Structural and phase transformations on zirconium surface after heat treatment with high-frequency currents

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Abstract. Research results on the surface morphological characteristics of zirconium samples after heat treatment with high-frequency currents have been described. It has been established that at temperature 600–1200 ºC and duration of heat treatment 30–300 s oxide coatings consisting of nano-grains are formed. The resulting oxide ZrO₂ coatings are a combination of two phases – monochinic (baddeleyite) and cubic.

1. Introduction
In order to protect metal surfaces from the environmental factors different methods of oxidation of metals are actively used, the basis of them comprise gas-thermal and electrochemical methods [1-5]. ZrO₂ coatings can also be produced by deposition methods [6]. In this regard, to create protective film systems and special functional coatings on zirconium surface a highly effective method of induction-thermal oxidation can be used, which has been tested successfully for commercially pure titanium, its constructional alloys, and chromium-nickel stainless steel [1,7]. As a result of this treatment on the surface of zirconium the processes of diffusion saturation with oxygen and formation of oxide compounds in the form of films and coatings are possible [8].

2. Methodology
The samples were cylinders with a diameter of 5.8–6 mm and a length of 2–2.5 mm fabricated from commercially pure zirconium grade E110. Their surface was exposed to the microtexturing air-abrasive (corundum with an average fineness of 200–300 μm) treatment. The resulting metal substrates of samples were also subjected to ultrasonic cleaning in aqueous-alcoholic solution. Further, the surfaces of the prepared samples were oxidized in the course of treatment with HFC [1]. Maximum power consumption of the laboratory device for the treatment with HFC during heating of the products with the geometry of this type was less than 550 W, the frequency of the current in the inductor – 89.5±0.5 kHz when the treatment temperature reached 600, 800, 1000 and 1200 ºC. In the course of the studies the effect of treatment with HFC was established in the temperature range of 600–1200 ºC on the morphological changes occurring in the surface during the formation of oxide coatings. The modes of coating production were given double numbers: the first number designated the heat treatment temperature of zirconium substrate measured in ºC; the second – treatment duration counted in seconds upon reaching the necessary temperature of treatment. For example, mode 800-030 corresponds to the temperature of 800±10 ºC and treatment duration of 30±1 s.

The surface morphology of the samples after the selected technological treatment was examined using scanning electron microscopy (SEM) in the micro- and nanoscale in order to identify the patterns of structure formation of the surface layer and coatings. SEM combined with energy-
dispersive X-ray spectroscopy (EDX) of the chemical composition of samples was performed on MIRA II LMU with INCA PentaFETx3 detector. Changes in the concentrations of zirconium and oxygen as well as other impurities measured in atomic percent (at.%) were analyzed in the areas of samples with different morphology types. Phase-structural surface state of the samples after IHT was studied by X-ray diffraction (XRD) on Gemini/Xcalibur (CuKα-radiation, λ = 1.541874 Å, 20º < 2θ < 110º).

3. Results

High oxygen content in the surface layer of zirconium samples showed its high adsorption capacity. Surface of zirconium was most active with respect to oxygen that can be traced throughout the range of heat treatment. The content of oxygen reached 49–57 at.%, which affected both the stabilization of initial phase α-Zr and formation of zirconium dioxide.

Treatment of zirconium with HFC lead to the activation of diffusion saturation of the near-surface layer with oxygen, oxidation, and formation of films of ZrO$_2-x$ and thicker coatings of ZrO$_2$ in different allotropic modifications: stable baddeleyite m-ZrO$_2$ (monoclinic system) and unstable c-ZrO$_2$ (cubic system) [8,9].

XRD data proved that untreated zirconium is characterized by the presence of α-Zr phase (Figure 1a). When the treatment temperature reached 600 ºC about 20–40% of the high-temperature phase of β-Zr appeared. In the near-surface layer of zirconium samples at a continuous treatment of about 300 s no more than 38% of baddeleyite m-ZrO$_2$ and about 11% of c-ZrO$_2$ were formed. At a short exposure of about 30 s no oxide phase was detected. Increase of the treatment temperature to 800 ºC lead to more intense oxidation of zirconium. At a short exposure the amount of zirconia (m-ZrO$_2$ + c-ZrO$_2$) equaled 18–20%. At a maximum exposure time of about 300 s the amount of zirconia reached a maximum of 75–80%. At the same time the number of the most stable baddeleyite was 55 % (Figure 1b).

![Figure 1(a, b). Results of XRD analysis of the zirconium surface: the untreated sample (a); the sample oxidized by HFC at 800 ºC (800-300 mode) (b).](image)

In the high-temperature range of treatment at about 1000 ºC the amount of zirconium dioxide reached 45–47% at the treatment time of 30 s. However, the maximum content of zirconia did not exceed 70% at the treatment time of about 300 s. This was probably related to the increase in defects in the form of pores and cracks.

With the temperature growth to 1200 ºC and at duration of HFC treatment of about 30 s there was an increase in the oxide phases to 59–60%. At the treatment duration of about 300 s the total amount of ZrO$_2$ did not exceed 65%.

Morphology of the initial microstructure of zirconium samples remained almost unchanged to the temperature of 1000 ºC and maximum duration of the oxidation (Figure 2a). When the temperature...
reached about 1200 °C and the treatment duration equalled about 300 s the crystals of the formed high-
temperature phase of zirconia had time to grow to submicron values that significantly altered the
surface relief after turning and air-abrasive treatment (Figure 2b).

![Figure 2(a, b). Microstructure of the surface after oxidation of zirconium samples at HFC mode
800-300 at different magnifications: ×10,000 (a); ×200,000 (b).]

The formed nanocrystals of the oxide film rapidly started to increase in size, which lead to their
further growth to submicron size and cracking (Figure 3d).

![Figure 3(a, b). Nanostructure of the surface after oxidation of zirconium samples at various modes
of treatment with HFC: mode 800-300 (×200,000) (a); mode 1200-300 (×100,000) (b).]
The resulting nanostructure of the oxide coating had grains with an average size within 40±10 nm. Intensive growth was observed with the increase in heat treatment temperature to 1200±30 °C and when the duration exceeded 30±1 s. Maximum values of zirconia grains after high temperature treatment (mode 1200-120 and 1200-300) were 100–250 nm. However, there was no spontaneous separation of the outer thick-layer oxide, which is typical for, e.g. commercially pure titanium and its alloys in this range of treatment with HFC [1].

4. Conclusions
Thus, the surface structure of zirconium samples treated with HFC was characterized by the formation of zirconia coatings, which are a combination of two phases: stable baddeleyite m-ZrO$_2$ (monoclinic system) and unstable c-ZrO$_2$ (cubic system). Functional coatings were formed mostly by nano-sized and submicron crystals of round and prismatic shapes. The samples of rough coatings with the highest parameters of morphological heterogeneity in the nanoscale corresponded to the following treatment modes: 800-120 (at $P = 150$ W, $t = 800$ °C, $\tau = 120$ s), 800-300 (at $P = 150$ W, $t = 800$ °C, $\tau = 300$ s), 1000-030 (at $P = 260$ W, $t = 1000$ °C, $\tau = 30$ s), 1000-120 (at $P = 260$ W, $t = 1000$ °C, $\tau = 120$ s), 1200-001 (at $P = 520$ W, $t = 1200$ °C, $\tau \approx 1$ s), and 1200-030 (at $P = 520$ W, $t = 1200$ °C, $\tau = 30$ s).

It should also be noted that zirconium products manufactured by conventional machining can be subjected to nanostructuring treatment with HFC in order to obtain the required surface morphology heterogeneity. Improving the quality of zirconium products is also be related to the control of the tribological parameters, particularly hardness, wear resistance, and coefficient of friction.

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