

# Study on improved tribological properties by alloying copper to CP-Ti and Ti-6Al-4V alloy



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## ABSTRACT

Copper alloying to titanium and its alloys is believed to show an antibacterial performance. However, the tribological properties of Cu alloyed titanium alloys were seldom studied. Ti-5Cu and Ti-6Al-4V-5Cu alloys were fabricated in the present study in order to further study the friction and wear properties of titanium alloys with Cu additive. The microstructure, composition and hardness were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and hardness tester. The tribological behaviors were tested with ZrO<sub>2</sub> counterface in 25% bovine serum using a ball-on-disc tribo-tester. The results revealed that precipitations of Ti<sub>2</sub>Cu intermetallic compounds appeared in both Ti-5Cu and Ti-6Al-4V-5Cu alloys. The tribological results showed an improvement in friction and wear resistance for both Ti-5Cu and Ti-6Al-4V-5Cu alloys due to the precipitation of Ti<sub>2</sub>Cu. The results also indicated that both CP-Ti and Ti-5Cu behaved better wear resistance than Ti-6Al-4V and Ti-6Al-4V-5Cu due to different wear mechanisms when articulated with hard zirconia. Both CP-Ti and Ti-5Cu revealed dominant adhesive wear with secondary abrasive wear mechanism while both Ti-6Al-4V and Ti-6Al-4V-5Cu showed severe abrasive wear and cracks with secondary adhesive wear mechanism due to different surface hardness integrated by their microstructures and material types.

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## 1. Introduction

Nowadays, titanium and its alloys are widely used as dental and orthopedic implant materials due to their excellent corrosion resistance, mechanical characteristics and biocompatibilities [1,2]. However, there are still some obstacles to be overcome for complete success in the application of titanium as false tooth or artificial joints. One of the biggest disadvantages is the implant loosening for its structural applications [3,4]. This phenomenon may lead to implant failure, revision surgery and even member amputation, associated with extremely high medical costs as well as the pain and suffering of the patients. The literatures have revealed that the dominant cause for implant loosening is related to the bacterial infection after implant replacement [5,6]. Reports showed that the annual infection rate for orthopedic implants is 4.3% in the USA [7]. Hence, the prevention of bacterial-related infection remains a major challenge for the implants.

It is well believed that the Cu or Ag ions released from the surface or coating of titanium and its alloys with modifications or additives possess antibacterial activity [8–10]. As an example, Zhang et al. [11] revealed that the silver nanoparticle-containing polyelectrolyte multi-layer coating on titanium alloy surface considerably enhanced the antibacterial activity. Bogdan et al. [12] also found that the porous TiO<sub>2</sub>-Ag composite layers on Ti-6Al-7Nb alloy significantly improved the in vitro antibacterial activity against methicillin-resistant *Staphylococcus aureus*. On the other hand, Hong et al. [13] revealed that adding a proper amount of Cu gave SUS 304 stainless steel an excellent antibacterial property. Some other studies [14,15] also confirmed the good antibacterial properties of Ti-Cu fabricated by powder metallurgy. Compared with antibacterial coatings, alloying with Cu or Ag additives in metals could release antibacterial ions over a longer period. Hence, the Cu alloying should offer a promising application for titanium alloy implants due to the excellent antibacterial properties.

Since bacterial infection is mainly related to the wear debris accumulation during the service of implant [16,17], the tribological properties of titanium and its alloys are also of great importance besides the antibacterial properties. Unfortunately, the main limit of titanium alloys is their poor tribological behavior, characterized by high coefficient of friction, severe adhesive wear and low abrasion resistance [18]. If the Cu alloyed titanium alloys could improve the tribological properties,

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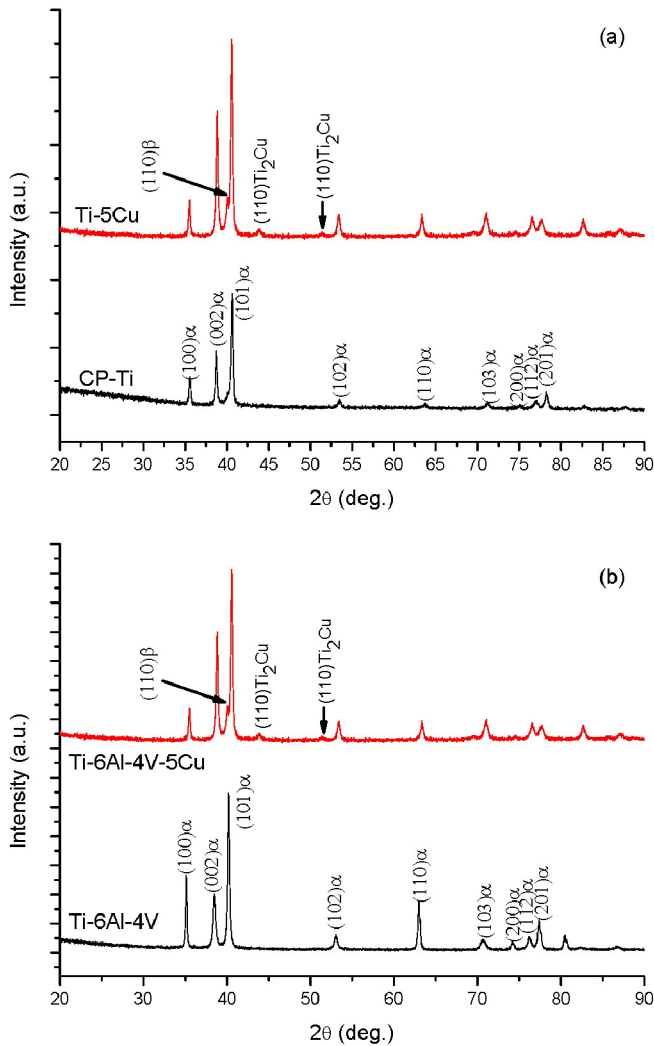


Fig. 1. XRD patterns of different samples, (a) CP-Ti and Ti-5Cu; (b) Ti-6Al-4V and Ti-6Al-4V-5Cu.

this method would be more promising to weaken and even avoid the implant loosening. Hence, the friction and wear properties as well as failure mechanism of the Cu alloyed titanium alloys are of great importance for the sake of decreasing the wear debris accumulation. However, there were less related reports focusing on the tribological properties of Cu alloyed titanium alloys. Ohkubo et al. [19] reported that the wear resistances of the experimental Ti-Cu and Ti-6Al-4V-Cu alloys were better than those of commercial pure titanium (CP-Ti) and Ti-6Al-4V alloy, respectively. However, the wear test was only conducted by repeatedly grinding upper and lower teeth under flowing water on a testing apparatus. The 25% bovine serum, a common simulated body fluid in the simulation test for artificial joints [20,21], was not considered in that study. In addition, they also did not contrast the friction coefficient as well as wear scars. Since the tribological properties of the Cu alloyed titanium alloys are still not well explained, this study was focused on this issue in order to clarify the improvements on friction and wear resistance of Ti-Cu and Ti-6Al-4V-Cu alloys.

In this study, the microstructure, composition and hardness of both Ti-5Cu and Ti-6Al-4V-5Cu alloys were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and hardness tester. Then, the friction and wear properties of Ti-5Cu and Ti-6Al-4V-5Cu alloys were measured and compared with those of pure titanium and Ti-6Al-4V alloy.

## 2. Materials and experimental details

### 2.1. Materials

According to our previous studies [22,23], Cu content in the Cu alloyed titanium alloys affected the state of Cu existence and the release behavior of Cu ions, which in turn influenced the antibacterial performance of the alloys. The antibacterial ability was enhanced with increase of the Cu content and the Cu content at 5 wt.% showed strong and stable antibacterial properties. Hence, Ti-5Cu and Ti-6Al-4V-5Cu alloys were adopted in this study.

Experimental materials by alloying copper to CP-Ti (commercial pure Ti) and Ti-6Al-4V alloy were prepared as follows. Ti-5Cu alloy was melted from CP-Ti and pure copper (99.99%) as the raw materials by vacuum arc melting in a 5 kg furnace. The ingot was re-melted for five times to ensure the compositional homogeneity, and then hot forged at 900 °C to round bars. Similarly, the Ti-6Al-4V-5Cu alloy was fabricated by melting high purity titanium, aluminum, vanadium and copper in a 30 kg consumable electrode arc melting furnace. The ingot was hot forged to bars of different diameter, starting from temperature of 1100 °C to the final temperature of 860 °C without any intermediate annealing. The medical grade CP-Ti and Ti-6Al-4V alloy with same dimension were used as control samples. The as-forged Ti-5Cu alloy and CP-Ti were heated at 900 °C with holding time of 1 h, followed by air cooling as the final heat treatment. The as-forged Ti-6Al-4V-5Cu alloy and Ti-6Al-4V alloy were machined into small samples, solution treated at 900 °C with holding time of 1 h, followed by quenching, and then aged at 550 °C for 6 h as the final heat treatment. Finally, samples with diameter of 10–30 mm and a thickness of 5 mm were sliced from these heat treated alloys for experiments. Before testing, these samples were successively ground using 60 to 1000 mesh SiC abrasive papers and polished in a polishing liquid with 1 μm SiC particles.

### 2.2. Microstructure, composition and hardness characterizations

The phase constitutions in the alloys were determined by the  $2\theta/\theta$  coupling method of X-ray diffraction (XRD) analysis using a Cu K $\alpha$  irradiation at an accelerating voltage of 40 kV and a current of 40 mA. The microstructure was observed and analyzed under both optical microscope (Axiovert 200 MAT) and transmission electron microscope (TEM, Tecnai G220). Hardness measurements were carried out by a micro-hardness tester (Tukon 2500 DM-400) under indentation load of 1 N and loading time of 10 s. Ten different fields were selected randomly and the result was a mean value with standard deviation.

### 2.3. Tribological test

The tribological tests were performed between control/experimental samples with ZrO<sub>2</sub> balls of 5 mm in diameter using a universal multifunctional tester (UMT) developed at CETR (Campbell, California) by ball-on-disc sliding style in 25% bovine serum lubrication. The tests were performed with load of 3 N and equivalent contact stress of ~450 MPa. The constant sliding time was 60 min and a steady-state condition could be obtained at a sliding frequency of 10 Hz with a stroke of 3 mm. Bovine serum was diluted to the concentration of 25%. The temperature was maintained at  $37 \pm 1$  °C during the wear process to simulate the physiological medium around the contact area of the prostheses in vivo. The details to control the experimental temperature were as follows. The UMT tribo-tester also provided a temperature control system, which included a platinum resistance thermometer and a liquid heating chamber. The measuring range was 0 to 350 °C for the temperature sensor (RTD-350, CETR, USA). The system was fixed on the lower reciprocating motion device and it could monitor the temperature of the lower “disc” sample. When a friction heat was generated during the process, the temperature control system would try to slow down the heating process.

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