Formation and properties of new Ni-based amorphous alloys with critical casting thickness up to 5 mm

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Abstract

New Ni-based bulk metallic glasses were synthesized in Ni<sub>a</sub>Cu<sub>b</sub>/Co<sub>c</sub>/Ti<sub>d</sub>Zr<sub>e</sub>Ai<sub>f</sub> (a ∼ b ∼ 45 at.%) system, based on a ternary alloy, Ni<sub>45</sub>Ti<sub>20</sub>Zr<sub>35</sub>. The additions of Al and Cu greatly increase the glass-forming ability (GFA). The best GFA is located around Ni<sub>40</sub>Cu<sub>5</sub> Ti<sub>16</sub>Zr<sub>28</sub>:5Al<sub>10</sub>, from which fully amorphous samples of up to 5 mm thickness were successfully fabricated by an injection mold casting method. These alloys exhibit high glass-transition temperatures T<sub>G</sub> ∼ 760 to 780 K, and relatively wide undercooled-liquid regions ΔT (defined by the difference between T<sub>G</sub> and the first crystallization temperature T<sub>x1</sub> upon heating) ∼40–50 K. Mechanical tests on these alloys show quite high Vicker’s Hardness ∼ 780 to 862 kg/mm<sup>2</sup>, Young’s modulus ∼ 111 to 134 GPa, shear modulus ∼ 40 to 50 GPa and high fracture strength ∼ 2.3 to 2.4 GPa. The effect of small Si-addition and a discrepancy between GFA and ΔT are also reported. The exceptional GFA and the all-metallic compositions give these new alloys excellent promise for both scientific and engineering applications.

Keywords: Metallic glasses; Ni alloys; Bulk amorphous materials; Casting; Compression test

1. Introduction

Because of their excellent glass-forming abilities (GFAs) and exceptional mechanical properties that include very high strength and elastic strain limit, bulk amorphous alloys have been of particular scientific and engineering interests in the past two decades. A large number of glass-forming alloys with critical cooling rates less than 1000 K/s have been successfully developed in Zr- [1,2], La- [3,4], Pd- [5,6], Pr- [7] and Y- [8] based systems, which has significantly broadened the promise of amorphous alloys for both scientific and engineering applications. As candidates for structural materials, current bulk metallic glasses (BMGs) still have limitations. These include limited thermal stability and elastic modulii, relatively high density and materials cost. As such, there has been a growing interest in developing novel BMGs with higher strength, higher elastic modulii, greater thermal stability, lower density and lower materials cost, which can be exemplified by Ni- [9–12], Fe- [13,14], Cu- [15], Al-, Ti-based alloys. As to Ni-based alloys, although quite a few glass-forming systems [9–12] with high strength have been reported, the GFAs achieved so far are very limited. Also, some of these reported systems [9,10] comprise metalloids in their chemical compositions, which limits the manufacturability of these alloys. For broader engineering applications or scientific studies on Ni-based glasses, it is necessary to develop new Ni-based alloys with higher GFAs and better manufacturability.

In this paper, we report on the formation, thermo-dynamic and mechanical properties of a new series of Ni-based bulk glass forming alloys with the formula Ni<sub>a</sub>Cu<sub>b</sub>/Co<sub>c</sub>/Ti<sub>d</sub>Zr<sub>e</sub>Ai<sub>f</sub> (a ∼ b ∼ 45 at.%), which show a critical casting thickness ranging from 2 to 5 mm.
2. Experiments

The ingots of the alloys studied in this work were prepared by arc melting mixtures of ultrasonically cleansed elemental metals having a purity of 99.5 at.% or higher. The arc melting was performed in a Ti-gettered high purity Argon atmosphere. Each ingot was re-melted in the arc melter for at least three times aimed at obtaining chemical homogeneity. The alloyed ingots were then re-melted under high vacuum in a quartz tube using high purity argon at a pressure of 1–2 atm. The copper molds have internal rectangular cavities with various thickness ranging from 0.5 to 5 mm. For comparison purposes, very thin samples (cut along a plane normal to the length of the samples) were examined by X-ray diffraction (XRD), using a 120° position sensitive detector (Inel) and a collimated Co Kα source. The amorphous structures of the bulk cast samples were further confirmed by transmission electron microscopy (TEM) analyses performed on their cross-sections. The glass transition and crystallization behaviors of all samples were examined with a differential scanning calorimeter (Perkin-Elmer DSC 7) at a heating rate of 0.33 K/s. Vicker’s hardness was measured on fully amorphous rectangular cast strips using a Leitz microhardness tester. Young’s modulus, shear modulus and Poisson ratio were obtained by measuring the longitudinal and shear sound velocities in the fully amorphous strips with an ultrasonic device and substituting the velocities into a set of formulas to be shown in Section 3.5.

3. Results and discussions

3.1. Ternary Ni_{45}Ti_{20}Zr_{35} alloy

Table 1 lists some examples of the newly discovered bulk metallic glasses in an order that reflects the sequential optimization of successive alloy additions which resulted in the improvement of the critical casting thickness for obtaining fully glassy samples.

The first phase of this work was the discovery of the ternary thin glass former, Ni_{45}Ti_{20}Zr_{35}, which produced a 0.5-mm thick partially amorphous strip using injection mold casting. The XRD and DSC scans of this ternary alloy are included in Figs. 1 and 2, respectively. Although there is some evidence of crystallinity on the XRD pattern in Fig. 1, the apparent diffuse background represents a large fraction of amorphous phase in the sample. This is further confirmed by the DSC scan in Fig. 2, which gives a total exothermic heat release of 52 J/g caused by the crystallization of the amorphous fraction of the specimen. The \( T_g \) and \( T_{x1} \) (marked in the figure by arrows) of this alloy are 725 and 752 K, respectively, and thus the stable undercooled liquid range is \( \Delta T = T_{x1} - T_g = 27 \) K.

3.2. Quaternary Ni_{45}Ti_{30}Zr_{35-x}Al\(_x\) alloys

Fig. 1 shows the structural effects of subsequent Al additions to the ternary alloy (in replacement of Zr). In Fig. 1, the quaternary samples used for taking XRD patterns are all 2 mm thick strips and the patterns were taken from the transverse cross-sections of the strips. The sample with 8% Al shows a weak broad background together with some nanocrystalline-like peaks, indicating a two-phase (amorphous phase + crystalline phase) partially crystallized structure. The sample with 10% Al only shows a series of broad diffraction maxima without any observable crystalline Bragg peaks, indicating a fully amorphous structure. The sample with 12% Al shows many crystalline peaks without any noticeable diffuse background, indicating the formation of one or more complex intermetallic compounds.

### Table 1

Examples of the new Ni-based amorphous alloys developed in this work (\( T_g \) and \( T_{x1} \) were measured with DSC at a heating rate of 0.33 K/s)

<table>
<thead>
<tr>
<th>Alloy composition (at.%)</th>
<th>Critical casting thickness (mm)</th>
<th>( T_g ) (K)</th>
<th>( T_{x1} ) (K)</th>
<th>( \Delta T = T_{x1} - T_g ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{45}Ti_{30}Zr_{15}</td>
<td>~ 0.5</td>
<td>725</td>
<td>752</td>
<td>27</td>
</tr>
<tr>
<td>Ni_{45}Ti_{30}Zr_{15}Al_6</td>
<td>&lt;0.5</td>
<td>761</td>
<td>802</td>
<td>41</td>
</tr>
<tr>
<td>Ni_{45}Ti_{30}Zr_{15}Al_8</td>
<td>2</td>
<td>773</td>
<td>818</td>
<td>45</td>
</tr>
<tr>
<td>Ni_{45}Ti_{30}Zr_{15}Al_12</td>
<td>&lt;0.5</td>
<td>783</td>
<td>832</td>
<td>49</td>
</tr>
<tr>
<td>Ni_{45}Cu_{10}Ti_{15}Zr_{25}Al_{10}</td>
<td>3</td>
<td>765</td>
<td>807</td>
<td>42</td>
</tr>
<tr>
<td>Ni_{45}Cu_{10}Ti_{15}Zr_{25}Al_{10}</td>
<td>4</td>
<td>762</td>
<td>808</td>
<td>46</td>
</tr>
<tr>
<td>Ni_{45}Cu_{10}Ti_{15}Zr_{25}Al_{10}</td>
<td>5</td>
<td>763</td>
<td>809</td>
<td>46</td>
</tr>
<tr>
<td>Ni_{39.5}Cu_{12.5}Ti_{19.5}Zr_{21.5}Al_{10}Si_{6.5}</td>
<td>5</td>
<td>768</td>
<td>815</td>
<td>47</td>
</tr>
</tbody>
</table>
alloy with 10% Al is the best glass former in this quaternary alloy series.

Fig. 2 presents the thermodynamic effects of the Al additions. As can be seen from these DSC scans, as well as from Table 1, the \( T_g \), \( T_x \), and \( \Delta T \) all increase monotonically as the Al content increases from 8% to 10% and 12%. It was previously proposed [16] that the GFA increases with \( \Delta T \) or, in other words, alloys with higher \( \Delta T \) values tend to have higher GFAs. However, the diffraction results in Fig. 1 clearly show that the highest GFA in the current quaternary alloy series occurs at 10% Al which does not correspond to the highest \( \Delta T \) value. The alloy with the highest \( \Delta T \) value, i.e., Ni\(_{45}\)Ti\(_{20}\)Zr\(_{23}\)Al\(_{12}\), seems to have the lowest GFA among the three alloys judging from diffraction patterns in Fig. 1. A similar discrepancy between GFA and thermal stability (i.e., \( \Delta T \)) has been observed in other alloy systems [17–19]. For the Vitreloy series of BMGs [17], a decomposition mechanism was used to explain why the best glass former does not have the highest thermal stability upon heating at a constant rate. Further work including small angle neutron scattering (SANS) experiments is needed to clarify if the same mechanism is involved in the current alloys. Aimed at a better prediction or description of the GFAs of various alloys, other parameters, including \( T_g/T_m \) [20] (where \( T_m \) is the melting temperature), \( T_g/T_l \) [18] (where \( T_l \) is the liquidus temperature) and \( T_g/(T_g + T_l) \) [19], have been utilized by different researchers. Due to the lack of data on the melting behaviors of the current alloys, these parameters are not discussed here.

3.3. Quinary Ni\(_{x}\)Cu\(_{a}\)/C\(_{0}\)xTi\(_{y}\)/C\(_{0}\)yZr\(_{b}\)/C\(_{0}\)bAl\(_{10}\) alloys (\( a \sim b \sim 45 \) at.%)

Figs. 3–5 present further major improvements achieved by adding copper to the above quaternary alloy Ni\(_{45}\)Ti\(_{20}\)Zr\(_{23}\)Al\(_{10}\). With small amounts of copper and small adjustments in compositions, thicker fully amorphous samples have been successfully prepared. Without Cu, the quaternary alloy is significantly crystallized at
3 mm thickness as shown in Fig. 3. The appropriate additions of Cu prevent the formation of the intermetallic compounds yielding fully amorphous samples. The best GFA was achieved from Ni_{40}Cu_{5}Ti_{16}Zr_{28}Al_{10} ('RAG2', in the following) which has a critical casting thickness above 5 mm. To best of our knowledge, this is the highest critical casting thickness ever obtained for Ni-based BMGs. To confirm the fully amorphous structure of the 5-mm thick strip of RAG2, TEM analysis was also performed on its transverse cross-section. From Fig. 4, one can see its electron diffraction pattern only comprises a series of diffuse halo rings. No distinct evidence of sharp crystalline rings was found anywhere across the specimen. Therefore, it is clear that the 5-mm strip of RAG2 indeed has a fully amorphous structure. TEM analyses were also performed on other bulk samples. The results, which are not shown here, are all in good agreement with the XRD analyses.

Fig. 5 shows the DSC traces of the quinary alloys. All these samples exhibit an endothermic glass transition and a fairly wide undercooled liquid region, followed by one or more exothermic events characteristic of crystallization. Their \( T_g, T_1 \), and \( \Delta T \) values are listed in Table 1. For a comparison, a DSC trace taken from a \( \sim60\mu \)m thick splat quenched sample of RAG2 is also included in Fig. 5. Within the measurement range, there is no appreciable difference in the \( T_g, T_1 \) and \( \Delta H_t \) (total enthalpy of crystallization) values of the splat quenched sample and the 5-mm thick strip of RAG2. This again confirms the fully amorphous structure of the bulk cast sample.

3.4. Effect of small Si additions

A small amount Si addition also appears to provide an improvement as illustrated in Fig. 6. Without Si, 4-mm thick Ni_{40}Cu_{5}Ti_{16}Zr_{28}Al_{10} strip shows an observable Bragg peak superimposed on the broad amorphous diffraction band, indicating that small nanocrystals have precipitated from the amorphous matrix. However, with 0.5% Si the alloy (Ni_{40}Cu_{5}Ti_{16}Zr_{28}Al_{10})_{99.5}Si_{0.5} is fully amorphous up to 5 mm, as shown by the absence of any sharp crystalline peaks on the XRD pattern in Fig. 6. The thermodynamic parameters of this Si-containing alloy are also included in Table 1, where it can be seen that the small Si addition enlarges the undercooled liquid region \( \Delta T \) by increasing the crystallization temperature (\( T_1 \)) while leaving \( T_g \) almost unchanged. This enhancement of GFA and stability of the glassy state by adding small amounts of Si agrees with previous reports for Zr-based BMGs [21].

3.5. Mechanical tests

Vicker’s hardness and elastic modulii were measured using those cast strips confirmed to be fully amorphous by both XRD and DSC. Selected results are shown in Table 2. The modulii and Poisson ratio were obtained by measuring the sound propagation velocities of plane waves (longitudinal and transverse, \( C_l \) and \( C_s \), respectively) in the alloys, then using the following relations (valid for isotropic materials such as glasses):

\[
v = \frac{(2-x)/(2-2x)}{\rho C_s^2} = \text{Poisson ratio}, \quad \text{where} \quad x = (C_l/C_s)^2,
\]

\[
G = \rho C_s^2 = \text{shear modulus}, \quad \text{where} \quad \rho \text{ is density},
\]

\[
E = G/2(1+v) = \text{Young's modulus}.
\]

Fig. 7 presents the compressive stress vs. strain curves for two selected alloys. The slopes have been calibrated using the Young’s modulus data measured from acoustic experiments. The strength data obtained from these compression tests are included in Table 2. These alloys have quite high fracture strength \( \sim2.3-2.4 \) GPa. The quaternary alloy, Ni_{45}Ti_{20}Zr_{25}AL_{10}, has a slightly higher strength than the quinary alloys (e.g., RAG2). This is associated with the small drop in \( T_g \) caused by
the addition of Cu (see Table 1). It is noteworthy that these alloys roughly obey the theoretical relation between Vicker’s hardness and strength: $H_v \sim \frac{42}{2.37}$ (in kg/mm$^2$, $H_v$ in MPa) for isotropic materials. Significantly premature failure, known for silica glass and some Ni-based BMGs [22] does not happen to these alloys.

4. Conclusions

The formation and properties of a new series of Ni-based bulk glass forming alloys with formula $\text{Ni}_{x}\text{Cu}_a\text{Ti}_b\text{Zr}_c\text{Al}_{10}$ ($a \sim b \sim 45$ at.%) are reported which have a critical casting thickness ranging from 2 to 5 mm. The best GFA appears around $x = 40, y = 16.5, a = b = 45$. These new amorphous alloys exhibit high thermal stabilities ($\Delta T \sim 40$ to 50 K) and excellent mechanical properties (e.g., $\sigma_f \sim 2.3$ to 2.4 GPa). Small amount Si-addition is found to enhance the GFAs and the thermal stabilities of these alloys. The GFA and $\Delta T$ of some quaternary alloys are found not in agreement with each other. The GFAs reported in this paper may be among the highest ever obtained for Ni-based alloys. Meanwhile, the all-metallic compositions endow these present Ni-based BMGs with excellent manufacturability.

Acknowledgements

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References

[12] Choi-Yim H, Xu DH. Unpublished work. We found Ni–Nb–Sn alloys reported in [12] fail prematurely; the apparent strength obtained from compression tests is quite lower than expected values.

Table 2

<table>
<thead>
<tr>
<th>Alloy composition (at.%)</th>
<th>Vicker’s hardness (kg/mm$^2$)</th>
<th>Poisson ratio</th>
<th>Shear modulus (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Fracture strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{45}$Ti$</em>{20}$Zr$<em>{25}$Al$</em>{10}$</td>
<td>791</td>
<td>0.36</td>
<td>42</td>
<td>114</td>
<td>2.37</td>
</tr>
<tr>
<td>Ni$<em>{40}$Cu$<em>6$Ti$</em>{16}$Zr$</em>{28}$Al$_{10}$</td>
<td>780</td>
<td>0.361</td>
<td>40.9</td>
<td>111</td>
<td>2.18</td>
</tr>
<tr>
<td>Ni$<em>{40}$Cu$<em>5$Ti$</em>{17}$Zr$</em>{28}$Al$_{10}$</td>
<td>862</td>
<td>0.348</td>
<td>48.7</td>
<td>133.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Ni$<em>{40}$Cu$<em>5$Ti$</em>{16.5}$Zr$</em>{28.5}$Al$_{10}$</td>
<td>800</td>
<td>0.355</td>
<td>45.2</td>
<td>122</td>
<td>2.3</td>
</tr>
<tr>
<td>Ni$<em>{39.8}$Cu$<em>5$Ti$</em>{15.9}$Zr$</em>{27.8}$Al$_{10}$</td>
<td>829</td>
<td>0.36</td>
<td>43</td>
<td>117</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Fig. 7. Compressive stress vs. strain curves of two selected alloys: (a) Ni$_{40}$Cu$_5$Ti$_{16.5}$Zr$_{28.5}$Al$_{10}$ and (b) Ni$_{45}$Ti$_{20}$Zr$_{25}$Al$_{10}$.