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Spark plasma sintering synthesis of porous nanocrystalline titanium alloys for biomedical applications

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Abstract

The reason for the extended use of titanium and its alloys as implant biomaterials stems from their lower elastic modulus, their superior biocompatibility and improved corrosion resistance compared to the more conventional stainless steel and cobalt-based alloys [Niinomi, M., Hattori, T., Niwa, S., 2004. Material characteristics and biocompatibility of low rigidity titanium alloys for biomedical applications. In: Jaszemski, M.J., Trantolo, D.J., Lewandrowski, K.U., Hasirci, V., Altobelli, D.E., Wise, D.L. (Eds.), Biomaterials in Orthopedics. Marcel Dekker Inc., New York, pp. 41–62]. Nanostructured titanium-based biomaterials with tailored porosity are important for cell-adhesion, viability, differentiation and growth. Newer technologies like foaming or low-density core processing were recently used for the surface modification of titanium alloy implant bodies to stimulate bone in-growth and improve osseointegration and cell-adhesion, which in turn play a key role in the acceptance of the implants. We here report preliminary results concerning the synthesis of mesoporous titanium alloy bodies by spark plasma sintering. Nanocrystalline cp Ti, Ti–6Al–4V, Ti–Al–V–Cr and Ti–Mn–V–Cr–Al alloy powders were prepared by high-energy wet-milling and sintered to either full-density (cp Ti, Ti–Al–V) or uniform porous (Ti–Al–V–Cr, Ti–Mn–V–Cr–Al) bulk specimens by field-assisted spark plasma sintering (FAST/SPS). Cellular interactions with the porous titanium alloy surfaces were tested with osteoblast-like human MG-63 cells. Cell morphology was investigated by scanning electron microscopy (SEM). The SEM analysis results were correlated with the alloy chemistry and the topographic features of the surface, namely porosity and roughness.

Keywords: Porous titanium surfaces; Spark plasma sintering; Cell morphology

1. Introduction

Porous interconnected scaffolds offer attractive solutions for the design of surface mechanical cues that stimulate cell adhesion and spreading (Temenoff et al., 2004; Niinomi et al., 2004). Adhesive cues regulate intracellular signalling pathways and cytoskeletal tension, which then modulate cell proliferation and differentiation (Liu et al., 2004). Beyond surface patterning by micromechanical/microfabrication processing, surface treatment (laser, plasma) or surface coating methods, new types of suitable biomaterials with controlled interconnected porosity, e.g. metallic foams, resulted recently from the advent of innovative material processing technologies. We used field-assisted spark plasma sintering (FAST/SPS) to obtain bulk titanium alloy substrates with surface porosity, which may readily be fine-tuned by an appropriate choice of the nanopowder precursors. Surface and near-surface-region porosity mainly aim to support osteoblast cell ingrowth, adhesion with better anchoring and ossification, however also to improve biological fluid diffusion, vascularization and to provide suitable surfaces for circulating growth factors. Surface porosity may later on serve as basis for the design of implants incorporating antibacterial functionalities. We have here tested the feasibility of the FAST/SPS technique for the synthesis of Ti-based alloy bulk solids with near-surface porosity. Preliminary cell adhesion and spreading results are shown for two surface porous alloys Ti–Al–13V–11Cr and Ti–Al–13V–7Mn–4Cr, in comparison to full-density conventional cp Ti and Ti–6Al–4V substrates also processed by FAST/SPS.

2. Experimental

2.1. Titanium alloys

For the present study the following alloys were selected: cp Ti (specimen E_0), Ti–6Al–4V (E_1), Ti–Al–13V–11Cr (E_2) and Ti–13V–7Mn–4Cr–Al (E_4).

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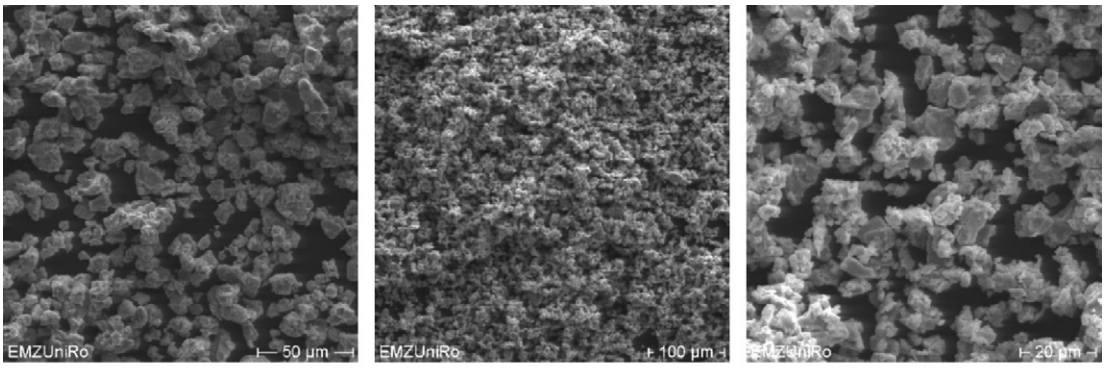

Fig. 1. (a–c) Morphology of the as-milled titanium alloy powders.

The alloy composition is given in weight percents. The start-up elements were high-purity (99.5% or better) gas-atomized powders with average particle sizes between 100–200 μm (Fluka). Mechanical alloying (MA) was performed with a high-energy PM400 planetary ball-mill (RETSCH, DLR), disposing of four vials mounted on a rotating platform. This enables the one-batch preparation of all alloy specimens under identical processing conditions. Chromium-hardened steel vials and balls were used as grinding media, with ball-to-powder ratio (BPR) equal to 18:1. Wet-milling in hexane was performed for 85 h at 250 rpm. Hexane was used as process control agent (PCA) to prevent oxidation and excessive contamination from the grinding media.

Thermal processing by dynamic heating of the as-prepared alloy powders to achieve predefined ratios of the α and β phases was investigated by thermal analysis (Netzsch 404C Pegasus) and by *in situ* synchrotron radiation powder diffraction (B2 beamline, DESY/HASYLAB). Field-activated densification of the alloy nanopowders was performed at FCT Systeme GmbH (Rauenstein, Germany) using proprietary FAST/SPS equipment (model HPD 25/1). Pulsed dc voltage (2–4 V; pulse cycle: 12 pulses ON/2 pulses OFF, pulse duration 3 ms) was used. The titanium alloy nanopowders were loaded into graphite die-punch units to sinter (20 mm diameter, thickness 2.8–3 mm) disc-shaped pellet substrates. The FAST/SPS experiments were conducted in vacuum (50 mTorr) under uniaxial pressure (55 MPa). The nanocrystalline powders were sintered for dwell times less than 5 min at the selected sintering temperature, chosen so that a certain degree of porosity is retained at the pellet surface. The heating rates were close to 50 °C/min, the cooling rates were close to 20 °C/min.

The surface morphology and composition of the as-milled alloy powders and of the FAST/SPS sintered pellets was examined by SEM/EDX at the Electron Microscopy Center (Rostock).

2.2. Cell culture

The sintered titanium alloys were placed into 6-well chambers (Greiner). Throughout the experiments we used the cell line MG-63, an osteoblast-like cell type obtained from ATCC (American Type Culture Collection, Manassas, VY, USA, CRL-1427). These cells represent an early-differentiated osteoblast. Cells were seeded onto the materials with a density of 5×10^4 cells/specimen and cultivated for 24 h with complete Dulbeccos modified Eagles medium (DMEM, Gibco Invitrogen, Karlsruhe) prewarmed to 37 °C, complemented with 10% fetal calf serum, 1% Gentamicin, and 5 μg/ml of Plasmocin for mycoplasm-prevention.

In order to investigate the cell morphology on the various titanium surfaces, the cells were prepared for SEM. After 24 h of cultivation cells were washed three times with PBS, fixed with 4% glutaraldehyde (1 h), postfixed with 0.5% OsO_4, dehydrated through a graded series of alcohol and dried in a critical point dryer (K 850, EMITECH, Taunusstein, Germany) at a pressure of 73.8 bar and a temperature of 31 °C. The conductivity of samples was achieved through homogenous gold sputtering (15–50 nm thickness) in vacuum with a coater (SCD 004, BAL-TEC, Balzers, Lichtenstein), and examined in the SEM DSM 960A.

3. Results

The scanning electron microscopy (SEM) analysis of as-milled alloy powders was performed using a Zeiss DSM 960A (Oberkochen, Germany) electron microscope operated at 10 kV. The morphology of the as-prepared alloy powders is shown in Fig. 1.

The morphology of the as-prepared MA powders does not vary significantly between the different alloys. The powders form agglomerates with typical average sizes between 10 and 20 μm. The particle size distributions are rather narrow (see for, e.g. specimen E_2: Ti–Al–V–Cr, Fig. 1(b)) and centred around

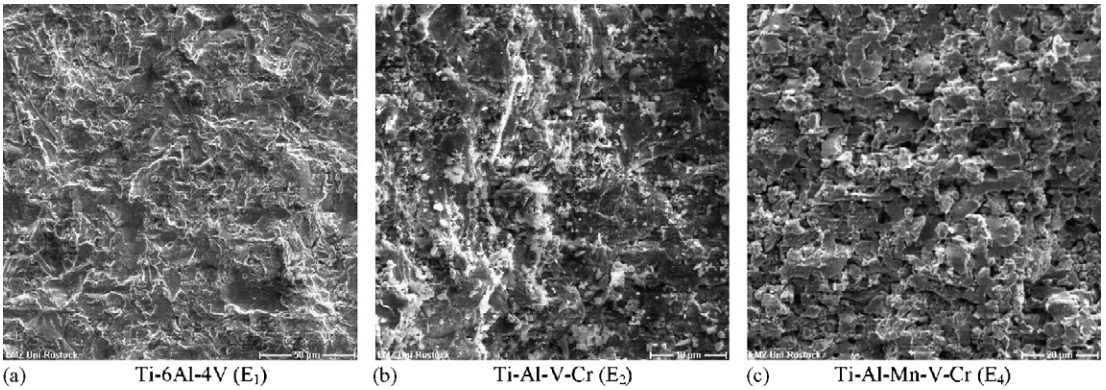

Fig. 2. (a–c) Surface morphology of the FAST/SPS sintered titanium alloys.