ARTICLE IN PRESS

Composite Structures xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

Surface morphology of zirconium after treatment with high-frequency currents

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ARTICLE INFO

Keywords:
Zirconium
Zirconia coatings
Induction heat treatment
Surface morphology

ABSTRACT

Coatings of zirconia were prepared by oxidation of zirconium grade E110 using induction heat treatment (IHT) with high-frequency currents. The IHT was performed at temperatures within 600–1200 °C for 30–300 s. According to the results of scanning electron microscopy, X-ray diffraction, energy dispersive analysis, and nanoindentation, zirconia coatings with high hardness (about 17 ± 0.4 GPa) and elastic modulus (about 270–320 GPa) were formed on zirconium surface after semi-rough turning followed by IHT at 1000 °C for 30 s. The coatings consisted of nanocrystals with an average size of 37 ± 2 nm. Zirconia coatings with high morphological heterogeneity (nanocrystals with an average size of 45 ± 2 nm), moderate hardness (about 4.5–5.5 GPa) and high elastic modulus (about 272–285 GPa) were formed on zirconium surface after abrasive blasting followed by IHT at 1000 °C for 30 s.

1. Introduction

Zirconia (ZrO_2) is applied in various fields of science and technology because of its unique properties, in particular thermal insulation, optimal combination of structural and chemical stability, as well as high strength under aggressive operating conditions. At present in many papers much attention is given to a more efficient use of zirconia for electronic devices and sensors [1], products operating at high temperatures (gas turbine engines in aerospace industry) [2] and under friction [3]. In medical engineering zirconia is widely used as a biocompatible ceramic material, which can be applied for the manufacture of dental crowns [4], extra-osseous components of dental implants (abutments) [5], acetabular components of hip joint endoprostheses [6], as well as morphologically heterogeneous coatings for metal implants [7]. The focus on zirconia and composite materials containing its various crystal modifications is related to its unique mechanical characteristics, in particular hardness and wear resistance [8].

Biocompatible zirconium alloys have also found application in implantology along with titanium alloys [9–11]. Much attention is paid to the surface morphology of metallic materials used for the production of various implants. For example, the surface of dental implants should have the required open porosity to ensure the osseointegration [12,13]. On the other hand, in the manufacture of structural elements operating under friction, it is important to minimize porosity and provide the necessary surface roughness.

The oxidation kinetics and stabilization of certain crystalline modifications of zirconia, e.g. t-ZrO_2 (tetragonal modification), are affected by doping of the zirconium alloy with yttrium, niobium and other elements [14]. Possible variants of the crystal structure of Zr/ZrO interface are also studied using *ab initio* theoretical calculations [15]. In order to improve the mechanical properties (strength, hardness, crack resistance), other nano-sized ceramic materials TiB_2, Al_2O_3, etc. are added to zirconia apart from Y_2O_3 [16]. As a result of high temperature treatment (sintering at 1100 °C for 120 min), the hardness of t-ZrO_2 rises from 11.20 to 13.48 GPa, and the resulting material finds application in the manufacture of tool ceramics.

In the course of thermal treatment of zirconium alloys, there are changes in the surface morphology and microstructure, in particular zirconia coatings with nano-sized (1–3 nm) pores are formed during oxidation [17]. Oxide coatings on zirconium alloys (Zr – balance, Nb ≥ 1 wt%, Sn ≥ 1–1.5 wt%) are obtained by thermal treatment (oxidation) in an oxygen-containing atmosphere (air, mixture of oxygen and argon) at temperatures from 700 to 1580 °C [18,19]. In the presented studies, the processes of formation of oxides, nitrides and gas-saturated (α-Zr(O), cZr(N)) near-surface layers where α-phase is stabilized by oxygen and nitrogen were described in sufficient detail. To obtain powders of nanoparticles, e.g. monoclinic and tetragonal modification of ZrO_2, the effect of arc discharges in an oxygen-containing

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https://doi.org/10.1016/j.compstruct.2018.01.055
Received 6 January 2018; Received in revised form 16 January 2018; Accepted 19 January 2018

Please cite this article as: Koshuro, V., Composite Structures (2018), https://doi.org/10.1016/j.compstruct.2018.01.055

atmosphere is used [20].

The oxidation of metallic materials also proceeds quite quickly when exposed to the superheated water steam [21]. A layer of ZrO_2 nanoparticles with the size varying from 4 to 50 nm is formed due to the treatment of zirconium with superheated water steam (at the temperature of 500–525 °C and pressure of 25 MPa) on its surface [22]. A thick loose scale is formed on the surface of zirconium products at a longer exposure to the high temperature (600–1200 °C) steam [23]. Thus, the duration of high temperature treatment strongly affects the chemical composition and microstructure of materials, which inevitably influences the mechanical properties.

ZrO_2 oxide coatings on the surface of chromium-nickel stainless steel are also obtained by the sol–gel method and subsequent laser modification [24]. Ceramic nanopowders are used to produce thick ZrO_2 coatings on the aluminum surface [25]. The phase composition of the resulting coatings is represented by several modifications of zirconia (m-ZrO_2, t-ZrO_2, c-ZrO_2), the average hardness value reaches 8.6 GPa, which is 1.6 times higher than that of conventional plasma-sprayed coatings. Spraying of nano-sized (up to 40 nm) ZrO_2 powder provides a significant increase in the microhardness of coatings to $HV_{0.02} = 1320$ ($\approx$13 GPa) [26]. The resulting value is equivalent to the hardness of the synthesized bulk ceramic material.

In earlier studies, it was shown that to change the morphological characteristics of the surface (the size of crystals and pores) of biocompatible metals, e.g. commercially pure titanium, and to improve the mechanical properties induction heat treatment (IHT) in the temperature range from 600 to 1200 °C with a high temperature exposure from 1 to 300 s was quite efficient [27]. As a result of IHT, there was a 3–4.5-fold increase in the hardness of commercially pure titanium (CP Ti Grade 2) compared to that of the untreated titanium (1.8–2.1 GPa) and it reached a maximum (about 9–9.5 GPa) at the treatment temperature of 1000 °C and exposure time of at least 120 s. Thus, in this paper, the influence of high temperature IHT of zirconium alloy E110 on the parameters of morphology, phase composition and hardness of the near-surface layer of oxide coatings is investigated.

2. Materials and methods

2.1. Preparation of coatings

Experimental samples were round plates (diameter of 5 ± 0.5 mm and thickness of 2.0–2.5 mm) fabricated from zirconium grade E110 (Zr – balance, Nb – 0.9–1.1 wt%). Their surface was subjected to semi-rough turning or abrasive blasting by corundum (Fig. 1). Morphologically heterogeneous surface after abrasive blasting was characterized by the presence of micrometric protrusions and cavities. Then the substrates were also subjected to ultrasonic cleaning in aqueous solutions of surfactants and alcohol.

The next step included the IHT and oxidizing in the air of the surface of zirconium samples. The temperature range for the production of coatings varied within 600–1200 °C with a step of 200 °C.

The current frequency equalled 89 ± 1 kHz and the electric power did not exceed 0.3 kW, which was chosen due to the mass and dimensional characteristics of the heated samples. At the same time, the difference between the temperature values of the near-surface and underlying layers was not more than 20–30 °C. The laboratory device for IHT ensured high efficiency of heating to the required temperature. The process was characterized by short heating duration to the certain temperature value – from 10 to 40 s and the velocity of heating – from 60 to 30 °C/s. The heating temperature was measured with an infrared pyrometer “DT-8828″.

2.2. Coating characterization

The chemical composition of the coatings was studied by energy dispersive X-ray fluorescent analysis (EDX). In order to perform the

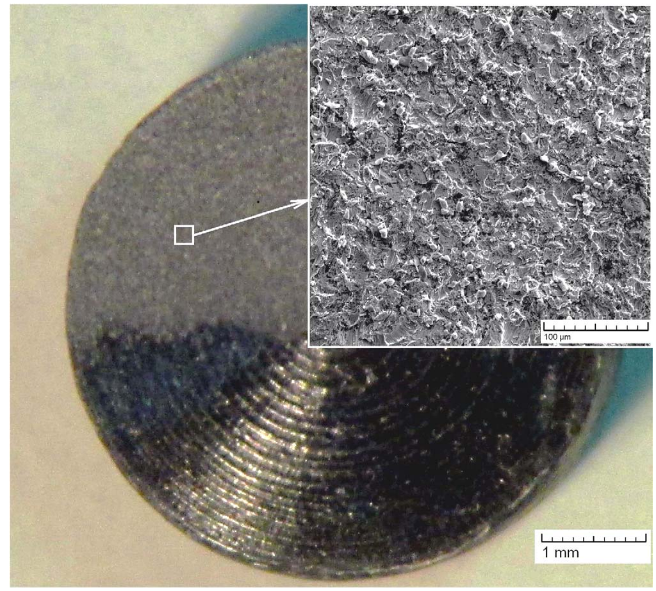

Fig. 1. Zirconium sample with the half-space after abrasive blasting (the upper area and its magnified fragment, ×1000) and after semi-rough turning (the lower area).

subsequent investigation of the phase composition of the near-surface layer of zirconium samples, it was necessary to determine the oxygen concentration (at.%).

Phase composition of the coatings was studied by X-ray diffraction (XRD) on “Gemini/Xcalibur” diffractometer using an X-ray tube with a copper anode (CuKα, $\lambda = 1.541874$ Å, $2\Theta = 25–110°$). The crystalline structure of the coatings was analyzed using the software processing of XRD patterns in order to remove the amorphous phase.

Surface morphology of the coatings was studied on micro- and nanoscale by scanning electron microscopy (SEM) to identify the structure formation patterns. Morphological parameters of the structure, e.g. dimensions of grains, were defined. Processing of SEM images was performed using software for the analysis of geometric parameters of micro-objects “AGPM-6M” and program “Metallograph” [28]. As a result of the morphological analysis of the coating surface images, the following parameters were determined: average linear dimension of microrelief elements (grains), their dispersion in size, and the number of these elements in the view field. SEM and EDX of the coatings were performed on “MIRA II LMU” with “INCA PentaFETx3” detector at the voltage of 20 kV.

Elastic modulus E and hardness H of coatings were evaluated by nanoindentation using mechanical properties tester “NANOVEA Ergonomic Workstation”. The selected load applied to Berkovich indenter equalled 100 mN and the indentations into the zirconia coating were about 0.5–1.5 µm.

3. Results and discussion

3.1. Chemical and phase composition

The chemical composition was analyzed using the EDX method in the investigation of the near-surface layer of zirconium samples after semi-rough turning or after abrasive blasting followed by IHT. Zirconium is a reactive metal, so its near-surface layer after machining had a high oxygen concentration of 54–59 at.%. On the morphologically heterogeneous surface the oxygen concentration reached 67–69 at.%, which corresponded to a natural thin layer of a chemically stable compound of zirconia, e.g. a monoclinic modification m-ZrO_2 (baddeleyite) [29].

After IHT at the temperature of 600 °C and short exposure of about 30 s the amount of oxygen increased insignificantly to 58–60 at.%.