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Electrochemical behavior and biocompatibility of Ti-Fe-Cu alloy with high strength and ductility

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ABSTRACT

The electrochemical behavior and biocompatibility of the micro/nano-structured α+β Ti−3.5Fe−3.9Cu alloy were investigated in this work. The alloy was produced by tilt-casting method and subjected to subsequent hot dual-axial forging at 1173 K. It is shown that the electrochemical behavior and biocompatibility of the Ti−3.5Fe−3.9Cu alloy are close to, or even better, than those of a typical commercial Ti-6Al-4V alloy widely used as implants. This demonstrates that the Ti−3.5Fe−3.9Cu alloy shows a good potential for application as biomaterial.

1. Introduction

The α+β - type alloys compose the most numerous group of industrial titanium alloys. These alloys have high heat resistance and can sustain their high strength even at elevated temperature [1]. On the other hand nanostructured materials have somewhat different physical properties in comparison with conventional microstructured materials [2]. Hypereutectic Ti-Fe [3,4] and Ti-Fe-Co [5,6] alloys obtained in the form of arc-melted ingots, have shown high compressive strength (over 2 GPa) along with excellent plasticity in compression up to 7 and 16% for binary Ti-Fe and ternary Ti-Fe-Co alloys, respectively. Large plastic deformation of 16.5% was obtained in $Ti_{70}Fe_{15}Co_{15}$ alloy while Cr, Mn and Ni additions caused brittle fracture owing to formation of the alternative intermetallic compounds. Later it has been shown that Sn addition further improves ductility of Ti-Fe and Ti-Fe-Co alloys [7–9]. The addition of B in small quantities (0.5 at.%) to Ti-Fe alloys increased mechanical strength up to 2470 MPa but decreased ductility [10]. Moreover, some other alloying additions like Cu and Nd were found to improve ductility of Ti-Fe alloys up to 8 and 11%, respectively [11]. However, alloys with large volume fraction of cP2 intermetallic (IM) compound exhibited brittle fracture. Deformation behavior and deformation-induced transformations of such alloys were studied in detail and nanoscale amorphous regions were found in $Ti_{60}Fe_{20}Co_{20}$ alloy [12].

Recently, we produced Ti−3.5Fe−3.9Cu alloy which exhibited good mechanical properties [13,14]. The tensile mechanical properties were further improved by dual-axial forging. An ultimate tensile strength of about 1200 MPa and elongation strain of about 9% have been achieved after dual-axial forging of the sample at 1173 K for 15 times. This Ti-based alloy contains only relatively cheap alloying elements (Fe and Cu). The tensile mechanical properties of this alloy are close to those of commercial Ti-based

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alloys containing more expensive alloying elements such as Mo, Nb, V etc. Especially vanadium is quite an expensive element [15].

It is noteworthy that Fe is one of the most efficient β phase stabilizing elements for Ti alloys which can increase mechanical strength, and improve the hot cracking resistance of Ti-based alloys [16–19]. It was suggested that in order to obtain good mechanical properties Fe content should be kept in the range of 1 at%-4 at% [20]. Copper is also a β stabilizing element. The addition of Cu to Ti-based alloy can provide high hardness, high strength and good wear resistance [21–24]. Furthermore Ti-based alloys with small amount of Cu exhibit adequate cell biocompatibility and Cu content has no influence on the cell proliferation and differentiation [25]. Also, Cu element has been widely used as an antibacterial agent, for example, metal implants after surface modification by ion implantation [26] and dual magnetron sputtering [27] show better antibacterial activity. It should be noted, that Ag has an almost similar antibacterial effect as Cu. The influence of Ag on the biocompatibility of the Ti-based alloys has been investigated and discussed in our previous work [28]. Thus, it is of interest to investigate the biocompatibility of the Ti–3.5Fe–3.9Cu alloy.

In this work we studied the electrochemical behavior and biocompatibility of the Ti–3.5Fe–3.9Cu alloy. The results were compared with the properties of a well-known industrial alloy, i.e. Ti–6Al–4V [29] which is widely used for implants [30–32].

2. Experimental procedure

2.1. Alloy preparation

The rods of the Ti–3.5Fe–3.9Cu alloy of 6 mm in diameter and about 50 mm in length are fabricated by arc melting the mixtures of pure metals in an argon atmosphere purified by Ti getter and subsequent tilt casting into a Cu mold. Before casting, the ingots are turned over and re-melted five times to ensure compositional homogeneity.

2.2. Analysis of the crystalline structure

The atomic structure of the alloys was examined by X-ray diffractometry with CuK_{α} radiation. The dimensions of crystallites in the samples were determined by the widening of the diffraction peaks with an accuracy of ±5 nm [33]. The microstructure of the ingots was examined by scanning electron microscopy (SEM) carried out at 15 kV.

Transmission electron microscopy (TEM) investigations were carried out using a JEOL JEM 2010 microscope operating at 200 kV and equipped with an energy dispersive X-ray spectrometer (resolution ~0.1 keV). The samples for TEM were prepared first mechanically (down to 10 μm thickness) and subsequently by an ion polishing technique (down to electron-beam transparency). In order to avoid structural damage to the specimen, the ion-beam energy was kept as low as 2 keV.

2.3. Dual-axial forging procedure and mechanical testing

According to our previous works [13,14] and the Ti-Fe and Ti-Cu phase diagrams [34], the forging procedure was performed for 15 times at 1173 K. The dimension reduction of the samples during forging procedure was about 60–70% per cycle.

2.4. Electrochemical behavior

The electrochemical behavior of the alloy were evaluated by polarization method in a 0.9 wt% NaCl solution at 298 K. This solution is regularly applied to estimate the corrosion characteristics of different alloys. The potentiodynamic polarization curves were measured at a scanning rate of 2 mV/min in three-electrode electrochemical SFG (ECSFG-sum-frequency generation at electrochemical interfaces) cell using a 10 × 5 mm^2 polycrystalline Pt counter electrode, and a Ag/AgCl reference electrode. The polarization measurements were carried out using Hokuto Denko HZ-5000 potentiostat. Electrochemical characteristic parameters, such as electrochemical corrosion potential and corrosion current density can be obtained by evaluating polarization curves. The electrochemical tests have been provided for 16 times on each sample.

2.5. X-ray photoelectron spectroscopy

The depth profiles of the oxide films were obtained by using X-ray photoelectron spectroscopy (XPS; Axis ultra DLD, Kratos), using a beam size and spot diameter of 300 × 700 μm and 2 mm, respectively. Step sizes of 1 and 0.1 eV were used in the survey and regional scans, respectively. Each regional scan was conducted for about 10 times. All binding energies given here are relative to the Fermi level, E_F, and all the spectra were obtained using incident monochromatized Al Kα X-rays (energy = 1486.61 eV). Depth-dependent XPS data were acquired by sputtering the surface layers with Ar ion beam. Chemical depth profiles were obtained by alternating sputtering and spectrum acquisition. The XPS profiles at each polishing depth were analyzed using built-in software.

2.6. Cell-based assays

Osteoblasts (hFoB 1.19 ATCC, US) were maintained in DMEM:-HAM F12 media with 10% (v/v) fetal bovine serum (FBS) and 1% penicillin/streptomycin, respectively. Typically, 100 μl cell suspensions (1 × 10^5 cells per ml) were seeded onto the surfaces of samples (1 cm in diameter and about 2 mm in thickness cylinders) which were placed in a cell culture plate. After 1 h, cells were adhered onto the samples, and another 800 μl cell suspensions were added into each well and then cultured for 7 days. After 1 day, 3 days and 7 days of culture, the cell number was determined using cell counting kit-8 (Sigma-Aldrich, USA) following the manufacturer's instructions. The samples were sterilized by immersion in 75% ethanol for 30 min. After that they were washed with sterilized deionized water for 5 times before cell seeding.

A Live/Dead kit (Invitrogen, USA) was used to distinguish between live and dead cells. After staining by this kit, the live cells exhibited green color and the dead cells exhibited red color. Data are presented as means ± standard error. Paired means were compared using unpaired Student's t-tests. P-values < 0.05 were considered statistically significant. The numerical P values are indicated in the legend of Fig. 4.

2.7. Ion release analyses

Mass of ion released in the simulated body fluid (HBSS (−) with Phenol Red) was analyzed by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Fisher Scientific IRIS Advantage DUO). The time of the sample immersing in the simulated body fluid was 31 days at the temperature of about 310 K.

3. Results and discussion

3.1. The crystalline structure analysis of the Ti–3.5Fe–3.9Cu alloy samples

As-prepared Ti–3.5Fe–3.9Cu alloy ingot, obtained by arc-melting and subsequent tilt-casting was quite brittle. The tensile