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Mechanical, corrosion and antibacterial properties of Ti-13Nb-13Zr-based alloys with various Cu contents

Yixiang Yuan¹, Zunyu Ke¹, Lei Zhang², Yehua Jiang¹ and Zhengyuan He¹

¹ School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, 650093, People’s Republic of China
² Department of Mechanical & Industrial Engineering, Northeastern University, Boston, MA02115, United States of America

E-mail: hzy-810@163.com

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Abstract

The development of Ti-based alloys with antibacterial properties and a low elastic modulus has become a major focus in recent years in metallic biomaterials. In this paper, the influences of Cu content on the microstructure, mechanical properties, corrosion properties, and antibacterial properties of Ti-13Nb-13Zr-xCu alloys were systematically discussed. The results showed that the Ti-13Nb-13Zr-xCu alloys were mainly composed of β-Ti, α-Ti, and Cu-containing phases (Ti₅Cu, Cu₁₀Zr₇ and CuZr). Compared with the Ti-13Nb-13Zr alloy, the compressive strength and yield strength of the Ti-13Nb-13Zr-xCu alloys increased with increasing Cu content, but the elastic modulus decreased. The Ti-13Nb-13Zr-10Cu alloy exhibited high strength and low elastic modulus. The electrochemical experiments showed that the corrosion current density (Icorr) displayed a decreasing trend. The Ti-13Nb-13Zr-10Cu alloy had the lowest corrosion current (1.23 μA cm⁻²) and passivation current density (2.47 μA cm⁻²), indicating excellent corrosion resistance. Antibacterial tests showed that the antibacterial rate of the Ti-13Nb-13Zr-xCu alloy with 10 and 13% Cu content against S. aureus and E. coli were over 99.0%. Therefore, it could be deduced that the Ti-13Nb-13Zr-10Cu alloy with excellent mechanical and antibacterial properties had the potential for biomedical applications.

1. Introduction

Ti and Ti alloys are widely used in bone implants and dental restorations due to their excellent biocompatibility, mechanical properties and corrosion resistance [1]. However, Ti and Ti alloys, as biologically inert materials, lack sterilization ability. During the implantation process, following strict aseptic operations and the application of antibiotics, the infection rate after implantation is still as high as 20% [2]. This challenge has persisted for many years and urgently needs to be solved.

In recent years, the commonly used antibacterial elements have been Cu and Ag. Zhi Yang et al [3] used a sputter coating method to fix silver ions onto the surface of a Ti-6Al-4V alloy-based biomedical material and studied the effect of adding silver on the microstructure and antibacterial properties of the Ti-6Al-4V alloy. The results showed that the silver ions formed an antibacterial silver-containing coating on the surface of the Ti-6Al-4V alloy, which gave the Ti-6Al-4V alloy excellent antibacterial properties while maintaining high strength and excellent mechanical properties. Compared with silver, copper has lower toxicity, but copper is also one of the essential trace elements for the human body and exhibits good cell compatibility and antibacterial properties [4]. Organic Cu complexes not only are used in the treatment of arthritis and achieve good curative effects but also have anticancer, antiepileptic, and antibacterial properties. Cu is effective in treating wound infections and skin diseases [5] and has been widely used as an antibacterial agent in many studies [6]. Ungureanu et al [7] used anodic oxidation to deposit a layer of Cu on the surface of TiO₂ for biological modification. The results show that the Cu-modified TiO₂/Ti surface with good biocompatibility and blood compatibility can effectively prevent the proliferation of Escherichia coli, Staphylococcus aureus, Enterococci, Bacillus subtilis, and Pseudomonas aeruginosa. Although the above studies have significantly improved the antibacterial properties of titanium and
titanium alloys through surface modification, coating exfoliation may occur after a long period of wear and corrosion after implantation in the human body.

Compared with surface-modified materials, Cu-bearing Ti alloys have attracted interest due to their potential to promote antibacterial activity. The antibacterial activity of a biomaterial was enhanced by the addition of Cu [8]. A Ti-Cu alloy containing the Ti2Cu phase and Cu-rich phase, synthesized by powder metallurgy, displayed enhanced antibacterial properties and high elastic modulus, strength and hardness values [9]. Moreover, Cu-bearing Ti-6Al-4V and Ti-5Al-2.5Fe alloys with potentially toxic elements, such as Al and V, also exhibited excellent antibacterial properties but still had a high elastic modulus [10]. It is well known that a high elastic modulus and potentially toxic elements can easily cause stress shielding [11] and toxic reactions causing inflammation, respectively. A new Ti-13Nb-13Zr based alloy with Cu element by the arc melting method overcomes the problems of a high elastic modulus and potentially toxic elements [12]. However, the Cu content affects the form in which Cu is found in the microstructure and therefore the antibacterial activity. Although some Cu-bearing Ti alloys have been studied, no reports can be found in the literature about the effects of Cu content on the microstructure, mechanical properties, and antibacterial properties studied in detail.

2. Materials and methods

2.1. Preparation of Ti-13Nb-13Zr-xCu alloys

In this study, Ti-13Nb-13Zr-xCu (30 g each, x = 0, 4, 7, 10, 13 wt.%) alloys were prepared in an Ar-arc melting furnace (DHL-300, China). The raw materials used in this experiment were Ti (purity > 99.99%), Nb (purity > 99.99%), Zr (purity > 99.99%), and Cu (purity > 99.99%) metal ingots. The Ti-13Nb-13Zr-xCu alloys were treated by solid solution in a vacuum tube furnace at 950 °C for 3 h and then water quenching.

Before the experiment, the samples were ground with SiC grinding papers with 180, 400, 800 and 1200 grit sizes in turn under running water, polished by a polishing agent, cleaned in alcohol by ultrasonication for approximately 5 min, and finally dried at room temperature.

2.2. Microstructural analysis

Ti-13Nb-13Zr-xCu alloys were cut into 10 × 10 × 5 mm pieces with a wire cutting machine for the phase identification and microstructural analysis. These alloys were corroded by a self-configured corrosive liquid (containing 50 ml of distilled water, 3 ml of HNO3 and 1 ml of HF), and the phase composition and evolution of Ti-13Nb-13Zr-xCu alloys were analyzed by x-ray diffraction (XRD, Bruker D8 Advance, Germany). After that, field emission scanning electron microscopy (FE-SEM, FEI Nova Nano SEM 450, America), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) (JEOL, JEM-2100, Japan) were used to analyze the microstructure and elemental and phase composition distributions of the alloy.

2.3. Mechanical property tests

Samples with dimensions of 9.4 × 8 mm were used for the compression test. The test was carried out on an AG-X100 electronic universal testing machine (maximum load: 100 kN) at room temperature. The movement speed of the crosshead was 1 mm min⁻¹, and the maximum deformation was 50%. Four experiments were conducted for each alloy specimen, and the final experimental results were averaged over four trials. The yield strength (σ0.2) and compressive strength (σbc) of Ti-13Nb-13Zr-xCu alloys were calculated by the following formulas:

\[
\sigma_{0.2} = \frac{F_{0.2}}{S} \quad (1)
\]

\[
\sigma_{bc} = \frac{F_{bc}}{S} \quad (2)
\]

where \(F_{0.2}\) is the yield load of the experiment, \(F_{bc}\) is the maximum load of the experiment, and \(S\) is the cross section of the cylinder.

Samples with dimensions of 10 × 10 × 5 mm were prepared to test the elastic modulus. The supersonic velocity of the alloys were measured by an ultrasonic echo representation system (TECLAB, UMS-100, France) at room temperature. Then, combined with the density of the alloy (P), the shear modulus (G), bulk modulus (K) and elastic modulus (E) of the alloy were calculated by the following formulas:

\[
G = 2P \times V_f \quad (3)
\]

\[
K = P(2V_f - 8/3V_i) \quad (4)
\]
E = 9KG/(3K + G)  

2.4. Electrochemical behavior

Samples with dimensions of $10 \times 10 \times 5$ mm were prepared. In this study, the corrosion performance of Ti-13Nb-13Zr-xCu alloys in simulated body fluid (SBF) was tested by a CHI660D electrochemical workstation. A platinum electrode was used as the auxiliary electrode of the experiment, and a saturated calomel electrode was used as the reference electrode of the experiment. Finally, the open circuit potential, polarization curve and AC impedance were obtained (analyzed by Zview software). When obtaining the open circuit potential of the sample, the open circuit potential-time curve of the alloy was recorded, and each measurement time was 20000 s. When testing the polarization curve of the sample, the scanning range of the polarization voltage was set to $-1.5 \sim 2$ V, and the scan rate was set to 1 mV s$^{-1}$, from which electrochemical parameters such as the self-corrosion current density ($I_{\text{corr}}$), self-corrosion potential ($V_{\text{corr}}$) and passivation current density ($I_{\text{pass}}$) could be obtained. When testing the AC impedance of the sample, the amplitude was set to 10 mV, and the frequency range was 1 to 10$^5$ Hz. Each electrochemical experiment test was conducted in triplicate, and the final result was averaged. New SBF was replaced when each sample needed to be replaced after the test.

2.5. Antibacterial property evaluation

Samples with dimensions of $4 \times 3$ mm were prepared, and the CP-Ti sample was prepared in the same way. First, inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the amount of Cu ions released after 7 days. In the antibacterial experiment, the antibacterial activity of Ti-13Nb-13Zr-xCu alloys against E. coli (ATCC 25922, Shanghai Esaybiocity) and S. aureus (ATCC 25923, Shanghai Esaybiocity) was verified by the plate counting method. E. coli and S. aureus were cultivated at 37° ± 1°C in the bacterial suspension (NB) to a concentration of $10^6$ CFU ml$^{-1}$ and then diluted 10-fold by SBF solution to a concentration of $10^4$ CFU ml$^{-1}$ (named the bacterial suspension) [9]. Before the antibacterial experiments, all glassware and samples were sterilized with UV irradiation for 60 min. Antibacterial properties were assessed according to the National Standard of China GB/T 2591 (JIS Z 2801-2000, ASTM G21-96, NEQ) [2]. Nutrient agar was spread onto a Petri dish as a negative sample, and the CP-Ti sample was used as a control sample.

3. Results and discussion

3.1. Microstructures

XRD was used to analyze the phase constituents of Ti-13Nb-13Zr-xCu alloys. From figure 1, the Ti-13Nb-13Zr-xCu alloys were mainly composed of the $\beta$-Ti, $\alpha$-Ti and Cu-containing phase (Ti$_2$Cu, Cu$_{10}$Zr$_7$ and CuZr). With the increase of Cu content, the peak of $\beta$ phase increased in intensity because Cu is a $\beta$-stabilizing element, while the diffraction peak intensity of the $\alpha$ phase was almost unchanged [13]. The Cu-containing phase increased with the increase of Cu content, which was in agreement with a previous study [14]. The changes in the Cu-containing phase were caused by a eutectic transformation between Cu and Zr at approximately 980 °C to form the Cu$_{10}$Zr$_7$ and CuZr phases [15], and by a eutectoid transformation between Ti and Cu at 790 °C to form the Ti$_2$Cu phase.

SEM micrographs of Ti-13Nb-13Zr alloys with different Cu contents are shown in figure 2. The alloy without Cu is mainly gray in the figure 2(a). Combined with the XRD results, it was inferred that the Ti-13Nb-13Zr alloy mainly consisted of the $\beta$ phase and the acicular $\alpha$ phase. With the addition of Cu, there were obvious reticular phases at the grain boundaries, as shown in figure 2(b). With increasing Cu content, the precipitated phases gradually increased, displaying more coarse reticular structure, especially for the alloy with 10 and 13% Cu, as shown in figures 2(d) and (e). The changes in the microstructure would affect the mechanical properties of the alloys. Furthermore, the EDS analysis was implemented to preliminarily verify the Cu-containing phase distribution in the figure 2(f).

To further analyze the element distribution of the alloy, the EDS mapping was carried out for Ti-13Nb-13Zr-10Cu alloy. The results were shown in figure 3. The morphology of scanning area is exhibited in figure 3(a). The element overlay graph is displayed in figure 3(b). The alloy matrix was mainly composed of Ti element (figure 3(b)). In addition, a large amount of Nb elements and little Zr element were also observed in matrix (figures 3(d) and (e)). Nevertheless, a generous amount of Zr element accumulated around the reticular structure (figure 3(e)). Combined with the analysis of figures (e) and (f), there was a clear clustering Cu element in the reticular structure, which was referred to Cu-containing phases (Ti$_2$Cu, Cu$_{10}$Zr$_7$ and CuZr). Based phase diagram [17], the CuZr and Cu$_{10}$Zr$_7$ phases were formed due to eutectic Transformation, and the Ti$_2$Cu phase due to eutectoid transformation. Moreover, the grain boundaries as effective nucleation particles would facilitate the formation of phases, and it therefore caused the precipitates growth as so to form Cu-containing phase. Combined with XRD analysis, these Cu-containing phases definitely presented in the alloy.
To verify the phase composition of the alloy, a high-resolution image of the Ti-13Nb-13Zr-10Cu alloy was taken by TEM. As shown in figure 4(a), a sample was obtained by removing the region of reticulated structure in the alloy to observe its appearance. Figure 4(b) shows a high-resolution enlarged images of the reticular structure and the diffraction pattern in the selected area. There were a large number of precipitated particles in the reticular structure. The diffraction patterns, appeared polycrystalline diffraction ring, were confirmed as the CuZr phase and the Ti$_2$Cu phase by electron diffraction pattern calibration. This result further proved the phase analysis of XRD, and was in line with the EDS results.

3.2. Mechanical properties

Figure 5 shows the changes in the yield strength, compressive strength and elastic modulus of Ti-13Nb-13Zr-xCu alloys with varying Cu content. With increasing Cu content, the compressive strength and yield strength of the alloys generally increased. The yield strength of the alloy with Cu contents of 4, 7, 10 and 13% increased by 5.2, 1.0, 6.2, and 18.5%, respectively, compared to that of the Ti-13Nb-13Zr alloy, which was higher than the compressive strength of the Ti-12Mo-5Zr alloy (1028 MPa) [18]. When the Cu content was 7%, this decrease in the yield strength can be attributed to the decrease in numbers of reticulated structure and a significant increase of the scale of the reticulated structure.
in the proportion of $\beta$-Ti [19]. However, Cu addition promoted the formation of CuZr, Cu10Zr7, Ti2Cu, etc., which achieved the effect of precipitation strengthening to improve the compressive strength of the alloy. After heat treatment, the Cu-containing phases precipitated or partial elements dissolved in matrix so as to enhance the strength of the Ti-13Nb-13Zr-xCu alloys. Combined with the analytical results shown in figure 2, the content of reticular phases increased with increasing Cu content. The reticular phases, however, could hinder brittle fracture significantly and improve the yield strength of the Ti-13Nb-13Zr-xCu alloys.

As shown in figure 5(b), when Cu was added into the Ti-13Nb-13Zr alloy. When the Cu contents were 4, 7, 10 and 13%, the elastic moduli were 64, 59, 66 and 76 GPa, respectively. These elastic moduli of the Ti-13Nb-13Zr-xCu alloys were significantly lower than those of the Ti-13Nb-13Zr alloy (79 GPa), the CP-Ti (120 GPa) [20], the Ti-7Cu alloy (107 GPa) [21], and the Ti-10Ag alloy (121 GPa) [22]. When the Cu content was less than or equal to 10%, the elastic moduli of the alloys decreased significantly. Because Cu was a stable element for the $\beta$ phase. The theoretically calculated elastic modulus of the body-centered cubic $\beta$ phase was only 32 GPa [23], resulting in a decrease in the elastic moduli of Ti-13Nb-13Zr-xCu alloys. When the Cu content was greater than 10%, the increase in the content of the Ti2Cu phase led to an increase in the elastic modulus of the alloys, which exceeded the decrease in the elastic modulus provided by the $\beta$ phase. It is worth noting that, among the tested
alloys, the Ti-13Nb-13Zr-10Cu alloy not only had a good elastic modulus but also had high strength that could satisfy the strength requirements of human bone (110 MPa) [24].

### 3.3. Corrosion resistance

Figure 6(a) shows that the change in the open circuit potential of Ti-13Nb-13Zr-xCu alloys with different Cu contents was similar. The potential of the alloy approached zero from a negative number over time until it gradually stabilized. These alloys formed a stable passivation film in SBF and had a tendency to resist corrosion. However, if too much Cu was added, the passivation film on the surface of the alloy was destroyed. This was the reason for the potential fluctuation of the Ti-13Nb-13Zr-13Cu alloy in the later stage.

The polarization curve in figure 6(b) shows that with increasing Cu content, the corrosion potential of the alloy generally increased, and the corrosion current first decreased and then increased. This result indicated that the addition of Cu protected the alloy against corrosion. At the same time, the rate of corrosion was also reduced. Ti-13Nb-13Zr-10Cu alloy corrosion current had a minimum value (1.23 μA cm$^{-2}$), and the potential also had a high value ($-0.52$ V), which exhibited strong corrosion resistance. The passivation phenomenon is related to the passivation current density. The smaller the passivation current density is, the easier it changes from the active zone to the passivation zone. From table 1, the passivation current density of Ti-13Nb-13Zr-10Cu alloy was the smallest, and it was easier to form passivation film, thereby improving the corrosion resistance. Compared with the α phase, the β and Ti$_2$Cu phases have better corrosion resistance. This was why the corrosion resistance of the alloy was improved when a small amount of Cu was added. When the Cu content was too high, the increase in the reticular structure led to an inability to eliminate the galvanic potential difference between the α phase and Ti$_2$Cu, resulting in enhanced galvanic corrosion between different phases [25]. Also, an uneven oxide film formed by Ti-13Nb-13Zr-13Cu alloy led to poor overall corrosion resistance [26]. It was also verified that the Ti-13Nb-13Zr-13Cu alloy open circuit potential was unstable in the later stage, which led to a poor passivation film and corrosion.

The diameter of the Ti-13Nb-13Zr-xCu alloys in the Nyquist plot (figure 6(c)) first increased and then decreased with increasing Cu content, and the corrosion resistance of the alloy also followed the same law. It was proven that the law obtained by the above polarization curve was correct. The Bode plot (figure 6(d)) shows that in the low-frequency region showed an overall downward trend. In the intermediate frequency region, a larger...
diameter and a time constant appeared. The phase angle of the alloy was smaller than the potential \(90^\circ\) of the pure capacitor, which showed the nonideal capacitor characteristics of the Ti-13Nb-13Zr-xCu alloys passivation film. In the high-frequency region, the phase angle gradually approached 0, which reflected the characteristics of artificial body fluids that were close to pure resistance.

According to the study of Kamimura et al [27], when titanium and titanium alloys underwent galvanic corrosion, a double-layer passivation film was easily formed on the surface of the alloy. Table 2 shows that the internal analog resistance (\(R_b\)) value of the alloy was much smaller than the external analog resistance (\(R_p\)) value. It can be inferred that the external dense layer of the alloy had strong corrosion resistance. According to the \(R_p\) value of the alloy at different Cu contents in table 2, the corrosion resistance of the alloy first increased and then decreased with increasing Cu content. When the Cu content was 7%, the resistance \(R_b\) of the Ti-13Nb-13Zr-xCu alloys passivation film was significantly smaller than that of the pure capacitor. This indicates that the Ti-13Nb-13Zr-xCu alloys have excellent corrosion resistance.

### Table 1. Dynamic potential polarization curve parameters of the Ti-13Nb-13Zr-xCu alloys.

| Alloy composition | \(E_{corr} (V)\) | \(I_{corr} (\mu A cm^{-2})\) | \(I_{pass} (\mu A cm^{-2})\) |
|-------------------|-----------------|-------------------|-------------------|
| Ti-13Nb-13Zr      | -0.97           | 4.06              | 3.50              |
| Ti-13Nb-13Z-4Cu    | -0.56           | 3.89              | 3.93              |
| Ti-13Nb-13Z-7Cu    | -0.75           | 2.50              | 9.33              |
| Ti-13Nb-13Z-10Cu   | -0.52           | 1.23              | 2.47              |
| Ti-13Nb-13Z-13Cu   | -0.40           | 3.58              | 8.77              |

### Table 2. Representative fitting parameters obtained from the EIS value of Ti-13Nb-13Zr-xCu alloys.

| Alloys          | \(R_s (\Omega cm^{-2})\) | \(CPEp (\mu F cm^{-2})\) | \(n_1\) | \(R_p (\Omega cm^{-2})\) | \(CPEb (\mu F cm^{-2})\) | \(n_2\) | \(R_b (K\Omega cm^{-2})\) |
|-----------------|--------------------------|--------------------------|--------|--------------------------|--------------------------|--------|--------------------------|
| Ti-13Nb-13Zr    | 6.78                     | 10.07                    | 0.91   | 808.2                    | 68.11                    | 0.65   | 141.06                   |
| Ti-13Nb-13Z-4Cu | 6.53                     | 6.95                     | 0.83   | 836.5                    | 51.03                    | 0.68   | 172.35                   |
| Ti-13Nb-13Z-7Cu | 5.90                     | 6.02                     | 0.90   | 850.6                    | 47.56                    | 0.59   | 233.75                   |
| Ti-13Nb-13Z-10Cu| 6.89                     | 7.16                     | 0.84   | 847.8                    | 52.35                    | 0.72   | 181.15                   |
| Ti-13Nb-13Z-13Cu| 6.05                     | 10.21                    | 0.87   | 788.3                    | 54.26                    | 0.72   | 122.31                   |
7Cu alloy increased to 233.75 KΩ.cm$^{-2}$, and the CPEb value decreased to 47.56 μF.cm$^{-2}$. As the Cu content continued to increase, the Rb value gradually decreased, and the CPEb value gradually increased. The Rp and CPEp values of Ti-13Nb-13Zr-xCu alloys with different Cu contents displayed little difference in the table2, which indicated that the Cu content had little effect on the corrosion resistance of the external passivation film of the alloy.

From figure 7(a), we can see that after the alloy was corroded in artificial body fluid, the main constituent elements on the alloy surface contained C, Ti, Cu, and a small amount of P and O. The presence of C and O could be due to contamination and oxidation of the alloy surface, respectively. The figure shows that as the amount of Cu gradually increased, the CuLMM and Cu2p peaks gradually increased in intensity. The main reason for this phenomenon was the addition of Cu to the alloy, which led to the gradual deposition of a large amount of Cu on the surface. The C1s, Ti2s and P2p peaks gradually increased in intensity with increasing Cu content. This observation was mainly due to a small amount of CO$_2$ and PO$_4^{3-}$ ions in the SBF [28]. And a small amount of C can also promote elemental deposition on the alloy surface, which was similar to the results of Y W Gu et al [29].

After the Ti-13Nb-13Zr-10Cu alloy was corroded in the SBF, the matrix elements on the surface of the alloy reacted with the ions of solution. Combining the binding energy analysis of Ti, Cu and Nb in figures 7(b)–(d) yielded that a dense composite oxide film consisting of TiO$_2$, Ti$_2$O$_3$, Cu$_2$O, CuO and Nb$_2$O$_5$ oxides was formed on the surface of Ti-13Nb-13Zr-10Cu alloy. A study [30] indicated that Nb$_2$O$_5$ can improve the thermodynamic stability of the passivation film formed by TiO$_2$ and Ti$_2$O$_3$. Therefore, the passivation film of the alloy was not prone to chemical decomposition, and the corrosion resistance of the Ti-13Nb-13Zr-10Cu alloy was more stable.

3.4. Antibacterial properties

Figure 8 shows the survival numbers of E. coli and S. aureus colonies at different Cu contents. The alloy without Cu content had a large number of colonies on the surface of the CP-Ti and Ti-13Nb-13Zr alloy, indicating no antibacterial properties. After adding Cu, the number of colonies of S. aureus and E. coli on the surface of Ti-13Nb-13Zr-xCu alloys were significantly reduced. The calculated antibacterial rate ($R(E. coli)$) values for 4, 7, 10, 13% Cu were 67.8, 90.4, 99.1, and 99.4%, respectively. When the antibacterial rate of 90 ~ 99% and >99% indicated antibacterial property and strong antibacterial property, respectively [31]. The Ti-13Nb-13Zr-7Cu alloy has an antibacterial effect, but the Ti-13Nb-13Zr-10Cu alloy and Ti-13Nb-13Zr-13Cu alloy have strong antibacterial effects. As the control group, Ti and the Ti-13Nb-13Zr alloy had no antibacterial properties. It can
be concluded that the release of Cu ions was the main reason for the observed antibacterial properties of the alloys. Therefore, Cu ion dissolution experiment was executed to evaluate the amount of Cu ions after 7 days immersion. The released Cu concentration was 50 μg l⁻¹ when the alloy Cu content was 10%, but the released Cu concentration was 86 μg l⁻¹ when the alloy Cu content was 13%. Therefore, the amount of ion released would affect the antibacterial properties of Ti-13Nb-13Zr-xCu alloys.

Figure 9 shows a diagram of the antibacterial mechanism of Cu ions. Cu ions were mainly precipitated from Ti₂Cu. Cu ions could diffuse into the SBF with the ion concentration gradient acting as a driving force. The Cu ions gradually would contact with the bacterial surface, destroying the integrity of the bacterial cell membrane and allowing proteins and some sugars in the bacteria to penetrate the cell membrane. Then, Cu ions in the interior of the bacterial cell reacted with the remaining proteins inside to produce reactive oxygen species and inhibit bacterial gene replication, eventually killing bacteria, in line with the conclusions of Muhammad Ibrahim [33] and WX Tian [34].
4. Conclusions

(1) The phase composition of Ti-13Nb-13Zr-xCu alloys varied with the Cu content. The alloys were mainly composed of $\beta$-Ti, $\alpha$-Ti, Ti$_2$Cu, CuZr and Cu$_{10}$Zr$_7$ phases. The reticular structure became denser and gradually connected with each other with increasing Cu content.

(2) The yield strength and compressive strength of the alloy generally increased due to the increase of Cu content. When the content was 4 ~ 10%, the elastic modulus of the alloy was low, which was beneficial to reduce the 'stress shielding' phenomenon. Therefore, the Ti-13Nb-13Zr-10Cu alloy had high compressive strength of 1360 MPa and low elastic modulus of 66 GPa.

(3) In the electrochemical corrosion of Ti-13Nb-13Zr-xCu alloys, Ti-13Nb-13Zr-10Cu alloy showed corrosion resistance, and surface analysis showed that Ti-13Nb-13Zr-10Cu alloy, a dense composite oxide film composed of TiO$_2$, Ti$_2$O$_3$, Cu$_2$O, CuO and Nb$_2$O$_5$ oxides, formed on the surface of the alloy.

(4) The precipitated Cu ions have strong antibacterial properties. When the Cu contents were 10 and 13% the antibacterial rates against S. aureus and E. coli were 99.0 and 99.1%, respectively, showing excellent antibacterial properties.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Zhengyuan He ORCID: https://orcid.org/0000-0001-7113-2930

References

[1] Shenglin M et al 2014 Antibacterial effects and biocompatibility of titanium surfaces with graded silver incorporation in titania nanotubes J. Biomaterials 35 4235–65
[2] Zhang E, Wang X, Chen M and Hou B 2016 Effect of the existing form of Cu element on the mechanical properties, bio-corrosion and antibacterial properties of Ti-Cu alloys for biomedical application Mater. Eng. C. Mater. Biol. Appl. 69 1210–21
[3] Du J-K et al 2017 Antibacterial properties and corrosion resistance of the newly developed biomaterial, Ti-12Nb-1Ag alloy Open Access Metallurgy Journal 7 506
[4] Liu R et al 2018 In vitro and in vivo studies of anti-bacterial copper-bearing titanium alloy for dental application Dent. Mater. 34 1112–26
[5] Michels H T, Noyce J O and Keevil C W 2009 Effects of temperature and humidity on the efficacy of methicillin-resistant Staphylococcus aureus challenged antimicrobial materials containing silver and copper Lett. Appl. Microbiol. 49 191–5
[6] Ibrahim M et al 2011 Copper as an antibacterial agent for human pathogenic multidrug resistant Burkholderia cepacia complex bacteria Journal of Bioence & Bioengineering 112 570–6
[7] Ungureanu C, Dumitriu C, Popescu S, Enculescu M and Pirvu C 2016 Enhancing antimicrobial activity of TiO$_2$/Ti by torularhodin bioinspired surface modification Bioelectrochemistry 107 14–24
[8] Yamanoglu R, Efendi E, Kolayli F, Uzuner H and Daoud I 2018 Production and mechanical properties of Ti–5Al–2.5Fe–x Cu alloys for biomedical applications Biomol. Mater. 13 025013
[9] Zhang E et al 2013 A new antibacterial titanium–copper sintered alloy: preparation and antibacterial property Materials Science & Engineering C Materials for Biological Applications 33 4280–7
[10] Peng C et al 2019 Optimization of annealing treatment and comprehensive properties of Cu–containing Ti6Al4V–xCu alloys Journal of Materials Science & Technology 35 2121–31
[11] Niinomi M 2008 Mechanical biocompatibilities of titanium alloys for biomedical applications J. Mech. Behav. Biomed. Mater. 1 30–42
[12] Ke H, Yi C, Zhang L, He Z, Tan J and Jiang Y 2019 Characterization of a new Ti-13Nb-13Zr-10Cu alloy with enhanced antibacterial activity for biomedical applications Mater. Lett. 253 335–8
[13] Kikuchi M and Niinomi M 2008 Mechanical biocompatibilities of titanium alloys for biomedical applications Intermetallic Compounds - Principles and Practice ed H Westbrook and R L Fleischer 3 (United States of America: Wiley) 32 681–705
[14] Schwarz R B 2002 Bulk Amorphous Alloys Intermetallic Compounds - Principles and Practice ed H Westbrook and R L Fleischer 3 (United States of America: Wiley) 32 681–705
[15] Schwarz R B 2002 Bulk Amorphous Alloys Intermetallic Compounds - Principles and Practice ed H Westbrook and R L Fleischer 3 (United States of America: Wiley) 32 681–705
[16] Yao X, Sun Q Y, Xiao L and Sun J 2009 Effect of Ti2Cu precipitates on mechanical behavior of Ti–2.3Cu alloy subjected to different heat treatments J. Alloys Compd. 484 196–202
[17] Yi C, Yuan Y, Zhang L, Jiang Y and He Z 2021 Antibacterial Ti-35Nb-7Zr-xCu alloy with excellent mechanical properties generated with a spark plasma sintering method for biological applications J. Alloys Compd. 879 160473

[18] Zhao C, Zhang X and Cao P 2011 Mechanical and electrochemical characterization of Ti–12Mo–5Zr alloy for biomedical application J. Alloys Compd. 509 8235–8

[19] Zhao X, Niinomi M, Nakai M, Ishimoto T and Nakano T 2011 Development of high Zr-containing Ti-based alloys with low Young’s modulus for use in removable implants Mater. Sci. Eng. C 31 1436–44

[20] Milner J L, Abu-Farha F, Bunget C, Kurfess T and Hammond V H 2013 Grain refinement and mechanical properties of CP-Ti processed by warm accumulative roll bonding Mater. Sci. Eng. A 561 109–17

[21] Hayama A O F, Andrade P N, Cremasco A, Contieri R J, Afonso C R M and Caram R 2014 Effects of composition and heat treatment on the mechanical behavior of Ti–Cu alloys Mater. Des. 55 1006–13

[22] Kikuchi M, Takahashi M and Okuno O 2008 Machinability of experimental Ti-Ag alloys Dent Mater J 27 216–20

[23] Ashton P J et al 2017 The effect of the beta phase on the micromechanical response of dual-phase titanium alloys Int. J. Fatigue 100 377–87

[24] Currey J D 1996 Biocomposites: micromechanics of biological hard tissues Curr. Opin. Solid State Mater. Sci. 1 440–5

[25] Chen J-R and Tsai W-T 2011 In situ corrosion monitoring of Ti–6Al–4V alloy in H2SO4/HCl mixed solution using electrochemical AFM Electrochim. Acta 56 1746–51

[26] Osorio W R, Cremasco A, Andrade P N, Garcia A and Caram R 2010 Electrochemical behavior of centrifuged cast and heat treated Ti–Cu alloys for medical applications Electrochim. Acta 55 759–70

[27] Kamimura T and Stratmann M 2001 The influence of chromium on the atmospheric corrosion of steel Corros. Sci. 43 429–47

[28] Bohner M and Lemaitre J 2009 Can bioactivity be tested in vitro with SBF solution? Biomaterials 30 2175–9

[29] Gu Y W, Khor K A, Pan D and Cheang P 2004 Activity of plasma sprayed yttria stabilized zirconia reinforced hydroxyapatite/Ti–6Al–4V composite coatings in simulated body fluid Biomaterials 25 3177–85

[30] Yu S, Brodrick C, Ryan M and Scully J 1999 Effects of Nb and Zr alloying additions on the activation behavior of Ti in hydrochloric acid J. Electrochem. Soc. 146 6429–38

[31] Liu J et al 2014 Effect of Cu content on the antibacterial activity of titanium–copper sintered alloys Mater. Sci. Eng. C 35 392–400

[32] Takada Y and Okuno O 2005 Corrosion characteristics of alpha-Ti and Ti2Cu composing Ti–Cu alloys Dent Mater J 24 610–6

[33] Ibrahim M et al 2011 Copper as an antibacterial agent for human pathogenic multidrug resistant Burkholderia cepacia complex bacteria J. Biosci. Biobeng. 112 570–6

[34] Tian W-X et al 2012 Copper as an antimicrobial agent against opportunist pathogenic and multidrug resistant Enteroabacter bacteria Journal of Microbiology 50 586–95