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THE SYNTHESIS OF TITANIUM ALLOYS FOR BIOMEDICAL APPLICATIONS

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Abstract. In a recent study, nanocrystalline Ti-based alloys were synthesized using mechanical alloying (MA) followed by annealing. The alloying elements Nb or Nb and Zr were added to titanium. The mechanical properties and the corrosion resistance of these materials were investigated and compared with microcrystalline Ti and the TiAl6V4 alloy. An enhancement of the properties due to nanoscale structures in consolidated materials was observed.

1. NTRODUCTION

During last years, interest in the study of nanostructured materials has been increasing. This is due to recent advances in materials synthesis and characterization techniques and the realization that these materials exhibit many interesting and unexpected mechanical as well as physical and chemical properties with a number of potential technological applications. For example, nanostructured Ti-based biomaterials are the key to the future of the biomedical industry [1-5].

Titanium and titanium alloys are widely employed in biomedical and dental applications. The use of titanium and its alloys in surgery has been growing steadily due to their superb combined properties compared to other metallic implant materials like stainless steel and cobalt-chromium alloys. Titanium and titanium-based alloys are characterized by: good fatigue strength; corrosion resistance and biocompatibility; relative low modulus; low densities, which give high specific strength-to-weight ratios allowing lighter and stronger structures. However, titanium and titanium alloys can not meet all of the clinical requirements because of its poor tribological properties [6].

One of the most popular titanium alloy, used today in medicine, is TiAl6V4 material. It is commonly accepted that titanium and its alloys exhibit a good corrosion resistance in vitro [7], although there are clinic researches, which show the accumulation of titanium ion tissue adjacent to the implant [8,9], signifying metal release and corrosion in vivo. Apart from that, some reports showed, that aluminum and vanadium can cause mutagenic, cytology and allergic reaction [10]. Therefore, the research has been commenced to modify the chemical composition of TiAlV type alloys as well as to change the processing method.

One of the new processing technique, that allows the production of nanocrystalline biomaterials is the mechanical alloying process. MA is one of the powder processing techniques. The starting materials used for mechanical alloying are commercially pure powders which are mixed in the right proportion in the mill along with the balls. During the MA process, the powder particles are repeat-

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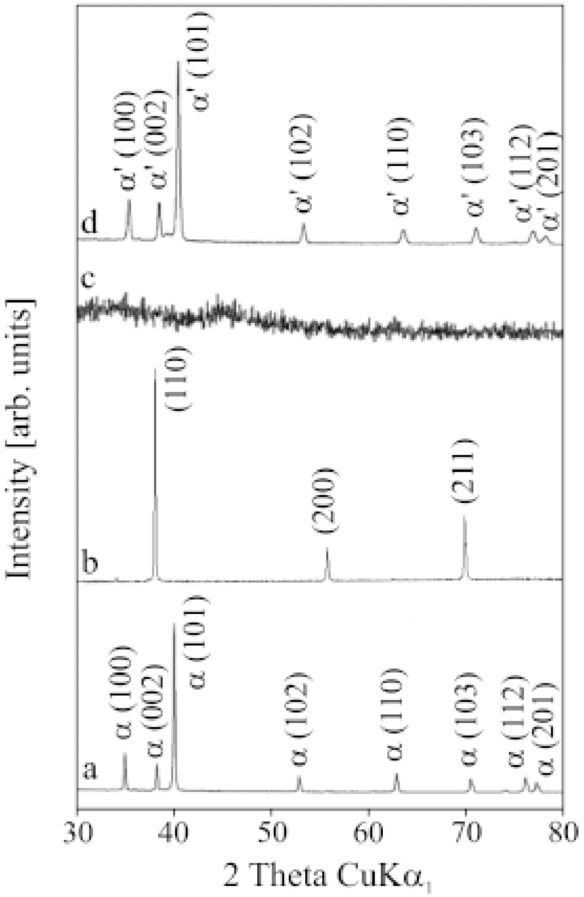

Fig. 1. XRD spectra of a mixture of Ti (a) and Nb (b) powders mechanically alloyed: after MA for 20 h (c) and heat treated at 1050 °C for 1h (d).

edly flattened, cold welded, fractured and rewelded. The milled powders are finally compacted and heat treated to obtain the desired microstructure and properties, which are a function of the milling conditions and the sintering temperature [11].

Recently, in our laboratory, titanium-ceramic nanocomposites are synthesized by mechanical alloying [12]. The experimental results show, that Ti-HA and Ti-SiO_2 nanocomposites have good corrosion resistance in comparison with microcrystalline titanium. On the other hand, in vivo studies indicate that Ti-20 vol.% HA composite has good biocompability and even better osteointegration ability than pure titanium, especially in the early stage after the implantation [13].

In this paper, bulk nanocrystalline TiNb13 and TiNb13Zr13 alloys prepared by mechanical alloying. The influence of the chemical composition of nanocrystalline Ti-based alloys on the corrosion resistance and the mechanical properties was compared to those of the microcrystalline titanium and the TiAl6V4 alloy.

2. EXPERIMENTAL PROCEDURE

The nanocrystalline Ti-based alloys were prepared using mechanical alloying followed by annealing. Mechanical alloying was performed under an argon atmosphere using a SPEX 8000 Mixer Mill. The round bottom stainless steel vial, which was equipped with a connection valve for evacuation or introduction of argon, was degassed for 12 h below 0.01 Pa. Then high purity argon was introduced into it, the pressure of which was up to 150 kPa. The vial was always handled in argon atmosphere to minimize uncontrolled oxidation. The composition of the starting powder mixture corresponded to the stoichiometry of the „ideal" reactions. The nanocrystalline TiNb13 and TiNb13Zr13 alloys were prepared. The high purity elemental powders (Ti: 44 μm, Nb: 1-5 μm, Zr: 44 μm) were mixed and loaded into the vial in the glove box (Labmaster 130) containing an argon atmosphere (O_2-2 ppm and H_2O-1 ppm). The mill was run up to 20 h for every powder preparation. The mechanically alloyed powders were then compacted at 18 MPa under argon. Finally, green compacts of Ti-based alloys were heat treated at 1050 °C for 1h in a gas atmosphere composed of 95% Ar and 5% H_2, under a pressure of 0.15 MPa to form ordered phases. The powders were examined by XRD analysis, using CuKα radiation, at various stages during mechanical alloying, prior to annealing and after annealing.

Commercially pure titanium (purity 98.8%) was manufactured by Studio Titanium Company Ltd. in an electric arc furnace, in vacuum. The microcrystalline Ti-6Al-4V alloy was prepared by arc melting in an argon atmosphere. The starting materials used were Ti, Al, V pieces. The composition of the starting materials corresponded to the stoichiometry of the alloys. Samples were remelted three times.

The Vickers' hardness was measured on polished surfaces under a load of 200 g. An electrochemical corrosion cell was used for in vitro potentiodynamic corrosion tests in 1M H_2SO_4 distilled water solution [14,15]. Saturated calomel electrode was used as the reference electrode and graphite rods were used as the counter electrode. The potentiodynamic polarization curves were obtained for each specimen and corrosion current

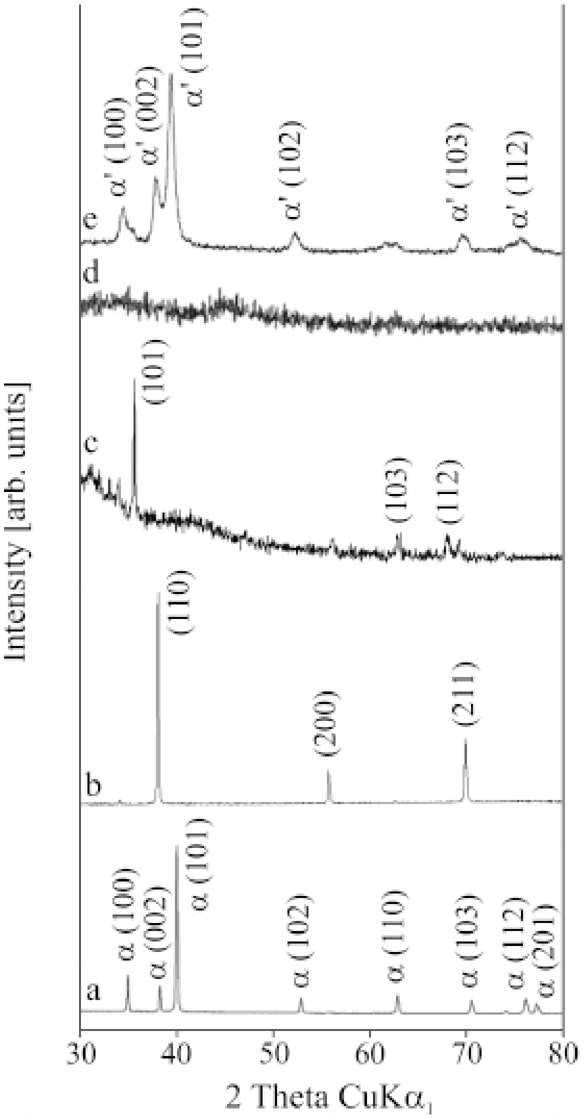

Fig. 2. XRD spectra of a mixture of Ti (a), Nb (b) and Zr (c) powders mechanically alloyed: after MA for 20 h (d) and heat treated at 1050 °C for 1h (e).

densities and corrosion potentials were determined by Tafel extrapolation methods.

3. RESULTS AND DISCUSION

The behaviour of MA process has been studied by X-ray diffraction and microstructural investigations. XRD diffraction patterns of the TiNb13 and TiNb13Zr13 alloys after mechanical alloying and heat treatment are shown in Figs. 1 and 2. Figs. 1a, 1b and Figs. 2a, 2b, 2c show the XRD patterns of the starting materials: Ti, Nb, and/or Zr. During mechanical alloying the originally sharp diffraction lines of the starting powders gradually become broader and their intensity decreases with milling time (not shown). The peak broadening represents a reduction in the crystallite size and an increase in the internal strain in the MA materials. The powder mixture milled for 20 h had transformed completely to an amorphous phase (Figs. 1c and 2d). But differentiation between a ”truly” amorphous, extremely fine grained or a material in which very small crystals are embedded in an amorphous matrix in so produced materials has not been easy on the basis of diffraction basis [11].

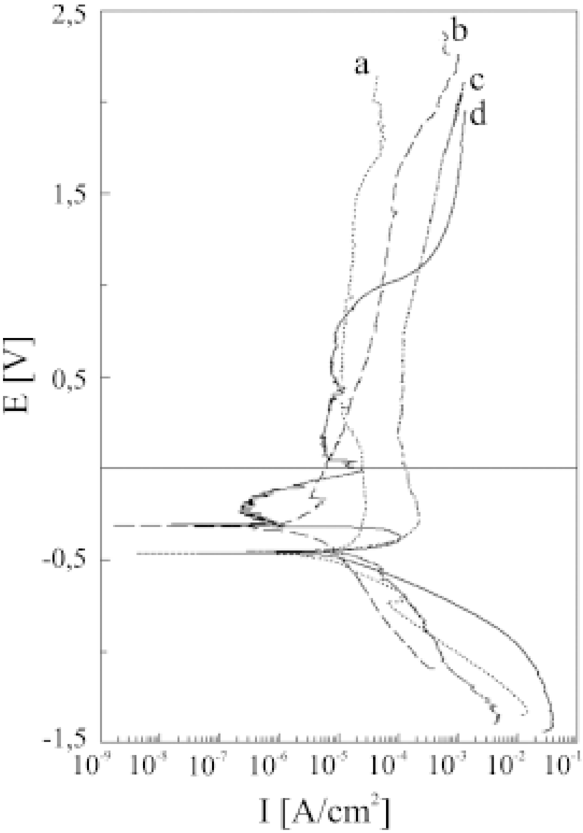

Fig. 3. Potentiodynamic polarization curves of: (a) microcrystalline Ti, (b) nanocrystalline TiNb13, (c) nanocrystalline TiNb13Zr13 and (d) microcrystalline TiAl6V4 in 1M H_2SO_4 distilled water solution.

Recently, we have studied the microstructure and possible local ordering in the mechanically alloyed TiNi biomaterial by TEM [16]. The sample milled for 5 h was mostly amorphous as appears from a high resolution image. SAED pattern contains broad rings at positions expected for TiNi with CsCl structure. There are, however additional

Table 1. Particle sizes, Vickers' hardness, corrosion current densities (I_c) and corrosion potentials (E_c) of studied Ti-type alloys.

alloy	structure	particle size (nm)	$HV_{0.2}$ (A/cm^2)	I_c	E_c (V)
Ti	micro	-	225	$1.49 \cdot 10^{-5}$	-0.47
TiAl6V4	micro	-	500	$1.06 \cdot 10^{-5}$	-0.46
TiNb13	nano	40	340	$9.15 \cdot 10^{-7}$	-0.31
TiNb13Zr13	nano	30	290	$2.13 \cdot 10^{-5}$	-0.44

weak, diffuse rings, most probably from TiO_2. It has been found that the amorphous alloy was unstable upon exposure to electron beam and underwent some crystallization. Apart from prevailing amorphous phase, the milled sample contained small amount of crystalline alloy with CsCl structure. Lack of any sharp reflections in the XRD pattern suggests that the amount of the crystalline phase is very low and/or it forms during in TEM observation.

The microstructure that forms during MA consists of layers of the starting material. The lamellar structure is increasingly refined during further mechanical alloying. After 20 h of mechanical alloying the sample shows cleavage fracture morphology and inhomogeneous size distribution. Bulk Ti-based materials with 98% theoretical density was prepared by sintering at 1050 °C for 1 h. The obtained spectra were dominated by a hexagonal á' phase (Figs. 1d and 2e). According to the Scherrer method for XRD profiles, the average size of heat treated TiNb13 and TiNb13Zr13 alloys is adequately 40 nm and 30 nm (Table 1).

The Vickers' hardness of the sintered samples prepared by mechanical alloying and powder metallurgical process is about 340 $HV_{0.2}$ for TiNb13 and 290 $HV_{0.2}$ for the TiNb13Zr13 alloy. Higher Vickers' hardness are measured for TiAl6V4 alloy ($HV_{0.2} = 500$). This material is typical an α/β alloy.

The potentiodynamic polarization curves of the nanocrystalline TiNb13 and TiNb13Zr13 alloys in the 1M H_2SO_4 distilled water solution in comparison with microcrystalline titanium and the TiAl6V4 alloy are shown in Fig. 3. The corrosion potentials and corrosion current densities of each specimen were determined from the potentiodynamic polarization curves by the Tafel extrapolation method and are summarized in Table 1. According to Table 1 and Fig. 3, the nanocrystalline TiNb13 alloy was more corrosion resistant ($I_c = 9.15 \cdot 10^{-7}$ A/cm^2, $E_c = -0.31$ V) than the microcrystalline TiAl6V4 ($I_c = 1.06 \cdot 10^{-5}$ A/cm^2, $E_c = -0.46$ V). The corrosion behaviour of the nanocrystalline TiNb13 alloy was also better than that of microcrystalline titanium ($I_c = 1.49 \cdot 10^{-5}$ A/cm^2, $E_c = -0.47$ V), as manifested by a shift of the polarization curve (Fig. 3b) to the right down of the microcrystalline titanium curve (a). The nanocrystalline TiNb13Zr13 alloy and microcrystalline TiAl6V4 have similar values of corrosion potentials and corrosion current densities. However the polarization curve (Fig. 2c) of the nanocrystalline TiNb13Zr13 alloy reveals a wider passive range, compared with curve (d), which is the microcrystalline TiAl6V4. The similar trend can be observed for microcrystalline titanium and nanocrystalline TiNb13Zr13 alloy.

Application of nanocrystalline Ti-based materials focused also other attention on the biocompatibility of synthesized alloys. The biocompatibility was investigated studying the behaviour of Normal Human Osteoblast (NHOst) cells from Cambrex (CC-2538). Two factors may influence cell growth on the disks. They are: adsorbing protein onto the disks and released metal ions from the disks. These studies are currently in progress and the results will be presented independently. Independently researchers demonstrated that metal surfaces utilizing low-micron to nanophase topography fostered increased adhesion of osteoblasts, the cells that create the matrix of bone [3].

4. CONCLUSION

In conclusion, the TiNb13 and TiNb13Zr13 bulk nanocrystalline materials have been successfully prepared by mechanical alloying and powder metallurgical process. The sintered materials were dominated by a hexagonal α' phase. An enhancement of the properties due to the nanoscale structures in consolidated materials was observed. The studies lead to the following conclusions:

- Vickers' hardness of TiNb13 and TiNb13Zr13 materials are about 50% and 30% higher than of pure microcrystalline Ti metal,
- nanocrystalline TiNb13 alloy is more corrosion resistant than the nanocrystalline TiNb13Zr13 and microcrystalline TiAl6V4 alloys as well as microcrystalline titanium,
- the results of this study continue to provide for the use of nanocrystalline Ti-based alloys for the design of the next generation of more successful implants.

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