



Characterization of electrical discharges during spark anodization of zirconium in different electrolytes



Janaina S. Santos^a, Sherlan G. Lemos^b, Wesley N. Gonçalves^c,
Odemir M. Bruno^c, Ernesto C. Pereira^{a,*}

^a Universidade Federal de São Carlos, P.O.Box 676, São Carlos, Brazil

^b Universidade Federal da Paraíba, P.O.Box 5093, João Pessoa, Brazil

^c Universidade de São Paulo, P.O.Box 369, São Carlos, Brazil

ARTICLE INFO

Article history:

Received 18 November 2013

Received in revised form 10 March 2014

Accepted 11 March 2014

Available online 22 March 2014

Keywords:

Zirconium

Oxide coatings

Anodic film

Spark anodization

ABSTRACT

The evolution of the electrical discharges parameters during spark anodization of metallic Zr under galvanostatic regime have been investigated by image analysis in phosphoric and oxalic acid electrolytes. The experiments were recorder using a high-speed video camera during the entire anodization with a resolution of 1.7 ms for determination of discharge lifetime and a standard resolution of 33 ms (real-time imaging) for determination of the average area and discharge population density. The discharge behavior was dependent of the current density, electrolyte composition and anodization time. During breakdown process, sparks discharges are progressively turned to micro-arcs, which can be seen by enlargement of discharge area, gradual increase of lifetime and reduction of discharge population density. A factorial design was used to estimate the effects of experimental conditions on the discharge behavior. The current density and electrolyte composition were the most important factors that affected the discharge population density. The anodization time and the electrolyte composition were the main factor that influenced the discharge area and lifetime. In comparison with the voltage vs. time curve, the results demonstrate important features of the process and the changes of the electrical discharges characteristics during the experiments.

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1. Introduction

The anodization under high electric field is known, in the literature, as Spark Anodizing, Plasma Electrolytic Oxidation (PEO) and Micro Arc Oxidation (MAO). This method is normally used for production of coatings in valve metals, such as Zr, Ti, Al and Ta, due to the formation of a thick oxide layer, rigidly adhered to the metal substrate, promoting corrosion resistance, thermal and wear protection [1–4]. This process is characterized by a series of simultaneous events such as voltage oscillations, oxygen evolution, local oxide crystallization and internal stress [5]. Besides, the formation of pores can occur if the electrolyte is oxide-dissolving [5]. The presence of a large number of short-lived electrical discharges at the electrode surface is also observed and it is associated to the localized electric breakdown of the growing oxide [1,5]. The breakdown is a complex phenomenon that influences the oxide properties. The anodic oxides obtained from valve metals have been

investigated since 50's, at the time, for development of new materials for capacitors [6–8]. Several models have been proposed in the literature in order to explain the electrolytic breakdown observed during the growth of the anodic oxides from valve metals, such as electron avalanche [9–11], mechanical breakdown [12,13] and pit formation [13–16]. However, due its complexity, there is not a generally accept complete mechanistic overview of the breakdown phenomenon in valve metal oxides. For this reason, studies are still being done in order to understand the fundamental aspects of breakdown [1,17,18].

In recent years, imaging techniques have been used to characterize the microdischarges parameters during the anodization of different metals such as Al, Ti, Mg and Ta under DC and AC regime [19–25]. Based on these studies, several mechanisms have been proposed to explain the electric breakdown phenomenon and the influence of the electrical microdischarges on morphology and microstructure of anodic films. Moreover, some authors suggest the modification of the morphology and microstructures properties of the oxide films by controlling the sparking during the process [22]. In order to investigate the relation between the growth of the oxide and the microdischarges during AC PEO of aluminium in alkaline

* Corresponding author.

E-mail address: ernesto@ufscar.br (E.C. Pereira).

solution, Yerokhin *et al.* [19] used digital video imaging of the electrode surface to obtain information as microdischarge size, density and spatial distribution in different stages of the coating formation process. The authors observed that microdischarge area monotonically increased whereas spatial density gradually decreased with the anodization time. In another study, Matykina *et al.* [20] also used digital video imaging to investigate the microdischarges during anodization of Ti in orthophosphate electrolyte and associate it with the oxide film morphology. They evaluated the size and lifetime of the electrical discharges and the evolution of the gas bubbles. The authors suggested that the pores could partially originate from extrusion of entrapped gas bubbles caused by high temperature and pressure of discharges events.

In spite of the rising number of papers dealing with the discharges characterization, there is no detailed description of the microdischarges behavior during the entire anodization of a substrate under different experimental conditions. Most of the papers studied the changes on discharge parameters under a unique anodizing condition [19,20,23–25]. Few papers investigated other experimental variables in their work [21,22]. Arrabal *et al.* [22] included different Mg alloys in their study and Moon *et al.* [21] expanded their investigation changing the electrolyte concentration and current density of DC PEO process of Al. It is important to stress out that different experimental conditions can lead to a lot breakdown situations than do different electrode composition [5]. This is a consequence of the breakdown voltage, which is affected not only by the oxide film properties but also by the oxide/electrolyte interface properties. Empirical observations reveals that the breakdown phenomenon depends on several parameters, such as electrolyte composition [16,26–28], applied current density [29–31] and electrolyte temperature [32]. Hence, the use of different experimental conditions is important to the comprehension of breakdown phenomena.

Considering the exposed above, the aim of this study was investigated the discharge evolution of DC PEO of zirconium in order to correlate the changes in discharge parameters profiles with the anodization curve, and observe the changes in the elementary process of the breakdown phenomenon, which are strongly dependent of the experimental conditions. Therefore, we used real-time imaging and high-speed video analysis to study the discharges emission during the anodization process. The changes in discharges parameters with the increase of the anodization time were monitored. The real-time imaging was used to count the number of discharges events on the electrode surface and calculate the average area. The high-speed video analysis was used to estimate the discharge lifetime, using a multivariate image analysis technique. This study was performed in phosphoric acid and oxalic acid solutions at different current densities. Based on literature and own previous studies [5,33–37], the experimental conditions chosen were those where the discharges events are intensified, such as DC regime, acid media, moderate dilute electrolyte and low temperature. A factorial design was used to analyze the effects of the experimental conditions on the spatial parameters and lifetime of the discharges events.

2. Experimental

2.1. Anodization of zirconium

The anodization experiments were carried out under galvanostatic regime on a zirconium substrate in 120 mL electrolyte solution containing $0.05 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$ or $0.05 \text{ mol L}^{-1} \text{ H}_2\text{C}_2\text{O}_4$. All solutions were prepared with reverse osmosis purified water and analytical-grade reagents. Table 1 depicts the experimental conditions used to perform the experiments. The electrolytic cell

was maintained at constant temperature using a thermostatic circulating bath (Cole-Parmer Polystat) and the electrolyte solution was stirred using a magnetic stirrer. Annealed zirconium (Zr) foils (Alfa Aesar 99.8%, 0.25 mm thick) were cut in flag shape pieces with dimensions $1.0 \times 1.0 \text{ cm}$ and exposed area of 2 cm^2 . Prior to the experiments, the working electrode was mechanically grinded with #600 SiC and then with #1200 SiC sandpaper followed by vigorous washing with deionised water. Two Pt sheets were used as counter electrodes to obtain a homogeneous electric field distribution over the electrode surfaces. A homemade DC power supply was used to perform the experiments. The voltage was recorded using an HP-Agilent model 3440A Digital Multimeter connected to a computer by an in-house software routine developed using HP-VEE® 5.0 software.

2.2. Image processing

The electrode surfaces were recorded during the experiments using a Casio Exilim F1 video camera with a shutter speed of $1\text{--}1/2000 \text{ s}$. The precision of the measurements was limited by the time resolution of video camera. A time resolution of 1.7 ms (600 frames per second) was used for a determination of the discharge lifetime. Due to low image resolution of the camera in this high-speed mode, a standard time resolution of 33 ms (30 frames per second) was used for determination of the average area and discharge population density (number of discharges per frame). The open source package FFmpeg® (www.ffmpeg.org) was used to extract the frames from the movies. Matlab® (Mathworks, USA) and ImageJ® [38], a public domain Java image processing software, were used to execute the image processing. The anodizations were carried out for 1,800 seconds, therefore each video with a temporal resolution of 33 ms generated around $\sim 54,000$ frames, whereas the videos recorded with a temporal resolution of 1.7 ms generated around $\sim 1,080,000$ frames. Due to the huge amount of data, a routine to batch processing was developed. The average area and discharge population density were calculated directly from analysis of each image. On the other hand, the lifetime of the discharges was determined by analyzing clusters of 10,000 images rearranged in a two-way array after unfolding video data. Unfolding is usually referred as 'Reshaping' in some software for multivariate image analysis [39]. As can be seen in schematic representation in Fig. 1, data video could be represented by a stack of \mathbf{K} congruent images with geometrical dimensions $\mathbf{M} \times \mathbf{N}$ (Fig. 1A) organized into a three-way array (Fig. 1B). Unfolding consists in converting this three-way array into a two-way array (Fig. 1C).

In this new two-way array, each original image is represented by a single column matrix of the new rearranged image; therefore, the number of columns is determined by the number of congruent images analyzed. The y-axis of the rearranged image is defined as the product of the geometrical variables ($\mathbf{M} \times \mathbf{N}$) of the original images, whereas the x-axis represents the number of the frames (\mathbf{K}). Consequently, the analysis of the width of the discharge events in the rearranged image allows evaluating the number of frames that an individual discharge will last. Therefore, considering an interval of 1.7 ms between the frames, the lifetime of the discharges can be estimated. Discharge lifetimes with low luminosity intensity and with values smaller than 1.7 ms might not be counted due to video camera temporal resolution (600 frames/s).

2.3. Chemometric analysis

To investigate the effects of the experimental conditions (variables) on discharges parameters (responses), a factorial design was used to plan the experiments. The advantages to use this chemometric procedure are the reduction of the number of experiments that are required for the analysis, and the quantification

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