Effect of copper-enriched layers on localized corrosion of aluminium-copper alloys

Efecto de las capas de enriquecimiento de cobre sobre corrosión localizada en aleaciones aluminio-cobre

Efeito das camadas de enriquecimento de cobre sobre corrosão localizada em ligas alumínio-cobre

María Ángeles Arenas-Vara[*]
Peter Skeldon[**]
Sandra Judith García-Vergara[***]

Abstract

Copper-enriched layers were developed onto aluminum-copper alloys using alkaline etching in sodium hydroxide, for both, sputter deposited and bulk conditions. Enriched alloys were evaluated by potentiodynamic polarization in sodium chloride solution in order to determine the effect of the enriched layers on the pitting potential of the alloys. Rutherford backscattering spectroscopy was employed to quantify the enrichments and their locations just beneath the alumina-based oxides remaining from the etching. For the sputter deposited aluminum-copper alloys, the results show some scattering of the pitting potential data, and no correlation between pitting potential and the alloy enriched layer. In the case of bulk Al-2wt.%Cu alloy, with the copper in solid-solution, the pitting potential increased for the enriched specimens, indicating also a different pit morphology, with respect to the non-enriched alloy.

Keywords: aluminium-copper alloys; anodizing; copper enrichment; pitting.

Resumen

Fueron desarrolladas capas de enriquecimiento de cobre mediante ataque alcalino en hidróxido de sodio sobre aleaciones aluminio-cobre. Se usaron aleaciones tanto depositadas por pulverización catódica, como vaciadas convencionalmente. Las aleaciones con las capas de enriquecimiento de cobre fueron estudiadas mediante polarización potenciodinámica en una solución de cloruro de sodio, para poder determinar si existe alguna correlación entre las capas de enriquecimiento de cobre y el potencial de picadura de las aleaciones. Los resultados no son concluyentes en el caso de las aleaciones depositadas por pulverización catódica; sin embargo, en el caso de la aleación en condición de vaciado, con el cobre en solución sólida, el potencial de picadura aumenta por la presencia de la capa de enriquecimiento, mostrando además una morfología diferente.

Palabras clave: aleaciones aluminio-cobre; anodizado; enriquecimiento de cobre; potencial de picadura.

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* Ph.D. Centro Nacional de Investigaciones Metalúrgicas – CENIM (Madrid, España). geles@cenim.csic.es.
** Ph.D. University of Manchester (Manchester, Reino Unido). peter.skeldon@manchester.ac.uk.
*** Ph.D. Universidad Industrial de Santander (Bucaramanga-Santander, Colombia). sagarver@uis.edu.co. ORCID: 0000-0002-4480-6255.

Resumo

Foram desenvolvidas camadas de enriquecimento de cobre mediante ataque alcalino em hidróxido de sódio sobre ligas alumínio-cobre. Usaram-se ligas tanto depositadas por pulverização catódica, como esvaziadas convencionalmente. As ligas com as camadas de enriquecimento de cobre foram estudadas mediante polarização potenciodinâmica em uma solução de cloreto de sódio, para poder determinar se existe alguma correlação entre as camadas de enriquecimento de cobre e o potencial de picadura das ligas. Os resultados não são concluintes no caso das ligas depositadas por pulverização catódica; porém, no caso da liga em condição de esvaziado, com o cobre em solução sólida, o potencial de picadura aumenta pela presença da camada de enriquecimento, mostrando além disso, uma morfologia diferente.

Palavras chave: ligas alumínio-cobre; anodizado; enriquecimento de cobre; potencial de picadura.

I. Introduction

Aluminum-copper alloys are widely used in aerospace and automotive industries due to their high strength to weight ratio and damage tolerance. These properties result from alloying with copper as the principal alloying element and appropriate thermomechanical processing. However, copper also has significant influence on the corrosion behaviour of the alloys. Copper-containing intermetallic particles often form microgalvanic couples with the surrounding alloy, consequently, increasing the susceptibility of the alloys to localized attack [1, 2].

In almost all applications of aluminum alloys, the fabricated alloys are pretreated and surface finished, thereby providing a functionalized surface. Etching, chemical polishing, acid picking, electropolished and anodized pretreatments of copper containing aluminum alloys normally results in the formation of a thin layer of alloy, about 2 to 4 nm thick and highly enriched in copper, immediately beneath the residual or anodic alumina film due to the less negative Gibbs free energy per equivalent for formation of copper oxide compared with that of alumina [3-6]. Further, for anodic oxidation of the alloys, once a steady enrichment of about 40 at% Cu, equivalent to about 5.4×10^{19} Cu atoms m^{-2}, is achieved, oxidation of copper proceeds and copper species are incorporated into the film at the alloy/film interface, in the alloy proportions [6]. The presence of copper in the anodic film leads to the generation of oxygen gas within the anodic films, resulting in oxygen gas containing bubbles at high pressure, consequently, introducing lateral porosity to the porous anodic films formed on copper-containing aluminum alloys [7].

Many studies have been devoted to the electrochemical behaviour of aluminium alloys in sodium chloride solutions [1-3]. All these studies reveal that the exposure of aluminium alloys to chloride ions results in localized corrosion (pitting corrosion). Pitting is the most common form of corrosion for aluminium and its alloys. Of the common electrochemical testing methods, potentiodynamic polarisation allows determining pitting susceptibility by revealing the pitting potential (E_p). Features like, inclusions, intermetallic particles (coarse or fine), surface roughness and electrochemical potential are factors that influence the nucleation and growth of metastable pits [8]. The aim of this paper is to study if there is a correlation between the enriched alloy layer and the pitting potential of aluminium copper alloys.

II. Experimental procedure

A. Sample preparation and characterization

Layers of Al-0.95at.%Cu alloy were prepared using an Atom Tech Ltd magnetron sputtering system with separate 99.999% aluminium and 99.95% copper targets. The alloy was deposited onto electropolished high purity aluminium substrates. The chamber was firstly evacuated to 6×10^{-7} mbar, and then deposition was carried out in 99.998% argon at 5.5×10^{-3} mbar. The substrates were attached to a large copper disk, whose temperature increased to 305 K during deposition of the alloys. Another set of experiments was carried out using heat-treated Al-2wt.%Cu alloy, with the copper in solid solution. Specimens of the alloy were heated to 550 °C for 3 h and then quenched in water. Rectangular pieces of the alloy were mounted in standard 00 size BEEM capsules, which were then filled with an epoxy resin. The filled capsule was cured in an oven at 60 °C for 48 h. Following the procedure used to prepare the samples for TEM by ultramicrotomy, the hardened resin blocks containing the specimens were trimmed using a glass knife in a Leica Ultracut UCT ultramicrotome. The final area was about 0.20 cm². This procedure was used to avoid inclusions or contamination by the normal polishing procedures. A high purity aluminum specimen was also prepared using the previous procedure.

The copper-enriched layer were generated, for both type of samples, by anodic etching at a constant current density of 5 mA cm⁻² in 0.1 M sodium hydroxide solution at 293 K by different times. Individual specimens were then connected, as the anode, to the power supply (METRONIX 6911 DC) and a stainless-steel sheet was connected as a cathode. The voltage-time responses of the anodic etching were recorded on a PC, with a PICOLOG recorder program. After the anodic etching, the specimens were quickly rinsed with deionized water and dried in cool air stream. The specimens were then immersed for 30 s in 15% nitric acid, to remove any smut layer, rinsed with deionized water and dried in a cool air stream.

The composition of the sputter deposited alloy and the specimens with the copper enriched layers were determined by Rutherford backscattering

spectroscopy (RBS) [9], using 2.00-2.5 MeV He+ ions produced by the 2.5 MeV Van de Graaff accelerator of the University of Paris. The beam current and the bean diameter were 60 nA and 0.5 mm, respectively, with the beam incident normal to the specimen surface. The scattered particles were detected at 165° to the direction of the incident bean. The data were interpreted using the RUMP program [10].

Specimens of freshly deposited and anodic etched alloy were sectioned to a nominal thickness of ~10 nm by ultramicrotomy and examined by Transmission electron microscopy TEM using a JEOL FX 200 II instrument.

B. Corrosion test

Potentiodynamic polarization curves of the aluminium-copper alloys, enriched aluminium-copper alloys and high purity aluminium were recorded in de-aerated 0.1 M sodium chloride solution at 293 K at a scan rate of 0.2 mV s^{-1}. The working area, defined with Lacomite, was about 0.2-1.0 cm^2, for the sputter deposited and bulk alloys, respectively. A three-electrode cell was employed, with a platinum counter electrode and a saturated calomel reference electrode (SCE). The data were recorded using a potentiostat-galvanostat EG&G 264, Solartron connected to a computer, using the Corr software.

III. Results

A. Enrichment of copper developed by alkaline etching

Table 1 lists the enrichments of copper from RBS and the expected amount of copper in the enriched layer generated in the Al-0.95at.%Cu alloy by alkaline etching in sodium hydroxide for 12 to 75 s. The average compositions of the copper enriched layer are also given assuming a layer of 2 nm in thickness with a weighted average of the atomic densities of aluminium and copper. Only for the longest time does copper oxidize during etching. The atomic density of the outer layer film material used in the simulations was 0.92 ´ 10^{23} atoms cm^{-3}, corresponding to that of anodic alumina of density 3.1 g cm^{-3}. The RBS analysis shows that the copper enrichment increases as the time of anodic etching increases.

Table 1
RESULTS OF RBS ANALYSES OF AL-0.95AT.% CU ALLOY AFTER ETCHING AT 5 MA CM^{-2} IN 0.1 M SODIUM HYDROXIDE SOLUTION AT 293 K

Time of etching (s)	Enrichment in alloy (Cu atoms cm^{-2})		Average composition of enriched layer (at.%Cu)
	RBS	Expected	
12	1.2 x 10^{15}	1.2 x 10^{15}	10
22	2.1 x 10^{15}	2.1 x 10^{15}	18
43	4.5 x 10^{15}	4.6 x 10^{15}	37
75	6.5 x 10^{15}	7.9 x 10^{15}	55

Figure 1 shows typical transmission electron micrographs of the Al-0.95at.%Cu alloy following deposition and after 75 s of etching in sodium hydroxide. The alloy is columnar-grained, with a typical grain width of ~ 40 nm, and the selected surface was locally flat to within ~ 8 nm, which are usual for the sputtering conditions. In the presented example, etching for 75 s reduced the alloy thickness by 148 nm, in reasonable agreement with the calculated reduction of 132 nm from the time of etching.
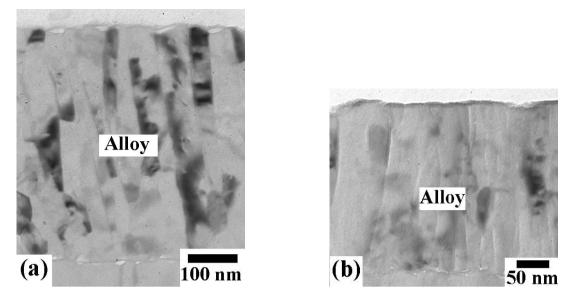
Fig. 1. Transmission electron micrographs of the Al-0.95at.%Cu alloy following (a) deposition and (b) etching for 75 s at 5 mA cm-2 in 0.1 M sodium hydroxide solution at 293 K.

B. Potentiodynamic polarization behaviour in sodium chloride solution

1) Sputtering-deposited Al-0.95at.%Cu alloy. Figure 2 shows the potentiodynamic polarization curves of Al-0.95at.%Cu alloy in de-aerated sodium chloride solution at 298 K, following alkaline etching. Individual specimens were immersed for 120 min prior to polarization. The potential was scanned at 0.2 mV s^{-1} starting at about 200 mV below the corrosion potential. The cathodic current density, due to decomposition of the water, does not show significant changes with the alloy enrichment, exhibiting values of 0.01–0.02 mA cm^{-2}. The corrosion potential increases as the etching time increases, due to the presence of the copper-enriched alloy layer, being the corrosion values about -1065 mV for the as-deposited alloy, -972 mV and -896 mV following 12 and 43 s of alkaline etching, respectively. Further, the curves suggest an slightly increased corrosion current density (i_{corr}) of 3.5 ´ 10^{-7} A cm^{-2} following 43 s of etching, when the enrichment is about 4.5 ´ 10^{15} Cu atoms cm^{-2} compare with the non-enriched alloy. The current density subsequently increases due to pitting. However, identification of the pitting potential (E_p) was hindered by absence of a clearly defined change in behaviour, which may relate to the use of thin alloy layers. E_p is here considered as the potential at which the current starts to increase rapidly above the background passive current [11]. Generally, the Al-Cu alloy appears to disclose an increase in the pitting potential in comparison with that of aluminium. This behaviour is in general agreement with previous work [12].
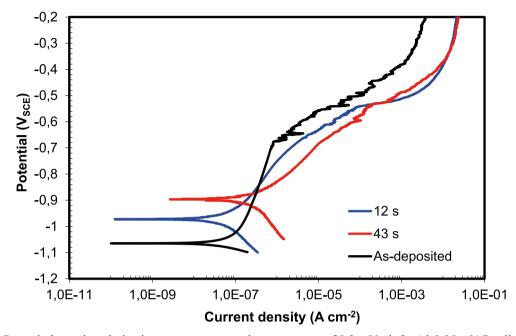
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Fig. 2. Potentiodynamic polarization curves, measured at a scan rate of 0.2 mV s^{-1}, for Al-0.95at.%Cu alloy in de-aerated 0.1 M sodium chloride solution at 293 K. The curves were measured for the as-deposited alloy, and following etching of the alloy for 12 and 43 s at 5 mA cm^{-2} in 0.1 M sodium hydroxide solution at 293 K.

Then, considering the results for the sputtering-deposited Al-0.95at.%Cu alloy in which copper does not oxidize, there is an increase in the corrosion potential by about 160 mV vs. SCE with enrichment by 4.5 ´ 10^{15} Cu atoms cm^{-2}. The influence of the enriched alloy layer on the free corrosion potential of aluminium alloys has been reported previously [13]. The present results confirm the key role of the copper enrichment in determining the corrosion potential of aluminium alloys. Further, the cathodic current density increases in the presence of the enriched alloy layer, suggesting changes in the cathodic kinetics. The pitting potential, however, is not well defined, probably due to the relatively low thickness of the initial alloy layers, which is further reduced by the anodic etching in sodium hydroxide solution. Although the thin layers have the advantage that surface preparation is not required prior to anodic etching, unlike bulk alloys that require mechanical treatment to generate a non-enriched initial surface, this is offer by their low thickness.

2) Bulk aluminium-copper alloy. The potentiodynamic polarization curves of the bulk Al-2wt.%Cu alloy, in both the as-received and alkaline-etched conditions, in de-aerated sodium chloride solution is presented in

Figure 3. The polarization curve of high pure aluminium is also included for comparison. The curves display a positive shift of the corrosion potential, as the enrichment of copper increases; however, the magnitude is smaller compared with that observed in Figure 2, for sputtering-deposited aluminium-copper alloy. The anodic region of Al-Cu specimens presents passive current densities in the range typically between 0.3–6 mA cm^2, with pitting subsequently commencing at potentials of about -600 mV vs. SCE. Pure aluminium exhibits a passive current density of about 0.4 mA cm^{-2} and a pitting potential of about -689 mV vs. SCE. After this point, the current density increases rapidly due to the pitting corrosion. Compared with the previous results for the sputtering-deposited alloy, the pitting potential is clearly distinguished for the bulk alloy. Further, measurements performed in triplicate for each specimen, show a very good reproducibility. The enrichment measured by RBS reveals a level of about 4.0 ´ 10^{15} Cu atoms cm^{-2} after 41 s of etching. However, no particular difference in the pitting potential is displayed between specimens in the as-received and alkaline-etched conditions, except for the possibly formation of metastable pits on the specimen in the as-received condition.
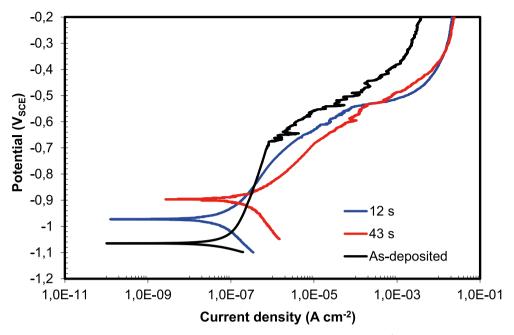
Fig. 3. Potentiodynamic polarization curves, measured at a scan rate of 0.2 mV s^{-1}, for Al-2wt.%Cu alloy in de-aerated 0.1 M sodium chloride solution at 293 K. The curves were measured for high pure aluminium, for as-received Al-2wt.%Cu alloy, and following etching of the alloy for 41 s at 5 mA cm^{-2} in 0.1 M sodium hydroxide solution at 293 K.

Pitting corrosion is considered to be one of the principal mechanisms for damage of high-strength aluminium alloys. Pitting corrosion occurs in the presence of aggressive anionic species, and chloride ions are usually, although not always, the cause. Chloride is an anion of a strong acid, and many metal cations exhibit considerable solubility in chloride solutions [12]. A critical factor in pitting corrosion is that the phenomenon is considered to be autocatalytic in nature; once a pit starts to grow, the conditions developed are such that further pit growth is promoted. The resistance to pitting for pure metals is usually measured in terms of the pitting potential, E_p, which characterizes the electrochemical stability of the passive film [14].

A better approach to understanding the effect of the alloy enrichment on the pitting potential was achieved using a bulk Al-2wt.%Cu alloy. Since the aluminium is a reactive metal, the homogeneous addition of almost any metal (except magnesium and zinc) to aluminium results in an increase in pitting potential, provided that the structure remains single phase [15, 16]. Galvele *et. al.* reported that the pitting potential of aluminium-copper alloys increased with copper concentration as long as copper was in solid solution [12]. They examined electropolished aluminium-copper alloys with copper content between 1 to 33 wt.%. The

pitting potential was increased by about 200 mV as the concentration of copper increased to 5 wt.%, with respect to aluminium. Enrichment of the alloying elements at the alloy/alumina film interface in aluminium alloys has been observed as a consequence of several surface treatments, including electropolishing [17]. Accordingly, the enrichment of copper was present in the specimens examined by Galvele *et al.*, and the observation regarding an improved resistance to pitting corrosion could reflect on the influence of this enriched alloy layer. Following their observations, a positive effect of the enriched alloy layer was expected in the present study. The pitting potential of the bulk aluminium-copper alloy increases in about 100 mV compared with aluminium. However, the potentiodynamic polarization curves show that the pitting potential for the specimens in as-received and alkaline etched conditions, exhibits approximately the same value around -600 mV vs. SCE. The thickness of enriched alloy layer is about 2–2.5 nm and the layer is probably consisted of copper-rich clusters, which are of size of the order of nanometres. Pits can penetrate the alloys in a fraction of seconds, and the effect of the enriched alloy layer cannot be detected. From the present observations, it is possible to conclude that the enrichment of copper in the alloy is not a key factor in the pitting corrosion of aluminium alloys. On the other hand, pits

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in aluminium alloys are typically associated with intermetallic particles [18, 19]. For aluminium-copper alloys, the presence of the intermetallic q-phase (Al$_2$Cu) reduces the resistance to pitting at levels similar to those achieved in aluminium alloyed with little copper [20]. In the commercial alloys, pitting corrosion is normally associated with the presence of two constituent particles, Al-Cu-Mn-Fe and Al-Cu-Mg containing particles [21]. Recently it was found that intergranular corrosion occurs first and crystallographic pitting initiates from the crevice wall behind the intergranular corrosion front of aluminium-copper alloys exposed to chloride solutions. Due to copper enrichment along the pit walls, the crystallographic pits in the AA2024 alloy are characterized with relatively irregular pit walls on a much finer dimension compared to the well-defined half-cube shape crystallographic pits in pure aluminium [22]. The present results confirm the influence of the enrichment of the alloying elements in the corrosion behaviour of surface-treated aluminium alloys. Also, they suggested that further investigation is necessary to clarify the behaviour of alloy enriched aluminium alloys in chloride solutions.

IV. Conclusions

The corrosion potential of an alkaline-etched, solid-solution Al-0.95at.%Cu alloy or bulk Al-2wt.%Cu, in de-aerated sodium chloride solution moves to more noble values as the level of copper enrichment in the alloy increases. The latter is determined by the extent of prior etching. The potential shift is more relevant for Al-0.95at.%Cu alloy after etching, about 160 mV as the enrichment rises to 4.5 ´ 10^{15} copper atoms cm^{-2}. Additionally, the absence of a clearly defined pitting potential of the sputtering deposited aluminium-copper alloys is related to the thickness of the alloy layers, suggesting that pit penetration of the alloy layers is very fast, and that the influences of the aluminium substrate cannot be avoided. Finally, the copper-enriched layer did not show a significant effect on the pitting potential, either in the as-deposited alloy or in the bulk alloy, suggesting that it is not a critical factor determining the resistance to pitting.

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