



## Effect of potassium fluoride in electrolytic solution on the structure and properties of microarc oxidation coatings on magnesium alloy

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### Abstract

Oxide coatings were produced on AM60B magnesium alloy substrate making use of microarc oxidation (MAO) technique. The effect of KF addition in the  $\text{Na}_2\text{SiO}_3\text{--KOH}$  electrolytic solution on the microarc oxidation process and the structure, composition, and properties of the oxide coatings was investigated. It was found that the addition of KF into the  $\text{Na}_2\text{SiO}_3\text{--KOH}$  electrolytic solution caused increase in the electrolyte conductivity and decrease in the work voltage and final voltage in the MAO process. Subsequently, the pore diameter and surface roughness of the microarc oxidation coating were decreased by the addition of KF, while the coating compactness was increased. At the same time, the phase compositions of the coatings also varied after the addition of KF in the electrolytic solution, owing to the participation of KF in the reaction and its incorporation into the oxide coating. Moreover, the coating formed in the electrolytic solution with KF had a higher surface hardness and better wear-resistance than that formed in the solution without KF, which was attributed to the changes in the spark discharge characteristics and the compositions and structures of the oxide coatings after the addition of KF.

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### 1. Introduction

Magnesium alloys have low density, outstanding strength to weight ratio, high dimensional stability,

good electromagnetic shielding and damping characteristics, and good machining and recycling ability [1]. Unfortunately, Magnesium alloys have some disadvantages such as poor corrosion resistance and poor friction-reducing and anti-wear behavior, which is especially so in aggressive and oxidizing environments [2]. Therefore, many surface treatment techniques such as electrochemical plating, conversion

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coating, gas-phase deposition, and anodizing have been developed for preventing the corrosion and increasing the anti-wear behavior of Mg alloys [2]. Among these techniques, anodizing is one of the most popular methods, owing to its ability to produce a relatively thick, dense, and hard film to improve surface properties [3–5]. Based on the anodic oxidation, microarc oxidation, also called “plasma electrolytic oxidation (PEO)” and “anodic spark deposition (ASD)”, characterized by higher voltage and current than anodic oxidation and spark discharge at the sample surface has been successfully developed, with which a plasma environment is generated and a ceramic coating can thus be synthesized on the metal surface through plasma chemical interactions [6,7]. Therefore, microarc oxidation technique has been used to produce hard ceramic coatings on valve metals such as Al, Ti, Mg, and their alloys [8–12]. As an example, the dense and hard microarc oxidation coating formed on Mg alloy contributed to greatly improve the wear and corrosion resistance of Mg alloy [12,13].

It has been found that the electrolyte compositions play a crucial role in the MAO process [14,15] and it is imperative to properly select the electrolyte compositions so that the rapid metal passivation can be promoted and the sparking voltage can be easily reached. Yerokhin et al. showed that the addition of compounds containing  $F^-$  ion into the electrolyte solution helped to increase the electrolyte conductivity and characterized by complex behaviour during MAO process [6]. As for Mg and Mg alloy, it could be fast passivated in the presence of  $F^-$ , with the generation of an undissolved  $MgF_2$  film on the surface [16]. This makes it possible to avoid the excessive anodic dissolution of the Mg alloy substrate with a high chemical reactivity in the initial stage of MAO treatment. However, little has been reported on the effect of the  $F^-$ -containing compounds added in the electrolyte solution on the structures and mechanical and tribological properties of the MAO coatings.

With that perspective in mind, the effect of KF added in  $Na_2SiO_3$ –KOH on the MAO process of AM60B Mg alloy is investigated in the present work, with the emphases being placed on the effect of the KF addition on the structure, composition, and mechanical and tribological properties of the oxide coating.

## 2. Experimental procedure

### 2.1. Preparation of the microarc oxidation coating

Prior to the oxidation process, the AM60B Mg alloy sheets with a size of 20 mm × 36 mm × 2 mm (mass fraction: Al 5.6%–6.4%, Mn 0.26%–0.4%, Zn ≤0.2%, balance Mg) were ground to an average surface roughness  $R_a \approx 0.18 \mu\text{m}$ , cleaned with a detergent, and washed with distilled water. The microarc oxidation process was conducted on a 20-kW microarc oxidation equipment consisting of a potential adjustable pulsed dc source, a stainless steel container with a sample-holder as the electrolyte cell, and a stirring and cooling system. The Mg alloy sample and the wall of the stainless steel container were used as the anode and the cathode, respectively. The electrolytic solutions were composed of 1.0 g/l KOH and 10.0 g/l  $Na_2SiO_3$  in distilled water without or with 8.0 g/l KF addition. The conductivity of the electrolytic solutions was determined on an MC226 conductivity meter (Mettler-Toledo). The temperature of the solutions was kept 25–30 °C during the oxidation. The current density on the sample surface was predefined as  $j = 6.0 \text{ A/dm}^2$  and maintained by modulating the voltage and the cathodic ( $I_c$ ) to anodic ( $I_a$ ) current ratio to be  $I_c/I_a = 1$ . All the samples were treated in the electrolytic solutions for 30 min.

### 2.2. Characterization of the microarc oxidation coatings

The thickness of the microarc oxidation coatings was measured with a MINITEST 1100 microprocessor coating thickness gauge (Elektro-physik Koln). The dimensions of the Mg alloy samples before and after the oxidation treatment were determined on a spiral micrometer, from which the values of the part of the coating growing towards the external surface and towards the substrate were calculated [17]. The surface roughness of the coatings was determined on a surface profilometer. A JY2002 analytical balance was used to measure the weights of the Mg alloy samples before and after the oxidation treatment, so as to determine the weight-gain of the substrate sample after the microarc oxidation process.

The surface morphology and microstructure of the oxide coatings were observed with a JSM-5600LV

scanning electron microscope (SEM). The phase composition of the coatings was analyzed by X-ray diffraction (XRD, D/max-rB), using a Cu K $\alpha$  radiation as the excitation source.

2.3. Hardness and tribological performance of the microarc oxidation coatings

The outer porous layer of the microarc oxidation coatings was removed by abrasion against SiC paper. Then the microhardness of the coatings was measured on a Vicker's microhardness meter at a load of 25 g and for a loading duration of 5 s. The final microhardness value quoted was the average of 10 replicate measurements. The hardness of the Mg alloy substrate was measured in the same manner.

The friction and wear properties of the microarc oxidation coatings sliding against Si<sub>3</sub>N<sub>4</sub> ball of a diameter 3 mm in a ball-on-disc configuration were evaluated on a UMT-2MT reciprocal-sliding test rig. The unlubricated sliding was performed at a load of 2 N, a sliding speed of 0.1 m/s, and sliding amplitude of 5 mm. A computer connected to the tester recorded the friction coefficient curves. The wear volume losses were determined by measuring the wear scar areas and widths with a profilometer, and the wear rates were calculated from dividing the wear volume loss by the total sliding distance and load.

3. Results and discussion

3.1. Effect of KF addition on the coating growth process

Table 1 gives the process parameters and the relevant conductivity, final voltage, and coating thickness with respect to the Na<sub>2</sub>SiO<sub>3</sub>–KOH solutions without and with KF addition. It is seen that the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution containing KF has a much

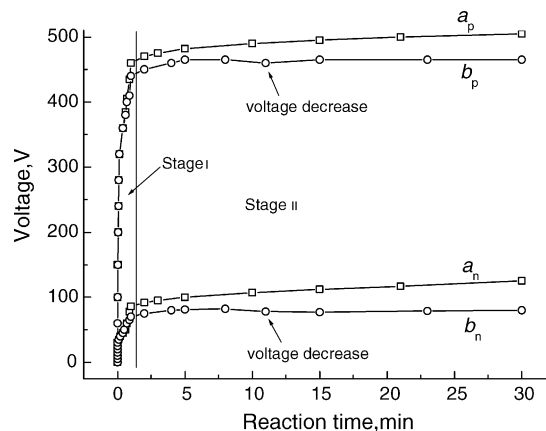


Fig. 1. Variation of positive and negative voltages in Na<sub>2</sub>SiO<sub>3</sub>–KOH solutions without and with addition of KF (*a<sub>p</sub>*, *a<sub>n</sub>*-positive and negative voltages in solution 1; *b<sub>p</sub>* and *b<sub>n</sub>*-positive and negative voltages in solution 2).

larger conductivity than the one without KF. Therefore, the work voltage in the process and the final voltage to maintain the same current density for the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution containing KF are somewhat smaller. Furthermore, the microarc oxidation coating prepared from the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution containing KF has a smaller total coating thickness than that prepared from the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution without KF. This could be attributed to the decrease in the work and final voltages of the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution containing KF during the microarc oxidation process.

Fig. 1 shows the variations of the positive and negative voltages with time during the microarc oxidation processes in the Na<sub>2</sub>SiO<sub>3</sub>–KOH solutions with and without KF in a constant current density mode. It is clear that the work voltage for the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution containing KF is smaller than that for the Na<sub>2</sub>SiO<sub>3</sub>–KOH solution without KF. The variations of the positive and negative voltages are similar for the two solutions and two stages can be classified according to the different rising rates of the voltages. Namely, the voltages quickly raise in stage I

Table 1

Process parameters and the relevant conductivity, final voltage, and coating thickness with respect to the Na<sub>2</sub>SiO<sub>3</sub>–KOH solutions without and with KF

Solution code	Solution composition	Solution conductivity (mS/cm)	Final voltage (V) (positive/negative)	Coating thickness (μm)
1	Na <sub>2</sub> SiO <sub>3</sub> , KOH	12.9	505/125	37
2	Na <sub>2</sub> SiO <sub>3</sub> , KOH, KF	19.1	465/80	32