Characterisation of plasma- and electrical parameters during plasma electrolytic oxidation of Al and Ti

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Abstract: Plasma electrolytic oxidation enables oxide-ceramic coatings on light-metals with high corrosion resistance and good adhesion of the coating to the substrate. In this work, the process is analysed with different concentrations of KOH electrolyte for aluminium and titanium anodes using a single microdischarge setup. Optical and electrical measurements are carried out to determine process parameters like the microdischarge lifetime, the gas temperature and electron density.

Keywords: Plasma electrolytic oxidation, liquids, coatings, corrosion, wear, light metals

1. Introduction

Light metals like aluminium, titanium, magnesium and their alloys are in increasing demand for transport or medical applications due to their relatively low density and high strength to weight ratio. The usage of light metal components in transport applications enables weight reduction, which transfers directly to an increasing fuel efficiency [1]. Titanium and magnesium can be used as body implants due their strength and biocompatibility [2,3]. A natural thin oxide layer on light metals with a thickness of several nm is not sufficient for wear and corrosion protection for most applications. Therefore, typical industrial methods like metal spraying, paints or anodising are used to create a protective layer [2,4].

Plasma electrolytic oxidation (PEO) is receiving increasing attention for the creation of a protective passivation layer with a thickness up to 200 µm [5]. It is a more ecologically friendly process compared to paints or anodising processes due to the usage of alkaline electrolytes [6,7]. The coating is characterised by a high corrosion and wear resistance as well as a good adhesion of the coating to the substrate. Additionally, the biocompatibility of titanium and magnesium metals is improved, which is especially important for medical implants [2,3]. The process is characterised by generation of anodic dielectric breakdowns in form of short-living microdischarges within the electrolyte solution. Additionally, it is accompanied by gas evolution in form of bubble formation. The process is influenced by several parameters like deposition time, electrical parameters (current, voltage), substrate composition as well as the electrolyte concentration and composition. However, the complex environment of microdischarge ignition makes an analysis of microdischarge behaviour challenging [5,6].

This work aims to improve the understanding of short-living microdischarges during the PEO process to control the composition and morphology of the created oxide layer. That is needed to adjust the PEO process to meet the demands of different applications.

2. Single microdischarge (SMD) setup

To analyse the short-living microdischarges during PEO, a single microdischarge (SMD) setup is used, which is shown in figure 1. The surface of an active anode is reduced to a tip of a wire with a diameter of 1 mm. As anode material, aluminium (Puratronic®, 99.9995 %) and titanium (Alfa Aesar, 99.99 %) wires are used. They are placed in a glass cylinder containing a mixture of an electrolyte varying concentration of potassium hydroxide (KOH) (0.5 – 4 g/l) in distilled water. The measurements are performed in a galvanostatic DC-mode with a current density of 1.27 A/cm^2 at the tip of the anode. The maximum voltage supply is set to 750 V resulting in no voltage limitation during the PEO process. Measurements are carried out over a treatment time of 10 minutes for a distinct KOH concentration.

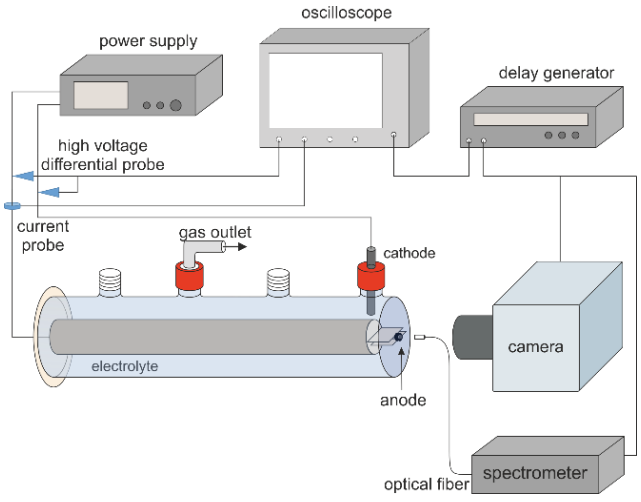

Fig. 1. Single microdischarge setup with an aluminium or titanium anode

3. Diagnostic methods

Diagnostic tools are placed in line-of-sight to the tip of the anode as seen in figure 1. This allows an investigation of the bubble dynamics and optical emission of the microdischarges. A high-speed camera (Phantom VEO 440l IMP, Vision Research) with an exposure time of 6.17 µs is triggered on the microdischarge current, which enables time-synchronised camera measurements. This

allows an analysis of the individual bubble as a function of time within the bubble and discharge event. Typically, microdischarges have lifetimes from tens to a few hundreds of µs. Furthermore, a determination of the bubble radius during the bubble formation is used as input parameter for the Rayleigh-Plesset equation, which allows an estimation of the bubble pressure during the bubble formation.

Optical emission spectroscopy is carried out with two spectrometers. A low-resolution spectrometer (QE65000, Ocean Optics) is used to measure the continuum radiation during the PEO treatment. The radiation can be estimated as the sum of Bremsstrahlung and Black-body radiation. Bremsstrahlung is caused by electron deflection by charged particles, whereas thermal radiation at the tip of the anode is estimated as Black-body radiation. Fitting both to the measured continuum spectrum allows an estimation of the electron temperature and the temperature of the surface during the PEO process.

A high-resolution spectrometer (ARYELLE Butterfly, LTB Lasertechnik Berlin GmbH) is used to determine the electron densities by measuring the broadening of the H_α-line. The shape of the measured H_α-line is approximated with a Voigt profile, which is a convolution of Gaussian and Lorentzian profiles. Broadening mechanisms considered in the analysis are shown in table 1. In particular, the Stark width enables an estimation of the electron density. The contribution of Stark broadening to the overall line width is estimated following an assessment of the other broadening mechanisms and a corresponding deconvolution.

Table 1. The following broadening are considered in this work to ultimately estimate the electron density.

Spectral line-broadening mechanism	Line-shape
Instrumental broadening	Gaussian
Doppler broadening	Gaussian
Van der Waals broadening	Lorentzian
Stark broadening	Lorentzian

4. Results

A typical output from the high-speed imaging synchronised with electrical measurements is shown in figure 2. The measured current is shown in black and the determined bubble radius in red for a KOH concentration of 1 g/l KOH at the beginning of the PEO process with an aluminium anode. Over a treatment time of ten minutes, the lifetime of microdischarges and bubbles increase up to several hundreds of microseconds. That is accompanied by a substantial increase of the peak microdischarge current and the maximum bubble radius, up to 100 mA and 600 µm after a treatment time of ten minutes, respectively. Simultaneously, the measured voltage increases gradually over the treatment time caused by an increasing oxide layer thickness at the tip of the anode. This demonstrates that the microdischarge properties are strongly linked to the process time and thickness of the oxide layer.

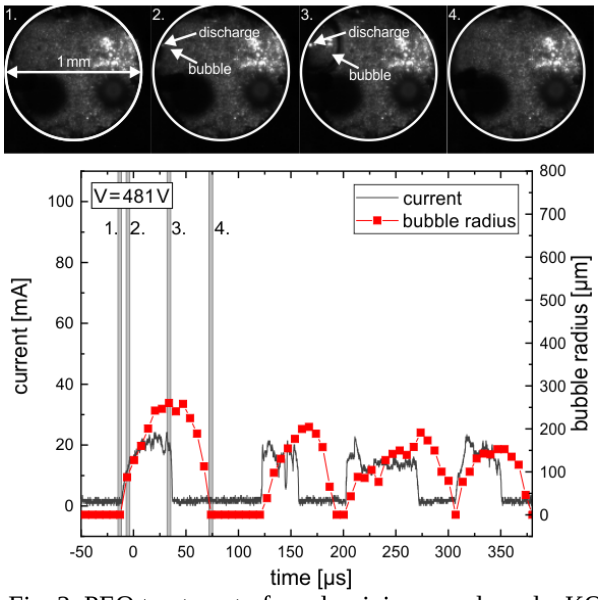

Fig. 2. PEO treatment of an aluminium anode and a KOH concentration of 1 g/l at the beginning of the process. The top images show a head-on view of the anode at the labelled time stages.

Furthermore, it was found that an analysis of bubble radii for a titanium anode is challenging due to lower image quality and faster bubble dynamics compared to a PEO process with an aluminium anode. Therefore, only KOH concentrations up to 2 g/l could be tested, while for an aluminium anode concentration up to 4 g/l were possible.

The surface temperature is determined in the range of 2800 K to 3200 K for an aluminium anode during a ten-minute PEO treatment, whereas the temperature for a titanium anode is about 1000 K lower.

A similar observation is made for the determined electron temperature, which is estimated to be in the range of 5000 K to 8000 K for an aluminium anode, while the temperature for a titanium anode is about 1000 K lower. However, an effect of the KOH concentration on the temperature could not be observed.

The electron density during a ten-minute PEO treatment with and aluminium as well as titanium anode is in the range of 10^{15} cm^{-3}. There are indications that, a higher KOH concentration leads to a higher electron density, which is especially noticeable at the end of the process. As an example, the difference of electron densities between 1 g/l KOH and 4 g/l KOH is approximately 2.5×10^{15} cm^{-3} after a ten-minute PEO treatment of an aluminium anode.

5. Conclusion

A single microdischarge (SMD) setup equipped with diagnostic tools for optical emission spectroscopy and camera measurements enables the determination of parameters like electron densities and bubble radius during a PEO treatment with an aluminium and titanium anode.

However, optical measurements for a PEO treatment with a titanium anode are more challenging due to faster bubble dynamics, lower image quality as well as lower spectral emission compared to a PEO treatment with an aluminium anode.

Nevertheless, it could be identified, that the electrolyte (KOH) concentration as well as the treatment time influences the bubble dynamics as well as parameters like electron density and bubble lifetimes. The bubble and microdischarge lifetime increase over treatment time for all tested electrolyte concentrations and additionally the electron densities are increasing for higher electrolyte concentrations.

Further analysis is needed to understand the effect of the electrolyte concentration and treatment time on the coating quality and how it is influenced by parameters like surface temperature and microdischarge lifetime during the PEO treatment.

6. Acknowledgement

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