Ni-Based Refractory Bulk Amorphous Alloys with High Thermal Stability

Minha Lee¹, Donghyun Bae¹, Wontae Kim² and Dohyang Kim¹,*

¹Department of Metallurgical Engineering, Center for Noncrystalline Materials, Yonsei University, Seoul 120-749, Korea
²Division of Applied Science, Chongju University, Chongju 360-764, Korea

*Corresponding author, E-mail: dohkim@yonsei.ac.kr

Enhancement of thermal stability and glass forming ability in Ni₆₀Nb₄₀−ₓTaₓ (x = 0, 3, 5, 10, 20 at%) alloys has been investigated. The crystallization temperature increases from 660°C in binary Ni₆₀Nb₄₀ amorphous phase to 721°C in Ni₆₀Nb₄₀Ta₂₀ amorphous phase. The fully amorphous rod with diameter of 2 mm is fabricated in Ni₆₀Nb₃₀Ta₁₀ alloy by an injection casting method. The compressive failure strength of the Ni₆₀Nb₃₀Ta₁₀ bulk amorphous alloy is 3346 MPa.

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1. Introduction

In the Ni-Nb alloy system, amorphous phase has been obtained in the wide range of alloy composition containing 30-60 at% Nb by rapid solidification process,¹ indicating high glass forming ability. Since the Ni-Nb based metallic glass shows excellent corrosion resistance and high strength,² enhancement of glass forming ability of Ni-Nb based metallic glass may enlarge the application field. Amorphous samples up to nearly 2 mm thickness have been prepared by quenching of highly undercooled Ni₆₀Nb₃₀ melts.³

In order to enhance the glass forming ability of the Ni-Nb alloy further, a few studies have been performed by adding other elements to form multi-component alloy.⁴⁻⁸ In the Ni-Nb-Cr-Mo-P-B system, bulk amorphous alloy rods with diameter of 1 mm have been fabricated by an injection casting method.⁴ The amorphous alloys exhibit high strength (~2.6 GPa) and high corrosion resistance.⁴ However, since large amounts of P (~15 at%) that has a high vapor pressure should be added to enhance the GFA, fabrication process of the Ni-based bulk amorphous alloys is complicated. Also bulk amorphous alloy rods with diameter of 2 mm could be fabricated in Ni-Nb-P and Ni-Nb-Ta-P systems.⁵ Recently, formation of bulk amorphous alloy has been reported in Ni-Nb based alloys containing no metalloid elements. Bulk amorphous alloy rods with diameter of 1 mm could be fabricated in Ni-Nb-Al alloys.⁶ Bulk amorphous Ni-Nb-Ti(-Hf) alloy rods could be fabricated up to the diameter of 1.5 mm, and exhibited high strength of ~3.1 GPa.⁶ More recently, bulk amorphous alloys with the critical cast thickness of 3 mm been reported in the Ni-Nb-Sn system.⁷⁻¹⁰

Considering the similar heat of mixing in Ni-Nb (~143 kJ/mol) and Ni-Ta (~133 kJ/mol), and similar atomic size of Nb and Ta (Goldschmidt atomic radius: 14.6 and 14.9 nm respectively), the effect of substitution of Nb with Ta in Ni₆₀Nb₃₀ alloy is investigated. Since the refractory metals have high melting temperature (Nb: 2467°C, Ta: 3014°C), the amorphous alloys containing the refractory metals are expected to have high thermal stability and high strength. In this study we report the thermal stability and glass forming ability of Ni₆₀Nb₄₀−ₓTaₓ (x = 0, 3, 5, 10, 20 at%) metallic glass alloys prepared by melt spinning and injection casting techniques.

2. Experimental Procedure

Alloys of nominal composition Ni₆₀Nb₄₀−ₓTaₓ (x = 0, 3, 5, 10, 20 at%) were prepared by arc melting pure metals Ni(99.9%), Nb(99.9%) and Ta(99.9%), under an argon atmosphere. Amorphous alloy specimens were produced by melt spinning and injection casting methods under an Ar atmosphere. For melt spinning, the alloys were remelted in quartz tubes, followed by ejecting with an over pressure of 35 kPa through a 0.5 mm diameter nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. The resulting ribbons exhibit thickness of about 30 μm and width of about 2 mm. In order to estimate glass forming ability, rod specimens with 1-3 mm in diameter and 35 mm in length were fabricated by injection casting. The Ni₆₀Nb₄₀−ₓTaₓ (x = 0, 3, 5, 10, 20 at%) alloys were remelted in quartz tubes, followed by casting into cylindrical cavity of a Cu mold. Structural change during heat treatment was studied by using X-ray diffractometry with monochromatic Cu Kα radiation (Rigaku, RINT2200) and transmission electron microscopy (TEM, JEOL, 2010F). Thin foil specimens for transmission electron microscopy were prepared by ion beam milling method. Crystallization and melting behaviors of the amorphous alloys were studied by using differential scanning calorimetry (DSC, Perkin Elmer, DSC7) and differential temperature analysis (DTA, Perkin Elmer, DTA7). Exothermic reactions during crystallization were monitored during continuous heating up to 700°C for DSC experiment and 1400°C for DTA experiment. Test specimens with a dimension of 1 mm diameter and 2 mm height were prepared for compression test. Uniaxial compression tests were conducted with an initial strain rate of 6 × 10⁻⁵ s⁻¹. The surface of the fractured specimen was observed by SEM.

3. Results

The X-ray diffraction results indicated that the melt-spun ribbons of Ni₆₀Nb₄₀−ₓTaₓ (x = 0, 3, 5, 10, 20 at%) alloys are composed of a single amorphous phase. Figures 1(a) and (b)
show typical DSC and DTA traces obtained during continuous heating as-melt spun Ni$_{60}$Nb$_{30-x}$Ta$_x$ alloys (x = 0, 3, 5, 10, 20 at%) with a heating rate of 40°C/min. The amorphous alloys show very high crystallization temperature, preventing from monitoring complete exothermic crystallization reactions during heating in DSC due to the temperature limit, the supercooled liquid region was 27°C. The amorphous phases in x = 0, 3 and 5 alloys did not show a clear glass transition event before crystallization, which is different from ordinary bulk glass forming alloys. However, as can be seen in the DSC trace (Fig. 1(a)), the amorphous phase in x = 10 alloy exhibited a clear glass transition at 661°C. Due to the temperature limit in DSC analysis the glass transition behavior in x = 20 alloy could not be identified clearly in the present study. The crystallization temperature of x = 10 alloy was 688°C, therefore the supercooled liquid region was 27°C. The DTA traces in Fig. 1(b) show that the melting ranges of the Ni$_{60}$Nb$_{30-x}$Ta$_x$ (x = 0, 3, 5, 10, 20 at%) alloys shifted to a higher temperature region with increasing Ta content. The glass transition temperature, the onset and peak temperatures of two exothermic reactions, and onset and end temperature of endothermic melting reaction are listed in Table 1.

To examine the glass forming ability of the alloys, rod specimens with diameters of 1, 2 and 3 mm were fabricated by injection casting. Fully amorphous alloy rod with maximum diameter of 2 mm could be successfully fabricated by injection casting Ni$_{60}$Nb$_{30}$Ta$_{10}$ alloy. For the alloys with the composition of Ni$_{60}$Nb$_{30}$Ta$_{10}$, (x = 0, 3, 5 at%) alloys fully amorphous alloy rod with diameter of max. 1 mm could be fabricated by injection casting. Figure 2 shows DSC traces obtained during continuous heating the injection cast Ni$_{60}$Nb$_{30}$Ta$_{10}$ rod with diameter of 2 and 3 mm with a heating rate of 20°C/min. For comparison, the DSC trace for the melt-spun Ni$_{60}$Nb$_{30}$Ta$_{10}$ ribbon is included. Although we could not measure the total amount of exothermic heat due to the temperature limit, the supercooled region, crystallization temperature and the maximum heat flow rate in 2 mm diameter rod sample and melt-spun ribbon

Table 1 Glass transition temperatures, onset and peak temperatures of the exothermic peaks and onset and end temperatures of the melting peaks of the Ni-Nb-Ta alloys investigated in the present study.

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>$T_g$ (°C)</th>
<th>$T_{1s}$ onset (°C)</th>
<th>$T_{1s}$ peak (°C)</th>
<th>$T_{2s}$ onset (°C)</th>
<th>$T_{2s}$ peak (°C)</th>
<th>$T_1$ onset (°C)</th>
<th>$T_1$ end (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{60}$Nb$</em>{30}$</td>
<td>—</td>
<td>660</td>
<td>673</td>
<td>714</td>
<td>728</td>
<td>1175</td>
<td>1211</td>
</tr>
<tr>
<td>Ni$<em>{60}$Nb$</em>{30}$Ta$_3$</td>
<td>—</td>
<td>661</td>
<td>674</td>
<td>725</td>
<td>735</td>
<td>1181</td>
<td>1270</td>
</tr>
<tr>
<td>Ni$<em>{60}$Nb$</em>{30}$Ta$_5$</td>
<td>—</td>
<td>662</td>
<td>677</td>
<td>730</td>
<td>743</td>
<td>1192</td>
<td>1284</td>
</tr>
<tr>
<td>Ni$<em>{60}$Nb$</em>{30}$Ta$_{10}$</td>
<td>661</td>
<td>688</td>
<td>697</td>
<td>716</td>
<td>727</td>
<td>1208</td>
<td>1286</td>
</tr>
<tr>
<td>Ni$<em>{60}$Nb$</em>{30}$Ta$_{20}$</td>
<td>*</td>
<td>721</td>
<td>735</td>
<td>761</td>
<td>772</td>
<td>1240</td>
<td>1303</td>
</tr>
</tbody>
</table>

* cannot be measured due to the temperature limit in the DSC equipment.
were almost same within experimental errors, as indicated in Fig. 2. However, the amount of exothermic heat in 3 mm diameter rod sample decreased significantly due to a partial crystallization during injection casting process.

To further verify the amorphous state of alloys, X-ray diffraction and TEM analysis were performed for injection cast 2 mm sample. Figure 3 shows XRD trace obtained from the as-melt spun ribbon and injection cast sample. XRD result shows a broad halo pattern, characteristic of the amorphous structure. TEM observation confirmed that as injection cast specimen is composed of single amorphous phase without any crystalline phase. Figures 4(a) and (b) show a typical bright field TEM image and the corresponding selected area diffraction pattern (SADP) for 2 mm diameter Ni_{60}Nb_{30}Ta_{10} bulk metallic glass specimen.

Figure 5 shows a stress vs. strain curve of the as-injection cast Ni_{60}Nb_{30}Ta_{10} (x = 10 at%) alloy rod tested under the uniaxial compressive condition at room temperature. The compressive failure strength value of this sample was 3,346 MPa that is the highest compressive strength level among those reported in Ni-based metallic glasses so far. The compressive plastic elongation of the Ni_{60}Nb_{30}Ta_{10} bulk metallic glass was about 1.5% as shown in Fig. 5. The compressive fracture took place along the maximum shear plane, which is declined by about 45° to the direction of compressive load. The secondary electron image in Fig. 6 was obtained from the specimen surface of the failed specimen. Multiple shear bands were well developed and propagated on the surface of sample. The shear bands occurred on habit planes oriented roughly at 45° to the loading direction.

4. Discussion

The alloy melt with the composition of Ni_{60}Nb_{30} solidifies at equilibrium to form eutectics consisting of the ordered orthorhombic Ni_{3}Nb and rhombohedral Ni_{6}Nb_{7} crystals both belonging to the class of topologically close-packed poly-

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**Fig. 2** DSC traces of Ni_{60}Nb_{30}Ta_{10} (x = 10 at%) alloy bulk specimen during continuous heating with heating rate 20°C/s.

**Fig. 3** XRD traces obtained from as-melt spun and bulk Ni_{60}Nb_{30}Ta_{10} (x = 10 at%) alloy.

**Fig. 4** Bright field TEM image and corresponding SADP of Ni_{60}Nb_{30}Ta_{10} (x = 10 at%) alloy: (a) Bright field image obtained from as-melt spun ribbon (b) SADP.

**Fig. 5** The stress vs. strain curve of the injection cast Ni_{60}Nb_{30}Ta_{10} (x = 10 at%) alloy rod tested under the uniaxial compressive condition at room temperature.

**Fig. 6** SEM images taken from the outer surface of the sample after uniaxial compression test.
creases from 660 \(^\circ\)C against crystallization. The crystallization temperature improves the thermal stability of the amorphous phase in metallic glasses. 11) Due to strong interatomic bonding between Ni-Nb, the Ni\(_{60}\)Nb\(_{40}\) alloy may be understood from the polyhedral structure with strong bond in liquid state. Due to the strong bond, individual diffusion of each atom becomes difficult hindering the formation of the competing crystalline phase during cooling. 12) Detailed study on the atomic structure of amorphous Ni\(_{60}\)Nb\(_{40}\) alloy showed that local atomic arrangement is essentially of polytetrahedral type, corresponding to random packing of polyhedral with a large number of distorted icosahedral coordinates. 13) The high glass forming ability of the Ni\(_{60}\)Nb\(_{40}\) alloy may be explained by the significantly improved thermal stability of the amorphous phase against crystallization when a part of Nb is substituted with Ta. The compressive failure strength of the \(x = 10\) bulk amorphous alloy Ni\(_{60}\)Nb\(_{40}\)Ta\(_{20}\) was 3,346 MPa that is the highest strength level among those reported in Ni-based metallic glasses so far. The compressive plastic elongation of the Ni\(_{60}\)Nb\(_{40}\)Ta\(_{20}\) metallic glass was about 1.5%.

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**REFERENCES**