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Materials Science and Engineering C 26 (2006) 14 – 19

MATERIALS SCIENCE & ENGINEERING C

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Ti alloy design strategy for biomedical applications☆

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Received in revised form 1 October 2004; accepted 14 March 2005
Available online 29 June 2005

Abstract

Based on the empirical rules for the composition design of bulk metallic glasses, a general composition formula for forming nano/ultrafine-structure is suggested. According to this formula a group of quinary Ti alloys have been developed. By controlling the solidification conditions an in situ formed bimodal microstructure consisting of micrometer-sized dendritic β-Ti solid solution dispersed in a nano/ultrafine-structured matrix has been obtained in these quinary Ti alloys. The β-Ti solid solution contributes to the ductility and the low Young's modulus, while the nano/ultrafine-structured matrix contributes to the high strength. The combination of high strength and low Young's modulus offers potential advantages in biomedical applications.

Keywords: Ti alloys; Biomaterials; Nanostructure; Young's modulus; Alloy design

1. Introduction

In the human body, bone-related degeneration and/or disease (e.g. degeneration and inflammation of joints; wear and corrosion of tooth; etc.) frequently occur. Patients may suffer from pain and partial or complete loss of the functionality due to these degenerative and inflammatory diseases. Replacement of diseased tooth, bone or even the joint by artificial materials is often required in orthopedic surgery in order to relieve pain and recover the functioning [1]. To meet the demands of longer human life and implantation in younger patients, the artificial materials used in orthopedic surgery should not only avoid short-term rejection and infection, but also provide long-term biocompatibility and long-term materials limitations, i.e., high strength, long lifetime, high-wear resistance, high resistance to corrosion in the human body environment, no toxicity to human body, etc. Ti-base alloys have excellent biocompatibility, low density, and excellent corrosion resistance [1–3], so that they are very good candidates as implant-materials. So far, the very frequently used Ti and Ti-alloys in orthopedic surgery are pure Ti and Ti–6Al–4V [3]. The problems are low shear strength and low wear resistance of Ti and Ti–6Al–4V when used in the orthopedic surgery [1]. Another key problem is the mismatch of Young's modulus between the Ti-implant (100–120 GPa) and bone (10–30 GPa), which is unfavorable for bone healing and remodeling [4]. For solving these problems and further improving the biological and the mechanical properties, many new Ti-alloys have been developed for the biomedical application [3,4]. For example, designing single β-phase type Ti alloys can obviously reduce the elastic modulus [3]. However, there is a contradiction between elastic modulus and other mechanical properties in those Ti alloys. When the elastic modulus is reduced, the strength of the Ti alloy is also decreased. Inversely, when the strength is enhanced the elastic modulus is also increased. In this study, a Ti alloy design strategy is proposed according to empirical rules for forming bulk metallic glasses. A nano/ultrafine-structure is introduced into the bio-Ti alloys. By the composition–modification and the microstructure-control we are trying to reduce the Young's modulus of Ti alloys, while maintain

☆ This manuscript is based on the talk at *The 2004 TMS Annual Meeting* (Charlotte, NC, March 14–18, 2004). The talk title was 'Nanostructured Ti-base alloys for biomedical applications'.

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doi:10.1016/j.msec.2005.03.007

their high strength, so as to develop high quality bio-Ti alloys for orthopedic applications.

2. Alloy designs

The drawbacks of the often-used Ti-base alloys (e.g. Ti–6Al–4V) in orthopedic surgery are: too high Young's modulus compared to the human bone; low shear strength; low wear resistance; and bio-toxicity of Al and V to human body. The improvement on both bio- and mechanical properties is necessary. The normal method to achieve better performance of Ti alloys in terms of their biomedical and mechanical properties is to modify their composition. Some strong β-phase forming elements such as Nb, Ta, Mo, and Zr, and some β-phase improving elements such as Fe, Cr, and Sn, are widely used in biomedical Ti alloys to form full or partial β-structure which has low elastic modulus and contributes to decreasing the bulk elastic modulus of the alloy. In addition, some alloying elements such as Cu, Co, Ni, Si are used to strengthen the alloys. However, these modified biomedical Ti alloys exhibit either high strength with high elastic modulus or low elastic modulus with low strength. Therefore, we must have a new idea for the alloy design to achieve low elastic modulus together with high strength.

For Ti alloys, hcp-α and bcc-β are basic phases. α-structure exhibits about 100–120 GPa of Young's modulus and β-structure exhibits about 60–80 GPa of Young's modulus [3]. It is clear that full β-structure has low Young's modulus. However, full β-structure must leads to low strength. There are two ways to strengthen the β-phase: one is alloying and the other is reducing grain size. The former may also lead to the increase in elastic modulus because the alloying must change the atom-bond of β-phase. Therefore, reducing grain size is the best way to strengthen the β-structure. Generally, when grain size is reduced into nanometer scale, the strength will significantly increase [5]. On the other hand, the volume fraction of grain boundary will also increase significantly. Due to high dense defects (such as voids, dislocation, etc.), the grain boundary is expected to have lower elastic modulus than that of grains. Accordingly, the grain boundary also contributes to the low elastic modulus. Based on the discussion above, nanostructured β-Ti alloys should exhibit high strength together with low elastic modulus. Therefore, the next attempt will be devoted to achieve nanostructure in β Ti alloys. There are different ways to synthesize or fabricate nanostructured alloys, for example, appropriate composition design and mold casting [6], nano powder sintering [7], severe deformation [8], etc. In this study, we are trying to fabricate the nanostructured Ti alloys by proper alloy design and copper mold casting.

To get ultrafine- or nanostructure during solidification, we must increase the nucleation and suppress the grain growth in the liquid alloy. This can be realized by increasing the stability of the supercooled liquid alloy and increasing cooling rate during solidification. It has been found that the alloy composition obeying the following three empirical rules exhibits highly stability in the supercooled temperature region [9]: (1) the alloy consists of multicomponent, (2) significant difference in atomic size among the main elements, and (3) negative heats of mixing among the main elements. Such multicomponent system can increase the degree of dense random packed structure in the liquid [9]. The dense structure includes short-range-orders which act as nuclei with decreasing temperature [10]. Due to the multi-component, the dense structure, and the high cooling rate, long-range atomic rearrangement is very difficulty. Thus the grain growth is effectively suppressed. As a result, an ultrafine- or nanostructure is formed during the solidification.

According to the three empirical rules, the possible nanostructured Ti alloys can be established as:

$$\mathrm{Ti}-\mathrm{M_a}-\mathrm{M_b}-\mathrm{M_c} \tag{1}$$

where $\mathrm{M_a}$=Ag, Cu, Pd, and Pt; $\mathrm{M_b}$=Co, Cr, Fe, Mn, Ni, Zr and Y; $\mathrm{M_c}$=Al, Ga, In, Sn, and Zn. Among them, a combination of Ti–Cu–Ni–Sn has shown the possibility to form nanostructure during solidification in our previous experiments [6].

Nanostructured metals or alloys usually follow a shear banding deformation-failure mechanism [11], which results in excessive shear banding in one or several deformation bands under loading. This makes them difficulty to deform and prone to catastrophic failure with small or zero plasticity [12]. A bimodal microstructure (nanostructure+ductile 'large' phase) has shown that the plasticity can be improved by the ductile phase while the high strength can be maintained by the nanostructure [13–15]. Thus, introducing the ductile phase into the nanostructure must be involved in the alloy design. A simple way to form a ductile bcc-β-phase at the primary solidification stage is adding refractory metals into Ti alloys. For example, Mo, Nb and Ta can be dissolved into liquid Ti and improve to form β-Ti solid solution during the solidification. Therefore, the general constituents of nanostructured Ti alloy should include:

$$\mathrm{Ti}-\mathrm{M_a}-\mathrm{M_b}-\mathrm{M_c}-\mathrm{M_R} \tag{2}$$

where $\mathrm{M_R}$=Hf, Mo, Nb, Ta, and W. So far, what we have tried for fabrication of the bimodal nanostructured Ti alloys includes following combinations: Ti–Cu–Ni(Co, Cr, Fe, Zr)–Sn–Nb(Mo, Ta). As examples, in next sections we will

Table 1
Compositions of the Ti–Cu–Ni(Fe,Co)–Sn–Nb(Ta) multicomponent alloys (at.%)

Alloys	Ti	Cu	Ni	Fe	Co	Sn	Ta	Nb
A	60.0	14.0	12.0	–	–	4.0	10.0	–
B	60.0	14.0	12.0	–	–	4.0	–	10.0
C	65.0	12.0	–	10.0	–	3.0	–	10.0
D	65.0	11.0	–	–	9.0	3.0	–	12.0

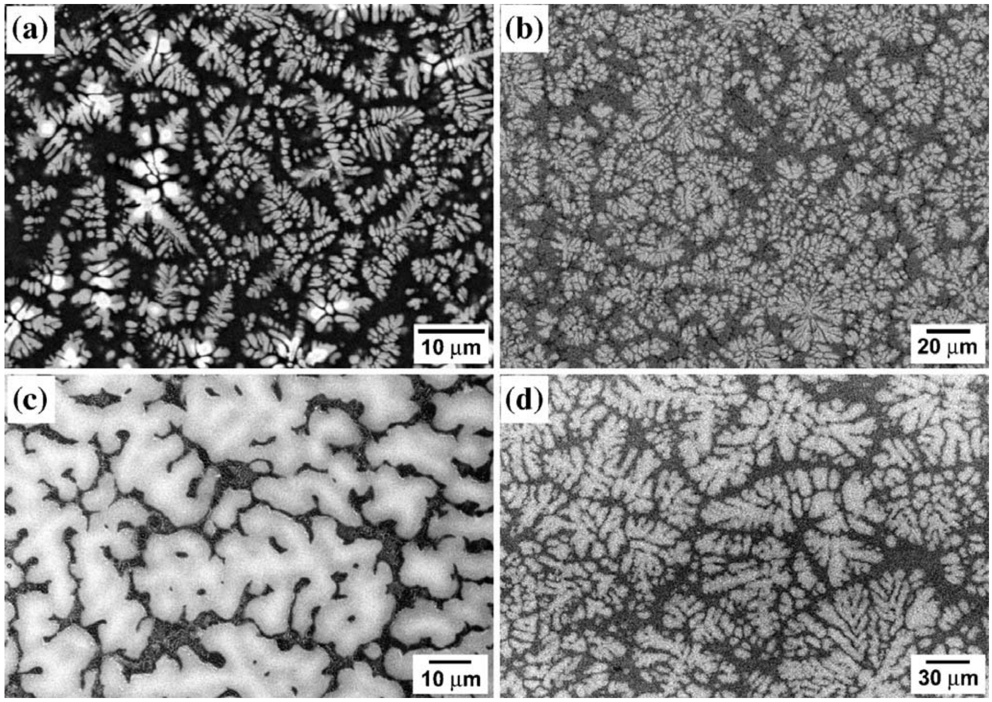

Fig. 1. SEM back-scattered electron images of the as-prepared microstructures: (a) alloy A, 3 mm in diameter; (b) alloy B, 3 mm in diameter; (c) alloy C, arc-melted; and (d) alloy D, arc-melted.

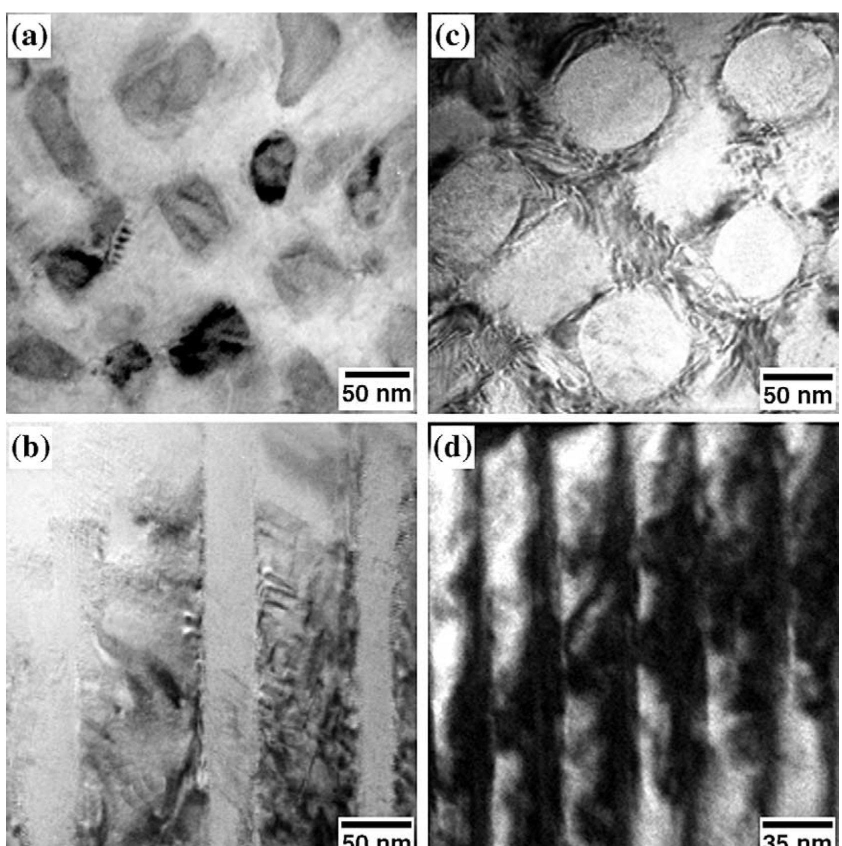

Fig. 2. Bright-field TEM images of the rod-like eutectic matrix phases in the as-cast alloys observed along (a) beta-[201] and (b) beta-[101] for alloy A, and (c) beta-[201] and (d) beta-[101] for alloy B.

present some results of the microstructure and the mechanical properties of four bimodal Ti alloys with different compositions (as listed in Table 1).

3. Experimental

The alloys were prepared by magnetic levitation melting or arc melting pure elements at argon atmosphere. Consequently, the cylindrical samples with different diameters were prepared by copper mold casting. Considering the influence of the liquid state on the microstructure, the overheating level and cooling rates will be carefully controlled. The cooling rates can be changed by using different casting methods or by changing sample thickness. The morphology, the microstructure and the composition of the as-prepared samples were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX).

The specimens for compression and tension tests were prepared according to American Standard. Both the compression and the tension tests were carried out with an Instron 8562 testing machine at a strain rate of 1×10^{-4}/s at room temperature. The compression stress–strain curves were calibrated by subtracting the strains of the test system (which was evaluated by going through the compressive test process with the same strain rate without a sample) from the recorded strains. The mechanical properties were evaluated directly from the calibrated stress–strain curves.

4. Results and discussion

Fig. 1 shows the as-prepared microstructure of alloys A through D. A typical bimodal microstructure, a dendritic phase dispersed in a matrix, has been obtained in all these alloys. Different dendritic morphologies and different size of the dendritic phase among these alloys are attributed to the different composition and the different cooling rate. The dendritic phase has been characterized to be bcc-β-Ti solid solution which is enriched by Ta(or Nb) and Sn. Since a few percent Sn dissolved in the alloy does not decrease the melting temperature of Ti (see Ti–Sn binary phase diagram [16]), the liquidus temperature of Ti alloy is significantly increased after Ta or Nb is dissolved. As a result, a Ta(or Nb)-rich β-Ti solid solution primarily precipitates at relative high temperature during solidification to form a dendritic phase. Such a β-Ti solid solution with bcc structure is expected to have very good ductility and low elastic modulus, but also low strength.

With precipitation of the dendritic phase, the remaining liquid is approaching a eutectic composition and finally takes a eutectic reaction below the eutectic temperature. The production of the eutectic reaction is a rod-like β-Ti arrays embedded in a γ-TiCu intermetallics as shown in Fig. 2. For as-cast 3 mm diameter alloy A, the rod-like β-Ti phase is 30–50 nm in the transverse direction (Fig. 2a) and about 1 μm in length. For as-cast 3 mm diameter alloy B, the rod-like β-Ti phase is 70–80 nm in the transverse direction (Fig. 2c) and about a few μm in length. Such nanometer scale structure is expected to have very high strength but low ductility [11,12]. The elastic modulus of such nanostructure depends on each volume fractions of the rod-like β-Ti phase, the γ-TiCu intermetallics and the boundaries between the two phases. Since the rod-like β-Ti phase and the boundaries are expected to have lower elastic modulus than the γ-TiCu intermetallics, larger volume fractions of β-Ti phase and boundaries lead to lower elastic modulus of the nanostructured matrix.

The bimodal microstructure with micrometer-sized dendrites dispersed in the nano/ultrafine-structured matrix combines the high strength of the nano/ultrafine-structure and the good ductility of the bcc-structured dendrites. As an example, the typical mechanical behavior of alloy B is shown in Fig. 3. The stress–strain curves exhibit a large elastic stage (~2% elastic strain) followed a long plastic strain with significant strain hardening. The as-cast 3 mm sample with a 70–80 nm structure exhibits 1312 MPa yield strength under compression. The as-arc-melted sample with ultrafine-structure also exhibits larger than 1000 MPa yield strength (Fig. 3a). Both samples exhibit a large plasticity, suggesting a combination of high yield strength and good

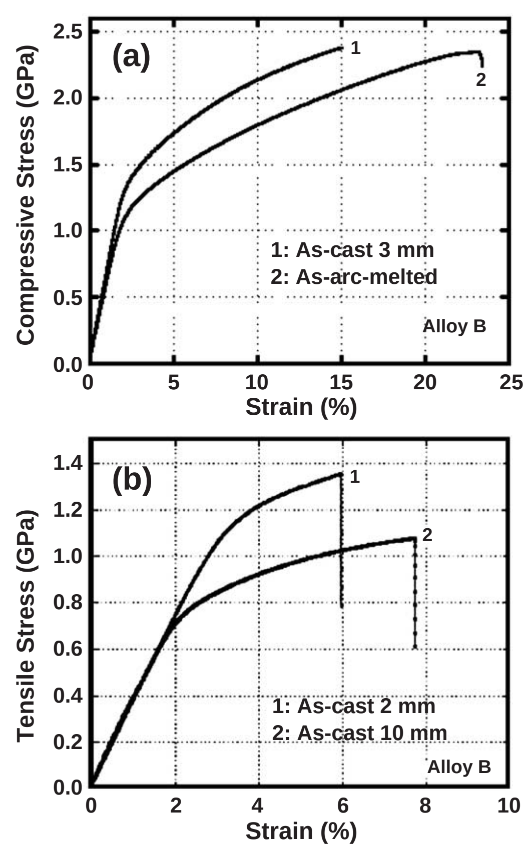

Fig. 3. Stress–strain curves of alloy B; (a) compression and (b) tension.

Table 2
Mechanical properties of alloys A through D

Alloys	Status	E (GPa)	σ_y (MPa)	ε_y (%)	σ_{max} (MPa)	ε_p (%)
Compression						
A	ϕ3 mm	73	1525	2.3	2282	6.0
	arc-melted	71	1037	1.7	2196	16.5
B	ϕ3 mm	66	1312	2.2	2401	14.5
	arc-melted	59	1052	2.1	2345	21.3
C	arc-melted	67	1167	2.0	1730	16.6
D	arc-melted	68	980	1.6	1440	16.2
Tension						
B	ϕ2 mm	40	1150	3.2	1350	2.8
	ϕ10 mm	40	680	1.9	1070	5.8

E: Young's modulus, σ_y: yield stress, ε_y: strain at the yield point, σ_{max}: ultimate compression stress, and ε_p: plastic strain.

ductility in this alloy. The tensile tests reveal a very similar behavior, i.e., a large elastic stage followed an obvious plastic stage with significant strain hardening (Fig. 3b). The as-cast 2 mm sample with a 30–50 nm structure exhibits 1150 MPa yield strength with about 2.8% plastic strain, while the as-cast 10 mm sample with about ~300 nm structure exhibits 680 MPa yield strength with about 5.8% plastic strain, indicating that the yield strength significantly depends on the nano/ultrafine-structure. The mechanical properties of alloys A through D are summarized in Table 2. All these alloys exhibit high yield strength, large plasticity and relative low Young's modulus. Even as expectation, the nano/ultrafine-structured matrix contributes to the high yield strength, while the micrometer-sized bcc-β-structured dendrites contribute to the large plastic strain. The low Young's modulus is attributed to the β-phase (including micrometer-sized dendritic β-phase and nanorod-like β-phase), the large volume fraction of boundaries and perhaps some voids formed during solidification (e.g., solidification shrinkage).

Above results support that to form bimodal microstructure, the Ti alloy constituents must obey the general formula (2). According to the experimental observation, the volume fraction of the dendritic β-phase depends on the percentages of Ti and M_R. Higher Ti+M_R content results in larger volume fraction of β-phase, leading to lower yield strength. Conversely, Higher M_a+M_b content results in smaller volume fraction of β-phase, leading to higher yield strength, but smaller plastic strains. This composition-microstructure-mechanical property relationship can be illustrated by Fig. 4. As an example, the fractographies of Ti–Cu–Ni–Sn–Nb bimodal alloys are shown in Fig. 4 on which the typical brittle (for higher Cu+Ni content) and ductile (for higher Ti+Nb content) fracture features are clearly observed. The stress–strain curves in Fig. 4 show

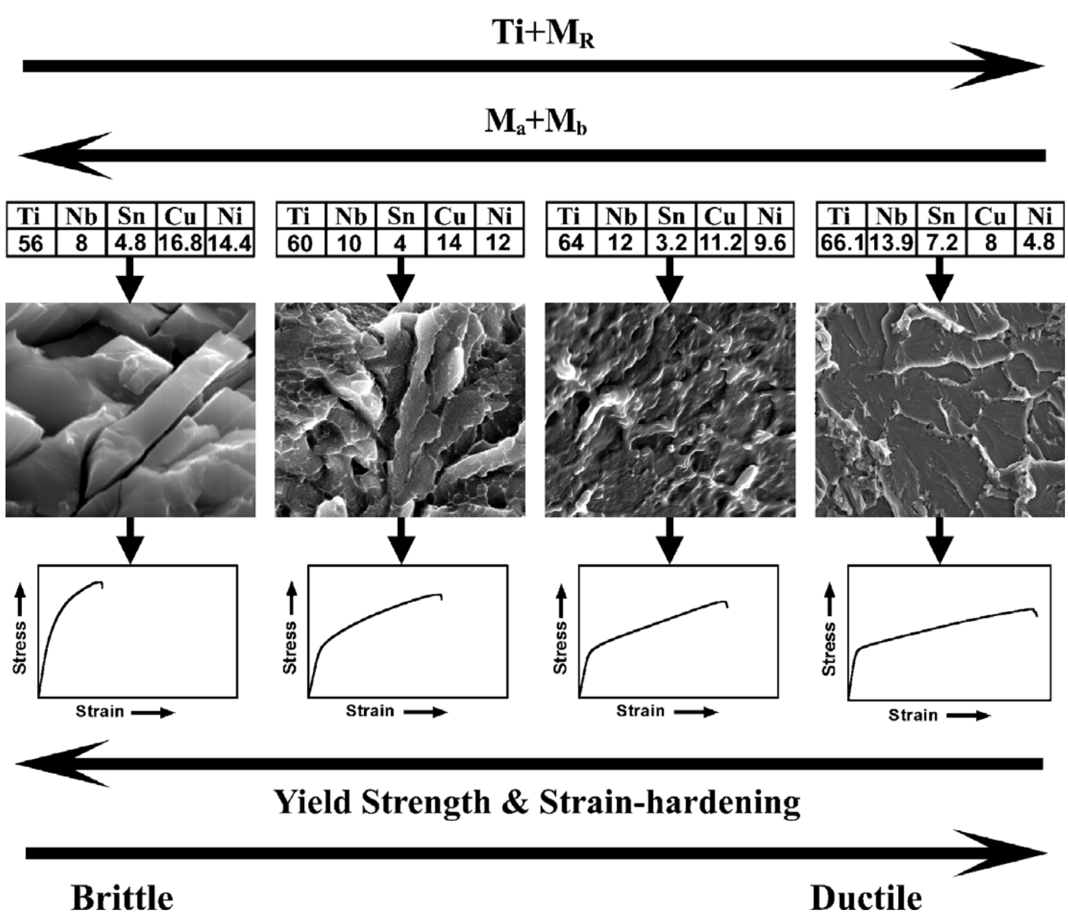

Fig. 4. Composition-dependence of mechanical properties of bimodal nanostructured Ti alloys.

that the strain-hardening becomes significant with increasing Cu+Ni in the alloy.

Although the elastic modulus depends on not only the compositions but also the processing conditions (e.g., cooling rate during solidification) [17], a fact is that all these alloys exhibit relative lower Young's modulus than other Ti or Ti alloys, e.g., pure Ti and Ti–6Al–4V. The combination of low Young's modulus and high yield strength is advantageous when these alloys are used as biomedical materials. Since Ni and Cu are deleterious to biocompatibility, the new bimodal nano/ultrafine-structured Ti alloys should exclude these elements when this strategy is applied for biomaterial design. Alloys C and D excluding Ni exhibit very similar mechanical properties with alloys A and B, indicating the possibility to achieve high performance on both mechanical properties and biocompatibility.

5. Conclusion

High strength together with low Young's modulus can be achieved in Ti alloys by proper composition design and copper mold casting. Such combination of mechanical properties and elastic modulus is attributed to the novel bimodal microstructure that consists of a micrometer-sized dendritic β-phase and a nano/ultrafine-structured matrix. The dendritic β-phase contributes to the plasticity and the low Young's modulus, while the matrix (consisting of nanorod-like β-Ti+γ-TiCu eutectic phases in Ti–Cu–Ni–Sn–Ta(Nb), for example) contributes to the high strength. The large volume fraction of boundaries in the nano-structured matrix may also contribute to the low Young's modulus. In Ni-free Ti alloys (e.g., Ti–Cu–Fe(Co)–Sn–Nb) a similar bimodal microstructure is obtained which also exhibits high strength and low Young's modulus, revealing that these bimodal Ti alloys have potential for biomedical applications.

Acknowledgements

The authors are grateful to J. Eckert, E. Ma and M.L. Sui for stimulating discussions, G.L. Dai, S. Emura, M. Frey, H. Grahl, M. Gründlich, Y.F. Gu, A. Güth, H.J. Klauβ, S. Kuszinski, W. Löser, S. Müller-Litvanyi, D.H. Ping, B.B. Sun, Y. Yamabe-Mitarai, and F.X. Yin for technical assistance.

References

[1] M. Long, H.J. Rack, Biomaterials 19 (1998) 1621.
[2] R.V. Noort, J. Mater. Sci. 22 (1987) 3801.
[3] M. Niinomi, Metall. Mater. Trans. 33A (2002) 477.
[4] M. Niinomi, Biomaterials 24 (2003) 2673.
[5] H. Gleiter, Acta Mater. 48 (2000) 1.
[6] G. He, W. Löser, J. Eckert, L. Schultz, J. Mater. Res. 17 (2002) 3015.
[7] Y.J. Wu, A. Bandyopadhyay, S. Bose, Mater. Sci. Eng. 380A (2004) 349.
[8] I.V. Alexandrov, R.Z. Valiev, Nanostruct. Mater. 12 (1999) 709.
[9] A. Inoue, Acta Mater. 48 (2000) 279.
[10] G.L. Chen, X.D. Hui, G. He, Z. Bian, Mater. Trans., JIM 42 (2001) 1095.
[11] J.R. Weertman, D. Farkas, K.J. Hemker, H. Kung, M. Mayo, R. Mitra, H. Van Swygenhoven, MRS Bull. 24 (1999) 44.
[12] C.C. Koch, D.G. Morris, K. Lu, A. Inoue, MRS Bull. 24 (1999) 54.
[13] R. Valiev, Nature 419 (2002) 887.
[14] Y.M. Wang, M.W. Chen, F.H. Zhou, E. Ma, Nature 419 (2002) 912.
[15] G. He, J. Eckert, W. Löser, L. Schultz, Nat. Mater. 2 (2003) 33.
[16] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak, Binary alloy phase diagrams, 2nd ed., William W. Scott Jr, 1992, p. 2078.
[17] G. He, J. Eckert, W. Löser, M. Hagiwara, Solid State Commun. 129 (2004) 711.