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Hard anodizing of AA2011-T3 Al-Cu-Pb-Bi free-cutting alloy: improvement of the process parameters

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ABSTRACT

The free-cutting Al-Cu-Pb-Bi alloy AA2011-T3 has been anodized in a traditional sulphuric bath with the aim of producing hard and uniform oxides of technological interest. H_2SO_4 concentration, electrolyte temperature, Al^{3+} concentration and current density have been modified. The effect of each process parameter has been evaluated through Potential-vs-time plot, coating hardness, coating thickness, volumetric expansion-ratio and coating defectiveness. SEM analysis has shown that Bi-based intermetallics are the main responsible for the severe defective state. Higher H_2SO_4 concentration and higher current density have improved coating hardness and defectiveness, however potentiodynamic polarizations have revealed that they do not enhance corrosion resistance.

1. Introduction

Aluminum, despite its many common applications, has its main and most indispensable use in the structural engineering field. Here, heat treatable alloys (series 2XXX, 6XXX and 7XXX) have great importance due to their significant high-mechanical-properties/low-density compromise. The latter peculiarity is fundamental when high performances or fuel saving issues are involved as in aircraft, vehicles and naval transports [1].

Often, aluminum components are processed through computer numerical controlled machines (CNC) where free-cutting properties are fundamental for high quality surface finish, high productivity and low tool-wear rates. The term 'Free-cutting' means that working chips easily flow away from the component being cut. This property is obtained through the addition in the alloy of proper elements with low melting point and low solubility which form dispersed inhomogeneities in the matrix; the high temperatures reached in the cutting area cause these dispersed phases to melt making chips breakage and removal easier [2]. AA2011 is an Al-Cu alloy with the addition of Pb and Bi as free-cutting elements which were observed to form eutectic globules at the grain boundaries; they are reported to greatly enhance machinability without compromising tensile properties [3].

On the other hand, every dispersed particle and inhomogeneity in the aluminum matrix acts as galvanic microcell thus decreasing the overall corrosion resistance of the alloy and making it more susceptible to dangerous localized forms of corrosion [4–9]. In order to avoid the onset of these localized phenomena, a common practice is to prevent the direct contact between the surrounding and electrochemically active metal through protective coatings such as paints, conversion coatings and/or anodic oxides.

Anodic oxidation is indeed a widespread electrochemical surface treatment in aluminum alloys which, in addition to corrosion resistance enhancement, creates a hard and wear-resistant film up to ~100 μm thick often fundamental in advanced structural applications [10,11]. Unfortunately, just those alloys which suffer more from corrosion and which requests harder surface for critic applications (highly alloyed casting and heat treatable alloys) are the most difficult ones to be anodized. All the constituents and precipitates which contribute to improve mechanical properties through precipitation hardening [12] or to improve machinability [2,13], create compositional and morphological inhomogeneities which make it difficult to obtain low-defected, well-adherent, hard and compact oxides [14–18].

Much research has been done on the influence on anodizing process of most common hardening precipitates and impurities found in aluminum alloys; $TiAl_3$, $NiAl_3$ and $MnAl_6$ were reported to oxidize slower than Al-matrix while Mg_2Si, $CuAl_2$, β-AlMg, Al-Zn-Mg at faster rate and $FeAl_3$ at similar rate [19,20]. Al–Fe and Al–Fe–Si particles are preferentially embedded into anodic oxide while Al-Cu intermetallics show the tendency to be primarily oxidized creating flawed oxides [17]. Other studies found that anodizing potential is crucial in determining the preferential oxidation of intermetallics; Al–Cu–Mg precipitates are oxidized faster also at low potentials while Al–Cu and Al–Cu–Fe

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particles show inert behavior at low potentials but they preferentially oxidize at high ones [21,22]. Furthermore the higher the Cu content and the faster preferential oxidation of intermetallic occurs due to increase of oxygen evolution and associated cyclic disruption of the anodic oxide [14]. Al-Fe-Mn-Si particles are dangerous for the good quality of anodic oxide; indeed high quantities of Fe and Mn impurities in those particles induce inhomogeneous growth of anodic coating and steep voltage rise during treatment [15,23].

While much data is available in literature on the influence of most common precipitates during anodizing, very little is present about uncommon alloying elements. Few studies report that Li-based intermetallics introduce possible cracking and oxide detachment caused by lithium Pilling-Bedworth ratio smaller than 1; moreover Li high tendency to oxidation creates inhomogeneities in electric field concentration which lead to unstable oxide growths [24,25]. One work focused on barrier anodic films formed on metastable solid solution Al–Ta alloys. It reports that Ta^{5+} ions migrate more slowly than Al^{3+} ones so leading to oxides characterized by outer layers rich in alumina and inner layers containing units of alumina and tantala [25]. Other uncommon alloying elements, in particular cadmium, indium and tin were studied with concern to void formation and alloy enrichment phenomena [26]. Indium and tin are said to be oxidized creating fine voids due to their relatively low Pilling-Bedworth ratio; on the other hand cadmium remained preferentially unoxidized causing no voids production.

Within this context, for the best of our knowledge, no studies concerning anodizing of aluminum alloyed with bismuth and lead have been carried out yet. However, cyclic voltammetry studies on Pb-Ca-Sn-Al alloys for batteries revealed that the addition of bismuth leads to the increase of the hydrogen and oxygen evolution rate [27]. Another similar work also reported that bismuth in the positive electrode promotes the evolution of oxygen [28].

Summing up, from a point of view of technological interest, the different precipitates and every compositional or morphological inhomogeneity in the aluminum matrix can cause: i) different electric field distribution between matrix and intermetallics so leading to an uneven anodic growth [10,25]; ii) entrapment of unoxidized metal particles into the anodic coating [10,15,23,29–33]; iii) oxygen evolution parasitic reaction typically caused by Al-Cu-Fe particles inducing voids and porosities [14,34–37]; iv) local tensions and micro voids due to oxidation of elements with low Pilling-Bedworth ratios [24,26]; v) defects along the barrier layer which hinder its compactness [38]. It is fundamental to study and overcome all the latter critical issues firstly to be able to obtain hard, compact and well adherent oxides; secondly it would limit the fatigue resistance decrease intrinsically introduced by anodizing treatment [39–42].

This work focused on the hard anodizing process of the AA2011-T3 Al-Cu-Pb-Bi free-cutting alloy in traditional sulphuric bath. With a standard set-up of variables suitable for other AA2XXX alloys, AA2011-T3 produced a spotted and extremely inhomogeneous coating really far away from possible acceptability in practical applications. Hence the values of temperature, H_2SO_4 concentration, Al^{3+} concentration and mean current density were modified in order to find out possible set-ups able to produce uniform, hard and compact oxides of technological interest.

2. Material and methods

2.1. Hard anodizing tests

Hard anodizing treatments were performed in a laboratory pilot plant whose schematic representation and details are well described elsewhere [37]. In general, it consists of a galvanostat/potentiostat connected to a programmable function generator and to other devices that ensure the acquisition of voltage *vs* time curves meanwhile the anodization experiment is being performed under galvanostatic control.

Table 1
Parameters set for hard anodizing experiments.

Sample	Bath Conditions			Electrical Parameters		
	H_2SO_4 [g/L]	T [°C]	Al^{3+} [g/L]	Description	Charge [C/cm^2]	Duration [min]
1	190	−2	8	Increase of	100	72
2	100	−2	8	2 mAcm^{-2}min^{-1} up to		
3	300	−2	8	25 mA/cm^2 and then		
4	400	−2	8	maintenance at 25 mA/		
5	190	10	8	cm^2 for 60 min		
6	190	20	8			
7	190	−2	2			
8	190	−2	11			
9	190	−2	8	Maintenance at 40 mA/		42
				cm^2 for 42 min		
10	190	−2	8	Maintenance at 60 mA/		28
				cm^2 for 28 min		
11	190	−2	8	Maintenance at 90 mA/		19
				cm^2 for 19 min		

The electrolytic cell is designed in order to guarantee good thermostatic control, good bath agitation and reproducible experimental set-up. The AA2011 (T3 temper condition) sample (Cu 5–6%, Bi 0.2–0.6%, Pb 0.2–0.6%, Fe < 0.7%, Si < 0.4%, Zn < 0.3%, others totally < 0.15%, each other < 0.05%) is exposed to electrolyte only through a constant circular area of 1.0 cm^2 and placed 1 cm distant from the cathode.

Every fundamental treatment variable was investigated and varied within large ranges of values to find possible ways to obtain oxides interesting for technological applications. Using a common set-up of variables suitable for AA2XXX alloys as a reference [36] (sample 1 in Table 1), one by one electrolyte bath temperature, H_2SO_4 concentration, Al^{3+} concentration and mean current density were investigated. When one variable was being varied, the others were kept constant and equal to the reference ones; compare Table 1 for every test settings. A common theoretical charge of 100 C/cm^2 was anyway imposed for every test in order to ensure the best comparability conditions; it was specifically chosen in order to obtain a thickness of around ~50 µm, largely adopted in industrial practice.

Just before each anodization, the sample disk was polished with FEPA#1200 SiC emery paper; afterwards it was cleaned with acetone and rinsed in distilled water. Sample 1, 6 and 10 were produced in two copies, one for mechanical and optical characterization, and the other for corrosion test. Once completed the anodizing treatment and before embedding it in resin or mounting it in the electrochemical cell (to perform polarization test), every sample was kept in atmospheric conditions (in a closed box at 19–23 °C, 60%–70% RH) for five days in order to let the oxide natural sealing occur.

2.2. Characterization techniques

Hard anodized samples were characterized with measures and parameters specifically described in our previous work [37]. In general, the following parameters were analyzed:

i) oxide defective state: a qualitative parameter obtained evaluating the oxide flaws condition taking into account the defects specified in the ISO standard 7585:2013, chapter 2.9. In particular, the samples studied in this work were characterized by crazing phenomena, punctual defects (as conical asperities), more or less accentuated roughness of the alloy/oxide interface and aesthetic inhomogeneities. This parameter qualitatively ranges from 0 to 10, where 0 means a totally defected oxide and 10 a perfect one. Observation in cross section was carried out at optical microscopy after sample embedment in resin, cut and polishing with emery papers and diamond suspensions. Furthermore, since this particular alloy often produced particularly poor oxides clearly visible also at