In-situ electrochemical characterization of “discharges initiation” during micro-arc oxidation of Mg alloys

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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. In the framework of the new ecological regulations, plasma electrolytic oxidation (PEO) appears as a promising process, thanks to the use of non-toxic electrolyte in a mono-step industrial process. It consists in a high-voltage oxidation until the dielectric breakdown at the interface metal/oxide/electrolyte (Fig.1a). The resulting coatings are dry ceramic layers, exhibiting interesting corrosion and wear resistance (Fig.1b). This process is generally performed in alkaline media containing fluorides and silicates. Previous studies have shown that the corrosion resistance of the treated Mg alloys is very likely linked to the properties of a first insulating layer, formed before the apparition of discharges. The purpose of this paper is to characterize the role of additives (fluorides and silicates) on the initiation of electric discharges and on the growth of the coating by an in-situ electrochemical study until and beyond the dielectric breakdown.

Experimental

Potentiodynamic scans (0-80V) were performed on AZ91 plates in KOH(3M)-based electrolytic baths by using a three-electrodes cell connected to a Modulab HV100 potentiostat. The effect of addition of fluorides (KF 0,5M) or silicates (Na$_2$SiO$_3$ 0,5M) to the reference bath was investigated.

The evolution of the electrochemical interface during polarization was in-situ characterized by electrochemical impedance spectroscopy: on the one hand, impedance spectra (100Hz-100000Hz, AC=20mV) were recorded every 10V; on the other hand, the impedance at 5000 Hz was continuously measured during a potential scan.

Surface analyses by FEG-SEM, EDS, XPS and vibrational spectroscopies were performed in order to characterize the evolution of the morphology and composition of the surface film during the anodization process.

Results and Discussion

The electrochemical mechanism until discharges occurrence can be divided in 3 steps (Fig.2)

Up to 5-7V, the current density remains low, which corresponds to a passive state of the surface. Then, the surface becomes active and very likely dissolves, as revealed by the current density peaks between 5 and 20 V. From 20V upwards, the material is passivated anew.
However, whereas the blocking properties of the passive layer seem to be significant in the presence of additives, the current density linearly increases with potential in KOH. After a potential threshold, electric discharges are detected by sharp current density peak. The potential of “breakdown” depends on the electrolyte composition: around 62 V in KOH 3M, 55 V and 47 V respectively in the fluorides and silicates containing medium. Between the discharges, the current density returns to its basic value.

![Figure 2: Potentiodynamic curves (0-80 V) recorded on AZ91 in KOH 3 M (a), KOH 3 M+ KF 0.5 M (b), KOH 3 M + Na$_2$SiO$_3$ 0.5 M (c)]](image)

The global impedance spectra, obtained in-situ at high potentials (Fig.3), were fitted with ZSimpWin software$^2$, by using a $R_e(QR_t)$ equivalent circuit: $R_e$ being assigned to the electrolyte resistance, the constant phase element $Q$ being assigned to the dielectric properties of the interface (double layer capacitance and/or passive film capacitance), $R_t$ being assigned to the charge transfer resistance. The refined parameters confirm the dissolution of the first protective layer between 0 and 10 V (dramatic decrease of $R_t$), followed by the growth of an insulating film from 10 V, which will be considered further as a pure capacitance, $n$ factor being higher than 0.9.

![Figure 3: Impedance spectra recorded at fixed potentials during the polarization in a fluorides containing medium (Bode phase (a), Bode modulus (b))](image)

By measuring continuously the complex impedance for $f = 5000$ Hz and assuming a $R_e(CR_t)$ equivalent circuit, the film capacitance $C$ and the resistance to charge transfer $R_t$ were calculated (Fig.4).
In the three electrolytes, from 10 V upwards, 1/C increases quasi-linearly with the applied potential, indicating the regular thickening of a homogeneous dielectric film. This growth regime is interrupted by the beginning of the discharge regime, occurring for a same value of the capacitance whatever the composition of the electrolyte.

However, the charge transfer resistance, improved by the formation of the insulating layer, evolves differently according to the electrolyte composition. Between 10V and 20V, it increases in the same proportions in the three electrolytes, consistently with the current density decrease observed on polarization curves. Beyond 20 V, the addition of fluoride or silicate in electrolyte provokes an increase of $R_t$ values until the discharge regime.

In pure KOH electrolyte, the appearance of sparks results in the stopping of the growth of the dielectric layer as revealed by 1/C values. In contrary, with fluorides and silicates, the discharge regime is associated with the resistance and 1/C increase, which corresponds to further growth of the coating as observed by metallographic observations.

Surface observations and analyses (SEM-EDS, Raman spectroscopy, XPS) allowed to explain the chemical role of additives in the formation of the first insulating film. Then, the electrochemical behavior of the anodized layers in a reference corrosive medium was correlated to the in-situ electrochemical measurement during the anodized process.

**Conclusions**

This in-situ electrochemical characterization showed that the growth of a first dielectric layer is necessary to reach the discharges regime of the plasma electrolytic oxidation process, occurring for a specific value of capacitance whatever the electrolyte composition.

The role of fluorides and silicates in both the reinforcement of the resisting properties of the coating and its further growth under sparks effect was highlighted.

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**References**