

# Obtaining Composite Zr–Al–O Coating on the Surface of Zirconium by Microplasma Oxidation

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**Abstract.** The paper describes the application of the microplasma oxidation for production of Zr–Al–O composition on the surface of zirconium. Certification of a new-type power supply for depositing oxide ceramic coatings by microplasma oxidation was also carried out. The growth rate of Zr–Al–O coating amounted around 0.2 nm/s, which around 10 times exceeds that for depositing similar coatings using the similar equipment. We have studied the change of surface morphology and the chemical composition of the formed ceramic coating by means of EVO 50 scanning electron microscope and X-ray spectral analysis.

**Keywords:** microplasma, zirconium, compositions, oxidation, ceramic coatings, electron microscope, morphology

## INTRODUCTION

The problems in the development of aviation and space technologies comprise the continuous improvement of existing structures and the development of advanced devices. They are closely connected with the constant toughening of operating conditions exposing the aircraft parts and components. In particular engineers always strive improving the life and reliability of parts and assemblies made from zirconium alloys. Their application involves the development of a modification methods involving, for instance, the formation of the surface layer, which will enable reducing or eliminating the stationary and periodic exposures of such dangerous operational parameter as high temperature. The modification of zirconium alloy was performed by microplasma oxidation [1, 7].

Microplasma oxidation is a method that enabled us to obtain a uniform coating on the outer and inner surfaces of parts with complex profile by sprouting into the metal surface for 70%, the coating having very high adhesion [2]. The method is environmentally friendly and relatively safe due to using slightly alkaline aqueous electrolytes easily neutralized to acceptable pH levels from 5.5 to 8.

## EXPERIMENTAL

We tested modes and electrolyte compositions for producing surface oxide layers on zirconium alloy, the oxides having uniform thickness and composition. The studies were conducted using the samples of zirconium with the dimensions of 30×8×3 mm.

Electrolyte composition was chosen basing on the analysis of available publications on the microplasma oxidation of zirconium alloys and out previous experience in the microplasma oxidation of aluminum alloys.

Generally, the microplasma oxidation of metal alloys implies application of the colloidal solutions of sodium silicates, i.e.  $\text{Na}_2\text{SiO}_3$ ,  $\text{K}_2\text{SiO}_3$  or potassium, complemented by the compounds that increase the conductivity (electrolytes):  $\text{NaF}$ ,  $\text{KOH}$  and  $\text{NaOH}$ . The microplasma surface modification method involved the spraying of zirconium silicate electrolyte [2, 4]. The traditionally used electrolytes were too aggressive and dissolved zirconium metal during the microplasma treatment.

In previous works it was experimentally established that the composition of the films formed by zirconium microplasma oxidation was very sensitive to pH of the electrolyte solution [3]. Using the electrolyte with high alkalinity (borate-phosphate-fluoride) or weakly acidic electrolytes lead to the etching (chemical and electrochemical dissolution) of zirconium and formation of a thin oxide coating. According to literature data, the microplasma treatment of valve metals (Al, Ti, Zr and their alloys) in aluminate-containing alkaline electrolytes results in the formation of high-quality oxide-ceramic coatings with uniform thickness [2]. During the oxidation using this electrolyte, metasilicate is introduced into the silicon oxide film. This conditioned the choice of the aluminate electrolyte.

Microplasma surface treatment was carried out in zirconium aluminate-alkaline electrolyte having the following composition: [sodium metasilicate] =  $3 \text{ g/dm}^3$ , [sodium aluminate] =  $6 \text{ g/dm}^3$ , [sodium hydroxide] =  $2.0 \text{ g/dm}^3$ . Formation of coatings was carried out in a pulsed microplasma mode at various processing time using a programmable power source.

A universal programmable power supply was designed, since the pulsed current discharge processes find a broad range of applications. The power supply can provide stabilization of voltage, current or power applied to the load by externally setting the parameters using the interface. The supply allows the power compensation due to switching regulator. The power supply is based on the high-voltage inverter converter regulated by a programmable controller, and the output of the supply allows modulating the output power signal in accordance with programmed parameters. This technical solution makes possible to control the following processes: set the output signal frequency within a wide range, set pulse power, deter critical control parameters (for example, prevent the formation of arc processes in the load) and apply recovery algorithms for conditional modes.

## RESULTS AND DISCUSSION

The goals of the work were to obtain the ceramic oxide coatings on zirconium, study their composition, morphology and properties depending on microplasma oxidation mode.

Testing included different modes and composition of electrolyte to produce oxide surface layers on zirconium containing 1% niobium and having uniform thickness and composition. In the entire investigated range of frequencies, a typical arcing was observed across the zirconium surface, the arcing being induced by an outgassing from the electrode.

The change of dimensions of the samples obtained by the oxidation method was determined using a micrometer. The thickness of the oxide layer was determined by a metallography of the sample transverse section.

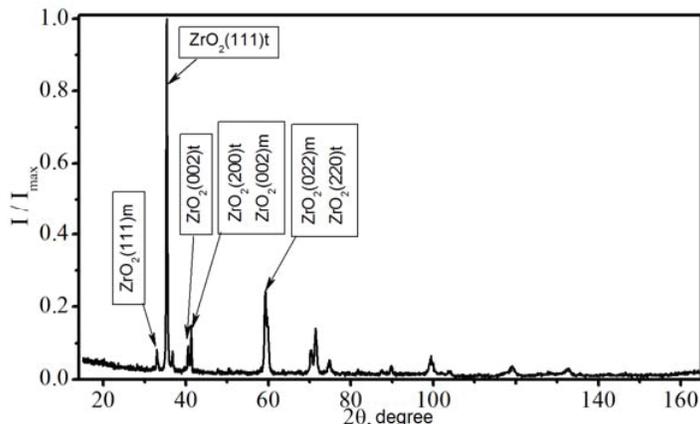
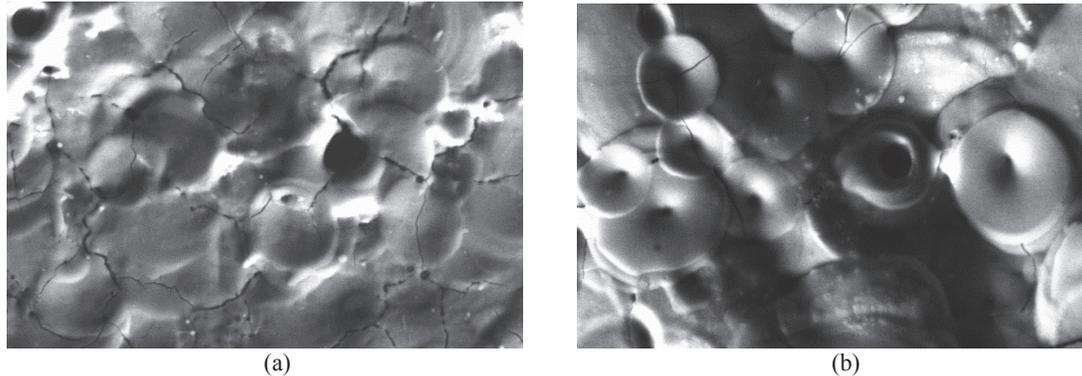


FIGURE 1. Radiograph of the oxidized surface of zirconium alloy sample

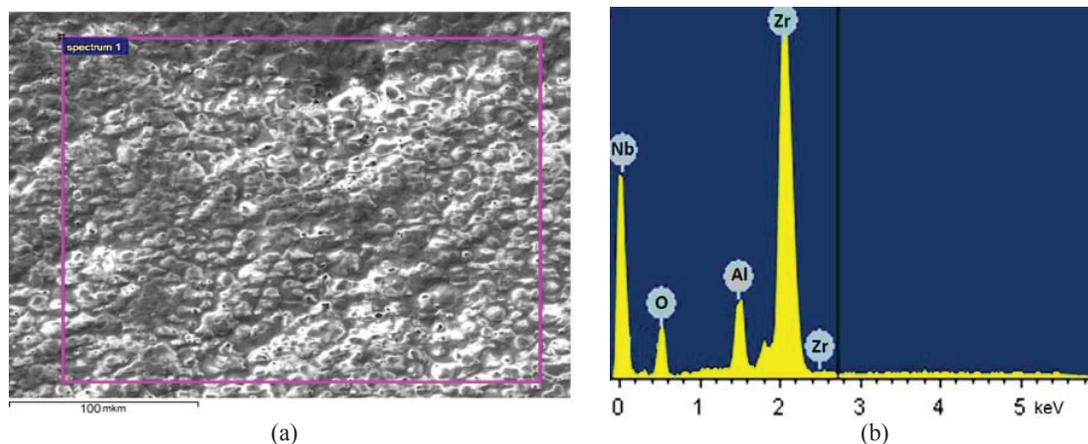


**FIGURE 2.** The morphology of the oxide-ceramic coatings obtained after zirconium microplasma oxidation. Scanning electron microscopy with  $\times 5000$  magnification: (a) oxide film thickness is around  $8\ \mu\text{m}$ , (b) oxide film thickness is around  $150\ \mu\text{m}$

X-ray structure analysis revealed the presence of the monoclinic and tetragonal phases on the surface of the sample. The portion of monoclinic phase was 18%, its lattice parameters were as follows:  $a = 5.3129\ \text{\AA}$ ,  $b = 5.2125\ \text{\AA}$ ,  $c = 5.1471\ \text{\AA}$ . Tetragonal phase portion was 72%. The lattice parameters were:  $a = 5.1200\ \text{\AA}$ ,  $c = 5.2500\ \text{\AA}$ . Thermodynamically equilibrium transition from the tetragonal to monoclinic phase occurs at the temperature of  $1200\ \text{°C}$ . Cubic zirconium oxide coating is stable at the temperature of  $2370\ \text{°C}$  and the presence of tetragonal zirconium is probably due to the stabilization of alumina, which was formed after oxidation of the sample surface with the aluminates contained in the electrolyte, and due to the rapid cooling of the oxide layer after the microplasma oxidation [5, 6].

Scanning electron microscopy showed that after the microplasma oxidation there is a typical coating with a porous structure, the surface coating is heterogeneous and rough. Increasing thickness of the oxide coating lead to the surface coating layer melt (Fig. 2(b)). With the growth of the oxide layer thickness, the energy injected into the cell micro arc discharge also increased due to the increased breakdown voltage. This lead to the increase of melting zone, and often to the formation of the dome over the discharge channel. This formations are hidden pores [7]. The power supply with a controlled pulse shape with negligible impact on the front allowed to conduct the continuous formation of the oxide layer with the depth of  $150\ \mu\text{m}$  within 10 and 6 minutes with the current density being equal to  $3.5$  and  $5.8\ \text{A/dm}^2$ , respectively.

This corresponds to the average rate of oxidation of the surface layer of about  $15\text{--}20\ \mu\text{m/min}$ . Thus, the microplasma oxidation has high efficacy at low specific energies.



**FIGURE 3.** Coatings produced by microplasma oxidation of zirconium alloy: (a) SEM EVO 50 image demonstrating the morphology the oxide-ceramic coating, (b) elemental composition of oxidized surface layers

TABLE 1. Chemical composition of Zr–Al–Nb–O coatings

Element	Zr L	Al K	Nb L	O K
Content, at. %	25.2	5.7	1.1	68.0

From Fig. 3 it is evident that the coating consists of grain aggregates with the dimensions ranging from 1 to 10  $\mu\text{m}$ . There are micropores on the surface with the diameter of up to 1  $\mu\text{m}$ . There is a small crack propagating predominantly along the grain aggregates. Figure 3(b) shows the spectrum obtained for the area highlighted in Fig. 3(a). Table 1 contains results of microprobe analysis of coating chemical composition which is similar to that of zirconium  $\text{ZrO}_2$ , containing Al and Nb as parts of solid solution. Data on the morphology of the surface layer coating produced by microplasma oxidation evidences the incorporation of electrolyte elements into the coating and formation of nanocomposite ceramics.

## CONCLUSIONS

The study enlightened the capability of a programmable power inverter to perform the microplasma oxidation for the purpose of the formation of oxide ceramic coatings with optimal characteristics. The growth rate of  $\text{ZrO}_2$ -based coating is about 14  $\mu\text{m}/\text{min}$ , which 10 to 15 times exceeds the rate of growth provided by industrial equipment. The microplasma zirconium processing equipment enabled the usage of aluminosilicate electrolyte and formation of ceramic Zr–Al–O coating with the uniform thickness ranging from 50 to 150  $\mu\text{m}$ .

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