Mechanical Property and Fracture Characteristic of Ti–Cu–Ni–Al_x Bulk Metallic Glasses under Different Strain Rates

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In this study, a Ti-based bulk metallic glass (BMG) was used to investigate the influence of the addition of Al on mechanical properties and glass forming ability (GFA). The experimental results show that the plastic flow stress value of the alloy will change with the change of strain and strain rate. As the strain rate increases, the plastic flow stress value increases. The fracture surface of the specimens can be observed through a scanning electron microscope. It can be seen that the fracture surface has the characteristics of a dimple-like structure. The appearance, distribution density, and grain density of the vein-like structure depend on the strain rate and the addition of the Al element.
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1. Introduction

Amorphous alloys are formed by rapid solidification of a molten metal, so amorphous metals are also referred to as liquid metals or non-crystalline metals. Because of this lack of symmetry short-range order structure and glass structure is similar, it is also called glass metallic or metallic glass (MG).¹⁾ In the previous scientific basis of metal materials, the occurrence of plastic deformation is often explained using dislocation theory. However, amorphous materials only have a short-range orderly arrangement, and there is no fixed slip system for sliding, so there is also no defect of the general crystalline material, and the dislocation theory is not applicable to explain. Because of this special structure and excellent performance, it has also attracted the attention of the academic community and the industry, and has been widely studied.^{2,3)} At present, the Ti-based MG has reached a strength of 2200 MPa, which is about twice the strength of traditional titanium alloys and has received much attention.^{4,5)} In the development of Ti-based MG, the thin ribbons synthesized by melt-spinning are still dominant at early stages, such as Ti–Be,⁶⁾ Ti–Ni,⁷⁾ and Ti–Ni–Si⁸⁾ etc. Bulk metallic glass (BMG) has many excellent properties such as large elastic limit, exceptionally high strength, good corrosion resistance, high yield strength, high hardness, and reduced sliding friction, which makes them considered as prospective candidates for engineering materials. Despite these excellent properties, the use of BMG as a structural material is limited. One of the major drawbacks of BMG compared to currently used crystalline alloys is their limited plasticity. Many studies have been performed to improve the plasticity of BMG. To enhance the plasticity, some inhomogeneities are introduced into the BMG matrix, atomic scale to micrometer (mm) scale, intended to enhance shear band nucleation or prevent shear band propagation. Ti-based BMG was explosively discussed until Inoue *et al.* added a small amount of tin to prepared a 6 mm diameter Ti–Cu–Ni–Sn BMG alloy by quench casting in 1988.⁵⁾ And Sundaresan *et al.* first use mechanical alloying to

synthesize Ti–Cu–Ni MG with a clearly supercooled liquid region in 1988.⁸⁾ Currently, scholars try to add zirconium, tin or niobium to improve the glass forming ability (GFA) of BMG.^{9–13)} But it is difficult to exceed the thickness of 6 mm, the main reason is that titanium metal is easily reacting with the oxygen and nitrogen in the air. In order to improve the poor ductility of BMG, recent studies have proposed to improve the mechanical properties by adding a strengthening phase to precipitate in the base phase of a BMG alloy. The addition of this type of material also promotes the GFA of the amorphous alloy. This new type of alloy is called bulk metallic glass composites (BMGC). BMG-based composites improved the plasticity and work-hardening ability through the addition of crystalline phases, and the determination of the properties of the additives had a significant influence on the mechanical properties of BMGC, such as the ductile crystal addition will reduce the plastic deformation capacity of BMGC.^{14–19)} However, in order to expand the field of application of BMG, more attention should be paid to the development of BMG based on ordinary metals such as Ni, Cu, Fe and Ti. Since Ti-based BMGCs have a low density that is almost matched to commercial Ti alloys, many Ti-based metallic glasses have been studied with the aim of improving the mechanical properties of Ti alloys.^{20,21)} In 2005, Guo *et al.* reported that the Ti-based BMGC rod of 12 mm in diameter exhibits a large compressive plastic strain of 5% with a strength of 1800 MPa.²²⁾ In 2007, Lee *et al.* reported that add Nb as an alloying element can strongly stabilize the formation of the β phase of Ti-based BMGC.²³⁾ In addition, Hofmann *et al.* reported that aluminum exhibits partial solubility in body centered cubic phase titanium, which is evenly distributed between the glass and dendrites. Therefore, a small amount of aluminum can be added to improve the GFA of BMGs.²⁴⁾ In this study, the mechanical behavior and microstructure evolution of Ti-based BMG specimens (Ti₄₄Cu₄₀Ni_{16–x}Al_x (x = 2, 4, and 6)) at room temperature under strain rates ranging from 10^{–3} ~ 3 × 10^{–3} s^{–1} were studied using a universal testing machine (MTS model) and compressive split-Hopkinson pressure bar (SHPB) system. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were used to examine the

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Fig. 1 The diagram of vacuum arc-melting device.

fracture morphology and crystalline properties of the Ti-based alloy system.

2. Experimental and Materials Preparation

Ingot alloys with a master chemical composition of $\text{Ti}_{44}\text{Cu}_{40}\text{Ni}_{16-x}\text{Al}_x$ ($x = 2, 4$, and $6 \text{ at\%}$) were prepared via the vacuum arc-melting (shown in Fig. 1) of a mixture of high purity constituent Ti (99.94 mass%), Cu (99.97 mass%), Ni (99.99 mass%), and Al (99.99 mass%) elements in an Ar atmosphere. After all the elements have melted, a cylindrical rod is formed in the copper mold using suction casting. Furthermore, to make the specimen have more uniformly, we re-melted the specimens four times. At the same time, the rods are cooled with subzero liquid and the cooling rate is about 1.3 K/s . In order to ensure the homogeneity of the microstructure, the ingot was melted and recast four times, and a cylindrical sample with a diameter of 4 mm was prepared for mechanical testing using a vacuum suction casting method. The quasi-static compression test was performed by the MTS tester at the strain rate of $10^{-3} \sim 10^{-1} \text{ s}^{-1}$ at room temperature conditions. In addition, a dynamic compression test was performed using a compression SHPB system at strain rates of $5.1 \times 10^3 \text{ s}^{-1}$, $6 \times 10^3 \text{ s}^{-1}$, and $7.2 \times 10^3 \text{ s}^{-1}$. The X-ray diffraction (XRD) analysis is used to examine the crystal structure, the differential scanning calorimetry (DSC) is used to study the GFA of BMG with different Al content at a heating rate of 20 K/min , and the scanning electron microscope (SEM) is used to observe the fracture surface of various Ti-based MGs.

3. Result and Discussion

3.1 XRD analysis

Figure 2(a)~(c) show the XRD patterns of the as-cast $\text{Ti}_{44}\text{Cu}_{40}\text{Ni}_{16-x}\text{Al}_x$ ($x = 2, 4$, and 6) specimens with diameter of 4 mm . A peak occurs at about 42° and 76° at 2θ , and this characteristic peak is corresponding to crystalline CuTi_2 phase,²⁵⁾ and no other component crystal peak appears. The peak of the brittleness phase is the strongest when 6% Al is added, and it can be inferred that the ductility of the 6% Al addition should be the worst. The Ti-based MGs with 4% Al addition shows that the peaks of brittleness phase are lower

Fig. 2 XRD patterns of the as-cast Ti-base MGs specimens with Al addition (a) 2, (b) 4, and (c) 6%.

than 2 and 6% Al addition, so the ductility is the best of the three specimens. According to the patterns above, we can know an amorphous structure with amorphous phase as a base containing a small amount of CuTi_2 brittle phase can be successfully prepared via the vacuum arc-melting.

3.2 DSC analysis

Figure 3 shows the DSC curves of the as-cast $\text{Ti}_{44}\text{Cu}_{40}\text{Ni}_{16-x}\text{Al}_x$ ($x = 2, 4$, and 6) specimens. It can be seen that there is a slight endothermic phenomenon in each component curve due to the amorphous phase structure transition at low temperature. The initial temperature of this phenomenon is defined as the glass transition temperature T_g . Then there will be a clear exothermic phenomenon, which means that the supercooled liquid state is successfully converted to the crystalline phase. The initial temperature of this phenomenon is defined as the crystallization temperature T_x . The supercooled liquid region is defined as $\Delta T_x = T_x - T_g$, a larger value of ΔT_x indication of the thermal stability of BMG materials and also represents the better GFA. From the DSC curve, we can observe that when the addition of 2 and 4% of Al, the double peak of the crystallization temperature T_x of the amorphous alloy is particularly significant. The temperature characteristics of

Fig. 3 The DSC curves of Ti-based MGs specimens with Al addition (a) 2, (b) 4, and (c) 6%.

Table 1 Glass-forming properties of Ti-based MGs with Al addition.

Composition (at %)	T _g (K)	T _x (K)	ΔT _x (K)
Ti ₄₄ Cu ₄₀ Ni ₁₄ Al ₂	585	639	54
Ti ₄₄ Cu ₄₀ Ni ₁₂ Al ₄	601	645	44
Ti ₄₄ Cu ₄₀ Ni ₁₀ Al ₆	598	638	40

these three alloys will shift to high temperatures as the amount of addition increases, but it is not particularly significant. The values of T_g, T_x, and ΔT_x of each specimen are summarized in Table 1. The value of ΔT_x with 2, 4, and 6% Al addition are 54, 44, and 40 K, respectively. With the increase of the addition ratio, the thermal stability and the ability to form metallic glass are reduced.

3.3 Stress-strain behavior

Figure 4(a)~(c) presents the stress-strain curves of the Ti₄₄Cu₄₀Ni_{16-x}Al_x (x = 2, 4, and 6) specimens under quasi-static strain rates and high strain rate. We found that when all specimens are subjected to different strain rate loads, all the plastic flow stress values increase with the strain rate. If the strain is fixed, the plastic flow stress value also increases with the increase of strain rate. At the same strain rate, the plastic flow stress value also increases with the increase of the strain, and the rising trend at high strain rates (5100 s⁻¹, 6000 s⁻¹, and 7200 s⁻¹) is more obvious than at low strain rates (10⁻¹ s⁻¹, 10⁻² s⁻¹, and 10⁻³ s⁻¹). It is speculated that the effect of strain rate enhancement at high strain rates is more pronounced than that at low strain rates.

Form the literatures,²⁵⁻²⁹⁾ they reported that the BMG materials deformed as a viscous flow behavior and depend on strain rates. In this study, it also very clear to see that the deformation behavior of Ti-based BMG materials also depend on strain rates. Whatever the content percentage of Al element, the Ti-based BMG materials obviously present viscous flow during the deformation. The more detail explanations will discuss on the fracture analysis in next section. On the other hand, we also found that the fracture strain will decrease with the increase of the strain rate, this is due to the earlier occurrence of adiabatic shear bands at high

(a)

(b)

(c)

Fig. 4 Stress-strain curves of: (a) Ti₄₄Cu₄₀Ni₁₄Al₂, (b) Ti₄₄Cu₄₀Ni₁₂Al₄, and (c) Ti₄₄Cu₄₀Ni₁₀Al₆.

strain rates. Furthermore, the decrease in free volume at the high strain rate induce the high temperature within the specimens, and it is expected to cause rapid decrease in viscosity. It caused the fracture earlier at high strain rate. Figure 5 shows the fracture strain properties of these

(a)

(b)

Fig. 5 Fracture strain of Ti-based MGs with different Al additions under (a) quasi-static strain rate; (b) high strain rate.

specimens under high strain rate and static conditions. It was found that when the Al content was 6%, the fracture strain has a minimum value, indicating that the ductility was the worst in all the specimens. This also proves that when Al is added to 6%, the XRD analysis of the brittle phase peak is the strongest. Although the ductility was not effectively improved by adding Al element, there was a slight increase in strength.

3.4 Strain rate effect

In order to investigate the strain rate effect on the mechanical property of $\text{Ti}_{44}\text{Cu}_{40}\text{Ni}_{16-x}\text{Al}_x$ BMG alloy, Figs. 6(a) and 6(b) show the variation of the flow stress with the logarithmic strain rate as a function of at true strains of 0.05 and 0.1. It can be seen that for both values of the true strain, the flow stress increases gradually with increasing strain rates. At the same rate, the flow stress also increases with true strain.

3.5 Surface morphology of fracture analysis

We observe and analyze the surface morphology of fracture specimens after static compression and dynamic

(a)

(b)

Fig. 6 True stress as function of strain rate at true strain of 0.05 and 0.1 under (a) quasi static strain rate (b) dynamic strain rate.

high-speed experiments. We can find that all fracture specimens are cracked along a plane oriented at 45° to the loading direction. Because this direction is the location of the maximum shear stress, the material fracture occurs in this direction. Figure 7 shows the failure morphology of the amorphous alloy after compressive stress deformation of the specimen. Through the observation of the fracture surface, we can find that the fracture surface is usually dominated by two deformation mechanisms, so the fracture surface is usually a combination of two different surface topographies, as shown in Fig. 7, indicating that the fracture surface is mainly composed of a shear surface and a tensile surface. In the shear area, it is caused by the shear stress, and in the tensile area, it is caused by the tensile stress. The fracture morphology of the amorphous alloy surface can be found in vein-like structures. The vein-like structure and fracture surface feature are different under quasi-static and dynamic experimental conditions, as shown in Fig. 8 and Fig. 9. The fracture surface of the Ti-Based BMG materials are exhibited vein-like feature within the shear bands, which was attributed to local viscous flow during the deformation.^{30–35} We can find that at the low strain rate deformation, the wider distribution of vein-like pattern and higher density, but at

Fig. 7 SEM micrograph of Ti₄₄Cu₄₀Ni₁₀Al₆ fracture surface.

high strain rate deformation the vein-like pattern is smaller and denser, and the morphology is flatter.

We know the relationship between the fracture strain and the vein-like structure by SEM observation. When the BMG material is fractured by a load impact, a vein-like structure is produced, and the phenomenon of melting droplets or fluid characteristics is found. This is because the large amount of heat generated in the plastic deformation area inside the material cannot be transmitted from the inside of the material within a short time, so that the temperature in the area is instantaneously increased, and the fluid appears inside when the material is deformed, as shown in Fig. 10. Localized small-scale fluid properties or melted droplets can be found at low strain rates, while large areas of fluid characteristics or melted droplet at high strain rates propagate in the direction of the shear band. Slipenyuk and Eckert³⁶⁾ also reported that

Fig. 8 SEM fractographs of Ti₄₄Cu₄₀Ni₁₄Al₂ specimens deformed at strain rates of (a) 10⁻¹ s⁻¹, (b) 10⁻² s⁻¹, and (c) 10⁻³ s⁻¹; Ti₄₄Cu₄₀Ni₁₂Al₄ specimens deformed at strain rates of (d) 10⁻¹ s⁻¹, (e) 10⁻² s⁻¹, and (f) 10⁻³ s⁻¹; Ti₄₄Cu₄₀Ni₁₀Al₆ specimens deformed at strain rates of (g) 10⁻¹ s⁻¹, (h) 10⁻² s⁻¹, and (i) 10⁻³ s⁻¹.

Fig. 9 SEM fractographs of Ti-based MGs deformed at strain rate of 5.1 × 10⁻³ s⁻¹: (a) Ti₄₄Cu₄₀Ni₁₄Al₂; (b) Ti₄₄Cu₄₀Ni₁₂Al₄; and (c) Ti₄₄Cu₄₀Ni₁₀Al₆.

Fig. 10 SEM image of $\text{Ti}_{44}\text{Cu}_{40}\text{Ni}_{12}\text{Al}_4$ with melted droplet and fluid properties at Strain Rate of 10^{-1} s^{-1} . (Scale bar = $10 \mu\text{m}$)

the free volume is proportional to the heat released during structural relaxation. Meantime, a small change in free volume will induce a dramatic effect on plastic flow behavior of BMG materials on high strain rate deformation. It means that the high strain rate deformation will cause the adiabatic deformation and have a smaller free volume and structural relaxation phenomenon.^{37,38)}

4. Conclusions

- (1) The amorphous alloy of the Al element added was analyzed on the microstructure by XRD. When Al is added, more brittle phases are precipitated, but the base phase is still present in an amorphous structure and slightly improves its mechanical properties.
- (2) The GFA was analyzed by DSC, although there is no obvious increase in thermal stability with the addition of an appropriate amount of Al, the temperature range of the supercooled liquid region will increase slightly when 2% of Al is added, and then increase with the Al content the supercooled liquid region will drop.
- (3) The addition of an appropriate amount of Al has no significant improvement in the ductility of the substrate, but it can be slightly improved in the strength of the material. When 4% Al is added, the strength and ductility of the amorphous alloy are the best.
- (4) When the Al content is 4%, the amorphous alloy has the most extensive distribution of vein-like structure, the highest density, the smoothest morphology, and the largest strain. This result is consistent with the mechanical property test results.

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