Mechanical Properties and Microstructures of Composites of Ti-Based Metallic Glass and $\beta$-Ti

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Microstructures and mechanical properties of Cu mold-cast Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ and Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$Ta$_5$ alloys were investigated by means of X-ray diffraction, electron microscopy and compressive testing. Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ alloys form microscopic composites consisting of Ti-based metallic glass as primary phase and $\beta$-Ti phases, while Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$Ta$_5$ alloys consisting of Ti-based metallic glass matrix and high density of nanocrystals dispersed in the matrix homogeneously. Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ bulk composite alloys showed 1.6% of plastic deformation and 2200 MPa of 0.2% of proof stress. The alloys also exhibited work hardening because of the presence of microscopic crystalline phases. Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$Ta$_5$ bulk alloys also deformed plastically after stress reached 2000 MPa without work hardening.

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1. Introduction

Ti-based bulk metallic glasses are attractive as well as Ti-based crystalline materials, because Ti is one of light and biocompatible metal elements and has high corrosion resistance. After Ti-based amorphous alloys1–3 were developed, many Ti-based metallic glasses have been reported.4–6 However, it is difficult to obtain Ti-based metallic glasses because they have high melting point when compared to conventional Pd- and Zr-based metallic glasses. As a result, only several Ti-based bulk metallic glasses have been reported.7–12 In order to enrich ductility of metallic glasses under compression, composites of metallic glasses with high strength and ductile microcrystalline phase were developed for Cu- and Zr-based alloys.13,14 For Ti-based alloys, ductile Ti-based nanocrystalline materials with high strength15–18 were prepared, but few studies have been reported for microscopic Ti-based metallic glass and crystalline composites. He et al.19 reported such composites, even though they contain less than 10 vol% of Ti-based metallic glass.

On the other hand, many metallic glasses in which nanocrystals are dispersed homogeneously also exhibit ductility20 by activating multiple shear bands during deformation. Various kinds of bulk metallic glasses become ductile under compression by this mechanism. Mechanical properties of Ti-based bulk metallic glasses were studied in several literatures,8–11 and Ma et al.10 and Men et al.11 found that Ti-based bulk metallic glasses deformed plastically. But microstructure of Ti-based metallic glasses has not been examined in detail by means of transmission electron microscopy (TEM).

In the present study, we investigated the effect of Ta addition to Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$ and Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$ alloys on the microstructure after rapid quenching. And we report the microscopic and nanoscopic ductile composites of Ti-based metallic glasses as the primary phase and crystalline phases for Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ and Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$Ta$_5$, respectively.

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2. Experimental Procedures

Ingots with nominal compositions of Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ and Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$Ta$_5$ were prepared by Ar-arc melting. Because the melting point of Ta is very high, Ti–Ta alloys were prepared at first and they were used to dissolve Ta homogeneously in the arc-melted ingots. The ingots were subjected to melt-spinning and mold-casting. Ribbons were prepared by melt-spinning using a Cu roll of 18 cm in diameter and silica nozzles. The ribbons were rapidly quenched by the roll rotating at 4000 rpm, which is equivalent to 37.7 m/s. Cylindrical bulk specimens whose dimension is 1 mm in diameter and 30 in length were prepared by Cu mold-casting. Differential scanning calorimetry (DSC) measurements were performed to determine glass transition temperature ($T_g$), crystallization temperature ($T_c$) and supercooled liquid region ($\Delta T_s = T_s - T_c$) at a heating rate of 0.67 K/s. Microstructures of the as-spun ribbons and as-cast bulk specimens were characterized by means of X-ray diffractometry (XRD) using a Cu rotating anode and TEM. Mechanical properties of the cylindrical bulk specimens were examined at room temperature by compression tests at a strain rate of $1 \times 10^{-4}$ using an Instron-type machine.

3. Results and Discussion

3.1 Microscopic Composite of Ti-based Metallic Glass and Crystalline Phases

Figure 1 shows the XRD pattern and DSC traces of Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ as-spun ribbons and bulk specimens. No sharp diffraction peaks are found in the XRD patterns of Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_5$Ta$_5$ as-spun ribbons, while several diffraction peaks of $\beta$–Ti and Ti$_2$Ni are found in that of the bulk specimens. In spite of the presence of those diffraction peaks, the bulk specimens exhibited glass transition at 715 K, which is almost the same as the $T_g$ of the ribbons. Moreover, about more than half of exothermic heat accompanied by crystallization is observed for the bulk specimens. Therefore, it is considered that almost half of the bulk specimen is the glass phase in the bulk specimens, although halo from glassy phase
is hidden in the background of the XRD pattern of the bulk specimens.

Figure 2 shows the microstructures of Ti\(_{50}\)Cu\(_{25}\)Ni\(_{15}\)-Sn\(_{5}\)Ta\(_{5}\) bulk specimens. Three kinds of phases were observed in the bulk specimens in accordance with the XRD pattern as shown in Fig. 1(a). The matrix phase in the bulk specimens were the glassy phase. As shown in Fig. 2(a), lattice fringes of nanocrystals were often observed in the glassy matrix phase. The major crystalline phase was \(\beta\)-Ti, whose size was larger than 1 \(\mu\)m as shown in Fig. 2(b). Ti\(_2\)Ni precipitates were sometimes found in the metallic glass phase as shown in Fig. 2(c), whose size is smaller than 1 \(\mu\)m. Thus, it is safe to say that the bulk specimens were composites of the metallic glass matrix and \(\beta\)-Ti.

The stress–strain curve of Ti\(_{50}\)Cu\(_{25}\)Ni\(_{15}\)-Sn\(_{5}\)Ta\(_{5}\) bulk specimen is shown in Fig. 3. The bulk specimen deformed plastically under compression, and the 0.2% proof stress and plastic strain of the specimen were 2200 MPa and 1.6%, respectively. During the plastic deformation, the specimen exhibited work hardening and was finally broken when the stress reached 2610 MPa.

### 3.2 Nanoscopic Composite of Ti-based Metallic Glass and Crystalline Phases

Figure 4 shows the XRD patterns and DSC traces of Ti\(_{45}\)Zr\(_{5}\)Cu\(_{45}\)Ni\(_{5}\) bulk specimens. The intensity of diffraction peaks of \(\beta\)-Ti, whose lattice parameter is 0.317 nm, and unknown phases in the XRD patterns increased, with increasing Ta content. On the other hand, the amount of exothermic heat accompanied by the first crystallization decreased with increasing Ta content. Thus, it is expected that Ti\(_{45}\)Zr\(_{5}\)Cu\(_{45}\)Ni\(_{5}\)Ta\(_{5}\) bulk specimens are Ti-based metallic glasses containing nanocrystals.

The TEM nanostructures of Ti\(_{45}\)Zr\(_{5}\)Cu\(_{45}\)Ni\(_{5}\) and Ti\(_{45}\)Zr\(_{5}\)Cu\(_{45}\)Ni\(_{5}\)Ta\(_{5}\) bulk specimens are depicted in Fig. 5. In both specimens, high density of fine nanocrystals, whose dimension was less than less than 10 nm, were found in the Ti-based metallic glass matrix and were homogeneously dispersed in the matrix. But in Ti\(_{45}\)Zr\(_{5}\)Cu\(_{45}\)Ni\(_{5}\) specimens, coarse nanocrystals, whose dimension was about 40 nm, were often found as indicated by the allow in Fig. 5(a). As far as the...
morphology of nanocrystals dispersed in the matrix, Ti$_{45}$-Zr$_5$Cu$_{44}$Ni$_5$Ta$_1$ specimens are more homogeneous than Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$. It seems that 1% of Ta addition suppresses growth of the nanocrystals during rapid quenching. In the SAED patterns of both Ti$_{45}$Zr$_5$Cu$_{45}$Ni$_5$ and Ti$_{45}$Zr$_5$Cu$_{44}$-Ni$_5$Ta$_1$, two sharp diffraction rings from nanocrystals are found. By careful observation, one more diffraction ring is found among the halo ring having the highest intensity. It is considered that the nanocrystals have a cubic structure, whose lattice parameter is 0.299 or 0.438 nm, but further studies are required to determine the crystal structure and lattice parameter of the nanocrystals exactly.

Figure 6 shows compressive stress–strain curves of Ti$_{45}$-Zr$_5$Cu$_{45-x}$Ni$_5$Ta$_x$ (x = 0, 1, 3, 5) bulk specimens. As we
Mechanical Properties and Microstructures of Composites of Ti-Based Metallic Glass and $\beta$-Ti

Fig. 6 Stress–strain curves of Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{5}$ bulk specimens. (a) $x = 0$, (b) $x = 1$, (c) $x = 3$ and (d) $x = 5$.

mentioned, Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$ and Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{5}$ specimens are Ti-based metallic glasses containing high density of fine nanocrystals. The others, Ti$_{45}$Zr$_{5}$Cu$_{42}$Ni$_{5}$Ta$_{3}$ and Ti$_{45}$Zr$_{5}$Cu$_{40}$Ni$_{5}$Ta$_{5}$, probably contain larger crystals than those found in Ti$_{45}$Zr$_{5}$Cu$_{45}$Ni$_{5}$ and Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$, because diffraction peaks are clearly observed in the XRD patterns in Fig. 4(a). Moreover, the amounts of crystalline phases in Ti$_{45}$Zr$_{5}$Cu$_{42}$Ni$_{5}$Ta$_{3}$ and Ti$_{45}$Zr$_{5}$Cu$_{40}$Ni$_{5}$Ta$_{5}$ were larger than those of Ti$_{45}$Zr$_{5}$Cu$_{45}$Ni$_{5}$ and Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$, because the amount of exothermic heat accompanied by crystallization is decreased drastically with increasing Ta content. The specimens containing larger crystals and large amount of crystals were broken without exhibiting large amount of plastic strain, while Ti$_{45}$Zr$_{5}$Cu$_{45}$Ni$_{5}$ and Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$ specimens exhibited plastic deformation with showing serration. The amount of plastic strain is 3.0% and is the largest for Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$. The 0.2% proof stress of Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$ specimen were 1922 MPa. Therefore, it is clear that homogeneous distribution of the high density of nanocrystals increases the amount of plastic strain, because large number of shear bands are activated during deformation.

4. Conclusions

Two types of composites of Ti-based metallic glass and crystalline phases were prepared by Cu mold-casting. Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_{5}$Ta$_{5}$ bulk specimens consisted of Ti-based glassy matrix phase and $\beta$-Ti phase. Ti$_{50}$Cu$_{25}$Ni$_{15}$Sn$_{5}$Ta$_{5}$ specimens exhibited work hardening. The amount of plastic strain was 1.6% and the fracture stress 2610 MPa. Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$ bulk specimens were Ti-based metallic glass in which high density of nanocrystals were dispersed homogeneously. Ti$_{45}$Zr$_{5}$Cu$_{44}$Ni$_{5}$Ta$_{1}$ was also deformed plastically at about 2000 MPa, and the amount of plastic strain was 3.0%.

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