Ti-Cu-Ni(Fe,Cr,Co)-Sn-Ta(Nb) Alloys with Potential for Biomedical Applications

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A group of multicomponent Ti-Cu-Ni(Fe, Co)-Sn-Ta(Nb) alloys were investigated in terms of the microstructure and the mechanical properties. A composite microstructure with a micrometer-sized dendritic bcc-β-Ti(RM) (RM = Nb, Ta) phase dispersed in a matrix was obtained. The TEM observation on the Ti$_{60}$Cu$_{14}$Ni$_{12}$Sn$_4$Ta$_{10}$ alloy shows that the matrix is composed of a nano/ultrafine bcc-phase with the size of 50–100 nm which is isolated by a tetragonal-phase. The designed Ti alloy exhibit very high yield strength (1050–1472 MPa) and relative lower Young’s modulus (67–105 GPa). Such combined properties, not easily achievable in previous Ti alloys, make these new designed Ti alloys promising candidates as biomedical materials.

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1. Introduction

The artificial materials used in orthopedic surgery should not only avoid short-term rejection and infection, but also provide long-term biocompatibility (no toxicity and excellent resistance to corrosion in the human body environment) and long-term material limitations (high-wear resistance, high fatigue strength and lower modulus to minimize bone resorption), so as to meet the demands of longer human life and of implantation in younger patients. As a biomedical material, Ti-base alloys have been paid more attention recent years due to their excellent biocompatibility, low density, excellent corrosion resistance and good balance of mechanical property. By either modifying the available Ti-base alloys or exploring new compositions one can achieve high performance of the Ti-base alloy in terms of biomedical and mechanical properties. However, some problems in Ti-base alloys are very difficult to solve. For example, the Young’s modulus of the available Ti-base alloys is very high as compared with that of bone. The low rigidity of the implants is considered effective for promoting bone healing and remodeling because they should imitate the elastic modulus of cortical bone. When attempts were made to reduce the Young’s modulus, the strength was also severely degraded. For example, Ti-35Nb-7Zr-5Ta exhibits a very low Young’s modulus of 55 GPa, but also very low yield strength of 530 MPa. Can we reduce the Young’s modulus of Ti-alloys, while maintaining their high strength so as to meet the demands of high quality Ti-alloys for orthopedic applications?

It was found that some multicomponent Ti-base alloys can be directly cast into nano/ultrafine-structured composites. When the grain sizes are reduced down to nanoscale range, the physical, the chemical and the mechanical properties of the alloys will significantly change. The well-known Hall-Petch relationship has predicted a great increase in strength with the grain refinement. This gain has already been obtained in many metallic materials. However, in most cases, these nanomaterials have low ductility (a reverse Hall-Petch relationship) which seriously restricts the application of the nanostructured materials. Recently, some progress has been made in enhancing the ductility of the nanostructured materials by introducing the micrometer-sized ductile phase into the nanostructure. This encouraged us to explore new enhanced nanostructured Ti-base alloys and their applications.

When the grain size is in the nanoscale regime, the elastic modulus of some nanomaterials goes down with decreasing the grain size. This behavior is completely different from or opposite to that of normal grain-sized materials. Though the reasons for this are unknown, the novel elastic behavior just meets the demand of biomedical application. This is worthy of further investigation on both science and technology. In this paper, we present a group of Ti-base alloys with β-phases enhanced nano/ultrafine-structure which exhibit high strength and large elastic strain. Some of them exhibit lower elastic modulus. These alloys are very promising candidates for the biomedical applications. Considering the bio-toxicity of Ni in the alloys, we try to replace Ni by Cr, Fe and Co. (The data of the biocompatibility of Cu or Ti-Cu is lacking so far. This needs further investigation.) The new alloys show very similar nano/ultrafine-structures with the Ni-contained alloy, and exhibit a good combination of mechanical properties.

2. Experimental Procedures

The compositions of Ti$_{60}$Cu$_{14}$Ni(Fe, Cr, Co)$_{12}$Sn$_4$Ta$_{10}$ (atomic percent) were selected based on the principles for the design of bulk nanostructured composites. The refractory metals, Nb and Ta, are used to form the micrometer-sized β-phase which contributes to the ductility of the materials. Cu, Ni, Fe, Cr and Co can improve to form the nano/ultrafine-structure which contributes to the high strength of the materials. Sn can improve the formation of the β-phase, as well as help to form nano/ultrafine microstructure. The alloys were prepared by arc melting the mixture of the pure elements (commercial purity) on a water-cooled copper hearth at argon atmosphere. About 60 mm × 15 mm × 12 mm ingots were obtained. The microstructures and the phases of the prepared ingots were characterized by using a...
JEOL-JSM5400 scanning electron microscope (SEM) coupled with energy-dispersive X-ray analysis (EDX) and a JEM-2010 transmission electron microscope (TEM) equipped with a UHR pole-piece at an accelerating voltage of 200 kV, as well as by using a JEOL JDX-3500 X-ray diffraction (XRD) facility with CuKα radiation. The mechanical behavior of the alloys was evaluated by compressive test, because tensile test is very sensitive to the cast defects. In present stage of the new complicated nano/ultrafine-structured alloys, the tensile behavior of the alloys may be seriously masked by the cast defects. Alternatively, compressive properties are not so strongly influenced by the cast defects and may give information about the yield strength and intrinsic ductility of the alloys. The samples were machined into $3 \times 6$ mm for compressive test. The compressive deformation behavior and the mechanical properties were investigated by using a Shimadzu AG-50kN testing machine at a strain rate of $1 \times 10^{-4}$ s$^{-1}$ at room temperature. In order to avoid the test-system errors, the tested stress-strain curves were calibrated by subtracting the strain of the test-system, which was evaluated by going through the compressive test process with the same strain rate without the test sample. The values of Young’s modulus and elastic strain were determined directly from the calibrated stress-strain curves. The slope of the curve at the initial elastic stage is defined as Young’s modulus. The yield point was determined at 0.2% plastic strain. The strain at the yield point corresponds to elastic strain and the strain at break point corresponds to total strain.

### 3. Results and Discussion

Figure 1(a) shows the backscatter SEM micrograph of the as-prepared Ni and Ta-contained alloy. The as-prepared alloy has a composite microstructure with a micrometer-sized dendritic $\beta$-Ti(RM) ($RM = Ta$) solid solution phase dispersed in a nano/ultrafine-structured matrix. The bright dendritic phase is the $bcc-\beta$-Ti(RM) solid solution which is confirmed by both XRD indexing (Fig. 2(a)) and the selected-area diffraction analysis (Figs. 3(a) and (b) insets). The matrix (dark phase in Fig. 1(a)) contains a complicated nano/ultrafine two-phase structure which includes a $bcc$-phase (as shown in Fig. 3) and a tetragonal-$y$-phase (Fig. 2(a)). For Cr and Nb-contained alloy, although the image (Fig. 1(b)) is very faint compared with the Ni and Ta-contained alloy, a developed dendritic morphology can be seen from the image. The volume fraction of the dendritic phase (about 80 vol%) is much larger than that of the Ni and Ta-contained alloy (about 35 vol%). The XRD analysis confirms that the alloy contains the $bcc-\beta$-phase (as shown in Fig. 3) and a tetragonal-$y$-phase (Fig. 2(a)). For Fe and Nb-contained alloy, a dendritic phase (bright phase in Fig. 1(c)) dispersed in a matrix (gray phase in Fig. 2(b)). For Fe and Nb-contained alloy, a dendritic phase (bright phase in Fig. 1(c)) dispersed in a matrix (gray phase in Fig. 2(b)). For Cr and Nb-contained alloy, a developed dendritic morphology can be seen from the image. The volume fraction of the dendritic phase (about 80 vol%) is much larger than that of the Ni and Ta-contained alloy (about 35 vol%). The XRD analysis confirms that the alloy contains the $\beta$-Ti(RM) phase (strong diffraction peaks in Fig. 2(b)). The $\alpha$-Ti(M) ($M = Cr, Cu$) is also indexed in the XRD pattern (Fig. 2(b)). For Fe and Nb-contained alloy, a dendritic phase (bright phase in Fig. 1(c)) dispersed in a matrix (gray phase in Fig. 1(c)) can be clearly distinguished. The XRD analysis indicates that the alloy contains the $\beta$-Ti(RM) phase and the $\alpha$-Ti(M) ($M = Fe, Cu$) phase (Fig. 2(c)). The volume fraction of the dendritic phase (about 40 vol%) is close to that of the Ni and Ta-contained alloy. For Co and Nb-contained alloy, a similar microstructure is obtained (Fig. 1(d)). The XRD analysis also confirms the $\beta$-Ti(RM) phase and the $\alpha$-Ti(M) ($M = Co, Cu$) phase (Fig. 2(d)). The volume fraction of the
dendritic phase (about 35 vol%) is very similar to that of the Ni and Ta-contained alloy.

Figure 3(a) is the bright-field TEM image of the as-arc melted Ti$_60$Cu$_{14}$Ni$_{12}$Sn$_4$Ta$_{10}$ alloy which shows the dendritic bcc-structured precipitate with sub-grain-boundaries. The inset in Fig. 3(a) is the select-area diffraction pattern (SADP) taken along the [011] zone axis of the dendritic phase corroborating its bcc-$\beta$-Ti(RM) structure. The HRTEM image of the dendritic phase (Fig. 3(b)) shows the detailed bcc-structure. The inset shows the SADP taken along the [100] zone axis of the bcc-phase. Figures 3(c) and (d) are bright-field TEM images of the matrix which show a two-phase structure marked as phase 1 and phase 2. The phase 1 is about 30–100 nm in size which is isolated by phase 2. The phase 1 is determined to be a bcc-structure by SADP analysis (inset in Fig. 3(d)), while the phase 2 is a tetragonal-structure. For other three alloys, the matrix was also confirmed to be a complicated ultrafine structure.

In the Ti-TM-Sn-RM multicomponent alloys, the RM can infinitely be dissolved into Ti to form a bcc-$\beta$-type solid solution in the temperature range of 1500–2200 K. Both RM and Sn are very good bcc-$\beta$-phase formers which result in the precipitation of the micrometer-sized dendritic $\beta$-Ti(RM) phase when cooling from the liquid. The residual liquid alloy is composed of Ti, TM and some remaining RM and Sn. The appropriate combination of these elements is close to the eutectic composition and satisfies the conditions

![Fig. 3 Microstructures of as-arc melted Ti$_60$Cu$_{14}$Ni$_{12}$Sn$_4$Ta$_{10}$ alloy. (a) Bright-field TEM image showing dendritic precipitate with sub-grain-boundaries. The inset is SADP taken along [011] zone axis of dendritic phase showing its bcc-$\beta$-Ti(RM) structure. (b) HRTEM image of the dendritic phase. The inset shows the SADP taken along [100] zone axis of bcc-phase. (c) Bright-field TEM image of matrix showing two-phase structure. (d) Detailed microstructure of matrix. The inset is the SADP taken along [111] zone axis of phase 1.](image)
of forming a highly dense random packed liquid structure, which can achieve a liquid→nano/ultraline-structure transformation in the continual cooling. In previous study, it is found that Nb and Ta play a same role in the alloys. Both can form an appropriate size, morphology and homogeneous distribution of the ductile dendrites in a nanostructured matrix in Ti-base multicomponent alloys. In this study, after the Ni was replaced by Cr, Fe and Co, the size of the dendritic \( \beta \)-Ti(RM) phase does not change, but the morphologies of the dendritic phase seems different (compared Figs. 1(a)–(d)), indicating that the significant effect of different TM on the formation of the primary dendritic \( \beta \)-Ti(RM) phase.

Due to the very fine microstructure of the matrix, the present alloys exhibit very high strength and relative low Young’s modulus (Table 1). Figure 4 shows the stress-strain curves of the as-arc melted Ti\(_{60}\)Cu\(_{14}\)(TM)\(_2\)Sn\(_4\)(RM)\(_{10}\) alloys. The Fe and Nb-contained, and Cr and Nb-contained alloys exhibit the yield strength of 1472 and 1370 MPa, and the Young’s moduli of 101 and 105 GPa, respectively. The Young’s moduli are comparable to that of the pure Ti, but the yield strength can reach about 1050 MPa, showing a very good balance of the strength and the elastic property which are superable to most of the available \( \beta \)-Ti alloys. The high strength may improve the reliability of the material against permanent shape change, which would benefit the patient when these materials are considered for implant or dental uses. The relative lower elastic modulus is very beneficial for the use as implants because an elastic modulus of around 67 GPa is much more close to that of the bone than for other high strength Ti-base alloys. Considering that the biomedical application also requires good fatigue properties, high corrosion resistance, and low density, the investigators must pay more attention on these aspects in further research so as to improve these properties and make the new Ti-base alloys being come into use as a biomaterial.

### 4. Conclusion

Using Cr, Fe and Co to replace Ni in multicomponent Ti\(_{60}\)Cu\(_{14}\)Ni\(_{12}\)Sn\(_4\)(RM)\(_{10}\) (RM = Nb, Ta), one can obtain a composite microstructure with a micrometer-sized dendritic \( bcc-\beta \)-Ti(RM) phase dispersed in a nano/ultraline-structured matrix. The matrix is composed of a \( bcc \)-phase of 50–100 nm in size which is isolated by a tetragonal or \( hcp \)-structured phase.

These alloys exhibit very high yield strength (1050–1472 MPa) and relative low Young’s modulus (67–105 GPa). The micrometer-sized dendritic \( bcc-\beta \)-Ti(RM) phase contributes to the ductility, and the matrix phase with a nano/ultraline structure contributes to the high yield strength of the alloys. Such combined properties, not easily achievable in previous Ti alloys, make these new Ti alloys promising candidates as biomedical materials.

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### REFERENCES


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**Table 1** Summary of the compressive test data of Ti\(_{60}\)Cu\(_{14}\)(TM)\(_2\)Sn\(_4\)(RM)\(_{10}\) Young’s modulus (\( E \)), yield stress (\( \sigma_y \)), strain at the yield point (\( \epsilon_y \)), ultimate compression stress (\( \sigma_{max} \)), and plastic strain (\( \epsilon_p \)).

<table>
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<tr>
<th>Alloys</th>
<th>( E ) (GPa)</th>
<th>( \sigma_y ) (MPa)</th>
<th>( \epsilon_y ) (%)</th>
<th>( \sigma_{max} ) (MPa)</th>
<th>( \epsilon_p )</th>
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<tr>
<td>TM=Ni, RM=Ta</td>
<td>71.0</td>
<td>1037.0</td>
<td>1.7</td>
<td>2196.0</td>
<td>16.5</td>
</tr>
<tr>
<td>TM=Cr, RM=Nb</td>
<td>105.0</td>
<td>1370.0</td>
<td>1.5</td>
<td>1610.0</td>
<td>9.1</td>
</tr>
<tr>
<td>TM=Fe, RM=Nb</td>
<td>101.0</td>
<td>1472.0</td>
<td>1.7</td>
<td>1600.0</td>
<td>6.2</td>
</tr>
<tr>
<td>TM=Co, RM=Nb</td>
<td>67.0</td>
<td>1050.0</td>
<td>1.8</td>
<td>1370.0</td>
<td>12.7</td>
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