Synthesis and Characterization of Highly Elastic TiCu-Based Amorphous Micro-Wires

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A series of TiCu-based quaternary amorphous wires from a deep eutectic alloy composition were prepared by arc-melting and melt-extraction methods. Continuous amorphous wires with good white luster and smooth surface were obtained in Ti₂₅Zr₁₅Cu₆₀−ₓNix (x = 0, 5, 10, 15 mol%) alloys. The TiCu-based amorphous wires exhibit high tensile strength exceeding 1.3 GPa and high elastic limit of over 1.4%. Good combine of mechanical properties make them viable for use in many micro mechanical systems. [doi:10.2320/matertrans.M2017153]

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1. Introduction

Amorphous alloys are defined as metallic compounds without long range order in atomic configuration yet with advantageous properties such as much higher strength and superior corrosion resistance over their crystalline counterparts¹–³. Despite their lack of plasticity due to localized shear banding, a series of novel metallic glassy materials (MG) have been produced⁴, including amorphous metallic micro wires with homogeneous chemistry, perfectly circular cross sections and excellent properties via rapid solidification of super cooled liquids, which have attracted intensive scientific interests and propelled more search for newer materials and other functional engineering applications. Amongst all the micro-wire manufacturing techniques in existence to date, supercooled liquid melt extraction (SLEM) in the super cooled liquid state has proved more successful, cost effective and highly efficient for the production of amorphous metallic micro wires from intrinsically brittle alloys on a large scale⁵–⁶. In this technique a high speed wheel with a sharp edge contacts the molten alloy surface and the molten layer is rapidly extracted and cooled to form amorphous wires⁷. According to Katsuya et al., melt extraction method can produce amorphous wires in alloy systems⁸⁹. The aim of this project was to produce and characterize amorphous micro wires from TiCu based metallic glasses with high glass forming ability (GFA) Ti₂₅Zr₁₅Cu₆₀−ₓNix (x = 0, 5, 10, 15) via super cooled liquid melt extraction technique.

2. Experiment

A high glass forming alloy ingots with nominal compositions Ti₂₅Zr₁₅Cu₆₀−ₓNix (x = 0, 5, 10, 15 mol%) were prepared by arc-melting a mixture of elements with a high purity level >99.9% in a Ti-gettered high purity argon atmosphere. The cylindrical wires with diameters about 40–100 μm and lengths upto 400 mm were prepared by melt extraction technique. The amorphous nature of the melt-extracted wires and the crystallization behavior of the amorphous phase were examined by X-ray diffraction (XRD) using CuKα radiation and differential scanning calorimetry (DSC) at a heating rate of 0.67 K s⁻¹. Tensile testing of more than 9 samples for each composition were carried out according to ASTM standard D3379-75 with gauge length of 10 mm under strain rate of 8.33 × 10⁻⁴ s⁻¹. The fracture morphology was examined using scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Amorphicity of the micro wires

Figure 1(a) shows XRD pattern of the melt extracted amorphous wires. XRD traces for x = 5, 10 and 15 shows broad diffuse diffraction maxima indicating that the alloys are fully amorphous in the as melt extracted state. Even though the XRD trace for x = 0 has some sharp peaks depicting some crystalline phases being embed in the amorphous phase, their intensities are quite low. In general, all alloys with compositions x = 5, 10 and 15 showed pronounced broad diffuse diffraction maxima at 2θ = 35°–48°. The diffractions become broader with increase of Ni mol%, which indicates an enhancement in the GFA. It’s also observed that the average position of 2θ of the broad diffraction peak shifts to lower 2θ angles with increasing Ni content, indicating an increase of the first nearest-neighbor distance between the atoms with the Ni addition. It confirms that the GFA increases with increasing nickel content, which is also attributed to decreasing free volume.

DSC curves of the amorphous wires are shown in Fig. 1(b). The plots reveal small endothermic peaks corresponding to the glass transition temperatures (Tg) which is followed by a super-cooled liquid region ΔTg (ΔTg = Tg − Tc). It’s noticed that the ΔTg value increases with increasing Ni content, indicating a rising stability of amorphous structure. Exothermic peaks shown in Fig. 1(b) (Tp1, Tp2, Tp3) correspond to the crystallization temperatures.
corresponds to crystallization reactions. The first crystallization peak (marked as $T_{p1}$) becomes higher with increasing Ni content. It suggests that the larger exothermic enthalpies for crystallization for $x = 5, 10$ and $15$ make them difficult for first crystallization to occur hence favoring solidification in amorphous structure comparing with $x = 0$. The alloys with $x = 0, x = 5$ and $x = 10$ have three crystallization peaks even though the third peak for $x = 5$ is very broad. The three peaks show clear three stage crystallization for the alloys. Especially, the alloy $x = 15$ has only two exothermic crystallization peaks, which is similar as a $\text{Cu}_{52}\text{Zr}_{16}\text{Ti}_{10}$ metallic glass ribbon\(^9\). The second and/or third peaks shifting to higher temperature values accompanied with increasing wider range between $T_{p1}$ and $T_{p2}$, which also indicates crystallization difficult to occur. In short, the above discussed DSC results suggest that increasing Ni content enhances thermal stability of $\text{Ti}_{25}\text{Zr}_{15}\text{Cu}_{60-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$) amorphous alloys.

3.2 Mechanical properties

During tensile measurements, the amorphous wires shows a sign of non-linear, inelastic deformation prior to failure unlike bulk metallic glass samples which are prone to catastrophic fracture with no plasticity under tension as showed in Fig. 2. This nonlinear deformation may be caused by the formation of sub-nanometer voids coalescing from flow defects under tensile stresses when the diameter of metallic glasses decreases\(^4\). It was only $x = 0$ that did not show appreciable non-linear inelastic deformation prior to failure. This type of behavior in amorphous wires had also been reported for ($\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 0, 2, 4, 6$ mol\%) wires at strain rate of $8.33 \times 10^{-5}$ s\(^{-1}\)\(^1\). It is important to note that the non-linear behavior is not caused by the tensile machine but inherent properties of the samples.

Figure 3 is the summary of the average mechanical properties; tensile fracture strength ($\sigma$), engineering fracture strain ($\varepsilon$), and the Young’s modulus ($E$) of the amorphous wires. From the results, it is observed that there is a general increase in the average tensile fracture strengths of the wires from 1235 MPa to 1609 MPa and elastic modulus from 88 to about 115 GPa as the content of Ni was increased from 0 to 15 mol\%. All the samples showed an average fracture strain of about 1.4\%. These trends observed for the Young’s modulus and the tensile fracture strengths showing a general increase with increasing Ni content was also observed in the crystallization temperatures and supercooled liquid regions of the amorphous wires. Liao et al. found that the Young’s modulus of annealed ($\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 0, 2, 4,$
6 mol%) amorphous wires was about 20% smaller than the value for (Cu_{20}Zr_{50})_{100-x}Al_{x} (x = 5, 6, 8 mol%) bulk metallic glasses, owing to homogeneous surface features of amorphous wires\(^{11,12}\). It can be also observed in Fig. 3, that the average standard deviations for the tensile fracture strengths of the amorphous wires were quite high. It is worth noting that such high values in the standard deviations had also been recorded by Ilankeeran et al.\(^{13}\) while investigating fracture strengths of single carbon and glass fibers where the standard deviation values reported were 19.86% and 17.06% for the carbon and glass fibers respectively. These variations are probably due to samples inheriting some geometrical imperfections such as surface defects and sides which are not perfectly parallel as adduced by Ref. 13).

3.3 Fracture surface

Figure 4(a) shows a typical SEM micrograph of a fractured test sample revealing two distinct regions resulting from different failure modes: pure shear mode (marked A in Fig. 4(a)) and vein patterned (marked B in Fig. 4(a)). A close up SEM image of the vein patterned, region B is shown in Fig. 4(b) showing a flower like structure which occurrence results from liquid like layer formation. The liquid like layer results from high temperature that leads to local melting of the shear bands. The fracture angle about 51° is a reflection of the failure mode as shown in Fig. 4(c). This value is within the range of shear angles reported by others metallic glasses, which were 54°\(^{14}\), 54°\(^{14}\), 50–60°\(^{15}\). For pure shear mode, material fractures at an angle of 45°, the angle for maximum shear stresses in a material. The fracture angle for the amorphous wire is not on the maximum shear stress plane of 45° with respect to the tensile stress axis because the energy barrier is too high for the atoms on the plane to flow hence the fracture does not occur on this plane\(^{14}\).

4. Conclusions

Super cooled melt-extraction method was used to prepare the Ti_{25}Zr_{15}Cu_{60-x}Ni_{x} (x = 0, 5, 10, 15) metallic glass wires. The amorphous wires showed excellent glass forming ability. With increase in the Ni content from 0 to 15 at%, tensile strengths and Young's modulus of the metallic glass wires increase from 88 GPa to about 115 GPa and from 1235 MPa to 1609 MPa, respectively. Micro-tensile testing of the wires revealed a nonlinear inelastic deformation, which is quite different from the usual catastrophic failure of bulk metallic glasses. These properties make the alloy wires suitable for application varied environments for fabrication of many micro sized materials and possible fabrication of luxury goods by liquid metal technology.

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