Formation of a Ni-Based Glassy Alloy in Centimeter Scale

Zeng Yuqiao¹, Nobuyuki Nishiyama² and Akihisa Inoue¹

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
²R&D Institute of Metals and Composites for Future Industries (RIMCOF), Sendai 980-8577, Japan

The effect of B addition on the glass formation in the Ni₆₀Pd₂₀P₂₀ alloy has been investigated. The composition containing 3 at % of B was found to show a drastically improved glass-forming ability. A glassy Ni₆₀Pd₂₀P₂₀B₃ alloy rod was prepared with a diameter of 12 mm by a water quenching technique. It is so far the first time to prepare a Ni-based bulk glassy alloy with a diameter over 1 cm. The glassy Ni₆₀Pd₂₀P₂₀B₃ alloy also exhibits good mechanical properties, such as high strength of 2060 MPa and a large plastic strain of 0.08 under a compressive load.

[Received March 30, 2007; Accepted April 18, 2007; Published May 25, 2007]

Keywords: glass, nickel-based system, glass-forming ability, high strength, plasticity

1. Introduction

Bulk glassy alloys (BGAs) with high glass-forming ability (GFA) and advantageous properties are believed to possess considerable potential as advanced engineering materials. In 1999, the first success in the formation of BGA with a diameter of 1 mm in Ni-Nb-Cr-Mo-P-B system was reported.¹ Ever since that, the Ni-based BGAs have attracted considerable interest due to their superior mechanical properties²-⁶ and excellent corrosion resistance.⁶,⁷ With the aim of producing Ni-based BGAs with larger size, much effort has been devoted to improve their GFA. As a result, new alloy systems with relatively high GFA such as Ni-Nb-Ti-Zr,² Ni-Ti-Zr-(Si,Sn),⁸ Ni-Nb-Ti-Zr-Co-Cu,² Ni-Ta-Sn⁹ and so on were developed, but the critical diameter for glass-formation (dₕ) was limited to less than 3 mm. In 2004, Lee, et al. found that a new Ni-based alloy with higher GFA could be obtained by adding Nb as a sixth alloying element into the Ni-Ti-Zr-Si-Sn alloy. The new alloy can be formed into BGA with a diameter up to 5 mm.⁵ However, there have been no data on the formation of Ni-based BGAs (Ni content ≥60 at%) in centimeter scale, while BGAs with diameters larger than 10 mm have been successfully prepared in Pd,¹⁰ Pd-Cu,¹¹ Pd-Pt,¹² Cu,¹³ Zr,¹⁴,¹⁵ and Fe,¹⁶ based alloy systems.

To develop a new Ni-based BMG with much higher GFA, we chose Ni₆₀Pd₂₀P₂₀ alloy as a base system. As one of the methods to improve the GFA, one can point out the addition of an alloying element that has different atomic size and negative mixing enthalpy against the main alloying elements. For the multi-component Ni₆₀Pd₂₀P₂₀ alloy, the atomic radii of the constituent elements are in the order of Pd (0.137 nm) > Ni (0.125 nm) > P (0.106 nm). The addition of small B atoms (0.082) may lead to a larger mismatch in atomic size, which is beneficial for glass formation. Hence B was chosen as the additional alloying element in this study.

2. Experimental Procedure

Mother alloys with nominal compositions of Ni₆₀Pd₂₀-P₂₀₋ₓBₓ (0 ≤ x ≤ 8 at%) were prepared by melting the mixture of pure Pd and Ni metals, B crystal and pre-alloyed Pd-Ni-P ingot in vacuumed fused silica tubes, followed by B₂O₃ flux treatment. From the mother alloy, ribbon samples with a thickness of 0.02 mm were prepared by a single-roller melt spinning technique. All the alloys exhibit an endothermic peak due to the crystallization, followed by a supercooled liquid region and then a sharp exothermic peak due to the crystallization.

3. Results and Discussion

Figure 1 shows the DSC curves of the as-spun Ni₆₀Pd₂₀P₂₀₋ₓBₓ ribbon samples prepared by melt-spinning technique. All the alloys exhibit an endothermic peak due to the glass transition, followed by a supercooled liquid region and then a sharp exothermic peak due to the crystallization.
With increasing B content, the glass transition temperature \( T_g \) increases gradually from 601 to 610 K, while the onset of crystallization temperature \( T_x \) first increases from 667 K at \( x = 0 \) to 683 K at \( x = 3 \) and then decreases to 667 K at \( x = 8 \). As a result, the supercooled liquid region \( \Delta T_s \) increases by a small amount of B addition, from 66 K at \( x = 0 \) to 78 K at \( x = 3 \), and then decreases significantly to 64 K with B content down to \( x = 6 \). The large \( \Delta T_s \) value of 78 K for Ni\(_{60}\)Pd\(_{20}\)P\(_2\)B\(_3\) alloy indicates the improvement of the GFA.

The \( d_c \) by copper mold casting was investigated for GFA evaluation for the Ni\(_{60}\)Pd\(_{20}\)P\(_2\)B\(_3\) alloys. The results are shown in Fig. 2, where the relationship between \( x \) and \( \Delta T_s \) is also shown for comparison. Rod samples with a single glassy phase were obtained in the diameter range up to 3 mm for the Ni\(_{60}\)Pd\(_{20}\)P\(_2\)B\(_3\) alloy, and 3.5 mm for the Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) and Ni\(_{60}\)Pd\(_{20}\)P\(_4\)B\(_4\) alloys. When the as-cast rod diameter increases to 4 mm, the Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) alloy contains a partially crystallized glassy phase, while the Ni\(_{60}\)Pd\(_{20}\)P\(_4\)B\(_4\) alloy is fully crystallized, indicating that the Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) alloy has the highest GFA among the Ni\(_{60}\)Pd\(_{20}\)P\(_x\)B\(_x\) system. This result is consistent with the tendency for \( \Delta T_s \).

A small amount of B addition into the Ni\(_{60}\)Pd\(_{20}\)P\(_2\)B\(_3\) alloy leads to a distinctive extension of the supercooled liquid region as well as the increase of the GFA. The extension of \( \Delta T_s \) and the enhancement of GFA for the 3 at % B-containing alloy are assumed to be caused by the retarded crystallization process. Therefore, the crystallization behavior was investigated. The Ni\(_{60}\)Pd\(_{20}\)P\(_{20-x}\)B\(_x\) (\( x = 0, 3, 6 \)) ribbon samples were annealed by DSC at the temperature of the first crystallization peak. As shown in Fig. 3, the diffraction peaks are identified as the mixture of Ni\(_3\)P, Ni\(_5\)P, and Pd\(_4\)P phases for the 0 at % B-containing alloy, Ni\(_3\)P, Ni\(_5\)P, and Ni\(_3\)B, Ni\(_5\)B, Ni\(_4\)B, and NiB phases for the 3 at % B-containing alloy, and Ni\(_3\)P, Pd\(_4\)P, Ni\(_5\)B, Ni\(_4\)B, and NiB phases for the 6 at % B-containing alloy. Compared with the Ni\(_{60}\)Pd\(_{20}\)P\(_2\) and Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) alloys, the Ni\(_{60}\)Pd\(_{20}\)P\(_4\)B\(_4\) alloy shows more complex precipitation phases. The crystallization of Ni\(_3\)P, NiP, and PdP phases are drastically depressed, accompanied with the appearance of Ni\(_5\)B, Ni\(_4\)B, and NiB. The small amount of B addition results in a large mismatch in atom size, and a higher degree of dense random packed structure is assumed be to formed, where the atomic rearrangement of the constituent elements is drastically depressed. Since the formation of these crystallized structures requires long-range atomic rearrangements, the complex precipitations upon devitrification for Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) alloy become more difficult. Thus the supercooled liquid region becomes more stable and GFA is enhanced correspondingly.

As described above, by copper mold casting, the Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) alloy can be formed into a glassy state in the diameter range up to 3.5 mm. However a much bigger glassy alloy rod can be obtained by using B\(_2\)O\(_3\) as a flux medium to remove the hetero-nucleates. In this study, a bulk cylindrical rod with a diameter of 12 mm was prepared by melting the mother alloy with B\(_2\)O\(_3\) in a quartz tube, followed by water quenching. The outer surface morphology of the

Fig. 2  \( d_c \) produced by copper mold casting and the supercooled liquid region \( \Delta T_s \) as a function of B content for Ni\(_{60}\)Pd\(_{20}\)P\(_x\)B\(_x\) alloys.

Fig. 3 XRD patterns of Ni\(_{60}\)Pd\(_{20}\)P\(_2\)B\(_3\) (\( x = 0, 3, 6 \)) ribbons annealed at the crystallization temperature.

Fig. 4 Formation of Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) glassy alloy in centimeter scale (12 mm). (a) Outer surface morphology (b) X-ray diffraction pattern and (c) DSC curve of the bulk Ni\(_{60}\)Pd\(_{20}\)P\(_3\)B\(_3\) glassy alloy.
water-quenched sample is shown in Fig. 4(a). The surface of the sample is mirror like lustrous and smooth. Neither concave nor cavity caused by a crystalline phase can be seen. The diffused halo diffraction peak in XRD pattern in Fig. 4(b) confirms the glassy structure. The DSC trace is shown in Fig. 4(c). \( T_g \) and \( T_x \) are 605 and 695 K, respectively. \( \Delta T_x \) is deduced to be as high as 90 K, which is the largest value among Ni-based alloys (Ni content > 60 at%) reported up to date. The \( \Delta T_x \) value of the bulk glass is larger as compared with the glassy Ni_{50}P_{20}P_{17}B_{3} as-spun sample. This may be due to the completed flux treatment for the bulk sample. Anyhow, this is the first evidence for a centimeter-size BMG formed in Ni-based alloy (Ni content > 60 at%).

The mechanical properties of the Ni_{60}Pd_{20}P_{17}B_{3} alloy were studied by using the as-cast sample. The nominal stress-strain curve is shown in Fig. 5 where the slope is calibrated by using a strain-gauge settlement. The alloy exhibits a high strength of 2060 MPa and a distinctive plastic strain of 0.08, corresponding to the largest plastic deformation reported for Ni-based glassy alloys so far. Figure 6 shows the fracture surface of the compressively deformed Ni_{60}Pd_{20}P_{17}B_{3} BGA. The fracture angle with stress axis is around 41–42°, which agrees with the previous data of other Ni- and Pd-based glassy alloys. On the fracture surface, a clear vein-like pattern is observed. Instead of a single shear band that leads to a catastrophic failure, multiple shear bands distribute on the outer surface of the deformed sample. In addition to the primary shear bands which are declined by about 42° to the loading direction, some secondary shear bands are formed with an angle of 30–42° to the primary ones. The similar phenomenon can be also observed in some other ductile Pd-Pt-Cu-Ni-P, and Ni-Pd-P glassy alloy systems. It was thought that the formations of these multiple shear bands might be due to the medium-range ordered (MRO) regions dispersed in the glassy matrix as shown in Fig. 7. The stress distribution around the MRO regions is changed to a three dimensional stress condition even under a uniaxial load. The three dimensional stress is expected to cause the suppression of highly localized shear band propagation through the generation of multiple shear stress condition. Consequently, the large plastic deformation of 8% was obtained.

4. Conclusions

A quaternary Ni-Pd-P-B alloy with high GFA was developed by adding B into the Ni_{60}Pd_{20}P_{20} alloy. The alloy containing 3 at% of B shows a distinctively improved GFA. A glassy rod with a diameter of 12 mm was obtained for

Fig. 5 Nominal compressive stress-strain curve of a Ni_{60}Pd_{20}P_{17}B_{3} glassy alloy.

Fig. 6 Glassy alloy rod subjected to fracture under a compressive load.

Fig. 7 HRTEM image of the as-cast Ni_{60}Pd_{20}P_{17}B_{3} sample.
Ni$_{60}$Pd$_{20}$P$_{17}$B$_3$ alloy by water-quenching technique. The glassy Ni$_{60}$Pd$_{20}$P$_{17}$B$_3$ alloy also exhibits good mechanical properties. High strength of 2060 MPa and large plastic strain of 0.08 were obtained under a compressive load. The large plastic strain is thought due to the homogenously dispersed MROs in the glassy matrix.

REFERENCES