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Optimization of mechanical properties, biocorrosion properties and antibacterial properties of wrought Ti-3Cu alloy by heat treatment

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A B S T R A C T

Previous study has shown that Ti-3Cu alloy shows good antibacterial properties (>90% antibacterial rate), but the mechanical properties still need to be improved. In this paper, a series of heat-treatment processes were selected to adjust the microstructure in order to optimize the properties of Ti-3Cu alloy. Microstructure, mechanical properties, biocorrosion properties and antibacterial properties of wrought Ti-3Cu alloy at different conditions was systematically investigated by X-ray diffraction, optical microscope, scanning electron microscope, transmission electron microscopy, electrochemical measurements, tensile test, fatigue test and antibacterial test. Heat treatment could significantly improve the mechanical properties, corrosion resistance and antibacterial rate due to the redistribution of copper elements and precipitation of Ti_2Cu phase. Solid solution treatment increased the yield strength from 400 to 740 MPa and improved the antibacterial rate from 33% to 65.2% while aging treatment enhanced the yield strength to 800–850 MPa and antibacterial rate (>91.32%). It was demonstrated that homogeneous distribution and fine Ti_2Cu phase plays a very important role in mechanical properties, corrosion resistance and antibacterial properties.

1. Introduction

Titanium and titanium alloys have been widely used in the biomedical implant field due to their excellent mechanical properties and biocompatibility [1,2], especially in repair and replacement materials such as artificial joint and dental implants [3,4]. But one of the big problems that plague the doctor is the infection or the inflammation. Once the infection occurs, it will seriously affect the healing process. Patients sometimes need to accept long-term antibiotic treatment even re-operation. Thus, the implant with strong antibacterial properties shows great potential for medical implant materials in clinic application.

Recently, many researches have been reported on the surface modification of titanium alloy to obtain good antibacterial properties. But surface coatings are susceptible to exfoliation and the antibacterial effect is greatly reduced over the time [5–8]. Alternatively, alloy-type antimicrobial titanium alloys in which antimicrobial elements are distributed uniformly have attracted much attention worldwide due to their long-term antibacterial property, good wear resistance, good corrosion resistance. Shirai et al. [9] first reported that titanium alloys containing 1% Cu and 5% Cu have antimicrobial activity and substantially reduce the incidence of pin tract infection. Then, Ti–Cu sintered alloy with 5 wt% or high Cu exhibits a strong and stable antibacterial rate (>99%) against *S. aureus* and *E. coli* [10,11]. Recently, ingot metallurgy as well as subsequent metal forming processing has been used to produce antibacterial titanium, such as Ti-6Al-4V-xCu (X = 1, 3, 5 wt%) [12], Ti-5Cu and Ti-10Cu [13], and Ti-Cu alloys with 2–4 wt% Cu [14]. Both Ti-Cu sintered alloy and Ti-Cu ingot alloy show excellent cytocompatibility and have no influence on the cell proliferation and differentiation [15,16]. It has been reported that the content of Cu and the existing form of Cu element had great influence on the antibacterial properties of Ti-Cu alloy. In order to get good antibacterial rate (>90%), the Cu content in Ti-Cu alloy has to be at least

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3 wt% [10,14].

However, for biomedical application, metallic materials should also have good mechanical properties as well as good corrosion resistance. Yao el. al [17] prepared Ti−2.5Cu alloy through hot rolling and indicated that acicular Ti_2Cu particles with tens of nanometers in width and 100 nm in length contribute greatly to the strength. Souza [18] found that cooling rate higher than 9 °C/s leds to the formation of the α-Ti and smaller Ti_2Cu spheres (~5 nm diameter), and the hardness was improved greatly due to the existence of nanoscale Ti_2Cu phases. Our previous study also reported that homogeneously dispersed and fine Ti_2Cu would provide strong strengthening effect, good corrosion resistance and strong antibacterial ability [13,14,19]. All these indicate the shape and size of Ti_2Cu phase significantly influences the antibacterial properties and mechanical properties as well corrosion properties.

It has shown that Ti-3wt%Cu alloy exhibited comprehensive high antibacterial, high ductility and strength [14], therefore, Ti-3 wt.% Cu was prepared in this paper by ingot metallurgy followed by forging. It was proposed to obtain good corrosion resistance and mechanical properties of Ti-3Cu alloy by adjusting the existing form of Ti_2Cu phase without reduction in antibacterial properties. The primary results demonstrate that the mechanical properties, bio-corrosion resistance and the antibacterial ability of Ti-3Cu alloy could be improved by microstructure control through proper heat treatment. In comparison with pure titanium and Ti-6Al-4V, it was suggested that Ti-3Cu with good comprehensive properties could be a candidate for long-term implant.

2. Experimental

2.1. Preparation of samples

Ti-3Cu bar with 15 mm in diameter was used. Different heat treatments were used to change the microstructure, as listed in Table 1. Samples for the following test were sliced from the bar.

2.2. Phase identification and microstructure observation

Phase identification was conducted on an X-ray diffraction (XRD) at an accelerating voltage of 40 kV and a current of 40 mA. For microstructure observation, all samples were ground by SiC sandpapers up to 2000 grits, polished with 1 μm polishing paste and etched with Keller's solution consisting of 1 vol% HF acid, 2.5 vol% HNO_3 acid, 1.5 vol% HCl acid and 95 vol% H_2O. Microstructure was observed on an optical microscopy (OM, Olympus GX71) and scanning electron microscopy (SEM, JSM-6510A) with an energy-dispersive X-ray spectrometer (EDS). Samples for TEM observation were manually ground to 100 μm, punched into Φ3mm discs and then ground to 50 μm with 1500 SiC sandpaper, and then ion milled at a low angle between 4° and 8°, finally observed under a transmission electron microscopy (TEM, JEOL-JEM2100).

2.3. Tensile test and fatigue test

Tensile specimen was 2 mm in thickness, 30 mm in length, with a head width of 6 mm. The tensile testing was carried out on an electronic universal testing machine (AG-Xplus100 KN) with a crosshead speed of 0.5 mm/min. At least three samples were tested for each condition.

Fatigue performance of Ti-3Cu(T6-16) was tested on INSTRON 8801. Specimen were prepared in accordance with National Standards and Requirements GB3075-82 [20] and ASTM E 466-96 (Reapproved 2002) [21], the minimum cross-sectional area is 6 mm in diameter, the parallel section length is 18 mm, the radius of the transition arc is 30 mm and the clamping end is 12 mm in diameter. Before test, all samples were surface polished to ensure the surface roughness Ra≤0.5 μm. The samples were tested by up-and-down test method [22] at a stress ratio of $R = -1$, at the frequency of 20 Hz in 20 °C.

2.4. Electrochemical test

Samples for electrochemical tests were put into a polymer sample holder with only one side of 12 mm in diameter exposed [23]. The test was conducted on a beaker containing 0.9% NaCl at 37 ± 1 °C using Versa STAT V3 automatic laboratory corrosion measurement system (Princeton Applied Research, USA). According to ISO 10271:2001 Standard [24], the open-circuit potential vs. time curve (OCP curve) was recorded for up to 3600 s to determine the open circuit potential (E_{OCP} at 3600 s). After the OCP measurement, the EIS test was carried out at an open circuit potential with a 10 mV amplitude sine wave potential and a frequency range of 10^{-2} Hz to 10^5 Hz. Then Tafel curve was recorded at a scanning range of −0.5 V ~ + 1.5 V (relative to open circuit potential) and the scanning rate was 1 mVs^{-1}. The Nyquist plot and Bode phase diagrams was analyzed and fitted by the ZsimpWin software. Three samples were measured at each condition. The corrosion rate (V) was calculated by Ref. [23]:

$$V = Mi_{corr}/nF \quad (1)$$

where, M is the molar mass of titanium (g mol^{-1}), i_{corr} is the average corrosion current density measured in the electrochemical tests (A cm^{-2}), F is Faraday constant (96,485 C mol^{-1}) and n is the valence of titanium.

Table 1
Samples and heat treatment processing.

Samples	Conditions	Processing
Ti-3Cu(F)	F	As-forged and annealed
Ti-3Cu(T4)	T4	900 °C/5 h
Ti-3Cu(T6-16)	T6-16	900 °C/5 h + 400 °C/16 h
Ti-3Cu(T6-24)	T6-24	900 °C/5 h + 400 °C/24 h
Ti-3Cu(T6-36)	T6-36	900 °C/5 h + 400 °C/24 h + 475 °C/12 h

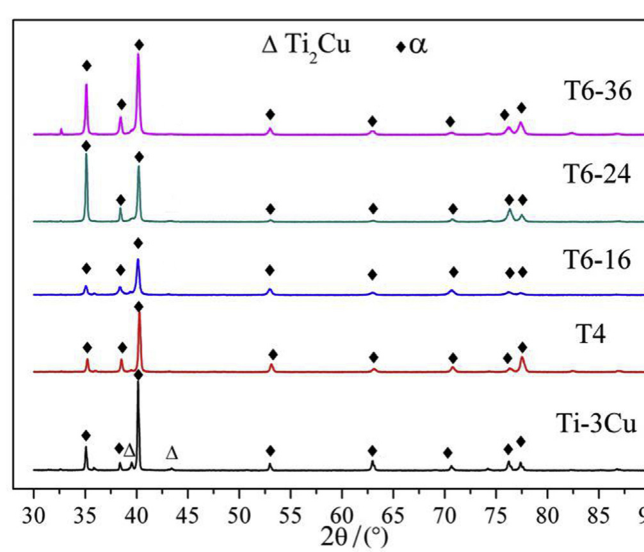

Fig. 1. XRD patterns of Ti-3Cu alloy under different heat-treatments.