Mechanoactivated TiNbZrSi powder for strong and wear-resistant biomedical coatings

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Abstract. The paper presents a study of morphology and chemical composition of the TiNbZrSi powder customized by mechanoactivation in an experimental high-energy vibration ball mill equipped with steel mortars and balls of different diameters. The initially synthesized as-cast TiNbZrSi tablet was preliminarily ground into a powder with fraction of about 400 µm using a conventional bench hammer. After that, the above powder was subjected to mechanoactivation within 4 hours in an Ar atmosphere at room temperature. In addition, the synthesized TiNbZrSi powder was deposited onto additively manufactured Ti-6Al-4V ELI substrates through their co-mechanoactivation followed by annealing for 1 hour at a temperature of 800 °C to ensure better adhesion. The characterization of the TiNbZrSi powder before and after co-mechanoactivation with the specified substrate was carried out by scanning electron microscopy.

1 Introduction

Mechanical activation is a promising method to synthesize and customize various multicomponent metal powders with improved physical and mechanical characteristics [1–3]. This method includes a use of high energy of mechanical impact on materials in special devices, such as vibration, planetary-ball, rotor-stator mills, etc. Intense mechanical forces leading to compression, grinding and mixing of materials arise during mechanoactivation process. As a result, this causes mechanical deformations, redistribution of chemical elements and dislocations in a crystal lattice of materials, including surface activation of atoms [3,4]. All this contributes to the acceleration of different kinds of reactions and the formation of new structural elements in material. In addition, mechanoactivation makes it possible to achieve a high degree of elements' homogenization, which improves physical characteristics and quality of the synthesized powder. Mechanoactivated metal powders are widely used in various industries, including metallurgy, chemical industry, electronics, and medicine [5].

The chemical composition of the initial TiNbZrSi alloy selected to synthesize a customized powder by mechanoactivation is a biocompatible material previously obtained in

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the form of the so-called bulk metallic glass through rapid quenching of a metallic melt [6]. According to the above study, the resulting amorphous TiNbZrSi coating has a great potential for application as implants, since its physical and mechanical characteristics are superior to well-established biocompatible crystalline analogues. In particular, the TiNbZrSi coatings possess improved anticorrosion properties, a high strength and wear resistance, an extended range of elastic deformations and a low Young's modulus. Due to the absence of literary data on crystalline TiNbZrSi alloys, in particular, coatings based on them, it is of great interest to obtain and study such materials customized by mechanoactivation process, which has a number of advantages compared to other traditional methods [7–10].

The paper goal is to synthesize a customized multicomponent TiNbZrSi powder by mechanoactivation in a high-energy vibration ball mill, as well as to study the morphology and chemical composition of the obtained powder to pre-evaluate its potential as biomedical coating for implants.

2 Materials and methods

Figure 1a shows as-cast TiNbZrSi tablet Ø 3 cm and 1 cm high, smelted using high-purity Ti, Nb, Zr and Si elements in an arc furnace. In order to grind the tablet in a vibration ball mill, it was previously divided into 5 parts (Figure 1a), from which one flat sample was taken for its further study by X-ray diffraction (XRD). The remaining 4 parts of the tablet were preliminarily crushed with a metal hammer to a powder fraction of about 400 μm.

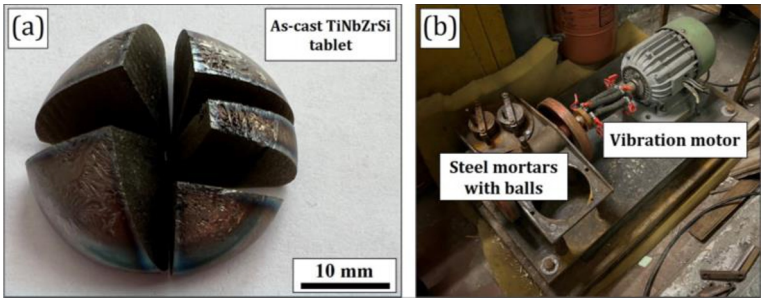

Fig. 1. (a) As-cast TiNbZrSi tablet Ø 3 cm and 1 cm high and (b) an experimental high-energy vibration ball mill.

After that, the resulting TiNbZrSi powder was placed in a steel mortar with steel balls of different diameters and subjected to mechanoactivation in an experimental vibration ball mill (Figure 1b). Mechanoactivation of the TiNbZrSi powder was carried out within 4 hours in an Ar atmosphere at room temperature.

The commercial spherical Ti-6Al-4V ELI powder (Table 1, TLS Technik GmbH & Co., Germany) was chosen to manufacture the substrates by selective laser melting (SLM) technology using 3D printer EOSINT M280 (EOS GmbH, Germany) equipped with an ytterbium fiber laser (IPG Photonics Corp., USA) operating at a wavelength of 1075 nm, a voltage of up to 400 V and a scanning speed of up to 2 m/s. The substrates' dimensions were 15 × 10 × 5 mm. This is important to note that the substrate and coating materials based on titanium alloys were especially chosen for co-mechanosynthesis, since matching their elemental composition is critical for future chemical bonding.

Table 1. The chemical composition of commercial Ti-6Al-4V ELI powder (wt.%).

Ti	Al	V	Fe	O_2	H_2	N_2	C
Base	5.5–6.5	3.5–4.5	<0.25	<0.13	<0.012	<0.05	<0.08

The microstructure and chemical composition of the synthesized TiNbZrSi powder before and after its deposition onto the Ti-6Al-4V ELI substrates through co-mechanoactivation were investigated by scanning electron microscope (SEM) Tescan MIRA LMS (Tescan s.r.o., Brno, Czech) coupled with energy-dispersive X-ray (EDX) and electron backscatter diffraction (EBSD) detectors.

3 Results and discussion

The morphology and chemical composition of the synthesized finely dispersed TiNbZrSi powder are shown in Figures 2 and 3. According to SEM analysis, the TiNbZrSi powder possessed a predominantly flake shape and a particle fraction in the range of 100–300 µm. The concentration of powder elements corresponded to the following values: Ti (65 at.%), Nb (12 at.%), Zr (10 at.%) and Si (13 at.%).

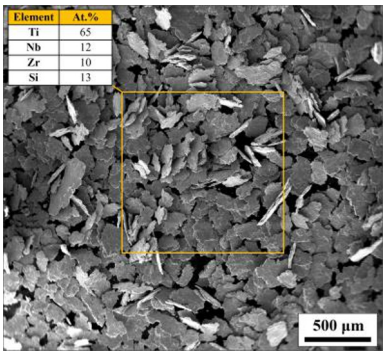

Fig. 2. Morphology and chemical composition of the TiNbZrSi powder (at.%).

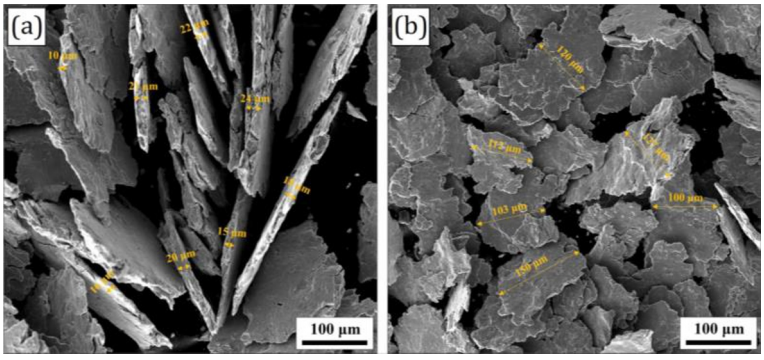

Fig. 3. Particle sizes of the TiNbZrSi powder: (a) thickness and (b) width.

Figure 4 demonstrates the elemental mapping of the TiNbZrSi powder at multiple magnification. Corresponding elements are marked with specific colors, in particular, Ti – burgundy, Nb – red, Zr – green and Si – turquoise. According to the mapping, the distribution of powder elements is homogeneous. Various defects, including cracks and pores, are observed on the synthesized powder.

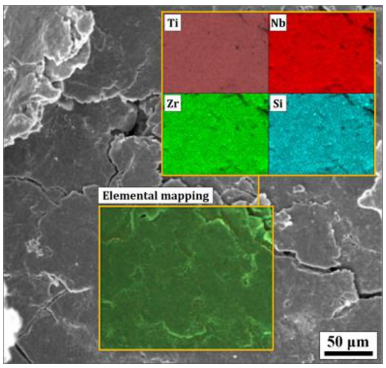

Fig. 4. Elemental mapping of the TiNbZrSi powder.

Figure 5a shows the custom Ti-6Al-4V ELI substrates manufactured by SLM method before and after their coating with mechanoactivated TiNbZrSi powder. The chemical analysis of the selected area is shown in Figure 5b.

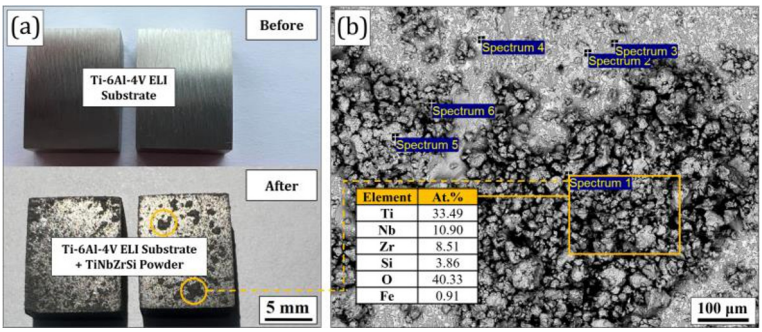

Fig. 5. (a) Additively manufactured Ti-6Al-4V ELI substrates before and after their coating with mechanoactivated TiNbZrSi powder and (b) chemical analysis of the selected area.

4 Conclusion

The paper is devoted to morphological and chemical composition studies of finely dispersed TiNbZrSi powder customized by mechanoactivation in a high-energy vibration ball mill, which allowed to pre-evaluate its potential as biomedical coating for implants. According to SEM analysis, the synthesized TiNbZrSi powder possesses a predominantly flake shape and a particle fraction in the range of 100–300 µm. The distribution of powder elements is homogeneous. Various defects, including cracks and pores, are observed on the surface. The co-mechanoactivation of the synthesized TiNbZrSi powder and additively manufactured Ti-6Al-4V ELI substrate, followed by annealing for 1 hour at a temperature of 800 °C in an Ar atmosphere, led to the formation of concentrated areas with oxidized TiNbZrSi powder on the substrate surface. The study results can be useful for understanding optimization regimes of the mechanoactivation process to obtain a TiNbZrSi powder with improved physical and

mechanical characteristics. To further determine the potential of the mechanoactivated TiNbZrSi powder as a biomedical coating, it is necessary to conduct additional structural and biochemical studies, including survey of adhesion between the above powder and substrate.

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