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Micro-arc oxidation of AZ91 Mg alloy: An in-situ electrochemical study

Delphine Veys-Renaux *, Emmanuel Rocca, Gérard Henrion

Institut Jean Lamour, UMR7198 CNRS-Université de Lorraine, BP 70239, 54506 Vandoeuvre-Les-Nancy, France

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ABSTRACT

The growth of coatings by micro-arc oxidation is based on the formation of spark discharges appearing at the metal/electrolyte interface over the dielectric breakdown potential. On Mg and Mg alloys, this anodizing process is usually performed in alkaline electrolytic baths in which fluorides or silicates are added. In concentrated KOH electrolytes, in-situ electrochemical impedance spectroscopy measurements are performed at high voltage (up to 80 V) and show that the dielectric breakdown occurs for a threshold capacitance at the electrochemical interface. The main positive role of fluorides and silicates in both the reinforcement of the resisting properties of the coating and its further growth under spark effect is highlighted.

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1. Introduction

The implementation of Mg alloys in the aircraft industry is more and more encouraged in order to lighten the structures. It requires a preliminary surface treatment due to the high sensitivity to corrosion of magnesium and its alloys [1]. Electrochemical conversion processes are generally preferred to chemical conversion processes as phosphatation [2,3] or chromatation [4], leading to thicker and more protective coatings. Various commercial anodizing processes have been developed for magnesium treatment such as HAE, DOW17, and ANOMAG [5]. In the framework of the new ecological regulations, micro-arc oxidation (MAO) (avoiding the use of heavy metals as chromium or manganese) appears as a promising process in a single-step industrial process. It consists in the application of high voltages (higher than the dielectric breakdown voltage of the oxide, depending on the stability and reactivity of the passive film [6]) in an alkaline based electrolyte, leading to the local formation of electric discharges/sparks. Thanks to the high temperature reached within the plasma during this sparking phenomenon, the resulting anodic coatings are dry ceramic layers, exhibiting interesting corrosion and wear resistance. These properties depend on all parameters of the anodizing process, namely the electrical parameters [7–10] and the composition of the electrolyte [10–15]. Two different kinds of electrolyte are usually used: KOH-silicates based solutions or KOH-KF based solutions. Phosphate, aluminate or borate ions are sometimes added. Recent studies have shown that the electrochemical behavior and the corrosion resistance of the treated Mg alloys are very likely linked to the

properties of a first insulating layer, formed before the apparition of discharges by classical anodizing [16]. The purpose of this paper is to characterize the initiation of electric discharges and the growth of the coating by in-situ electrochemical impedance spectroscopy at high voltage in a KOH-based electrolyte until and beyond the dielectric breakdown. Particular attention is paid to the role of additives (silicates, fluorides) on the electrochemical behavior of the interface during the anodizing process and the further reinforcement of the grown layer.

2. Experimental

The growth of anodized coatings on AZ91 plates (circular samples, area 3 cm^2) was performed by applying potentiodynamic scans from 0 to 75 V, with a scan rate of 100 mV s^{-1}, in KOH (3 mol L^{-1})-based electrolytic baths (pH = 13.4; χ = 400 mS cm^{-1}). A three-electrode cell connected to a Modulab HV100 potentiostat was used with the studied sample as a working electrode, a saturated calomel electrode as a reference electrode and a platinum grid (area 5 cm^2) as a counter electrode. The effect of addition of fluorides (KF 0.5 mol L^{-1}, pH = 13.4; χ = 400 mS cm^{-1}) or silicates (Na$_2$SiO$_3$ 0.5 mol L^{-1}; pH = 13.4; χ = 350 mS cm^{-1}) to the reference bath was investigated.

The evolution of the electrochemical interface during polarization was in-situ characterized by electrochemical impedance spectroscopy (EIS). On the one hand, potentiodynamic scans were interrupted every 10 V for a 3 s long potentiostatic step, during which an impedance spectra was recorded within a 100,000 Hz to 100 Hz frequency range and a 20 mV sinusoidal perturbation. The obtained EIS data were fitted with ZsimpWin Software [17]. On the other hand, single

* Corresponding author. Tel.: +33 3 83 68 46 30; fax: +33 3 83 68 46 11.
E-mail address: delphine.veys-renaux@univ-lorraine.fr (D. Veys-Renaux).

frequency impedance values (for f = 5000 Hz) were continuously measured during a potential scan.

The presence of fluorine or silicon in the coatings grown until 40 V respectively in fluorides and silicates containing electrolytes was investigated by X-ray photoelectron spectroscopy (XPS) with a Kratos AXIS Ultra DLD spectrometer after argon ion sputtering. The spectra were recorded by using a monochromatized Al-K$_\alpha$ X-ray radiation (1486.6 eV), with 20 eV pass-energy in the hemispherical analyser and a take-off angle of 90°. For internal calibration, C1s peak (285.0 eV) was used.

3. Results and discussion

3.1. Electrochemical behavior between 0 and 80 V

The obtained polarization curves, shown in Fig. 1, exhibit the same shape whatever the composition of the electrolyte.

Before the electrical discharge voltage range, the electrochemical behavior of Mg can be divided in 3 steps. Up to 5–7 V, the current density remains low, which corresponds to a first passive state of the surface with a current density of about 0.2 to 0.3 mA cm^{-2}.
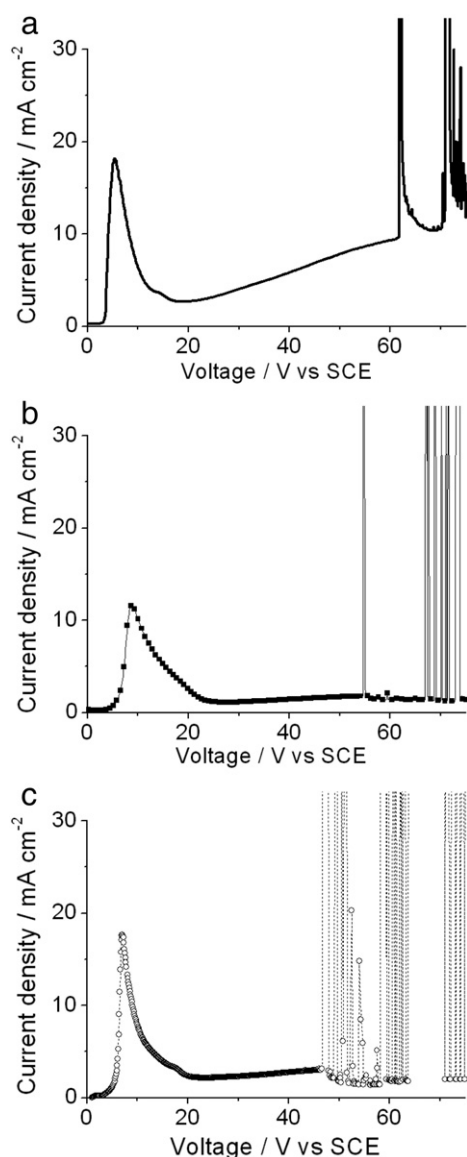
Then, the surface becomes active and very likely dissolves, as revealed by the large current density peak between 5 and 20 V observed in all cases. From 20 V upwards, the alloy is passivated anew with larger anodic current densities around 1 to 10 mA cm^{-2}. In this voltage region, the blocking properties of the passive layer are more significant in the presence of additives (fluorides and silicates) with a current density less than 5 mA cm^{-2}. In inhibitor-free KOH electrolyte, the current density linearly increases with potential until 10 mA cm^{-2} at 60 V.

After this second pseudo-passivation plateau, sharp peaks of current density occur beyond a potential threshold value. These sharp current peaks correspond to electric discharges following the dielectric breakdown at the substrate/electrolyte interface that can be visually observed in the electrolytic cell. The apparition voltage of this "sparking" regime depends on the electrolyte composition: around 62 V in KOH 3 mol L^{-1}, 55 V and 47 V in the fluorides and silicates containing media respectively. Between the discharges, the alloy returns to the pseudo-passive state, as revealed by the values of current density measured between the sharp current peaks.

3.2. Electrochemical impedance spectroscopy at high voltage

The global impedance spectra, obtained in-situ at fixed potentials during the anodizing, show the same evolution in the three KOH-based electrolytic baths. As an example, impedance spectra recorded in the fluoride containing electrolyte are depicted in Fig. 2. According to previous studies [10,18], anodized layers on Mg alloys can be considered as thin oxide films with some small free areas. The impedance spectra recorded in the considered frequency range can be well described with a single time constant and were therefore fitted with ZSimpWin software [17] by using a simple R$_e$(QR) equivalent circuit.

In the three cases, R$_e$ is assigned to the electrolyte resistance and its value is closed to 5 Ω cm^2. Indeed, the electrolyte conductivity is buffered by the high concentration of KOH in the three electrolytes.

The Q constant phase element (the admittance of Q is defined as $Y = Q \cdot (j\omega^n)$) takes into account all the dielectric contributions of the interface: the double layer capacitance and the oxide capacitance
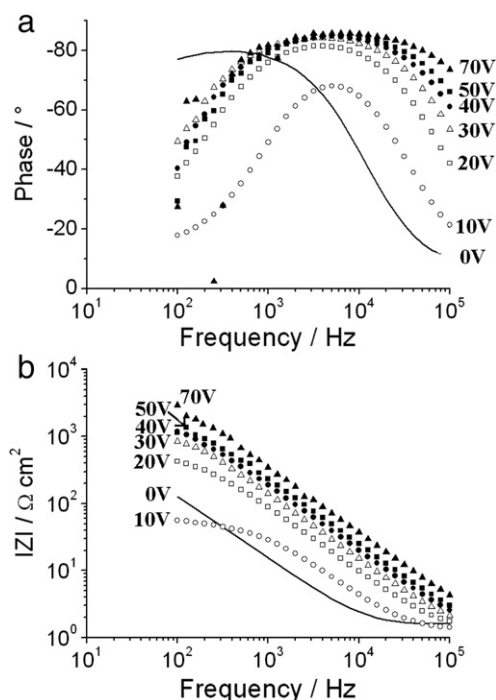

Fig. 1. Potentiodynamic curves (0–80 V) recorded on AZ91 in KOH 3 M (a), KOH 3 M + KF 0.5 M (b), and KOH 3 M + Na$_2$SiO$_3$ 0.5 M (c).

Fig. 2. Impedance spectra recorded at fixed potentials during the polarization in a fluoride containing medium (Bode phase (a), Bode modulus (b)).