Structure and properties of ceramic-like coating on zirconium alloy produced by microarc oxidation in electrolyte with submicron yttria powder additives

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Abstract. Ceramic-like coatings were formed on zirconium-niobium (Nb – 1%) alloy by microarc oxidation (MAO) in slurry electrolyte with the addition of submicron yttria powder. The coatings were investigated using scanning electron microscopy, x-ray diffraction analysis, microhardness tester and roughness meter. The addition of submicron yttria powder in electrolyte leads to content reduction of zirconia monoclinic phase in MAO coating. The inhibition effect increases with the MAO coating thickness rise and with an increase of the process current density up to 30 A/dm².

1. Introduction

Microarc oxidation (MAO) is a promising method for obtaining ceramic-like zirconia coatings [1]. For example, MAO zirconia coatings have been studied for biocompatible zirconium implants, for water corrosion protection of fuel elements of nuclear power reactors, for thermal barrier coatings production. These coatings have layered structure and low thermal conductivity: it can reach 0.2 W/m•K [2–3]. Stabilization of the tetragonal phase in MAO coating allows improving its functional properties. It was shown that MAO in slurry electrolyte with additives of yttria nanopowder allows to obtain tetragonal phase zirconia coatings [4–5]. However, the use of nanopowders is quite expensive and requires additional operations to prepare the electrolyte to prevent the nanoparticles from sticking together into conglomerates. Submicron powders are cheaper and less addicted to agglomeration.

The aim of this work was formation and study of zirconia tetragonal phase coatings by MAO method with the addition in electrolyte of yttria submicron powder.

2. Experimental

Segments of zirconium-niobium alloy (Nb – 1%) were used as a substrates for coatings. MAO treatment was carried out in an aqueous solution of sodium hypophosphite (5 g/l) and sodium silicate (9 g/l) with addition of 6 g/l of submicron yttria powder. Coatings were formed in AC electrical mode at equal values of anode and cathode currents and total current densities 20, 30, and 40 A/dm² for 60 min using MAI setup.
The thicknesses of MAO coatings were measured using the eddy current thickness gauge VT-201 and on cross-sections using a scanning electron microscope (SEM). The structure of the coatings was studied by SEM Quanta 600. Phase analysis of the coatings was carried out in copper Kα1.2 radiation using x-ray diffractometer PANalytical Empyrean. Phases were identified by database ICDDPDF-2. Microhardness was analyzed using Micromet 5114 hardness tester with the load on the indenter of 0.25 N. The time from the start of supplying the load to the nominal value was 5 seconds. Exposure under load was 10 seconds. Roughness assessment was carried out using a portable roughness meter TIME TR100 with 10 measurements on each coating samples.

3. Results and discussion

The thickness of the coatings varies in different areas of the samples. In the center parts it varies in the range 73..100 μm and increases at the edges of the samples to ~ 143..175 μm. Table 1 shows the average thickness of MAO coatings formed at different current densities.

| Table 1. MAO coatings thickness. | Current density, A/dm² | Thickness, μm |
|---------------------------------|------------------------|--------------|
| Sample 1                        | 20                     | 35           |
| Sample 2                        | 30                     | 126          |
| Sample 3                        | 40                     | 160          |

The study of the cross-sections revealed 3 layers in the coatings (figure 1(a)): a thin barrier (1), medium (2) and technical outer layer with large pores (3). MAO coating obtained at a total current density of 20 A/dm² has a large number of craters with pores in the center as well as areas containing electrolyte components on the surface (figure 1(a)). It is also noticed areas of globular structures with the size of 3÷5 μm (figure 1(b)) and adsorbed yttria particles with the size from 0.18 to 0.45 μm.

With an increase of current density up to 30 A/dm² the coating become less porous, the number of craters and microcracks decreases on the surface of the coating. At higher magnification (figure 1(c)) the coating grains with size up to 0.02 μm are visible. The density of adsorbed particles increases on the surface, them size varies from 0.05 to 0.3 μm (figure 1(d)).

MAO coating produced at a current density of 40 A/dm² has more regions with a predominance of electrolyte components on the surface. There are melted disc areas with globular inclusions shaped like powder particles on the coating grains (figure 1(e)).

Zirconia coatings microhardness increases with MAO process current density rise. So, microhardness of the top layer of coating № 1 varies from 1060 to 1800 HV, coating № 2 - from 1300 to 2050 HV, and coating № 3 - from 1410 to 2180 HV.

The study of the roughness of the coatings showed that the value of Ra parameter increases with the rise in the current density of MAO process. Ra parameter is ~0.5 μm for coatings №1 and №2. It increases to 0.8 μm for coating №3.

X-ray phase analysis has shown that the coating № 1 contains ~ 34% monoclinic (m) and ~ 66% tetragonal (t) phases of zirconia. With an increase in the total current density to 30 A/dm², the increase of the t-phase of zirconia up to 96% and decrease of the m-phase up to 4% is observed (figure 2). In the coating №3 produced at a current density of 40 A/dm² the content of t-phase is about 86%, and m-phase is ~ 14%. The peaks of the tetragonal phase are wider in the center, which shows the presence also of the cubic phase (figure 3). It could occur due to the high current density and as a result of higher temperatures during oxidation process. In work [3] it is shown that during the MAO process in this electrolyte without yttria additives, only monoclinic modification of zirconia is in the coating.
Figure 1. SEM images of the cross-section (a) (1 – barrier layer, 2 – medium layer, 3 – outer layer) and the surface (b, c) of the MAO coating formed at current density 20 A/dm$^2$; the MAO coating surfaces formed at current densities 30 A/dm$^2$ (d, e) and 40 A/dm$^2$ (f).

Figure 2. X-ray diffraction patterns of sample №2.
4. Conclusions
The addition of submicron yttria powder in electrolyte leads to the content reduction of zirconia monoclinic phase in MAO coating. The reduction effect increases with the thickness rise of the MAO coating and with an increase of the current density in the electrolyte up to $30 \text{ A/dm}^2$. The current density increasing up to $40 \text{ A/dm}^2$ promotes not only the tetragonal phase, but also the cubic phase formation in zirconia MAO coatings.

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References
[1] Apelfeld A V, Belkin P N, Borisov A M, Vasin V A, Krit B L, Ludin V B, Somov O V, Sorokin V A, Suminov I V and Frantskevich V P 2017 Modern Technologies for Modification of Materials Surface and Formation of Protective Coatings 1 648
[2] Savushkina S V, Polyansky M N, Borisov A M, Vinogradov A V, Lydin V B, Dankova T E and Agureev L E 2016 J. Surf. Invest.: X-Ray, Synchrotron, Neutron. Tech. 10 406
[3] Apelfeld A V, Borisov A M, Krit B L, Ludin V B, Polyansky M N, Romanovsky E A, Savushkina S V, Suminov I V, Tkachenko N V, Vinogradov A V and Vostrikov V G 2015 Surf. Coat. Technol. 269 279–85
[4] Savushkina S V, Ashmarin A A, Apelfeld A V, Borisov A M, Vinogradov A V, Polyansky M N and Bogdashkina N L Journal of Physics: Conference Series 2017 857 1 012037
[5] Apelfeld A V, Ashmarin A A, Borisov A M, Vinogradov A V, Savushkina S V and Shmytkova E A 2017 Surf. Coat. Technol. 328 513–7