

Electrochemical behavior of intermetallic phases in sulfuric acid at high voltage – anodization of $\text{Al}_7\text{Cu}_2\text{Fe}$ and MgZn_2 phase

Joffrey Tardelli Emmanuel Rocca

Institut Jean Lamour, UMR7198 CNRS – Université de Lorraine, BP 70239, 54506 Vandoeuvre-Les-Nancy, France - emmanuel.rocca@ijl.nancy-universite.fr

Abstract

The purpose of this article is to characterize the electrochemical behavior and the corrosion layer of bulk phases, $\text{Al}_7\text{Cu}_2\text{Fe}$ and MgZn_2 , in the anodization electrolyte H_2SO_4 200 g/l at the open-circuit potential and at high voltage until 20 V. A rapid dealloying phenomenon was characterized with the formation of a nanometric sponge of copper on surface. Surprisingly, MgZn_2 has a “metal valve” behavior in sulfuric acid at high potential despite a relatively high dissolution rate. The consequences of the electrochemical behavior of these phase was discussed in the case of the anodization of 7050 alloy.

Introduction

The aluminum alloys with high mechanical properties, the 2xxx and 7xxx series are very sensible to corrosion because of the presence of numerous intermetallic phases in these materials. These phases are responsible of the formation of many defects in the anticorrosion coatings, especially in the anodized layers as displayed in the figure 1.

The objective of this work is to study the behavior of two main phases, $\text{Al}_7\text{Cu}_2\text{Fe}$ and MgZn_2 present in the 7050 alloy in the condition of anodization process of aluminum alloys.

Birbilis et al. [1] have studied the corrosion behavior of $\text{Al}_7\text{Cu}_2\text{Fe}$ in NaCl solution by capillary microelectrode technique directly on 7075 alloy or model alloys. However, this technique is difficult to use in very corrosive media such as sulfuric acid and with high voltage. For MgZn_2 (η) phase, some electrochemical measurement was realized by Li et al. [2] in NaCl solution on bulk- MgZn_2 sample.

The purpose of this article is to characterize the electrochemical behavior and the corrosion layer of bulk phases in sulfuric acid and at high voltage.

Experimental

For that, the bulk phases, $\text{Al}_7\text{Cu}_2\text{Fe}$ and MgZn_2 , was synthesized from the pure elements by melting small pieces (3-8 mm) under argon gas in a high frequency inductive furnace. After several inducting fusions, the samples were annealed at several temperatures during 96 hours, to make compact and dense samples at a centimeter scale. The electrochemical measurements were performed in 2 mol L^{-1} sulfuric acid in three-electrode cell until 20 V using Modulab potentiostat with HV100 booster, a SCE reference electrode and a working surface of 1 cm^2 . Bulk phases and thick corrosion layer were analyzed by X-ray diffraction and FEG-SEM coupled with EDX analysis. The composition of thin passive layer, especially on MgZn_2 phase, was investigated by X-ray Photoelectron Spectroscopy.

Results and discussion

Bulk- $\text{Al}_7\text{Cu}_2\text{Fe}$

Potentiodynamic curves of $\text{Al}_7\text{Cu}_2\text{Fe}$ phase measured until 20 V show that this phase is very active in sulfuric acid. Indeed, after a first anodic peak, the current density rapidly raises

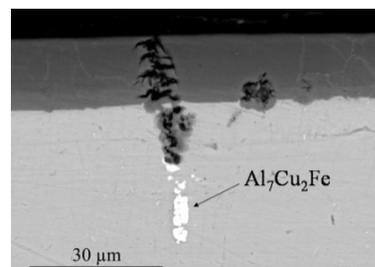


Figure 1: Defect in anodized layer on 7050 alloy

1 A cm⁻² (Figure 2a). At corrosion potential and at high potential, the Al₇Cu₂Fe phase is dissolved, but its dissolution is not homogeneous. Surface analysis show nanoparticles of pure copper which form a nanometric sponge.

Impedance measurements confirm that the active electrochemical surface is mainly metallic and increase with immersion time and/or anodization voltage (Figure 2b and c). According to surface and cross section observations, the important value of double layer capacity of electrode, around 100-300 mF cm⁻², is explained by a simple geometrical model of metallic nanoparticle assembly with a double layer capacity of 20 to 30 μF cm².

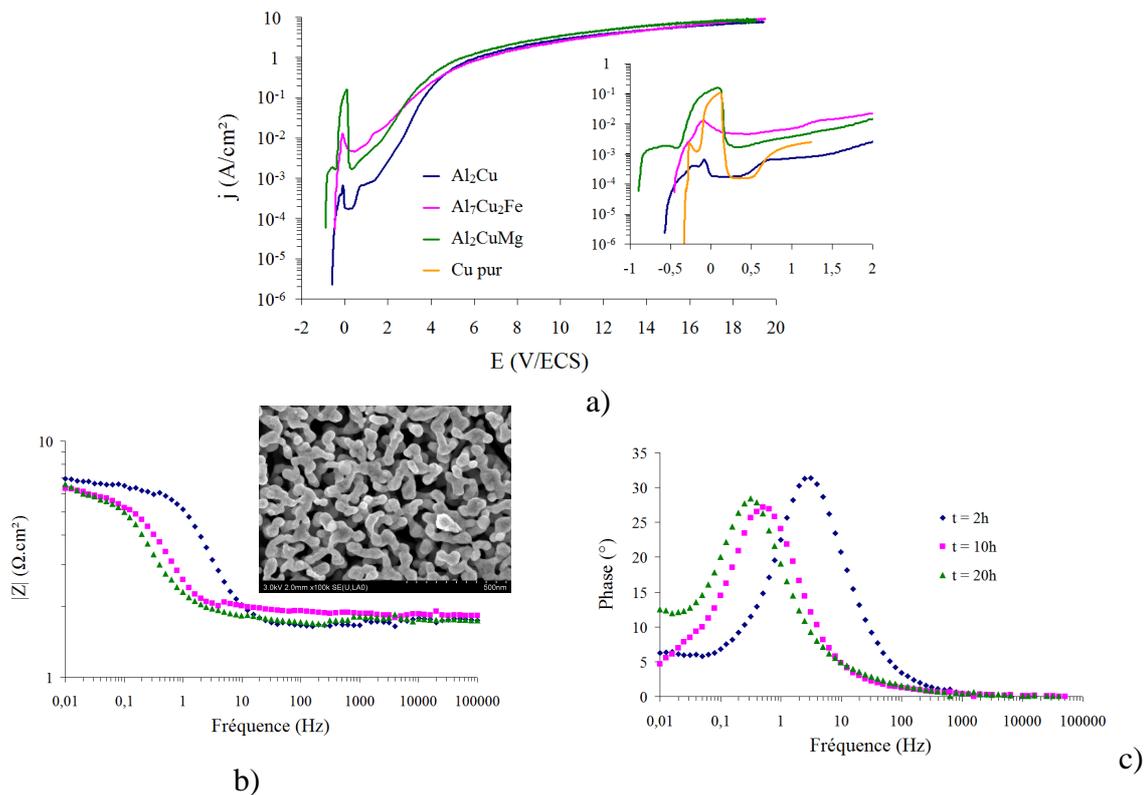


Figure 2: (a) Potentiodynamic curves of Al₇Cu₂Fe in 2 mol L⁻¹ sulfuric acid until 20 V ; (b,c) EIS spectrum of Al₇Cu₂Fe versus immersion time in 2 mol L⁻¹ sulfuric acid at corrosion potential

The capacity evolution of electrode allows evaluating the kinetic of formation of copper nanosponge layer on Al₇Cu₂Fe.

Bulk-MgZn₂

In sulfuric acid, the MgZn₂ phase, the second main particle in 7050 alloy, show a passive behavior at high voltage. In fact, after a first anodic peak, the anodic current density reaches around 20 μA cm² above a voltage of 5 V.

Surface analysis done by FEG-SEM and XPS indicate the presence of a tin oxide film of composition Mg_{1-x}Zn_xO.

Impedance diagram at high voltage can be simulated by two constant phase: a first one attributed to the charge transfer, and the second one at low frequency attributed to the solid-state diffusion across the film. The thickness of the film was determined from capacity measurements around 50 to 200 nm versus voltage and time and is matched with surface analysis.

At low voltage (5 V), the low-frequency measurements can be fitted with a Warburg-like element simulating the diffusion in a finite-length region, the film thickness. Although at

higher voltage (10 and 20 V), the electrode has a blocking behavior, which explains the stabilization of a thin oxide film [3].

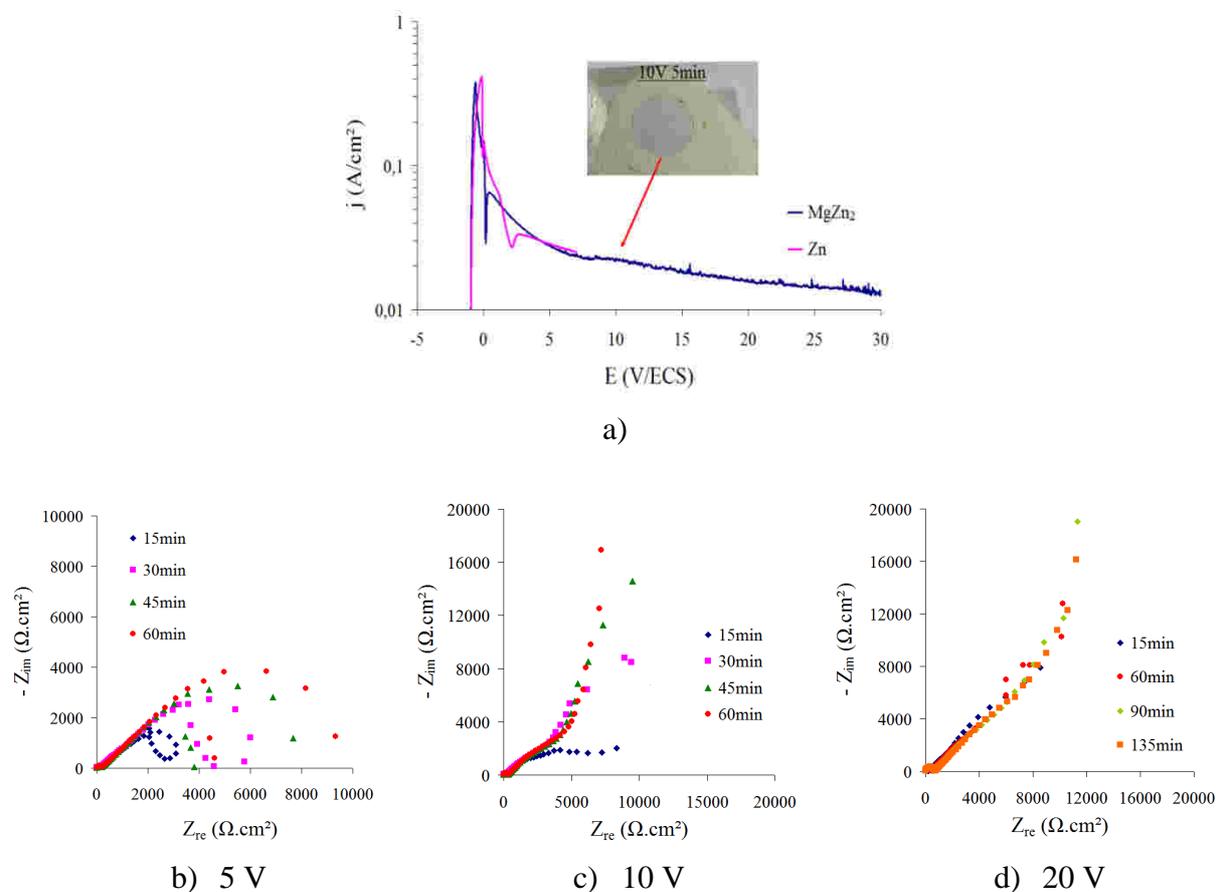


Figure 3: (a) Potentiodynamic curves of MgZn₂ in 2 mol L⁻¹ sulfuric acid until 30 V ; (b,c) EIS spectrum of MgZn₂ at different voltage in 2 mol L⁻¹ sulfuric acid versus immersion time

Concluding remarks

The electrochemical behavior of these two phases in sulfuric acid at high voltage explains the formation of holes or copper on surface during the etching or anodization step on 7050 alloy. The consequences of the presence of these defaults on the corrosion behavior of anodized 7050 alloy were also studied by electrochemical methods (EIS) and non-electrochemical methods (salt spray test).

Acknowledgements

This study was performed in the framework of MODELIA project funded by the French Agence National de la Recherche.

References

1. N. Birbilis, M.K Cavanaugh, R.G Buccheit, Corrosion Science 48 (2006) 4202-4215
2. J.F Li, Z.Q Zheng, W.J Chen, W.D Ren, X.S Zhao, Corrosion Science 49 (2007) 2436-2449
3. J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, P.R Bueno, Journal of Electroanalytical Chemistry 475 (1999) 152–163