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Fabrication and evaluation of bulk nanostructured cobalt intended for dental and orthopedic implants

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ABSTRACT

Bulk nanostructured cobalt (Co) was fabricated by a combination of high energy ball milling and warm pressing. The obtained cobalt has an average grain size of 35 nm with measured hardness and elastic modulus of 7.32 GPa and 211.4 GPa, respectively. Dry sliding wear testing shows such bulk nanostructured Co has high sliding wear resistance. However, electrochemical study shows that such Co has a relatively high corrosion rate and no passive behavior in the artificial saliva solution. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis further reveal that the corrosion product is composed of insoluble cobalt (II) phosphate and cobalt hydroxide. The evaluation results suggest that bulk nanostructured cobalt can be a promising wear resistant material but may not be suitable for dental/orthopedic implants.

1. Introduction

Bulk nanostructured metals are increasingly becoming a significant class of biomaterials due to their unusual physical and mechanical properties compared to conventional coarse-grained counterparts. Among these metals, cobalt (Co) and Co based alloys are reported to be potentially suited for some dental prostheses and orthopedic implants since they have combined high strength, wear resistance and corrosion resistance (Lowe and Valiev, 2014). The dental uses are either as implants embedded within the jawbone with an external superstructure containing the fabricated ceramic dental crown attached or as removable partial denture frameworks (Rosenstiel, Land and Fujimoto, 2015). Orthopedic hip implants are generally cemented to the bone, although a cement-less technique has been used. For such dental and orthopedic implants, Co is often alloyed with Cr and Mo to increase its corrosion resistance. However, the conventional cast Co-Cr-Mo alloys have coarse grain size and dendritic structure which will cause lower tensile and fatigue strength (Çelik et al., 2008) and their irregular hard interdendritic Cr and Mo-rich carbides precipitates can cause brittleness and are detrimental to the wear and corrosion resistance if the distribution, volume fraction, size and/or morphology are not well controlled (Caudillo et al., 2002; Chen et al., 2014; Chiba et al., 2007; Clemow and Daniell, 1979; Liao et al., 2012; Ramírez-Vidaurri et al., 2009; Wimmer et al., 2001). Wrought Co-Cr-Mo alloys often have non-uniform grain size distribution due to inhomogeneous strains introduced during hot working process, which will cause the mechanical properties varying from area to area (Kurosu et al., 2010).

Furthermore, there have been concerns raised about the effects of ions and particles released from Co-Cr-Mo based orthopedic implants on the body's inflammatory and/or immune response (Gilbert et al., 2015). The conventional Co-Cr-Mo alloy usually contains ~1 wt% of Ni and the continuous release of Ni ions during in vivo service may possibly cause an allergy and carcinogenicity (Savarino et al., 2003; Setcos et al., 2006). The release of Cr ions from the alloy increases the adverse biologic effects such as toxicity or even carcinogenic issues (Cohen et al., 1993). Alloying can also increase stress shielding due to much higher elastic modulus (Chen and Thouas, 2015). Nanostructured metals have been previously reported to have improved corrosion resistance (Balyanov et al., 2004). Therefore, bulk nanostructured metals are promising candidates for dental/orthopedic applications.

Extensive efforts have been devoted to fabricating nanostructured Co by either top-down or bottom-up strategy (Fellah et al., 2012). In the top-down process, ultrafine structured or nanostructured Co are made from bulk material via severe plastic deformation (SPD) such as high pressure torsion (HPT) (Edalati et al., 2013). However, such ultrafine grained (UFG) Co obtained by HPT has shape and size limitation which are not suitable for many industrial applications and the distribution of the microstructure is inhomogeneous across the diameter (Edalati and Horita, 2010). The bottom-up strategy is based on either a one-step processing method such as electrodeposition (Karimpoor and Erb, 2006; Karimpoor et al., 2003), or two-step processing approach in which nanoparticle synthesis is followed by consolidation (Barry et al., 2014; Fellah et al., 2010; Fellah et al.,

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2012). The nanocrystalline Co processed by ED is generally in the form of thin film or coating with limited thickness which is not suitable for fabrication of bulk nanostructured samples. Two-step processing approach performed at high consolidation temperature usually leads to grain coarsening even crystallite size of the chemically synthesized starting Co powders is at the nanoscale. For example, Co nanopowder synthesized by *chimie douce* with average crystallite size of 10 nm has coarsened to be ~300 nm after consolidated by hot isostatic pressing (HIP) (Fellah et al., 2010). The consolidation processed by spark plasma sintering (SPS) also induces the mean grain size 3–7 times larger than that of the initial powders (Barry et al., 2014; Fellah et al., 2012).

Furthermore, previous work mainly focused on hcp-fcc phase transformation, microstructure and mechanical properties of nanocrystalline Co. There have been rather limited studies on wear and corrosion behaviours of bulk nanostructured Co (Metikoš-Huković and Babić, 2007). In the present work, we aim to fabricate bulk nanostructured Co by a combination of high energy ball milling and warm pressing, and concentrate on its dry sliding wear behaviour and the corrosion resistance in artificial saliva solution (ASS). Chemical composition of the corrosion products formed during polarization will be in-depth analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The findings are expected to help to evaluate the feasibility of bulk nanostructured Co as a potential candidate for dental implants.

2. Experimental

2.1. Fabrication of bulk nanostructured Co

5 g of commercially pure Co (Alfa Aesar, 1.6 μm, 99.8%) powder and 25 g of hardened steel balls (powder-to-ball weight ratio 1:5) were loaded into a 65 mL hardened steel vial and subjected to high energy ball milling using a SPEX 8000D mill in an argon glove box for 12 h at ambient temperature. Then, the ball milled powder was directly fed to the die (in a circular tube shape with an inner diameter of 10 mm) of the custom-designed pressing assembly through a tube integrated with the bottom of the glove box and consolidated into bulk at temperature of 300 °C for 1 h under a constant load of ~1 GPa and high vacuum of 2×10^{-6} Pa. The whole process was performed either in argon atmosphere or high vacuum environment to prevent oxidation of the sample. The density of as-compacted cylinder was measured by Archimedes method (ASTM B962-15, 2015) and the result was averaged by three separated samples.

2.2. Microstructural characterization

The phase of the obtained sample was identified by X-ray diffraction (XRD) pattern recorded on a PANalytical Philips X'pert PRO-MPD diffractometer in the 2θ range from 30° to 100° using Cu-Kα radiation (λ=1.54056 Å, 40 kV, 40 mA) with a step size of 0.02° and a count time of 1 s. The microstructures of the sample prior to and post wear were characterized by transmission electron microscopy (TEM) using JEOL 2010 microscope operated at 200 kV. The TEM samples were prepared by focused ion beam (FIB; Helios NanoLab™ 600i) milling using the standard lift-out technique. The grain size was determined from TEM micrographs by measuring and averaging the diameters of more than 200 grains. For the worn sample, the directions normal to the sliding surface, along the sliding direction and perpendicular to the sliding direction in the sliding plane were defined as ND, SD and TD, respectively. An ND-SD cross-sectional TEM sample was prepared. To protect the original worn surface, a protective platinum strip of thickness ~1 μm was deposited before the FIB milling. To minimize surface damage by Ga^+ ion implantation, during the final step of polishing the foil, the acceleration voltage was reduced to 5 kV and ion beam current was reduced to 15 pA.

2.3. Mechanical characterization and pin-on-disk dry sliding wear test

The nanohardness and elastic modulus (Oliver, 1992; Oliver and Pharr, 2004) of the mechanically polished sample were measured using a Hysitron TI-950 Triboindenter with a diamond Berkovich tip and calibrated with standard aluminum and fused quartz. Arrays of 36 indentations were performed and the average values were provided. Micro-hardness (ASTM E384-16, 2016) was measured using a Vickers diamond pyramidal indenter (HXD-1000TMC/LCD, Shanghai Taiming Optical Instrument Co., Ltd., Shanghai, China) under a load of 300 gf for 10 s.

The pin samples were cut into 3 mm in diameter and length of 10 mm from the as-compacted cylinder using a wire-cut electrical discharge machine. Pin-on-disk wear tests (Anton-Parr Pin-on-Disk Tribometer, Australia; ASTM G99-05, 2016) were performed in air under load of 9.8 N (corresponding to nominal contact pressure of 1.38 MPa). After preliminary wear test against martensitic stainless steel 440 C (SS440C) disk, we found that no weight loss of the pin sample was detected but the counterface material was severely worn. Therefore, we chose to take the highly wear-resistant alumina as our counterface material, which is reasonable for wear test of dental alloys. A constant slow sliding velocity of 0.1 m s^{-1} was selected to suppress flash heating at the contacting surfaces. Steady-state wear rates were calculated by weight loss measurements after sliding distances of 720 m.

Before starting the wear tests, the contacting surfaces of both the pin sample and the disk were first polished with sequential silicon carbide papers down to 1200 grit and then vibrationally polished with alumina suspension of 1 and 0.05 μm, and finally silica suspension of 0.02 μm. Three separate tests were run and the average wear rate and coefficient of friction were provided. The morphology of the worn pin surface was analyzed by scanning electron microscopy (SEM). The size, morphology and chemical composition of the wear debris were characterized by SEM and energy dispersive X-ray spectroscopy (EDX).

2.4. Electrochemical corrosion test

The corrosion behaviour of the bulk nanostructured Co samples was investigated by electrochemical polarization tests using a Princeton Applied Research Versa Studio (PARSTAT 4000). The tests were performed in a conventional three-electrode cell configuration using a saturated calomel reference electrode (SCE) as reference electrode and a platinum plate as counter electrode. All the potential values are reported vs. SCE hereafter. Prior to electrochemical tests, the Co discs with 10 mm in diameter were ground with SiC emery paper down to a 1200 grit and then vibrationally polished to a mirror finish with 0.02 μm silica suspension. After ultrasonically rinsed in ethanol and double distilled water for 10 min, respectively, the samples were insulated with epoxy resin with 78.5 mm^2 exposed area as the working electrodes. Measurements were performed at 37 °C in ASS: 1.5 g/L NaCl, 1.5 g/L $NaHCO_3$, 0.5 g/L $NaH_2PO_4\cdot2H_2O$, 0.5 g/L KSCN, and 0.9 g/L lactic acid, with pH of 6.2 (Vincent et al., 2014). All electrolytes were prepared from analytical reagent-grade chemicals using double distilled water. The test was repeated three times to confirm reproducibility of the data. The working electrode was immersed in test solution for 40 min to attain a stable open circuit potential (OCP). Potentiodynamic polarization curves were recorded by scanning from (OCP value, −0.75 V) to (OCP value, +0.75 V) at a scanning rate of 10 mV/min. The corrosion potential E_{corr} as well as the corrosion current density i_{corr} were automatically extracted from the polarization curve by the Versa Studio 2.44 software through Tafel slope extrapolation.

The corroded surface after polarization test was examined using an SEM. The chemical composition and phase of corrosion products were analyzed by EDX, XRD and X-ray Photoelectron Spectroscopy (XPS,