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Materials Letters 60 (2006) 474–478
materials letters
www.elsevier.com/locate/matlet

Effects of spark discharge on the anodic coatings on magnesium alloy

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Received 10 May 2005; accepted 8 September 2005
Available online 13 October 2005

Abstract

Spark discharge was the representative phenomenon of Micro-arc oxidation (MAO) method distinguished from other electrochemical oxidation methods. Under the spark discharge treatment, characteristics of the anodic layer were significantly changed. To investigate the influences of the spark discharge, a piece of magnesium alloy AZ91D specimen was partly treated by MAO method in alkaline silicate solution. And the microstructure, element distributions as well as the surface potential distributions of the specimen were studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and scanning Kelvin probe (SKP) technique. As a result of intensive spark discharge treatment, porous external layer with dense internal layer were formed on Mg alloy surface. At the same time, the depositions of OH^- and SiO_3^{2-} ions were accelerated, which resulted in the enrichment of element oxygen and silicon at the spark discharge region. Moreover, due to the compact internal layer, the intensive spark discharge region exhibited more positive potentials with respect to other regions, which meant this region could restrain the ejection of electron and provide effective protection to the substrate. In addition, it was found that oxygen played a vital role in determining the intensity and size of sparks, and abundant oxygen resulted in intensive and larger sparks.

Keywords: Spark discharge; Micro-arc oxidation; Magnesium alloy; Oxygen; Element distribution; Surface potential

1. Introduction

In recent years, micro-arc oxidation (MAO) technique has been widely investigated as a novel technique to deposit thick, dense and ultra-hard ceramic coatings on the surface of valve metals. Essentially, the MAO process combines electrochemical oxidation with a high voltage spark treatment [1–3]. The MAO process is environmental friendly and the ceramic coatings synthesized by this process have exhibited superior mechanical property and high growth rate as compared with other anodic oxide coatings [4,5]. The difference can be attributed to the influence of the spark discharge, which is the primary character of the MAO process. Much attention has been given to the structural, mechanical, thermal and electrical properties of MAO coatings [6–10], but few studies have focused on the influences of the spark discharge [11,12].

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doi:10.1016/j.matlet.2005.09.015

So far, it was known that sparking normally occurred when anodizing voltage was greater than the dielectric breakdown voltage of the film formed before. Under the treatment of sparking, a great deal of heat accompanied with oxygen and water vapor was released, and high temperature was achieved at the local regions on the surface. Concurrently, owing to the high temperature, magnesium and alloying elements were melted out of the substrate, entered the discharge channels and got oxidized [13]. The final anodized coating was a result of breakdown and smelting of the coating by sparking. Accordingly, the surface condition such as the structure and composition of the oxide coating were significantly changed.

It was of significant to investigate the spark-treated anodic coatings, understand and control the spark discharge, for the purpose to obtain anodic coatings with good properties. So, in this work, a piece of magnesium alloy was partly treated by spark discharges, and then the morphologies and element distributions of which were examined by SEM and EDS techniques. At the same time, in order to detect the changes of the surface electrochemical conditions, a SKP technique was also introduced.

2. Experimental

Magnesium alloys AZ91D of 10 × 10 × 5 mm dimensions were used as the substrate in the experiment. An alkali–silicate solution was used as the electrolyte, and the coating deposition was carried out at current density less than 20 mA/cm^2 by a DC power supply. The voltage was increased gradually to 130 V without spark discharges, then the power supply was switched off, and the sample was taken out of the electrolyte, washed in distilled water and dried. Again, part of this specimen was immersed in the electrolyte, oxidized to 180 V with the appearance of sparks, then taken out, washed and dried.

The surface appearance of the coating was studied by scanning electron microscopy (SEM, KYKY2800B) and the element distribution was analyzed by energy dispersive spectroscopy (EDS, Oxford Ins). The surface potential distribution over the specimen was also detected under 80% RH at 20 °C by a self-constructed scanning Kelvin Probe (SKP) instrument.

SKP is one of the very few non-destructive methods in surface analysis and its theoretical background has been described in the literature [14]. It is based on the vibrating-capacitor technique to measure the lateral distribution of the Volta potential at a microscopic scale, which correlates with the difference in the electron work function of metals. The work function, defined as the minimum energy required for removing an electron through the surface region, is a very sensitive parameter of surface condition. Any change in the electrical character of the specimen surface will change the work function [15]. Therefore, the Volta potential measured by SKP technique can reflect the structural and chemical changes on the specimen surface. In this work, the maximum potential, step resolution and the data acquisition rate for the performance of this Kelvin probe setup are 3 mV, 1 μm and 5 points/s, respectively.

3. Results and discussion

3.1. Electrolytic voltage

During the oxidation process, electrolytic voltage behaved quite differently with treatment time, as shown in Fig. 1. When the current was applied, electrolytic voltage increased rapidly in the beginning, afterwards retarded. When the voltage reached the value of breakdown (140 V), numerous micro-sparks appeared and moved quickly over the specimen surface. At the same time, the voltage oscillated within the range of 1∼2 V. Apparently, this oscillation behavior should be attributed to the spark discharge and might imply an occurrence of different growth mechanisms. Moreover, the oscillation range increased with the prolonging of MAO treatment time.

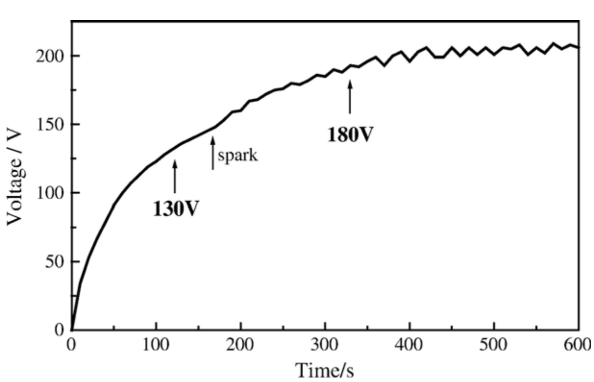

Fig. 1. Variations in electrolytic voltage with oxidation time at current density less than 20 mA/cm^2.

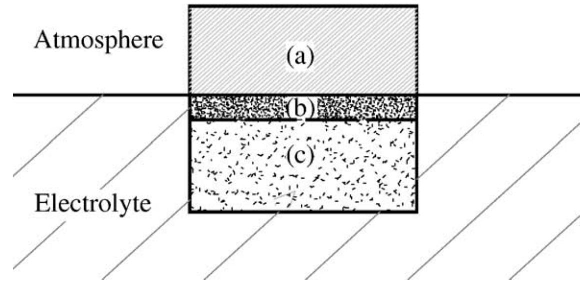

Fig. 2. Schematic diagram of magnesium alloy during the MAO treatment.

To investigate the influences of spark discharge, two parts of a magnesium alloy specimen were treated to different voltage, respectively. The schematic diagram of magnesium alloy during the MAO treatment was shown in Fig. 2. Part (a) was anodized to 130 V without spark discharge, and the rest was anodized to 180 V with the occurrence of sparks. During the treatment process, the parts immersed in the electrolyte presented different phenomena. Region (b) was near the interface of the atmosphere/electrolyte, where large amount of bubbles and intensive sparks were observed. While region (c) was far from the interface, only sparse sparks appeared. The boundary between the two regions was not quite definite.

3.2. Surface morphology

To examine the specific microstructure of the specimen, SEM photograph was taken as shown in Fig. 3. Corresponding to the regions in Fig. 2, the entire photograph could also be divided into three regions (a), (b) and (c). Region (a) was corresponding to the part without spark discharge treatment; region (b) and (c) corresponding to the part treated by spark discharge. The bold line between region (a) and (b) was related to the interface of the atmosphere/electrolyte.

Without spark discharge treatment, the substrate only lost its metal brightness and covered by a thin transparent passive film as shown at region (a). This region was smooth and uniform, with some grinding

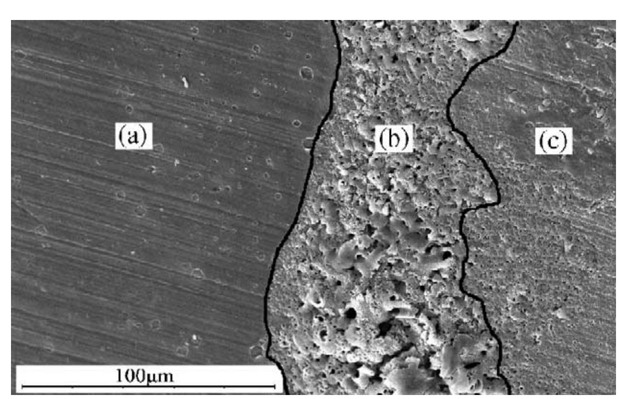

Fig. 3. Influences of spark discharge on the surface morphologies of the specimen.