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The effect of the solute on the structure, selected mechanical properties, and biocompatibility of Ti–Zr system alloys for dental applications

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ABSTRACT

New titanium alloys have been developed with the aim of utilizing materials with better properties for application as biomaterials, and Ti–Zr system alloys are among the more promising of these. In this paper, the influence of zirconium concentrations on the structure, microstructure, and selected mechanical properties of Ti–Zr alloys is analyzed. After melting and swaging, the samples were characterized through chemical analysis, density measurements, X-ray diffraction, optical microscopy, Vickers microhardness, and elasticity modulus. In-vitro cytotoxicity tests were performed on cultured osteogenic cells. The results showed the formation essentially of the α′ phase (with hcp structure) and microhardness values greater than cp-Ti. The elasticity modulus of the alloys was sensitive to the zirconium concentrations while remaining within the range of values of conventional titanium alloys. The alloys presented no cytotoxic effects on osteoblastic cells in the studied conditions.

1. Introduction

Titanium alloys have been widely used as biomaterials, especially for orthopedic prostheses and dental implants. Titanium has replaced Co–Cr alloys and 316L stainless steel due to its excellent corrosion resistance, mechanical properties, and biocompatibility. The aim of the development of titanium alloys is to create materials with improved properties for use as implants that can be used for a long period of time [1].

The Ti–6Al–4V alloy has been singled out as a good alternative for application in orthopedic prostheses because it possesses good mechanical and corrosion resistance, as well as a much lower elasticity modulus than cp-Ti [2]. However, there are reports that vanadium and aluminum ions can lead to neurological problems, such as Alzheimer's disease, and adverse reactions in tissues over an extended period [3]. Therefore the need exists for the development of new titanium alloys, mainly with the addition of niobium, molybdenum, tantalum, and zirconium, i.e., elements that have no cytotoxicity.

Titanium displays allotropic transformation at around 883 °C, changing from an α phase (hcp crystalline structure) to a β phase (bcc crystalline structure). Titanium also presents metastable phases, which are dependent on processing conditions, as hexagonal martensite α′ and orthorhombic α″ phases. With respect to their microstructure, titanium alloys are classified according to their phase proportion and can be near α, α, α + β, near β, and β. The mechanical properties of titanium alloys are directly related to their microstructure [4].

The α-type titanium alloys are characterized by good corrosion resistance and resilience, and higher elasticity modulus than β-type alloys. The main applications of α-type titanium alloys are in dentistry because they have significant weldability, hardness, and tensile strength, which are favorable properties for this application [5,6]. Although the standard material for removable partial denture framework is still cobalt–chromium alloy. The major difference between titanium alloys and cobalt–chromium alloys lies in their modulus of elasticity. It is known that the modulus of elasticity of titanium alloys is about half that of cobalt–chromium alloy, which increases its resiliency and makes it more like gold alloys. Because these applications are located in a region of the body where there is intense mechanical work and interaction with different corrosive substances, α alloys are used predominantly as removable partial dentures and dental crowns [5,7]. This property would allow for the retentive clasp arm of removable partial denture to construct shorter arm length than it is possible with cobalt–chromium alloy and to be placed in deeper undercut and on abutment tooth. This characteristic is useful in clinical situations when the abutment tooth is not a molar tooth and has to be concerned about an esthetic or periodontal health case.

Zirconium is considered a neutral element when added to a solid solution with titanium because it has an identical allotropic transformation with a similar phase transition temperature. When in a solid solution with titanium, in both α and β phases, it promotes hardening and slows the speed of phase transformation. This element has great solubility in both crystalline phases of titanium and can form alloys of various proportions, as well as increase mechanical strength (such as tensile strength, hardness, and flexural strength) and improve corrosion potential. Earlier studies have shown that the formation of solid solutions with

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zirconium can decrease the α′ martensitic transformation temperature of titanium [5,8]. The addition of zirconium can also decrease the melting temperature of titanium, which can reduce the cost of casting and swaging [9,10]. Li et al. [11] investigated the shape memory behavior of Ti–Zr alloys and showed that the alloys have great potential for dental applications.

The biocompatibility and mechanical properties (Young's modulus and hardness) are important to the development of dental implants; these properties are dependent upon the crystalline structure and microstructure of the alloy. The purpose of this paper is to analyze the structure, microstructure, selected mechanical properties, and biocompatibility of Ti–Zr alloys with 5%, 10%, and 15% zirconium weight. The structural and microstructural analyses were obtained by means of X-ray diffraction and optical light microscopy, respectively, while the mechanical properties were assessed with measures of hardness and elasticity modulus. Biocompatibility was analyzed using in vitro tests.

2. Experimental part

The alloys were prepared from titanium cylindrical bars (Aldrich Inc., 99.7% purity) and zirconium foil (Aldrich Inc., 99.8% purity). The samples were melted in an arc-voltaic furnace with a cooled copper crucible in an argon atmosphere. To guarantee the samples' homogeneity, the produced ingots were remelted five times. The chemical composition of the samples was obtained by optical emission spectroscopy (Spectra, SPECTROMAXx equipment) and thermoconductivity difference (LECO, TC-436DR equipment). The density measurements were performed using the Archimedes' principle in an Ohaus analytical balance.

The ingots were submitted to a hot swaging process using a swaging machine (Fenn Model 3F). After this mechanical processing, the samples acquired a cylindrical shape with a diameter of approximately 4 mm.

The structure of the samples was obtained by X-ray diffraction (XRD) measurements in a Rigaku D/Max 2100/PC diffractometer using the powder method with Cu-Kα ($\lambda = 1.544$ Å) radiation in fixed time mode with a step of 0.02, a permanence time of 1.6 s, and a scan of 20° to 80°. The determination of the diffraction parameters and the quantitative phase analysis was made by the application of Rietveld's method using GSAS® software [12].

A microstructural analysis was performed by optical microscopy using an Olympus BX51M microscope. The cylindrical samples were mechanically grinded on abrasive paper until they were 2000 grade, and they were then polished to a mirror surface by alumina paste (1 μm). Thereafter, the samples were chemically etched with a solution of 5% HF, 10% HNO_3, and 85% H_2O.

The mechanical properties, specifically hardness and Young's modulus (E), were determined. The microhardness tests were performed in a Shimadzu HMV-2 model microdurometer with a load of 1.961 N for 60 s. Five measurements were carried out, and the reproducibility was very good. The dynamical elasticity modulus was obtained using a torsion pendulum operating with a frequency of 30 Hz using the expression [13,14]:

$$E = \frac{32}{3}\pi^2 \Lambda I f^2 \quad (1)$$

where I is the inertia momentum of the system, f is the oscillation frequency, and Λ is the geometrical factor, such that a sample with a cylindrical shape was provided by:

$$\Lambda = \frac{32L}{\pi d^4} \quad (2)$$

where L is the length, and d is the diameter of the sample.

MC3T3-E1 cells are a preosteoblastic lineage obtained from the calvaria of *Mus musculus* (ATCC, Rockville, MD, USA). Cells were grown in a completely alpha-minimum essential medium (α-MEM, Invitrogen, Carlsbad, CA) supplemented with 10% fetal bovine serum (FBS) and 1% gentamicin (Invitrogen) at 37 °C in a humidified atmosphere with 5% CO_2. The MTT test was measured by absorbance reading [15]. The MC3T3-E1 cells (p5 to p15) were plated on disks placed on 96-well microplates (density of 2×10^4 cell/well). Polystyrene (culture plate) was used as negative control while a solution of α-MEM, 10% of FBS, and 1% phenol was the positive control for cytotoxicity. Following incubation for 72 h, MTT (5 mg/mL) was added to each well, and the plate was incubated at 37 °C for 3 h. After this period, the medium was removed and replated with 100 μL DMSO to dissolve the formazan crystals. The product was quantified spectrophotometrically by measuring absorbance at 562 nm using a microplate reader [16,17]. For scanning electron microscopy (SEM) analysis, the cells were plated under the surface of the alloys. After 24 h, the cells were fixed in 4% paraformaldehyde + 0.1% glutaraldehyde buffered with sodium cacodylate, pH 7.2, for 1 h at room temperature and routinely processed for SEM. Briefly, the samples were postfixed with 1% osmium tetroxide, dehydrated in increasing concentrations of ethanol, and desiccated after treatment with hexamethyldisilazane. The specimens were mounted onto Al stubs and sputtered with gold. Morphological analyses of the adhesion of these cells to the alloy surface were made using a LEO 430 SEM (Tokyo, Japan). Cells grown on a glass coverslip were used as the negative control.

3. Results and discussion

The chemical compositions of the produced samples are presented in Tables 1 and 2. The results show that the zirconium concentration in the substitutional solute was very close to the stoichiometry, and the metallic and the interstitial impurities were in low quantities, thus demonstrating the good quality of the produced alloys. These impurities related to the processing of the precursor elements by the manufacturer and to the melting process.

Fig. 1 shows a comparison of the theoretical value, calculated from the nominal concentration of the elements, and the density values that were obtained for each prepared alloy. It can be observed from the results that the addition of zirconium increased the density of the material when compared to the value for pure titanium (4.51 g/cm^3). This occurs as a result of the great difference in density with zirconium (6.50 g/cm^3) [18]. The density values after melting and swaging made no great differences to the theoretical values, indicating that the components were near the desired stoichiometry, and thus certifying the quality of the produced samples.

Fig. 2 presents the X-ray diffraction patterns of all the prepared alloys in comparison to pure titanium. Table 3 shows the lattice parameters and the results of the quantitative phase analysis obtained with the refinement of the diffractograms using Rietveld's method. Peaks related with the α-phase in the cp-Ti and with the α′-phase in the alloys are present in the diffractograms, showing that the addition of the solute did not significantly change the crystalline structure of the material. The diffraction peaks of the alloys presented a little shift to lower angles, due the distortion of the crystalline structure by substitutional Zr and the formation of α′-phase. The results follow those indicated by the phase diagram of the Ti–Zr system, which only provides for the formation of the α′ phase for these concentrations of zirconium. Ho et al. [9] obtained the same results for Ti–10Zr, observing peaks related to the β phase only following the addition of small amounts of iron and chromium to the alloy.

Table 1
The chemical composition of the Ti–Zr produced alloys.

	Mo	Zr	Al	Cr	Fe	Mn	Ni	Ti
Ti–5Zr	<0.001	4.89	<0.001	0.010	0.029	<0.001	0.009	Balance
Ti–10Zr	<0.001	9.76	0.006	0.009	0.030	<0.001	0.008	Balance
Ti–15Zr	<0.001	15.60	0.092	<0.005	0.042	<0.001	<0.005	Balance