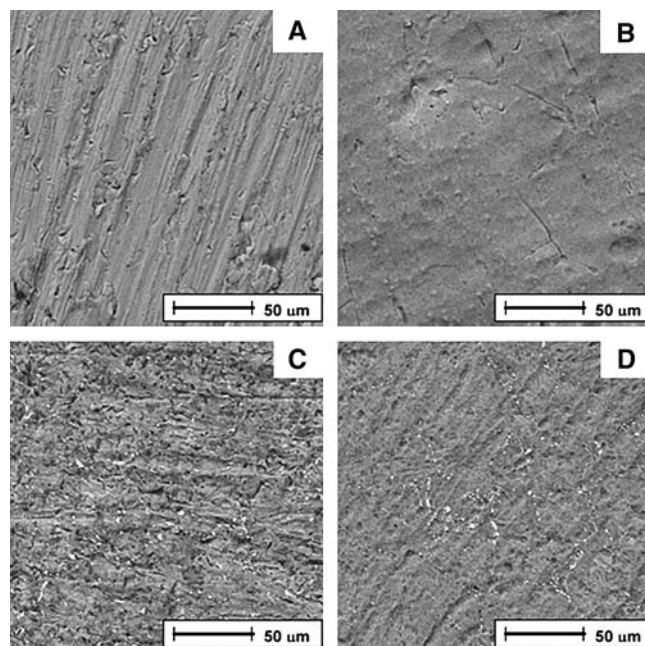


Fig. 1 The SEM micrographs showing the surface morphology of the differently heat-treated Al-2.1 at.% Ag. **a** Solution heat-treated after mechanical polishing, **b** solution heat-treated after chemical polishing, **c** solution-aged heat-treated after mechanical polishing, **d** solution-aged heat-treated after chemical polishing

appearance. Silver-rich regions are particularly prevalent for the aged alloy, reflecting the increased amount of silver in the alloy (Fig. 2c, d). Occasional silver-rich

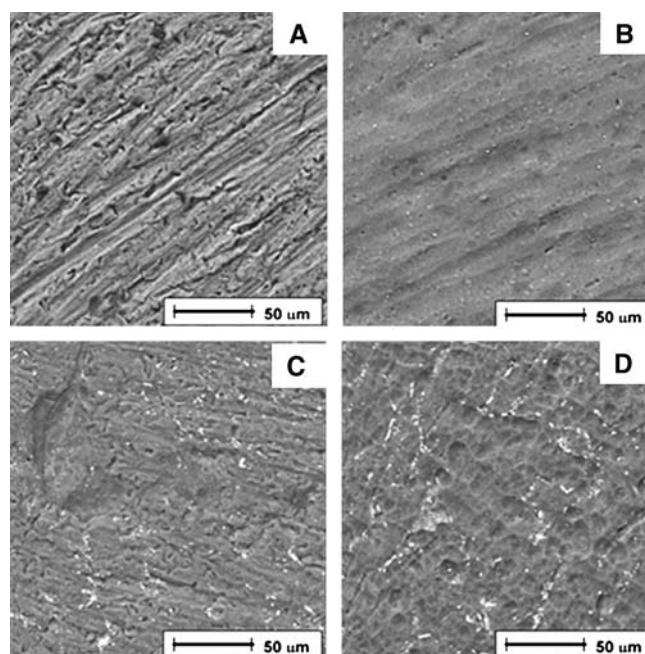


Fig. 2 The SEM micrographs showing the surface morphology of the differently heat-treated Al-4 at.% Ag. **a** Solution heat-treated after mechanical polishing, **b** solution heat-treated after chemical polishing, **c** solution-aged heat-treated after mechanical polishing, **d** solution-aged heat-treated after chemical polishing

particles were also observed for the solution heat-treated alloy.

Voltage–time responses

The mechanically polished solution-treated Al–2.1 at.% Ag alloy displays a linear increase of voltage with time of 1.1 V s^{-1} to 200 V (Fig. 3a). In contrast, for the Al–4% Ag alloy, the initial rate of 1.3 V s^{-1} increases to 1.6 V s^{-1} above 90 V (Fig. 3b). The low rates compared with that of anodizing aluminium at 100% efficiency, 2.3 V s^{-1} , are due to influences of abraded regions and locally increased alloying, which promote oxygen evolution during anodizing [8, 9]. After chemical polishing, increased initial rates of voltage rise of 2.7 V s^{-1} and 2.8 V s^{-1} were evident to 50 V for the solution-treated Al–2.1 at.% and Al–4 at.% Ag alloys, respectively (Fig. 3a, b) which are related to the alloying element behaviour during chemical polishing and anodizing, as discussed later. With further anodizing, the rates of

voltage rise decreased progressively to 2.1 and 2.3 V s^{-1} for the Al–2.1 and Al–4 at.% Ag respectively.

Both the chemically and mechanically polished Al–2.1 at.% Ag alloy in the aged condition revealed similar initial rates of voltage rise of about 1.8 V s^{-1} to 75 V (Fig. 4). Above 75 V, the rate of voltage rise decreases slightly to 1.7 and 1.6 V s^{-1} for the mechanically and chemically polished, respectively. With the mechanically and chemically polished Al–4 at.% Ag alloy, the voltage rose at a rate of 2.1 V s^{-1} from the start of anodizing up to 200 V. In contrast, the initial rate for the chemically polished alloy was only 1.3 V s^{-1} , but increasing progressively above 50 V to about 2.0 V s^{-1} at 200 V; extensive oxygen evolution was observed throughout anodizing.

With mechanical polishing, the voltage rises faster for the solution-treated and the aged Al–4 at.% Ag alloy respectively, than for the Al–2 at.% Ag alloy in the corresponding conditions. The behaviour indicates enhanced resistance to the ionic current, probably due to the presence of fine oxygen bubbles within the film [4, 7, 10]. On the other hand, for the chemically polished

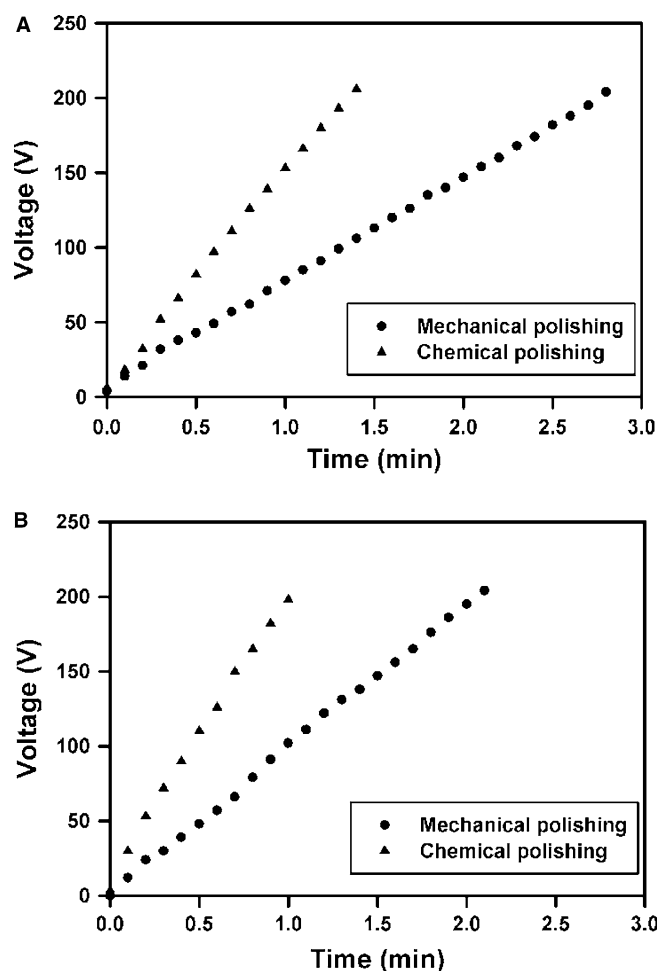


Fig. 3 Voltage–time responses showing the influence of surface treatment on anodizing the solution heat-treated Al–Ag alloys. **a** Al–2.1 at.% Ag, **b** Al–4 at.% Ag

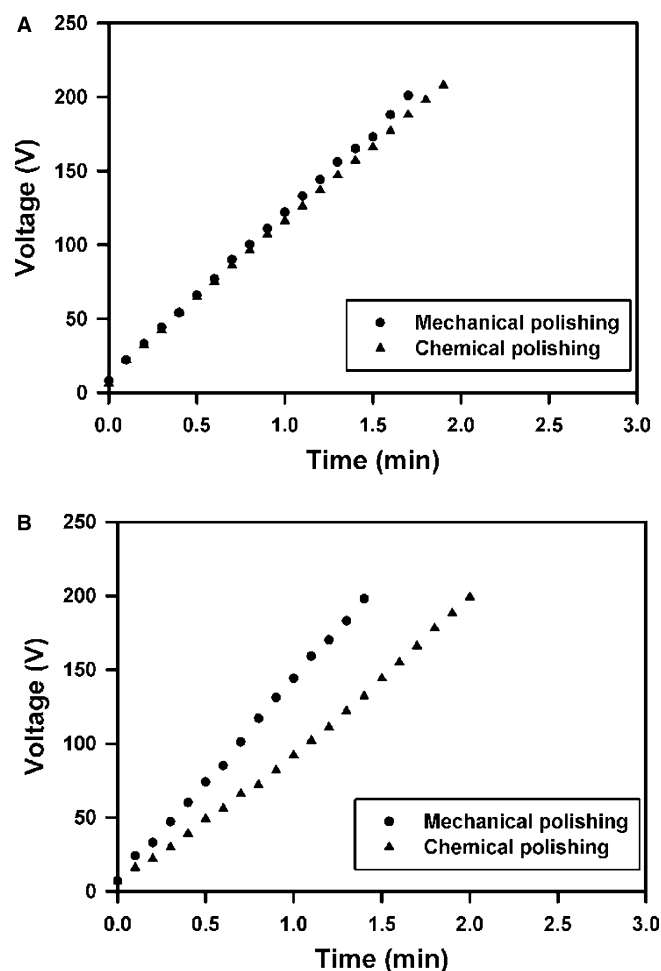


Fig. 4 Voltage–time responses showing the influence of surface treatment on anodizing the solution-aged heat-treated Al–Ag alloys. **a** Al–2.1 at.% Ag, **b** Al–4 at.% Ag

solution-treated alloys, increasing silver content results in an increased rate of voltage rise from the commencement of anodizing. For the aged alloys, however, the rate of voltage rise with the anodizing time is decreased slightly for the Al-2.1 at.% Ag and markedly for the Al-4 at.% Ag.

Potentiodynamic polarization: aluminium and silver

The voltammograms, between -1.5 V and 0.4 V, for mechanically polished aluminium reveal anodic oxidation from about -0.65 V, with progressive current increase with increased the limiting anodic potential (Fig. 5a). After chemical polishing, anodic oxidation occurs at about -1.0 V, with rapid achievement of the approximately constant current density, associated with thickening of the alumina film. As expected, the oxidation current is displaced to more positive potentials as the oxide thickens during successive cycles.

For silver (Fig. 5b), the current response correlates with its high standard oxidation potential, about 0.56 V

(SCE). Thus, oxidation of silver leads to a current increase at about 0.2 V, with further increase above 0.5 V and change in the electrode appearance from metallic to yellow. During cathodic polarization, two current peaks, marked I and II, starting at 0.40 and -0.13 V correspond respectively to a reduction of silver species formed during the anodic scan, and oxygen reduction. Peak II is absent when oxygen is purged from the solution by bubbling nitrogen.

Potentiodynamic polarization: solution-treated Al–Ag alloys

For the mechanically polished Al–Ag alloys, oxidation of aluminium starts above -0.4 V, compared with about 0.25 V for high purity aluminium, mainly due to the nobility of silver (Fig.6). With increase of the anodic potential limit to about -0.1 V, the cathodic scan reveals a peak (indicated by an arrow) in the potential range of oxygen reduction on silver, which is attributed to oxygen reduction above local silver-rich regions in the

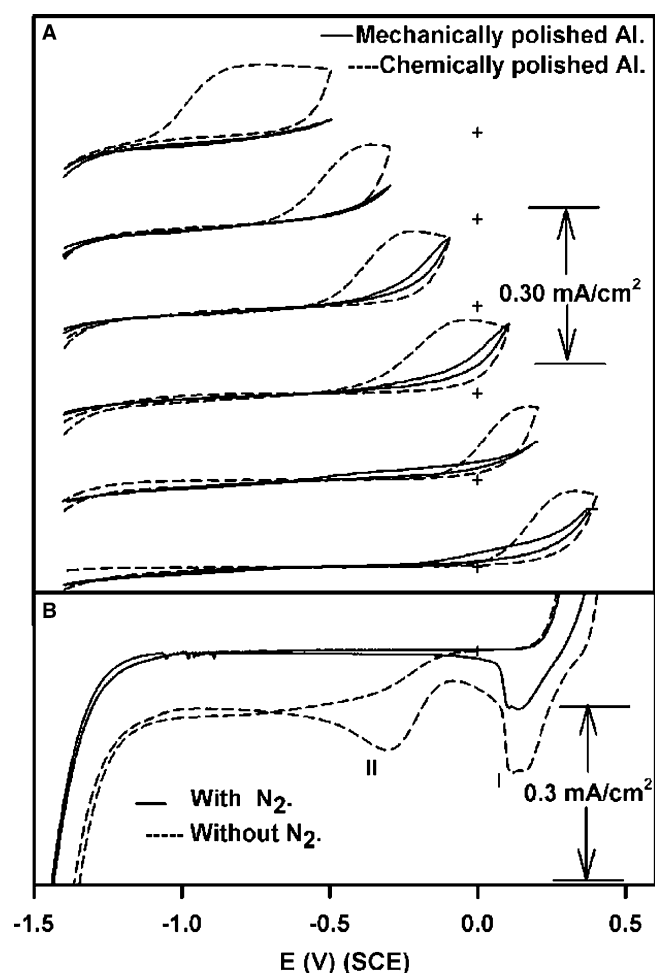


Fig. 5 Potentiodynamic polarization of aluminium (a) and silver of high purity (b), at 10 mV s^{-1} , after different surface treatments

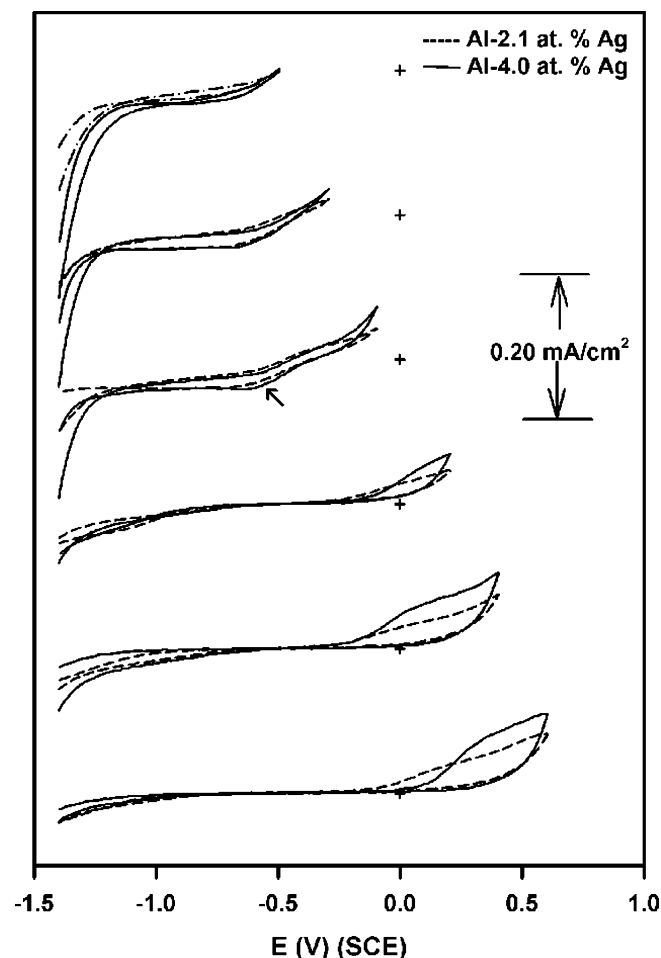


Fig. 6 Potentiodynamic polarization at 10 mV s^{-1} of the solution heat-treated Al-2.1 and 4 at.% Ag alloys after mechanical polishing

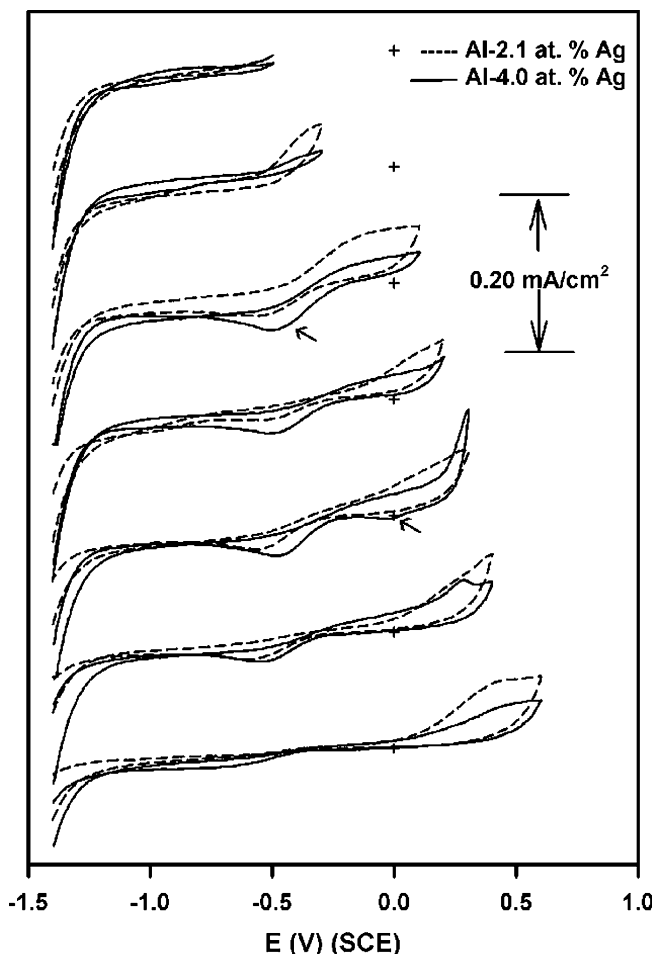


Fig. 7 Potentiodynamic polarization at 10 mV s^{-1} of the solution-aged heat-treated Al-2.1 and 4 at.% Ag alloys after mechanical polishing

alloy (Fig. 5b). The peak is not found for higher anodic potential limits. The anodic charges in Fig. 6 are greater for the alloy of high silver content.

With the chemically polished Al–Ag alloys, aluminium oxidizes from -0.5 V (Fig. 7), 0.1 V lower than that of the mechanically polished alloy (Fig. 6). With limiting anodic potentials beyond -0.1 V , a current peak, starting about -0.15 V , during cathodic polarization is attributed to oxygen reduction, as previously. The peak is absent for limiting anodic potentials above 0.5 V . However, a second cathodic peak, starting about 0.15 V (indicated by an arrow) is located in a similar potential range to that of reduction of silver species on the silver electrode (Fig. 5b). The charge due to oxygen reduction is greater with chemical polishing than with mechanical polishing.

Potentiodynamic polarization: aged Al–Ag alloys

Potentiodynamic polarization of the mechanically polished aged alloys (Fig. 8) reveals oxidation of aluminium above -0.4 V , similar to that of the solution-treated

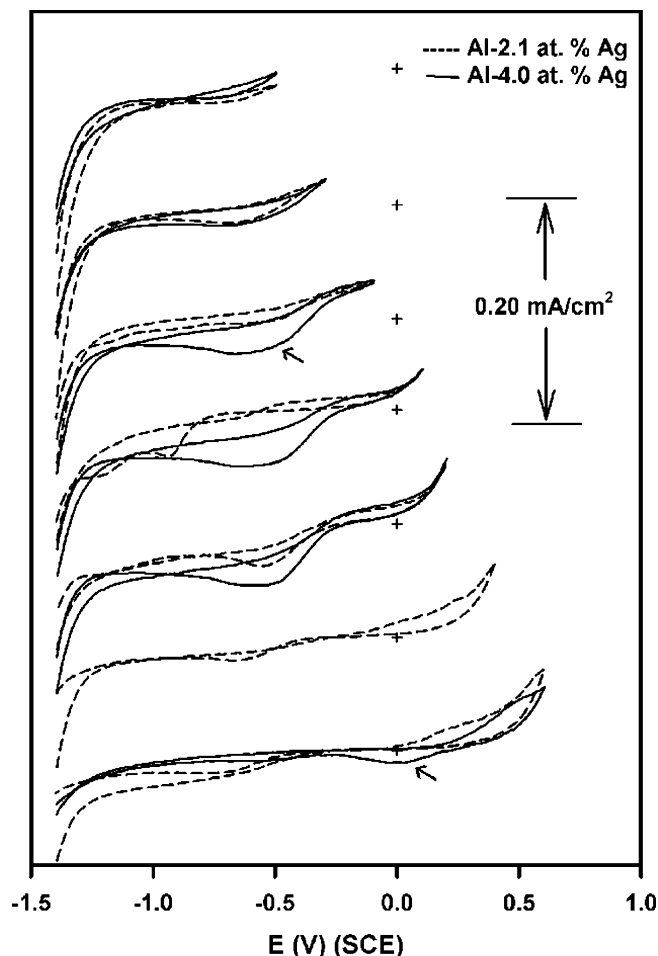


Fig. 8 Potentiodynamic polarization at 10 mV s^{-1} of the solution-aged heat-treated Al-2.1 and 4 at.% Ag alloys after chemical polishing

alloys (Fig. 6). The current responses of the aged alloys are similar to the chemically polished, solution-treated alloys (Fig. 7). However, the charges associated with the reduction of oxygen and silver species are greater for the mechanically polished aged alloys (indicated by arrows). The behaviour of the aged alloy is possibly associated with the presence of second phase material. Silver oxide reduction, between -0.2 and $+0.2 \text{ V}$, is not detected for the Al-2.1 at.% Ag alloy, with reduced precipitation.

From the current response of the chemically polished aged alloy (Fig. 9), oxidation of aluminium starts at about -0.35 V , similarly to the potential with mechanical polishing. Notably, chemical polishing and increase of the silver content of the aged alloy lead to enhanced reduction of oxygen and silver species.

The polarization behaviour of the chemically polished, aged Al-4 at.% Ag alloy, over the potential range between -2 V and 8 V , at 100 mV s^{-1} is compared with that of the solution-treated alloy and the silver electrode in Fig. 10. In addition to the secondary reactions considered previously, a high over-potential arises above 2.7 V due oxygen bubbles, evident by stereoscopic microscopy, that envelop the alloy and silver electrodes.

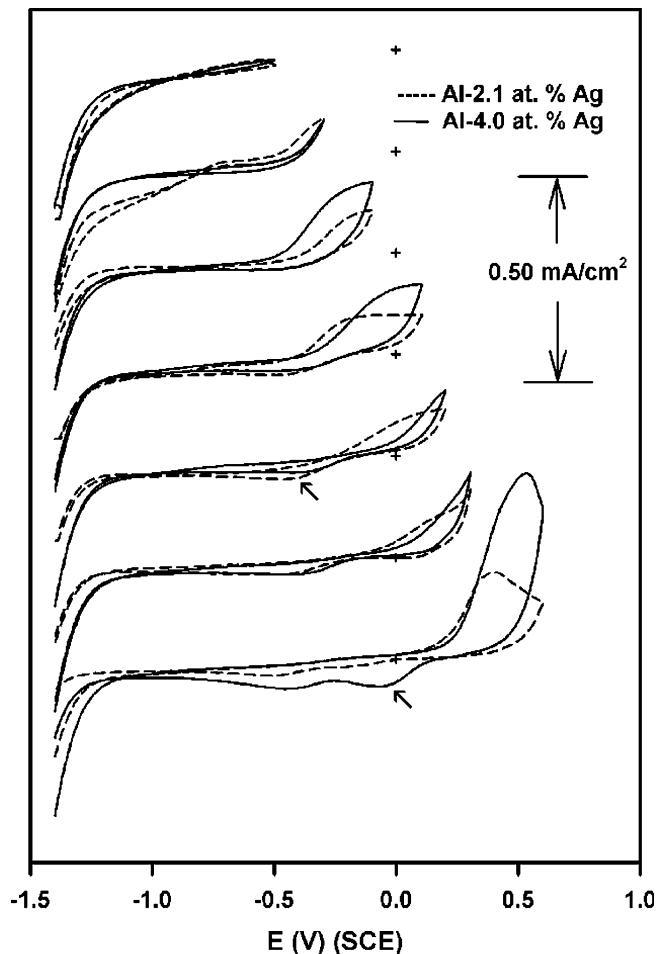


Fig. 9 Potentiodynamic polarization at 10 mV s^{-1} of the solution-aged heat-treated Al-2.1 and 4 at.% Ag alloys after chemical polishing

Discussion

The anodic behaviour of the present alloys is dependent upon the amounts and distributions of silver. The silver is mainly in solid solution and in GP zones following solution treatment, with additional Al_3Ag_2 after ageing, the amounts of the latter being increased for the alloy of higher silver content. Silver in solid solution, and possibly in fine GP zones, enriches during chemical polishing and anodizing treatments [4]. Enrichment of the intermetallic may also occur, but possibly limited by the pre-existing high concentration of silver. The enriched silver during anodizing is oxidized on achieving the required level of enrichment. The anodic film above such regions will be composed of amorphous alumina, with a reduced concentration of silver relative to that of the alloy, since silver species migrate faster than aluminium species in the film. Oxygen gas is generated, by oxidation of O^{2-} ions of the alumina, at silver-rich regions within the film, leading to bubbles of oxygen gas. The bubbles can grow, with continued thickening of the film, co-

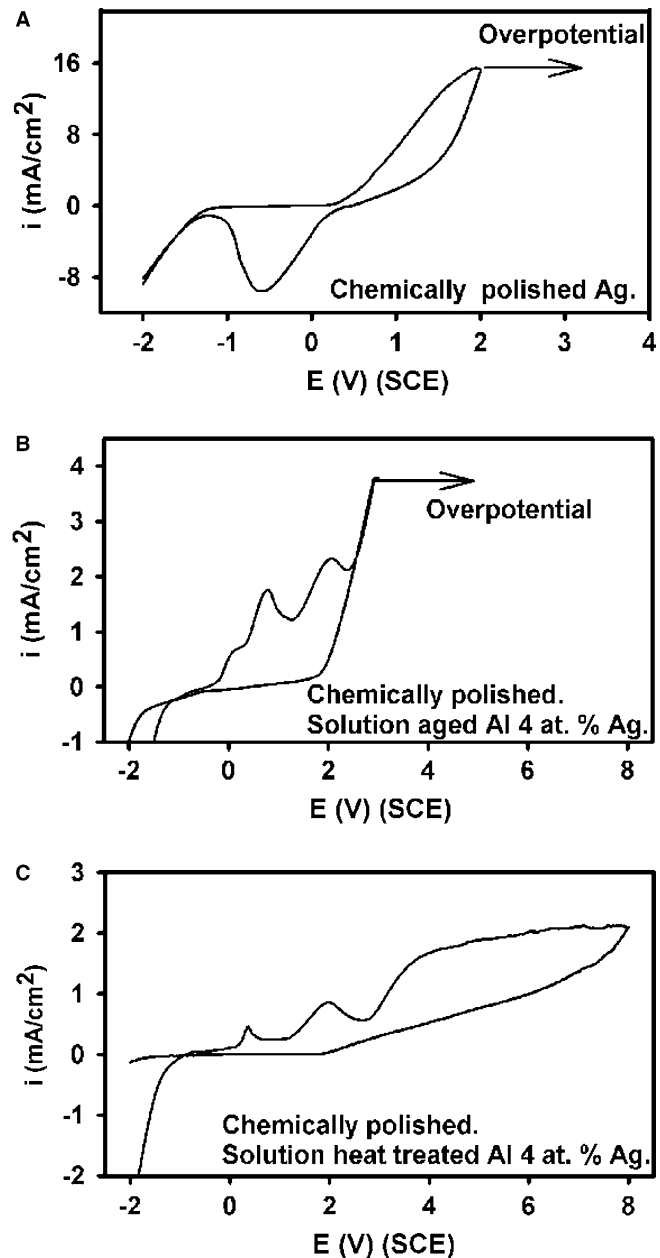


Fig. 10 Potentiodynamic polarization at 100 mV s^{-1} of silver and the differently heat-treated Al-4 at.% Ag after chemical polishing **a** silver, **b** solution-aged heat-treated alloy, **c** solution heat-treated alloy

lesce, and then burst, resulting in local damage to the film. The breach in the film is rapidly healed by growth of new oxide, but leading to an irregular film thickness. At intermetallics, such processes are accelerated by the high concentration of silver. Thus, growth of silver-free alumina, enrichment of silver in the intermetallic, incorporation of silver into the film, oxygen generation, film rupture and healing may build up layers of broken film material that can be penetrated by the electrolyte. Current may or may not flow preferentially to the intermetallic, depending upon the resistivity of the local

Table 1 The initial slope of the voltage–time response (dV/dt) during anodizing of Al-2.1 at.% Ag and Al-4 at.% Ag alloys to 200 V at 5 mA cm⁻² in 0.1 M ammonium pentaborate electrolyte at 293 K

	Solution-treated		Aged	
	MP	CP	MP	CP
Al-2.1 at.% Ag				
dV/dt (V s ⁻¹)	1.1	2.7	1.8	1.8
Slope ratio (%)	0.48	1.17	0.78	0.78
Time ratio (%)	0.54	1.1	0.9	0.83
Al-4 at.% Ag				
dV/dt (V s ⁻¹)	1.3	2.8	2.1	1.3
Slope ratio (%)	0.57	1.22	0.91	0.57
Time ratio (%)	0.73	1.5	1.1	0.75

The alloys were initially either mechanically polished (*MP*) or chemically polished (*CP*). The ratios of the initial slopes, and the times to reach 200 V, for the alloys with respect to that for high purity aluminium (2.3 V s⁻¹, 85 s) are also given

film material. With chemical polishing, similar enrichment occurs, but whether silver oxidizes or is incorporated into the oxide as nanoparticles of metal is uncertain. The level of enrichments due to chemical polishing and anodizing are expected to be similar. Silver can, therefore, immediately enter the anodic film at all regions of the surface during anodizing of chemically polished alloys. In contrast, enrichments are absent following mechanical polishing, and must be developed in the initial stages of anodizing. Enrichments proceed more rapidly at intermetallics than in matrix regions. Greater oxygen evolution and film damage is expected near intermetallics, due to the increasing availability of silver. Intermetallics were most prevalent for the aged alloys, especially those of higher silver content. Occasional intermetallics may be present in solution-treated material. Chemical polishing of the surface appeared to have little or no influence on the distribution of silver-rich regions.

Comparison of the voltage-time responses of the alloys and of high purity aluminium allows assessment of the processes taking place on the anode during anodizing. The response for electropolished aluminium is linear, with slope 2.3 V s⁻¹ under the present conditions of anodizing. This behaviour indicates growth of a uniform, amorphous alumina film on a relatively smooth and flat initial surface, with practically no side reactions or loss of aluminium to the electrolyte, i.e. corresponding to growth of oxide at 100% efficiency. The response for a second material may differ from that of the control aluminium for one or more reasons [4, 7–13]. Several factors can lead to a reduced slope: (1) A rough initial surface, for instance produced by mechanical polishing, will increase the surface area, and hence reduce the local current density [9], (2) embedded grinding and polishing particles can provide sites for oxygen evolution, with current being diverted from film growth [8], (3) cracking, rupture or detachment of the film will lead to voltage irregular falls, with net effect on the voltage-time re-

sponse dependent upon their scale and frequency, (4) incorporation of alloying element species into the alumina can alter the film density and the electric field requirements, although there is also the possibility of an increased slope [7, 10], (5) dissolution of film material, under the electric field, can slow the rate of film thickening [4, 8], (6) side reactions at second phase particles, such as oxygen evolution and particle dissolution [13]. An increased slope can arise from (1) formation of crystalline material within the film [14, 15] and (2) generation of oxygen gas, with development of bubbles within the amorphous alumina hindering ionic current flow [11, 12].

In Table 1, the ratios of the initial slopes of the voltage-time responses and the ratios of the times to reach 200 V for the alloys and aluminium are given. Chemical polishing of the solution-treated alloys results in relatively high values of both ratios. The behaviour may be most readily attributed to oxygen generation within the anodic films from the commencement of anodizing, with oxygen bubbles hindering ionic transport. The relatively low concentrations of silver species in the film are not anticipated to affect the electric field and film density significantly. Further, previous transmission electron microscopy did not indicate development of crystalline oxide. In contrast, mechanical polishing leads to significantly reduced ratios, reflecting enhanced surface areas, possible film cracking on the roughened surface, and influence of side reactions on the silver-rich phase, including dissolution of silver species and oxygen evolution. General oxygen generation at matrix regions does not occur initially, since silver enrichment must first be developed, unlike with chemical polishing. Side reactions also occur with the chemically-polished alloy, but the influence of the matrix appears to dominate, since any silver-rich intermetallics are of relatively low volume fraction. For aged alloys, the behaviour is less systematic, with most conditions giving reduced values of both ratios, consistent with increased numbers and influence of intermetallics, generating oxygen, dissolved silver species and damaged film material. The time ratios appear anomalously high for the chemically-polished and mechanically-polished alloys containing 2.1 and 4 at.% Ag respectively, suggesting that the overpotentials associated with oxygen generation offset losses of current to side reactions.

Cyclic voltammetry for aluminium reveals the expected behaviour of a chemically-polished surface, with growth of a barrier film. Mechanical polishing delays the current rise due to film growth to increased potentials, possibly due to differences in the initial film thickness for the two pre-treatments and influences of oxygen generation with the mechanically-polished surface. Further, the selected voltage sweep rate results in low current density for film growth, about 0.2 mA cm⁻², such that some hydration and dissolution of film material may occur. For solution-treated alloys, significant reduction of silver species was only occasionally detected, consis-

tent with the relatively low amounts of intermetallics. In contrast, the aged alloys disclosed more consistent indications of reduction of silver species and also oxygen, which is presumed to occur at silver-rich intermetallics.

Conclusions

1. The anodizing behaviour of Al–Ag alloys, containing 2–4 at.% Ag, during growth of barrier films in ammonium pentaborate electrolyte at constant current is strongly influenced by heat treatment of the alloy and pre-treatments of the alloy surface. In general, solution treatment combined with chemical polishing results in relatively uniform behaviour, due to the negligible presence of silver-rich intermetallics and smoothing of the alloy surface by the pre-treatment. Mechanical polishing leads to less efficient film growth due to side reactions, particularly oxygen evolution.
2. Ageing of Al–Ag alloys develops silver-rich intermetallic particles, which are preferred sites for oxygen generation, dissolution of silver species and formation of damaged film material. Accordingly, film formation occurs at reduced rates.
3. The form of the voltage-time response is dependent on the interplay of film growth, generation of oxygen bubbles within film, evolution of oxygen at silver-rich particles, film damage and healing associated with oxygen generated at matrix and intermetallic regions and dissolution of silver species.

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