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Effect of Cu on microstructure, mechanical properties, corrosion resistance and cytotoxicity of CoCrW alloy fabricated by selective laser melting

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ABSTRACT

In the study, CoCrWCu alloys with differing Cu content (2, 3, 4 wt%) were prepared by selective laser melting using mixture powders consisting of CoCrW and Cu, aiming at investigating the effect of Cu on the microstructures, mechanical properties, corrosion behavior and cytotoxicity. The SEM observations indicated that the Cu content up to 3 wt% caused the Si-rich precipitates to segregate along grain boundaries and in the grains, and EBSD analysis suggested that the Cu addition decreased the recrystallization degree and increased the grain diameter and fraction of big grains. The tensile tests found that the increasing Cu content led to a decrease of mechanical properties compared with Cu-free CoCrW alloy. The electrochemical tests revealed that the addition of Cu shifted the corrosion potential toward nobler positive, but increased the corrosion current density. Also, a more protective passive film was formed when 2 wt% Cu content was added, but the higher Cu content up to 3 wt% was detrimental to the corrosion resistance. It was noted that there was no cytotoxicity for Cu-bearing CoCrW alloys to MG-63 cell and the cells could spread well on the surfaces of studied alloys. Meanwhile, the Cu-bearing CoCrW alloy exhibited an excellent antibacterial performance against E.coli when Cu content was up to 3 wt%. It is suggested that the feasible fabrication of Cu-bearing CoCrW alloy by SLM using mixed CoCrW and Cu powders is a promising candidate for use in antibacterial oral repair products. This current study also can aid in the further design of antibacterial Cu-containing CoCrW alloying powders.

1. Introduction

Selective laser melting (SLM) is an additive manufacturing technique, which can directly produce parts with high geometrical complexity from 3D computer-aided design (CAD) data by selectively melting layers of powder (Prashanth et al., 2014; Song et al., 2014). Compared to traditional manufacturing means, the SLM technique has many advantages, including high levels of process flexibility, time safe, and complex shape parts obtained without using dies or molds, and so on. Therefore, the technique is attractive to manufacture complex shapes of individual implants made from biocompatible metals, such as dentures and bone implants (Han et al., 2017). To date, some commercialized biomedical materials have been manufacturing by SLM, such as titanium alloys (Kang et al., 2017; Liu et al., 2016; Zhao et al., 2016b; Zhou et al., 2016), stainless steel (Divinski et al., 2015; Ma et al., 2016), 17-4PH (Hu et al., 2017), and Co-Cr based alloys (Liverani et al., 2016; Lu et al., 2016a; Takaichi et al., 2013). Among them, Co-Cr based alloys have been widely used as implants in orthopedic (artificial hip and knee joint replacements) and dentistry (coping materials) due to their superior mechanical properties to excellent wear resistance and corrosion resistance (Demir and Previtali, 2017; Yamanaka et al., 2014).

However, implant associated bacterial infection is currently regarded as the most severe and devastating complication associated with the use of implants and has significant social, clinical and economic impact, especially for dental environment with diversity of bacteria. It

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has been suggested that bacteria can readily colonize the different types of surfaces including teeth, prosthetic devices and dental implants (Achtman and Wagner, 2008). The formation and maturation of biofilms on dental biomaterial surfaces may lead to the development of peri-implant diseases, such as peri-implant mucositis or peri-implantitis, resulting in the failure of dental implant seriously (Lee and Wang, 2010). One approach to reduce the clinical infection or inflammation is developed some novel antimicrobial alloys for biomedical applications by the addition of antibacterial alloying elements during material making process, such as Zn, Cu and Ag (Schrand et al., 2010). Cu is one of the most important trace elements for human beings, playing crucial nutritional function in human body, as it serves as a cofactor for a variety of enzymes (Klevay, 1997). Cu deficiency will lead to compromised bone health by a decrease in lysyl oxidase, which strengthens collagen fibril crosslinking (Medeiros, 2016). It is reported that proper quantity of Cu ions can inhibit active bone resorption and promote the osteogenesis (Guo et al., 2016; Mir et al., 2007). In addition, Cu is well known for its antimicrobial activity since the 19th century. Given those, some novel kinds of Cu-bearing alloys with antimicrobial activity have been developed recently for reducing implant associated infection, such as 317L-Cu stainless steel (Ren et al., 2014), 17–4PH-Cu (Wang et al., 2015), Ti-Cu (Hayama et al., 2014; Zhang et al., 2013) and Ti6Al4V-xCu (Guo et al., 2016), and so on. In the work of Zhang et al.'s research (Zhang and Liu, 2016), a sets of Cu-bearing CoCrMo alloy with 1–4 wt% Cu was fabricated by sintering processing. They found that the addition of Cu limited influence on the tensile property and corrosion resistance of CoCrMo alloy as well.

Recently, a novel Cu-bearing Ti6Al4V based alloys for biomedical application combining the antimicrobial activity of Cu and the advantages SLM technology have been designed and fabricated by SLM in our previous study using mixed spherical powders of Cu and Ti6Al4V for the first time (Guo et al., 2016). Whereafter, the SLMed CoCrW-3Cu (wt%) alloy were directly fabricated by the mixed CoCrW and Cu powders for denture application (Lu et al., 2016b). The bonding strength of metal–porcelain was evaluated systematically, which indicated that the average metal-porcelain bonding strength is significantly higher than the minimum value in the ISO 9693 standard for denture, indicating that Cu-bearing CoCrW based alloys is a promising candidate for use in antibacterial oral repair products. As for a new biomedical alloy, however, the effect of Cu content on the microstructure, mechanical property, corrosion behavior, and cytotoxicity of SLMed CoCrW based alloys has not been investigated in detail. Therefore, it is of great importance to clarify the above materials data for optimizing the alloying powders design and properties with the purpose of providing support for its application as coping materials in clinical field.

2. Experimental details

2.1. Materials preparation

Referencing to our previous studies and the Ref. (Zhang and Liu, 2016), it has been found that the Cu content less than 1 wt% will limit the antibacterial activity is limited whereas higher Cu content will severely negatively impact on the mechanical properties and biocompatibility. Given this, in this study three kinds of Cu bearing CoCrW alloys, containing 2, 3 and 4 wt% Cu, were designed and fabricated by SLM using the mixed powders consisting of CoCrW and Cu powders. The average chemical composition of CoCrW powders is listed in Table 1. The size distribution of CoCrW powders is between 15 and 45 μm, while that of Cu powders is less than 10 μm. The two powders were uniformly mixed together for 30 min before SLM processing. The morphologies of the CoCrW powders and Cu powders are shown in Fig. 1. The most of CoCrW powders are appeared to be spherical (Fig. 1a), while pure Cu powders are irregular shape (Fig. 1b). The Cu-bearing CoCrW alloys with relative density of higher than 99.5% then were fabricate by SLM processing using line scanning strategy according to our previous study (Lu et al., 2015), listed in Table 2. Fig. 2 shows the optical photographs of the polished CoCrW based alloys with different Cu content (XY-plane). In all cases, a compact surface with few pores can be obtained by selective laser melting. Then those alloys were solution heated at 1200 °C for 1 h in an annealing oven with high purity argon, and then were quenched in water. The heat treatment that used in this study was referenced our previous study (Lu et al., 2016a), in which the microstructure, mechanical property and corrosion resistance of the CoCrW alloy can significantly be improved. To rapidly assess the property of the Cu-bearing CoCrW alloy, therefore, the CoCrW alloys with differing Cu content only were treated under the small condition from practical application point of view. Herein, the samples with different Cu contents were denominated as CoCrW-2Cu, CoCrW-3Cu and CoCrW-4Cu, respectively.

Table 1
The chemical composition of the CoCrW powders.

	Chemical Composition (mass %)							
Co	Cr	W	Si	Mn	N	Fe	Ni	Be
Bal.	28.00	9.00	1.50	≤0.01	≤0.002	≤0.05	/	/

2.2. Microstructural and mechanical property characterization

Specimens with the dimensions of 10 mm × 10 mm × 8 mm for microstructural observation were grinded with water proof emery paper up to 2000 grit under running water, and finally polished with diamond paste, then ultrasonically cleaned in acetone for 30 min. Microstructural observation was observed using Scanning Electron Microscope (SEM, SU-8010) on the surface etched by an etching solution consisting of 20% H_2O_2 and 80% HCl for 10 s at room temperature.). Electro-Probe Microanalyzer (EPMA, JXA-8230) was conducted to analyze the element distribution. Field Emission Transmission Electron Microscope (TEM, Tecnai F20) was used to observe the microstructures of the CoCrW based alloys. The energy-dispersive X-ray spectroscopy (EDS) was performed to identify the chemistry of precipitate The EBSD scanning data were collected and analyzed by using an recrystallized fraction and grain detect system (FEI Quanta 650 F). Tensile tests were performed on a universal testing machine (AG-X 100 kN, SHIMADZU, JAPAN) with a tensile rate of 2 mm/min at room temperature. Three specimens were tested for each group. Fracture surfaces were observed using SEM.

2.3. Electrochemical measurements

The electrochemical tests on the samples were carried out in the 0.9%NaCl solution at 37 °C solution using a Gamry Reference 600 + electrochemical station. The three-electrode electrochemical setup included a platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The surface of the samples served as working electrode with an area of 1.0 cm^2. Prior to polarization and Electrochemical impedance spectroscopy (EIS) tests, the open circuit potential (OCP) test was measured for 1 h from beginning of work electrode putting into the electrolyte. The potentiodynamic polarization curves were performed from potential range of −0.5 V to + 1.0 V versus OCP at a sweep rate of 1 mV/s. EIS was acquired at the OCP potentiostatically running over the frequency range of 100 kHz to 10 mHz with an amplitude of 10 mV. The corrosion current density, corrosion potential and corrosion rate from the experimental data was fitted with the ZSimpwin 3.20 software. The corrosion tests were repeated at least three times for data reproducibility.