Structure and phase structure of electro-spark Zr coatings on titanium alloys

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The article is cover investigation microstructure and phase composition of electro-spark Zr-coatings on titanium base. Coatings were obtained in protective (Ar) and saturation (N_2) atmosphere. The properties of coatings were investigated by SEM and X-ray diffraction, microstructure and microhardness analysis.

It has been shown that microhardness increase till 16 GPa in intermediate layer after ESA in saturation atmosphere.

Keywords and phrases: titanium alloys, electro-spark alloying (ESA), coatings, microhardness, microstructure, SEM.

Introduction

Titanium and zirconium is wide known as biocompatible materials. Their oxides are used for obtain different coatings for implants. There is made a decision to obtain coatings from titanium and zirconium by high-energy treatment method — electro-spark alloying in different atmosphere (air, protective and saturation atmosphere). The TiZr system shows as a complete solid solution for both the high temperature beta phase and the low temperature alpha phase, a wide variation of alloy design is available. Hence, it may be possible to design TiZr alloy having a superior corrosion resistance and good biocompatibility, like pure Ti, but with better mechanical properties than those of Ti-6Al-4V alloy [1]. Last time in USA, Canada, India and China high-energy methods are popular for biocompatible coatings obtaining [2–4]. Because, electro-spark alloying is a micro alloying and coating technique, which utilizes a brief power discharge (typically, 1–10 μs) between an electrode and the work-piece in the frequency range 10–1000 Hz, with the maximum arc temperature reaching 5000–25,000 K at the discharge micro-site [5]. It can transfer material from the electrode tip to the work-piece and strengthens the surface by alloying to improve the physical, chemical and mechanical performance of the substrate. Therefore, the ESA treatment provides several benefits such as (1) because very little heat is transferred to or accumulated in the work-piece, the substrate has a small temperature increase and suffers minimal mechanical damage; (2) a strong metallurgical bond is established with the substrate; (3) wear proof, anti-corrosion and other functional properties can be obtained by choosing the appropriate electrode material or treatment medium; and (4) its simplicity, easy operation, and relatively low cost is invaluable for surface engineering [6].

Materials and methods

Cylindrical form samples were used for experiment (h = 10 mm, Ø = 10 mm). Electro-spark alloying (ESA) was carry out on air and in camera with protective (Ar) or saturating (N_2) atmosphere during 180 sec (3 min). For electro-spark alloying was used electro-spark device "Elitron-22". The main operation principle of electro-spark device is generation electro-spark discharge between two electrodes (cathode — sample, which alloying, and anode — material for alloying). So, work-piece of titanium was situated on platform and it was cathode, the cuboid peace of zirconium was situated in device holder and it was anode. The scheme of electro-spark alloying process is presented in Fig. 1.

Microscopic, microhardness, X-ray and SEM analyses were used for investigation Zr-coatings on titanium base.

For microscopic investigation used metallographic microscope "MIM-10". Before microscopic investigation,

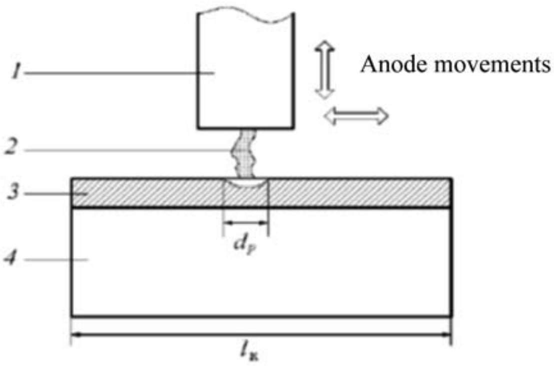

Fig. 1. Scheme of electro-spark alloying process. 1 — Anode; 2 — Electric discharge; 3 — Coating; 4 — Cathode; l_k — Width of cathode; d_p — Diameter of discharge operating zone.

samples were prepared. It were consists of grinding, next polishing by Cr_2O_3-pasta and finishing polishing on water.

For microhardness investigation was used device “PMT-3M”. Microhardness appreciation conduct by diamond pyramid indentation with square base and two sided angle at top 136° and with loading 0,05 kg during 10 sec. Diagonal from print of diamond pyramid was measuring, and by table data microhardness in GPa was determ.

For SEM analysis was used electron microscope SELMI.

Results and discussion

After ESA in protective atmosphere we don’t see clear--cut line division between alloying layer and base material. Besides of them, solid homogeneous small with metalescent “dots” are formed in some places on the coating (Fig. 1). Microhardness of this “dots” is come up to 9…10 GPa. There is hardened region in surface layer were find by microhardness analyses and width of this region is about 1500 µm, hardening value about 2.4 GPa (Fig. 2).

After ESA in saturating atmosphere, division line between layer and base material were observed. Layer structure has solid nature with small amounts of cracks (Fig. 3).

During alloying on saturating atmosphere (N_2) was formed layer with nigh microhardness, that come up to 16 GPa. It’s about 10 times higher, than initial microhardness of base material (Fig. 4).

Possible, that this microhardness distribution is due to forming of fine-disperse Zr or Ti nitrides, concentration of which chosen from surface to the deep of sample.

In samples, which alloying by zirconium in protective medium (Ar) were find layered structure by SEM investigation. It is confirms by microprobe analysis.

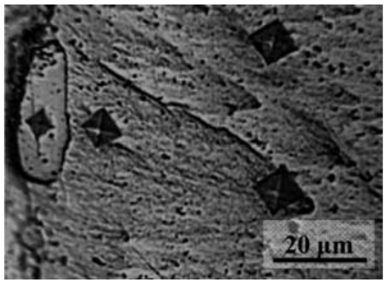

Fig. 2. Surface layer microstructure of titanium sample after ESA, anode — Zr, I = 2,8..3 A; τ = 180 s (3 min), atmosphere — Ar.

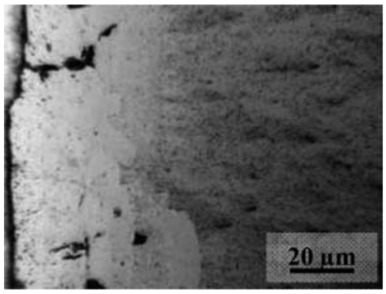

Fig. 3. Surface layer microstructure of titanium sample after ESA, anode — Zr, I = 2,5 A; τ = 180 s (3 min), atmosphere — N_2.

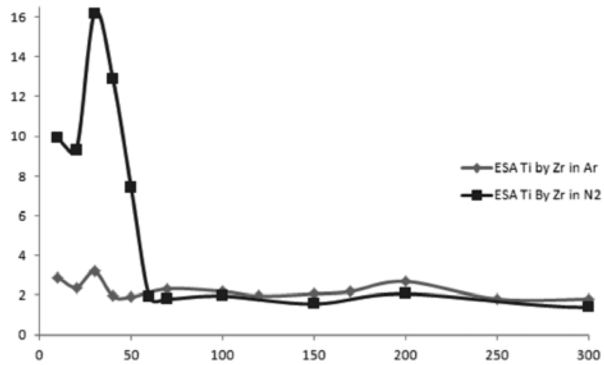

Fig. 4. Microhardness distribution in surface layer of titanium sample, ESA, anode — Zr, medium — Ar, N_2; I = 2,5 A; τ = 180 sec (3 min).

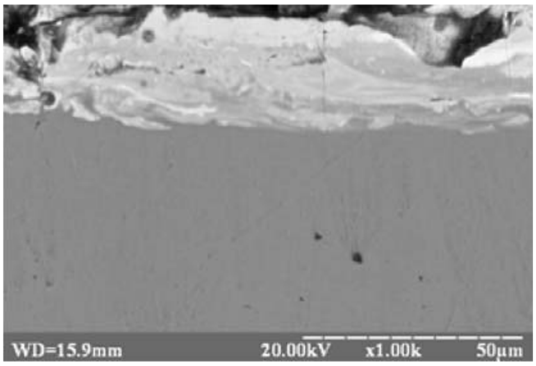

Fig. 5. Micrograph of titanium sample alloying layer, SEM (secondary electrons), ESA, anode — Zr, medium — Ar; I = 2,5 A; τ = 180 sec (3 min).

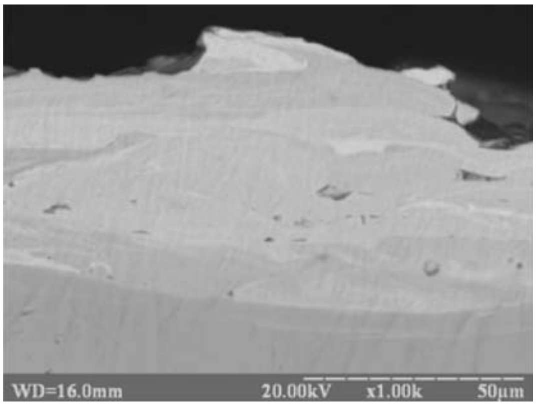

Fig. 6. Micrograph of titanium sample alloying layer, SEM (secondary electrons), ESA, anode — Zr, medium — N_2; I = 2,5 A; τ = 180 sec (3 min).

Results of X-ray investigation are adjust with analytical data. Solid solution α-Ti(Zr) is forming in surface layer in case of isomorphic crystal lattice of Ti and Zr. Parameter of lattice is determined by Zr concentration [7].

Conclusions

Obtaining of composite biocompatible coating with required properties is one of contemporary material science tasks. One of method for obtaining this kind of coatings could be high-energy methods like electro-spark alloying, different types of laser treatment.

It is possible to obtain Zr-coatings on titanium base by electro-spark alloying in different atmosphere. This is first stage for obtaining biocompatible coatings.

Effect of increasing microhardness till 16 GPa (hardening coefficient = 8,7) in intermidiate layer after ESA of titanium sample were established. Possible, it is due to nitride saturation from interelectrode medium.

The final idea of this experiment is obtain biocompotible metal composite coatings. So, for the conclusions about this possiblity, results of mechanical properties and corrosion resistance, and in vitro analysis are needed.

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