Formation and Thermal Stability of Ni-Based Bulk Metallic Glasses in Ni-Zr-Nb-Al System

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An Al element was selected as an alloying metal to improve the glass-forming ability (GFA) of Ni-Zr-Nb alloys. The thermal stability and glass-forming ability of Ni-Zr-Nb-Al alloys were investigated. It was found that the partial substitution of Nb by Al led to significant shift of the onset crystallization temperature \( T_c \), the reduced glass transition temperature \( T_g / T_c \), while the glass transition temperature \( T_g \) was less composition sensitive. The supercooled liquid region, \( \Delta T_g = ( T_c - T_g ) \), the reduced glass transition temperature \( ( T_g / T_c ) \) and \( \gamma = T_g / ( T_f + T_c ) \) increased with increasing Al content up to 5 at\%. The best GFA was found at Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\)Al\(_{2}\) with a critical diameter of 3 mm. The characteristics parameters are: \( \Delta T_g = 54 \) K, \( T_g / T_c = 0.615 \) and \( \gamma = 0.405 \). The maximum values of \( \Delta T_g \) and \( T_g / T_c \) were 72 K and 0.617, respectively, at Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\)Al\(_{2}\). The compression tests showed that the Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\)Al\(_{2}\) BMG possessed high fracture strength of 2900 MPa, Young’s modul of 152 GPa, and plastic elongation of 2.5% at room temperature.

Keywords: bulk metallic glass, glass-forming ability, mechanical property

1. Introduction

Bulk metallic glasses (BMGs) are new alloys associated with extraordinary high glass-forming ability (GFA), which can be made at cooling rates as slow as 1~100 K/s.\(^{1-4}\) The alloys possess advanced physical and mechanical properties, and have been the subject materials in tremendous research endeavors by now.\(^{1-4}\) Among those BMGs which are composed of metallic elements only, Ni-based alloys possess the highest fracture strength, higher Young’s modulus and good ductility. They are one of the most promising engineering BMGs.\(^{5,6}\) Ni-based BMGs have been obtained in following alloy systems, namely, Ni-Nb-(Ti,Zr,Hf), Ni-Nb-Sn, Ni-Nb-Ti-Zr-Co-Cu, Ni-Zr-Ti-Si-Sn and Ni-Cu-Ti-Zr-Al.\(^{6-12}\) Recently, new Ni-based glass-forming alloys were developed in the Ni-Zr-Nb system.\(^{13}\) These alloys exhibited high thermal stability, for instance, the largest value of the supercooled liquid region was found to be about 50 K for Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\) alloy. More interestingly, high hydrogen permeability was also observed in these alloys.\(^{14}\) The unique property combination gives rise to promise the hydrogen permeable membrane application at high temperatures. However, the GFAs of these Ni-Zr-Nb alloys are very limited, and it is worth exploring new compositions with improved GFA. According to the well-known three empirical principles for BMGs formation,\(^{1,15}\) Al was selected as the addition element to a basic Ni-Zr-Nb alloy. The glass-forming ability, thermal stability and mechanical property of Ni-Zr-Nb-Al glassy alloys thus formed are investigated in the present work.

2. Alloy Compositions and Experimental Procedure

The above mentioned Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\) composition was chosen as the basic alloy. Considering that the Goldschmidt radius of Al atom (0.143 nm) is close to that of Nb (0.147 nm),\(^{16}\) a series of Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\)Al\(_{2-x}\) alloys were designed in the manner of Al substituting Nb. The immediate experimental results showed that an optimum content for Al addition in Ni-Zr-Nb alloys was about 5 at\%. So in the subsequent alloying treatment we fixed the Al content and changed the ratio of Zr to Nb content. The composition dependence of thermal stability and glass-forming ability in the second serial alloys, namely, Ni\(_{60}\)Zr\(_{35-x}\)Nb\(_{5}\)Al\(_{x}\), was investigated.

Buttons of Ni-Zr-Nb-Al alloys were prepared by arc melting the constituent elements under a Ti-gettered high purity argon atmosphere. The purities of metals are 99.5 mass\% for Zr, 99.99 mass\% for Al and 99.9 wt\% for Ni and Nb. In particular, Ni-Nb intermediate alloys were produced first for the subsequent co-melting with Zr and Al elements. The ingots were remelted four times to ensure homogeneity in composition. Using these alloy ingots, ribbon samples with a cross section of about 0.05 \( \times 1.0 \) mm\(^2\) were prepared by a single roller melt-spinning apparatus with a wheel surface velocity of 40 m/s, and alloy rods were made by copper mold casting.

X-ray diffraction (XRD) for phase identification was conducted by a Rigaku RINT-ultima IIIsp diffractometer with Cu-\(K_α\) irradiation (\( λ = 0.15406 \) nm), TA-DSC Q100 type differential scanning calorimetry (DSC) and TA-STD Q600 type differential thermal analysis (DTA) were employed to study the thermal stability. The heating rates for DSC and DTA measurements were 40 K/min and 20 K/min, respectively.

Cylindrical specimens, with dimensions of 2.0 \( \pm 0.03 \) mm in diameter and 4.0 \( \pm 0.05 \) mm in length, were adopted for uniaxial compression testing. Quasistatic loadings were performed at a strain rate of \( 5 \times 10^{-4} \) s\(^{-1}\) with an Instron testing machine at room temperature, and the strain was measured by using a strain gauge. The morphology observation of the fractured samples was made with a SEM.

3. Results and Discussion

3.1 Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\)Al\(_{2-x}\) Alloy Series

XRD patterns indicated that all the melt-spun Ni\(_{60}\)Zr\(_{35}\)Nb\(_{5}\)Al\(_{x}\) \(( x = 0, 2.5, 5, 7.5 and 10; \) at\%) samples...
Alloying effect on the enhancement of GFA was pronounced in the Ni-Zr-Nb system. Inoue has proposed three empirical principles for BMG-forming systems, \(^1,15\) i.e., (1) consisting of more than three elements, (2) significant atomic size mismatches about above 12\% among the predominant constituents, and (3) suitable negative heats of mixing among their elements. For the Ni-Zr-Nb-Al system, the negative mixing enthalpy is \(-44\,kJ/mol\) for Al-Zr, \(-18\,kJ/mol\) for Al-Nb and \(-22\,kJ/mol\) for Al-Ni.\(^{20}\) The atomic radii of Al is 0.143 nm, 0.160 nm for Zr, 0.147 nm for Nb, and 0.125 nm for Ni.\(^{16}\) The ratios of the atomic radius \((R)\) are 1.12 for Zr/Al, 1.03 for Nb/Al, 1.14 for Al/Ni. Therefore, the addition of Al element in the Ni-Zr-Nb system satisfies all the above three rules, which lead to formation of bulk metallic glasses in Ni-Zr-Nb-Al system.

### 3.2 Ni\(_{60}\)Zr\(_{35}\)-xNb\(_{3}\)Al\(_{x}\) alloy series

A family of Ni\(_{60}\)Zr\(_{35}\)-xNb\(_{3}\)Al\(_{x}\) \((x = 0\sim 35;\ \text{in}\ \text{at}%)\) alloys were then designed to examine the effect of Zr/Nb ratio on the thermal stability and glass-forming ability. Melt-spun amorphous alloys were obtained at all the compositions designed. Their DSC traces are shown in Fig. 4(a). A distinct glass transition is observed for the compositions with Nb contents ranging from 0 to 25 at\%. At higher Nb concentrations \(T_g\) got to be concealed. With DTA results (Fig. 4(b)), \(T_g\), \(T_l\), \(\Delta T_x\), and \(\gamma\) were calculated for the glassy alloys showing distinct glass transitions. All the data obtained are suma-
rized in Table 1. The variation of $T_x$ is irregular. The largest values of $\frac{\Delta T_x}{T_g}$ and $\frac{\Delta T_y}{T_l}$ are obtained at the 10 at% Nb composition, while $\frac{T_{rg}}{T_l}$ maximum appears around 20 at% Nb (Fig. 5). $\Delta T_x$ and $\gamma$ thus are not consistent with $T_{rg}$ in GFA assessment. Alloy rods of 2 mm in diameter at these compositions were made to reveal the difference in GFA. The BMGs can be made in the composition range containing 12.5–20 at% Nb (Fig. 6). The best former was achieved at Ni$_{60}$Zr$_{35}$Nb$_{15}$Al$_5$. The Ni$_{60}$Zr$_{25}$Nb$_{10}$Al$_5$ BMG has the largest $\Delta T_x$ of 72 K, while the critical BMG size is less than 1.5 mm. The above results show that GFA assessments by $T_{rg}$, $\frac{\Delta T_x}{T_g}$, and $\frac{\Delta T_y}{T_l}$ are not well consistent with the experimental results on the present alloy series. The DTA curves (Fig. 4(b)) show that the best BMG has a single peak melting process associated with a minimum melting span of 27 K. This suggests that the best glass former is located near a eutectic composition. It was very alike the case in the Ni$_{60}$Zr$_{35}$Nb$_{15}$Al$_5$ alloy series (see in Fig. 2).

### 3.3 Strength and fracture behavior

The mechanical properties of the as-cast Ni$_{60}$Zr$_{20}$Nb$_{15}$Al$_5$ glassy alloy rod were examined at room-temperature. The stress-strain curve under uniaxial compression is shown in Fig. 7. The curve exhibits an elastic deformation followed by a distinct plastic elongation of 2.5 % after yielding. The compression fracture strength ($\sigma_c$) and Young’s modulus (E) of this sample are approximately 2900 MPa and 152 GPa, respectively. As shown in Fig. 8, the Ni$_{60}$Zr$_{20}$Nb$_{15}$Al$_5$ glassy alloy exhibits typical fracture behavior of BMGs. The fracture surface is inclined by an angle of about 45° to the loading direction. Fracture surfaces show typical microscopic vein patterns. Localized shear bands are also observed on the surface of the deformed specimen.

### Table 1: Thermal analysis data of the melt-spun Ni$_{60}$Zr$_{35-x}$Nb$_x$Al$_5$ (x = 0–35 at%) ribbons and critical diameter for BMG formations.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$T_x$/K</th>
<th>$T_{rg}$/K</th>
<th>$\Delta T_x$/K</th>
<th>$T_m$/K</th>
<th>$T_l$/K</th>
<th>$\gamma$</th>
<th>$\Delta T_y$/K</th>
<th>$T_l$/K</th>
<th>$\gamma$</th>
<th>$D_c$(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 at% Nb</td>
<td>809</td>
<td>843</td>
<td>34</td>
<td>1320</td>
<td>1355</td>
<td>0.597</td>
<td>0.390</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 at% Nb</td>
<td>820</td>
<td>877</td>
<td>57</td>
<td>1331</td>
<td>1365</td>
<td>0.601</td>
<td>0.401</td>
<td>&lt;1</td>
<td></td>
<td></td>
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<tr>
<td>10 at% Nb</td>
<td>830</td>
<td>902</td>
<td>72</td>
<td>1339</td>
<td>1373</td>
<td>0.605</td>
<td>0.409</td>
<td>&lt;1.5</td>
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<tr>
<td>12.5 at% Nb</td>
<td>836</td>
<td>902</td>
<td>66</td>
<td>1339</td>
<td>1372</td>
<td>0.609</td>
<td>0.409</td>
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<td></td>
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<tr>
<td>15 at% Nb</td>
<td>842</td>
<td>896</td>
<td>54</td>
<td>1343</td>
<td>1370</td>
<td>0.615</td>
<td>0.405</td>
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<tr>
<td>17.5 at% Nb</td>
<td>853</td>
<td>894</td>
<td>41</td>
<td>1340</td>
<td>1384</td>
<td>0.616</td>
<td>0.400</td>
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<tr>
<td>20 at% Nb</td>
<td>861</td>
<td>897</td>
<td>36</td>
<td>1342</td>
<td>1396</td>
<td>0.617</td>
<td>0.397</td>
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<tr>
<td>25 at% Nb</td>
<td>873</td>
<td>900</td>
<td>27</td>
<td>1370</td>
<td>1417</td>
<td>0.616</td>
<td>0.393</td>
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<tr>
<td>30 at% Nb</td>
<td>*</td>
<td>908</td>
<td>*</td>
<td>1398</td>
<td>1445</td>
<td>*</td>
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<tr>
<td>35 at% Nb</td>
<td>*</td>
<td>915</td>
<td>*</td>
<td>1446</td>
<td>1476</td>
<td>*</td>
<td>*</td>
<td>&lt;1</td>
<td></td>
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</table>

**Glass transition temperature, $T_x$; onset temperature of the first crystallization peak; under-cooled liquid region, $\Delta T_x = T_{rg} - T_x$; onset temperature of melting, $T_m$; liquidus temperature, $T_l$; reduced glass transition temperature $T_r/T_l$ and $\gamma = T_r/(T_x + T_l)$; critical size for BMG formation, $D_c$.**
4. Conclusions

New Ni-based BMGs were developed in Ni-Zr-Nb-Al alloy system. It was confirmed that the GFA of the Ni-Zr-Nb alloys was improved significantly by the addition of Al. Glassy alloys with distinct glass transition were obtained in a wide composition range: 10 at% ≤ Zr ≤ 35 at%; 0 at% ≤ Al ≤ 10 at%; 0 at% ≤ Nb ≤ 25 at%. The Ni$_{60}$Zr$_{35}$Nb$_{10}$Al$_5$ glassy alloy had the maximum $\Delta T_x$ of 72 K. In the Ni$_{60}$Zr$_{35}$Nb$_x$Al$_5$ alloy series, glassy alloy rods with 2 mm in diameter were obtained at compositions of 12.5~20 at% Nb contents. The highest glass forming ability was achieved near an eutectic composition of Ni$_{60}$Zr$_{20}$Nb$_{15}$Al$_5$, where the glassy alloy rod of 3 mm in critical diameter was produced by copper mold casting. This BMG exhibits high fracture strength of 2900 MPa, Young’s modulus of 152 GPa, and plastic elongation of 2.5% at room temperature.

Acknowledgments

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REFERENCES