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MORPHOLOGICAL ASPECTS OF ZIRCONIA COATING ON Ti-Zr ALLOY OBTAINED WITH ATHMOSPHERIC PLASMA SPRAYING TECHNIQUE

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In recent years different types of titanium alloys have been investigated with the aim of utilizing materials in biomaterials field, and Ti–Zr system alloys are very promising materials. In this paper, microstructure and morphology of ZrO_2-CaO coating deposited on Ti-55Zr alloy is investigated. Zirconia ceramic coating was deposited using Sulzer Metco 9MCE atmospheric plasma spraying, in order to improve corrosion resistance and biocompatibility. Microstructure and phase analysis of based material and ceramic coating were investigated using scanning electron microscopy, X-ray diffractometry (XRD). The coated layer presents a homogenous aspect with an average thickness layer of 120 microns and some small cracks and splats.

Keywords: ZrO_2-CaO coating, Ti-Zr alloy, SEM, XRD.

În ultimii ani diferite tipuri de aliaje de titan au fost analizate în scopul utilizării lor în aplicaţiile biomedicale, sub diverse forme de proteze şi implanturi. În această lucrare au fost analziate microstructura şi morfologia stratului de ZrO_2-CaO depus pe un aliaj Ti-55Zr. Acoperirea ceramică de zirconiu a fost realizată utilizând o instalaţie de depunere în jet de plasmă Sulzer Metco 9MCE, în scopul îmbunătăţirii rezistenţei la coroziune şi a biocompatibilităţii. Microstructura şi analiza de faze a materialului de baza şi stratului ceramic depus au fost efectuate utilizând microscopia cu scanare de electroni şi difracţia de raze X. Stratul depus a prezentat un aspect omogen cu o grosime medie a stratului de 120 microni şi cu prezenţa unor "splat-uri" şi mici fisuri.

Cuvinte-cheie: strat de ZrO_2-CaO, aliaj Ti-Zr, SEM, XRD.

INTRODUCTION

Titanium and its alloys are especially used as biomaterials, for orthopedic field and dental implants. Titanium alloys are the second generation biomaterials and replaced Co–Cr alloys and 316L stainless steel due improving corrosion resistan Young modulus, tensile strenght, and biocompatibility. The most important fact of these alloys is to obtain materials with better properties for implants for a long time [1]. In order to improve characteristics of material it is necessary alloying with several elements like Nb, Mo, Ta, and Zr, elements that do not present cytotoxicity in the human body. Several authors reveal that Ti has hexagonal metastable phases α′ and orthorhombic α and orthorhombic α″ [2].

Li et al. [3] showed the shape memory aspect of Ti–Zr alloys and revealed that these alloys are suitable for dental implants in medical field.

Zr is known to be as an element with identical allotropic transformation with Ti. α and β phases of zirconium, exhibts hardening and decreases the phase transformation velocity [4, 5]. Zr is non-toxic element and it is in the class of allergy-free element [6]. It has strong corrosion resistance alloying with Ti [7]. Ti alloys with 25%Zr prevent calcium phosphate formation, which is an important aspect of the human bones [8]. Ti alloys up to 56%Zr It is also reported that the tensile strength maintains fairly high, however, elongation decreases when Zr content exceeds 56 wt.% [9].

APS (atmospheric plasma spraying) technique is shown in fig. 3a having as main components: plasma gun, powder feeder and control unit. The equipment must contain four types of gases: H_2, Ar, He, N_2. Between anode and cathode, by high voltage discharge a continuous current arc is established that ionizes Plasma gas, leading to good electrical conductivity. At the exit of the nozzle gas ions recombines, yielding the energy absorbed in a very short time, leading to the formation of a plasma jet with a temperature of 10000-16000°C. The powder is injected directly into the plasma jet which accelerates to surface area [10].

Commercial ZrO_2 oxide ceramics are basically known as partial stabilized zirconia and tetragonal zirconia crystals. The addition of „stabilizing" oxide, like CaO, to pure ZrO_2 allows forming multiphase materials, but in last period of time authors keep their focus on ZrO_2-CaO ceramics [11]. Ceramic coatings generated by plasma spraying have been used as anti-corrosion layers for metallic components [11].

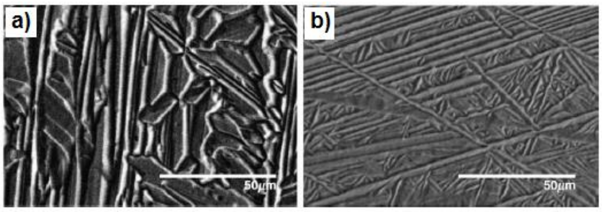


Fig. 1. SEM images of Ti-Zr alloys: a) Ti-30Zr; b) Ti-40Zr [12]

Kim et al. [12] reveals in fig. 1 the microstructures of the Ti–Zr alloy with Zr content of 30% (wt.), respectively 40% (wt.). The microstructures of the Ti–30Zr and Ti–40Zr alloys have two constituents compose of a lamellar structure and a needle-like structure.

Cao et al. studied ZrO_2 stabilized by CaO and MgO as thermal barrier coatings [13] and could be a reasonable phase for obtaining a protective coating and promoting adhesion in Ti-ceramic dental restorations. The purpose of this paper is to observe the morphology and phase analysis of a ZrO_2-CaO ceramic layer deposited with APS technique on Ti-55Zr based material.

MATERIALS AND METHODS

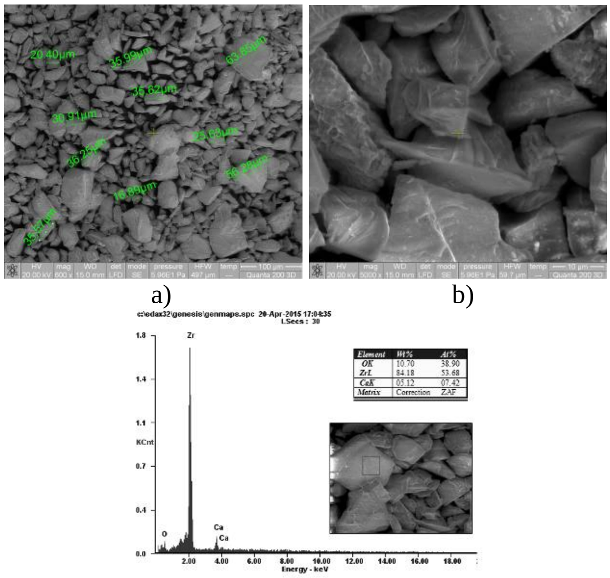
A binary Ti-Zr alloy was prepared in a high frequency induction furnace, followed by a process of rolling to a thickness of 600 microns. Authors used raw materials of high purity.

Table 1. Deposition parameters for plasma-sprayed coating

Coating	ZrO_2CaO 95-5
Powder Supplier	MTS 8013
Feeding mode	Internal
Arc current(A)	500
Arc voltage(V)	50
Working gases	Ar, H_2
Torch traverse	layer-6 passes
Spray distance (mm)	150

Final chemical composition was obtained by repeted melting with the following chemical composition, presented in fig. 7b).

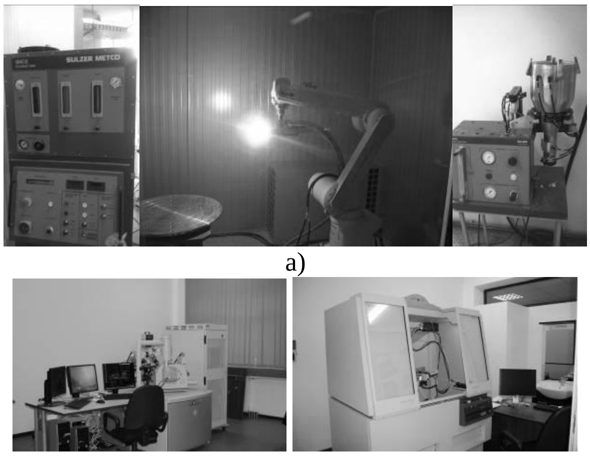
ZrO_2 - CaO coating was deposited using atmospheric plasma spraying system SULZER METCO 9MCE – SPRAYWIZARD. Spraying parameters are shown in table 1.



a) b)

c)

Fig. 2. SEM images of ZrO_2CaO powder (a-b) and EDAX analysis (c)



a)

b) c)

Fig. 3. a) Sulzer Metco 9MCE facility; b) SEM QUANTA 2003D; XRD X'Pert PRO MPD

Samples of Ti-55Zr were investigated by scanning electron microscopy – FEI SEM Quanta 200 3D with EDS detector for chemical composition and X –ray diffraction using an X'Pert Pro MPD diffractometer with the following parameters: continous scan, 2θ – (10º-90º), Step size: 0.0131303, Time per step: 61.20, Scan speed: 0.05471, 45 KV and 40 mA using a copper anode X-ray tube. The equipments used for coating process and materials characterization are shown in fig. 3 [14]. ZrO_2CaO powder morphology and chemical composition is presented in fig. 2 having a grain range between: 5µm-60µm.

RESULTS AND DISCUSSIONS

Structural analysis. The surface SEM images of the ZrO_2-CaO are shown in fig. 4 (a-d). The metallic surface covered by ZrO_2-CaO exhibited pores and splats. Coating presents some unmelted particles of ZrO_2 and CaO, which are revelead by their aspects and chemical compostion (fig. 4d and fig. 5b).

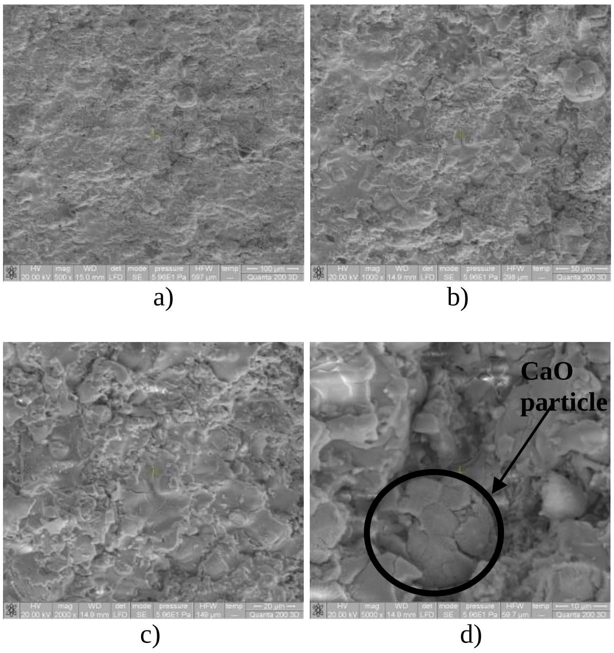


Fig. 4. SEM images of ZrO2-CaO surface coating

The surface SEM images of the ZrO_2-CaO are shown in fig. 6 (a-d). Thickness of the deposited layer is in the range of approximately 120µm. Plasma deposition led to a compact layer with small cracks and specific morphology of a ceramic layer called “splats” (fig. 6). In fig. 7 are shown cross section EDAX analysis for the coating and the base material. Fig. 8 reveals a uniform distribution of elements in the deposited layer.

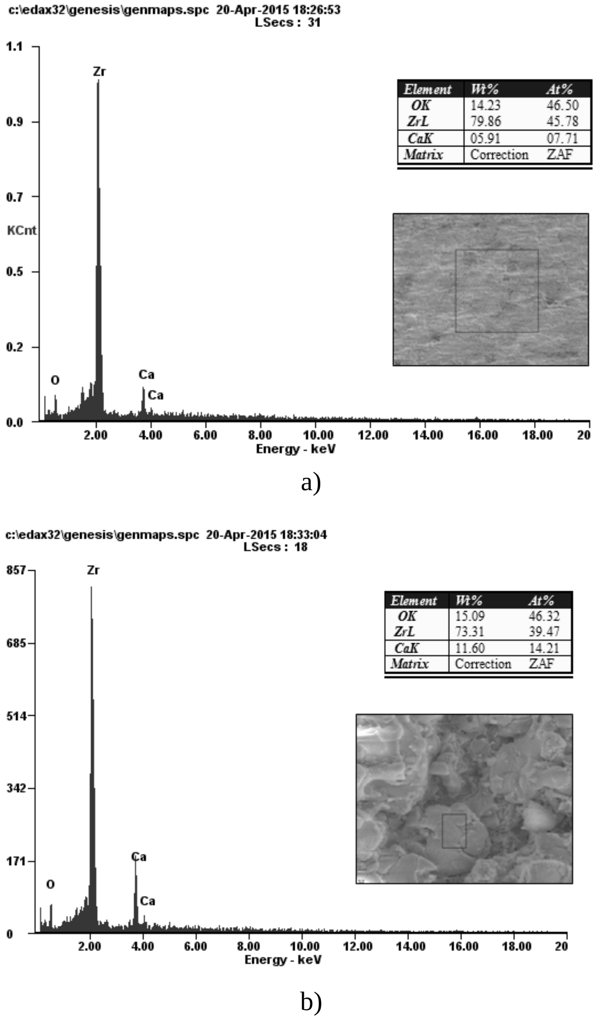


Fig. 5. EDAX analysis of surface coating

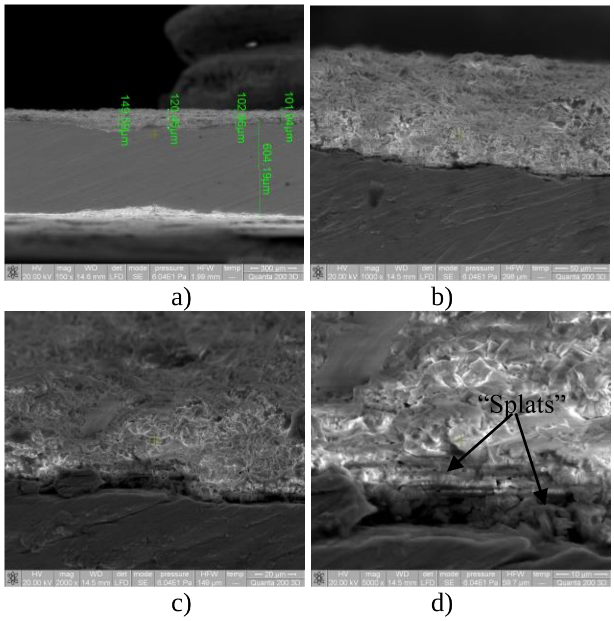
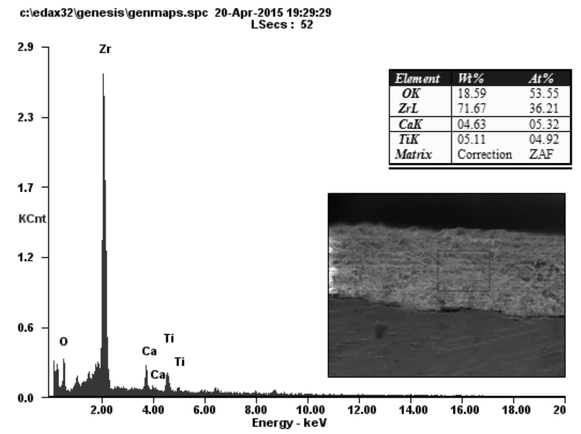
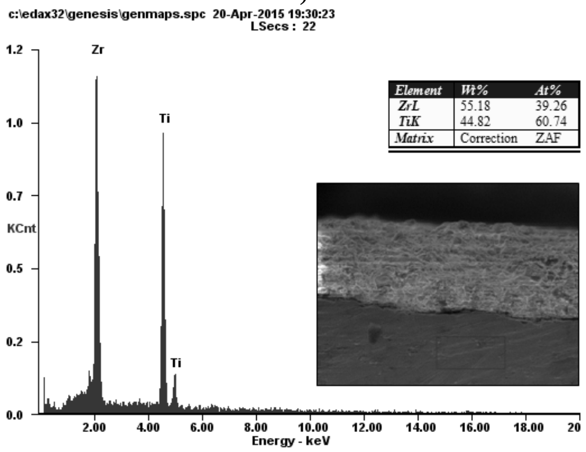


Fig. 6. SEM images of ZrO2-CaO cross-section coating



a)



b)

Fig. 7. EDAX analysis of cross-section coating

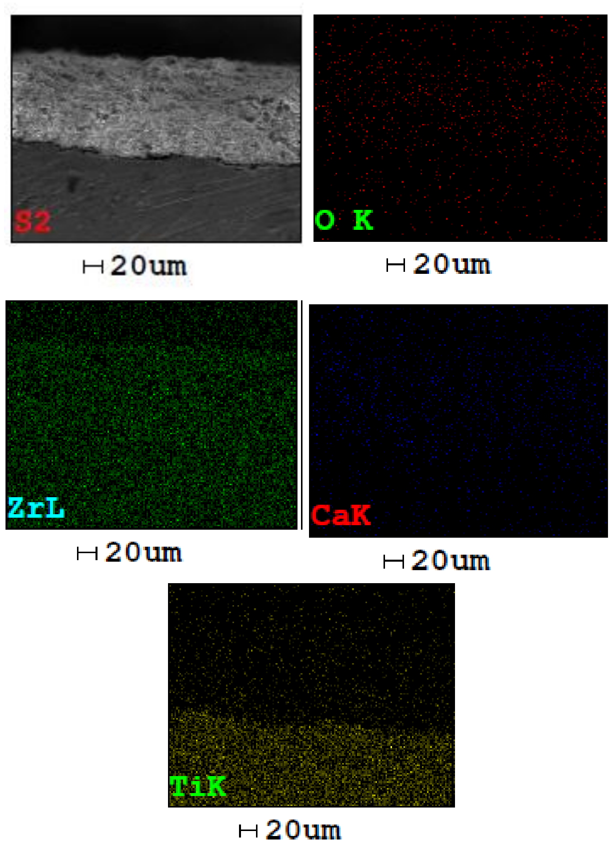
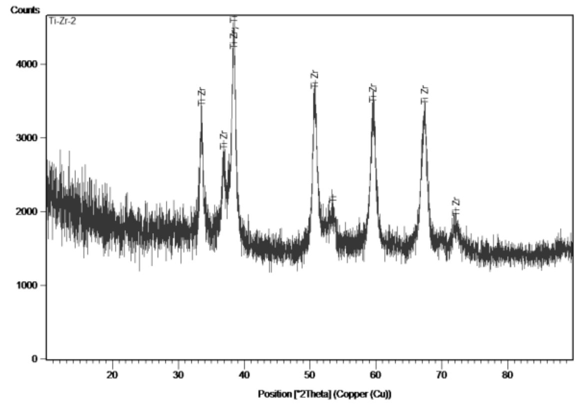
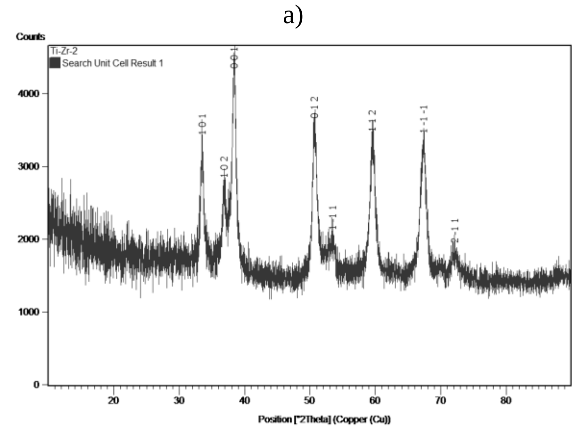


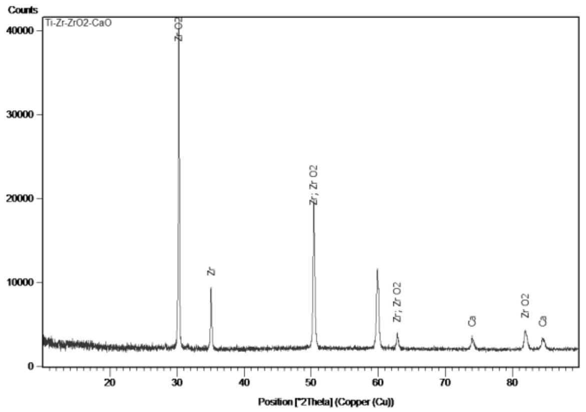
Fig. 8. Distribution map of the elements



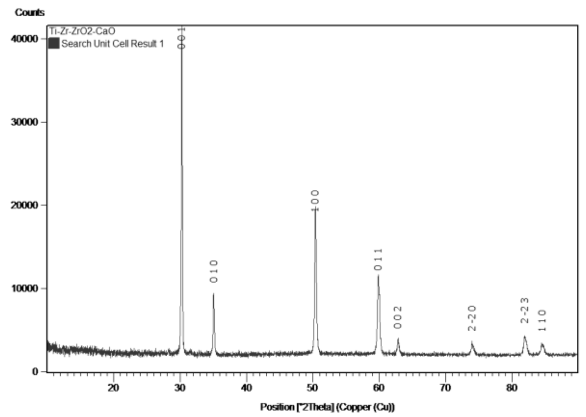
a)



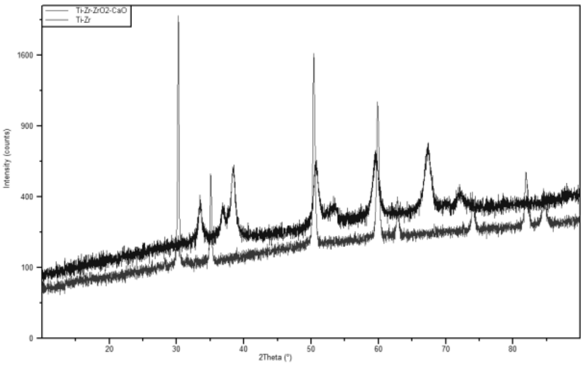
b)



c)



d)



e)

Fig. 9. X-ray diffraction of sample and Miller parameters: a), b) – Ti-55Zr alloy; c) ,d) ZrO_2-CaO coating; e) comparative results

XRD analysis. XRD results, phase analysis, respectively Miller parameters of as cast Ti-55Zr and ZrO_2-CaO coating alloys are shown in fig. 9 (a, b, c, d).

Fig. 9 and table 2 presents XRD pattern with typically peaks of Ti-Zr alloy and ZrO_2-CaO layer. Ti-Zr alloy consists two compounds (Ti-Zr and Ti) in hexagonal crystal system. Zirconia coating presents four phases: ZrO_2 (tetragonal form), β-Zr (cubic form) and two α-Ca phases in cubic crystal system.

Table 2. Compound parameters

	Compound	Crystal system	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Cell volume (10^6 pm^3)
Ti-Zr uncoated	Ti-Zr	Hexagonal	3,1100	3,1100	4,9010	90	90	120	41,05
	Ti	Hexagonal	2,9064	2,9064	4,6667	90	90	120	34,14
ZrO_2CaO coated Ti-Zr	ZrO_2	Tetragonal	3,5961	3,5961	5,1770	90	90	90	66,95
	β-Zr	Cubic	3,6162	3,6162	3,6162	90	90	90	47,29
	α-Ca	Cubic	5,5884	5,5884	5,5884	90	90	90	174,53
	α-Ca	Cubic	5,6120	5,6120	5,6120	90	90	90	176,75

CONCLUSIONS

In this paper authors used a modern plasma deposition technique of a ZrO_2-CaO ceramic layer on a Ti-55Zr substrate. SEM, EDAX, XRD analysis showed the uniformity of the deposited layer and also the morphology and chemical composition.

Structural analysis revealed the presence of some CaO unmelted particles, segregated during the spraying process with a negative effect on the structural uniformity. “Splat” type morphology of a specific ceramic layer has been highlighted.

The analysis of the deposited thickness layer showed an irregular thickness layer with a possible negative effect (flaking effect). It is needed an automatic deposition process with control over the plasma jet deposition.

It was noticed a large surface roughness of the coated layer, aspect which can be useful for bone implants, because it accelerates the phenomenon of osteosynthesis

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