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Hard anodizing of AA2099-T8 aluminum lithium copper alloy: Influence of electric cycle, electrolytic bath composition and temperature

Massimiliano Bononi [a,*], Manuela Conte [a], Roberto Giovanardi [a], Andrea Bozza [b]

[a] *University of Modena and Reggio Emilia, Department of Engineering 'Enzo Ferrari', Via Vivarelli 10, 41125 Modena, Italy.*
[b] *Microntech s.r.l., GPS-Mochem Group, Via A. Boito 431, Soliera, MO, Italy*

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ABSTRACT

AA2099-T8 samples have been hard anodized in a traditional sulphuric bath with the aim of studying the influence of i) electrolyte temperature, ii) Al^{3+} concentration and iii) different electric cycles in direct current, multi-step direct current and pulsed current (both completely anodic cycles and with cathodic "off" pulses). Anodic oxide thickness, volumetric expansion ratio (V_{ox}/V_{Al}), mean hardness ($HV_{0.05}$), faradic efficiency and defective state have been analyzed. As temperature decreases, the oxide hardness increases but defectiveness steeply worsens; similarly a middle compromise of Al^{3+} concentration ensures the best performances. Regimes of high current, from one side, and of low current and current transient, from the other side, strongly affect oxide defective state introducing different types of flaws; an appropriate balance is crucial for a performing non-defected oxide. High current induces the occurrence of parasitic reactions which produce rough and defected Al/ox interface. Low current and current transient induce diffused cracking and detachments of coating fragments which decrease corrosion resistance as shown by potentiodynamic polarization tests. Li-based intermetallics play a crucial role in the last mentioned flaw-creation phenomena since they produce inhomogeneities in electric field distribution and contribute to create unstable oxide structures.

1. Introduction

Anodic oxidation is a surface treatment widely used in the field of aluminum alloys thanks to its reasonable price if compared to the benefits it can offer in terms of corrosion resistance and mechanical, functional and aesthetic properties. In particular, the hard anodizing version can increase the tribo-corrosive performances of components thanks to the growth of a hard and compact oxide up to several tens of microns [1]. Therefore it finds large application in advanced structural engineering sectors as automotive, motorsport, aerospace and military. In these sectors, heat treatable aluminum alloys are materials of extremely great interest thanks to an optimal mechanical-properties/density ratio; hence they open the possibility to lighten structures to the limit in those applications where also a small gain in weight reduction represents a great improvement [2]. In order to further optimize the performances in these sectors, in the last decades the metallurgical research has led to the development of third generation heat treatable aluminum lithium alloys. The critical issues of brittleness and anisotropy which were limiting the application in the previous generations, now on the third one have been overcome [3,4]. Proper addition of lithium as alloying element and the optimization of the alloy thermo-metallurgic treatment [5–13] have allowed to gain improvements if compared to traditional heat treated alloys belonging to 2XXX and 7XXX series. In particular better yield strength, corrosion and fatigue resistance, fracture toughness and weldability have been achieved; moreover a further decrease of density and an increase of Young modulus have been obtained. In the context of the third generation aluminum lithium alloys, AA2099-T8 is a consolidated and commercially diffused alloy adopted in those advanced sectors which request high material performances without high economic constraints [3,4]. Regarding anodizing treatment on this alloy, currently few studies have been performed; they concern the film composition and morphology in function of applied potential [14] and the intermetallics role on the oxide growth process [15,16]. At low voltage values, well defined pore morphology occurs with the incorporation of Cu-rich nanoparticles into the oxide; with potential increase, pores dimensions get bigger and an increase of lateral porosity occurs instead. The latter derives from gaseous oxygen evolution occurring during the oxidation of Cu-rich particles and depends upon grain orientation [14]. Concerning the aspects of technological interest, the different precipitates affect the process and contribute to the formation of cavities, defects and irregular structures in the oxide [16]; therefore the obtainment of a performing hard and compact oxide is hindered. In literature, several studies have already proven that the film properties in many heat treated aluminum alloys are seriously affected by intermetallics, microstructural and compositional

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[*] Corresponding author.
E-mail address: massimiliano.bononi@unimore.it (M. Bononi).

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inhomogeneities [17–19]. Unoxidized intermetallics can remain entrapped into the anodic film [20–22] and parasitic reactions as gaseous oxygen evolution may occur [23–25]. Furthermore distorted distributions of electric field are possible and they can lead to inhomogeneous oxide growths [1]. Moreover, the peculiar presence of lithium introduces other critical issues due to its tendency to form an oxide with molar volume smaller than the base metal one; as a result many microvoids are created along the aluminum/oxide interface so compromising coating adhesion [15]. Previous works on different classes of alloys show that some critical issues can be attenuated through the modification of the electrolytic variables [20,26,27] or adopting specific electric cycles as the pulsed current [28–35]. Through the optimization of the latter variables, a good compromise between hardness, compactness and low defectiveness can be achieved. The resulting thick and performing oxide is fundamental for the typical field of application of AA2099-T8. Indeed, the structural components in aerospace, automobile and marine sectors are often in relative contact and aluminum suffers from wear due to its low hardness [36]. Indeed the vibrations produced by flight or any kind of motion make the contacting parts rub against each other; as a result wear phenomena occurs and damage the structure [37,38]. The presence of a hard, thick and well adherent oxide provided by hard anodizing ensures the improvement of wear resistance properties [1,39]. In the light of this scenario, this work focuses on studying the hard anodization of the Al-Cu-Li alloy AA2099-T8 in traditional sulphuric bath. In particular, concerning electrolytic bath variables, Al^{3+} concentration and temperature influence has been explored; as for electric cycle, many different procedures in direct current, multistep direct current and pulsed current have been tested in order to achieve the best technological oxide properties (hardness, compactness, defectiveness). Potentiodynamic polarization tests have then been carried out on the most representative samples to understand how anodic oxide and different defective states affect the corrosion resistance.

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 [29]. 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 was being performed under galvanostatic control. The electrolytic cell is designed in order to guarantee good thermostatic control, good bath agitation and reproducible experimental set-up. The AA2099 (T8 temper condition) sample (Cu 2.4–3%, Li 1.6–2%, Zn 0.4–1%, Mg, Mn 0.1–0.5%, Zr 0.05–0.12%, Ti $< 0.1\%$, Fe $< 0.07\%$, Si $<0.05\%$) is exposed to electrolyte only through a constant circular area of 1.0 cm^2 and placed 1 cm distant from the cathode. The mean grain size of the material was calculated with the linear intercept method, according to ASTM standard E112. 5 micrographies at 50× magnification and 5 micrographies at 100× were analyzed. They were captured with the optical microscope after 20 s of material etching into the Dix-Keller reagent. Due to significant grain anisotropy in the plane of the samples subjected to anodizing, two different averages were calculated in two perpendicular directions, defined as longitudinal and transversal. The longitudinal mean grain size is (462 ± 54) μm and the transversal one is (65 ± 5) μm.

Firstly, bath associated variables were studied (Table 1). Twelve cross variables test were performed testing three values of Al^{3+} concentration (2 g/L, 5 g/L, 8 g/L) and four temperatures (−2 °C, 0 °C, 2 °C, 4 °C). These values were chosen because they belong to the range which gave the best results in our previous works [28,30]. For all these first anodization experiments, H$_2$SO$_4$ concentration was kept constant and equal to 186 g/L; the same was done with electric cycle, a constant direct current ramp (compare Table 1 for description) was applied transferring 100 C/cm^2 of charge.

Table 1
Parameters adopted for studying the influence of electrolytic bath variables.

Sample	Bath conditions			Electrical parameters		
	H$_2$SO$_4$ [g/L]	T [°C]	Al^{3+} [g/L]	Description	Charge [C/cm^2]	Duration [min]
1	186	−2	8	Increase of 2 mA cm^{-2} min^{-1} up to 25 mA/cm^2 and then maintenance at 25 mA/cm^2 for 60 min	100	72
2		0				
3		2				
4		4				
5		−2	5			
6		0				
7		2				
8		4				
9		−2	2			
10		0				
11		2				
12		4				

Analyzing the results obtained from the first run of experiments, the optimal Al^{3+} concentration (5 g/L) and the most interesting anodizing temperatures (2 °C and −2 °C) were defined; hence the latter conditions were chosen for the following tests which tried to achieve improvements through the modification of electric cycle (Table 2). In particular i) with $T = -2$ °C the best oxide hardness was achieved, but the coating was moderately defected, so a soft pulsed current cycle was applied in order to improve the defective state (PC1 in Table 2); DC (duty cycle) = 50%, I$_{on}$ = 24 mA/cm^2, I$_{off}$ = 6 mA/cm^2 and 0.05 Hz were chosen because in a previous study [28] they had allowed to greatly reduce the number of defects in another AA2XXX series alloy; ii) with $T = 2$ °C the best compromise between mechanical properties and defectiveness of the oxide had been achieved, so different pulsed current cycles were tested in order to further improve the oxide properties (i.e. hardness and volumetric expansion ratio). Different settings were tested (frequencies, current levels and times), all of them falling in the most adopted ranges found in literature and already tested in other alloys in our previous work [29]. Contrarily, PC5, PC6 and PC7 were specifically designed in this work to understand more about the influence of low and high currents on the process. I$_{on}$ was kept at 40 mA/cm^2 for all the three samples, while 3, 6 and 24 mA/cm^2 were adopted as I$_{off}$. These tests allowed to have better evidence of the defective state provoked on the oxide by low currents which emerged to be crucial in the previous tests. A common theoretical charge of 100 C/cm^2 was anyway maintained for every test of this work in order to ensure the best comparability conditions.

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 7, PC2 and PC4 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 the 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 natural sealing of the oxide occur.

2.2. Characterization techniques

Hard anodized samples were characterized with the same procedure adopted in our previous work [29]. In general, the following parameters were analyzed:

i) oxide state of defects: a qualitative parameter obtained evaluating the oxide flaws condition taking into account the defects specified in the ISO standard 7585:2013, Section 2.9. In particular, the samples studied in this work were characterized by crazing phenomena, punctual defects (as conical asperities) and