Bulk Amorphous Co–Ni-Based Alloys with a Large Supercooled Liquid Region

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An amorphous alloy with a large supercooled liquid region above 80 K was synthesized for Ni_{40}Co_{20}Fe_{10}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6}. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of the amorphous alloy are 710, 791 and 1162 K, respectively, and the reduced glass transition temperature (T_g/T_m) is as high as 0.61. The amorphous alloy crystallizes through a single exothermic reaction and the crystallized structure consists of Ni, Ni_{3}B, Ni_{5}P, Cr_{5}P, Ni_{5}Mo_{5}P and Co_{72}Nb_{2}P_{7} phases. The high thermal stability of supercooled liquid results from the crystallization mode requiring the necessity of long-range redistribution of alloy components. By use of the alloy with the high T_g/T_m value, bulk amorphous alloy rods were prepared in the diameter range up to 1 mm by copper mold casting. No difference in the thermal stability and crystallization mode is recognized for the amorphous rods. The tensile fracture strength and elongation of the amorphous alloy rod with a diameter of 1 mm are 2800 MPa and 1.88%, respectively. The tensile fracture takes place along the shear-type fracture mode and its surface consists mainly of a well-developed vein pattern. The extension of bulk amorphous alloys to the Ni–Co-based system is encouraging for the future prospect of bulk amorphous alloys as basic science and engineering materials.

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1. Introduction

Since the synthesis of bulk amorphous alloys in Mg,\(^1\) Lanthanide (Ln),\(^2\) and Zr,\(^3\)\(^-\)\(^9\) based systems, the alloys have attracted much attention as new materials in science and engineering fields.\(^5\) Their alloy systems have been significantly extended for the last decade. In particular, the extension of bulk amorphous alloys to Fe-, Co- and Ni-based systems is important because of the expectation of high mechanical strength, soft magnetic properties and high corrosion resistance. Since the first synthesis of Fe-based bulk amorphous alloys in Fe–(Al, Ga)–(P, C, B) and Fe–M–(Al, Ga)–(P, C, B) (M = Cr, Mo, Nb) systems by copper mold casting in 1995,\(^6\) Fe-based bulk amorphous alloys have also been formed in the other alloy systems such as Fe–(Zr, Nb)–(Cr, Mo, B),\(^7\) Fe–(Al, Ga)–(P, C, B, Si),\(^8\) Fe–Cr–Mo–Ga–(P, C, B),\(^9\) Fe–Mo–Ga–(P, C, B),\(^10\) and Fe–Ga–(P, C, B).\(^11\) The bulk amorphous alloys are divided into two groups of Fe–(Al, Ga)–(P, C, B) and Fe–(Zr, Nb)–B base systems.\(^5\) All these amorphous alloys have a large supercooled liquid region exceeding 50 K before crystallization and the high resistance of the supercooled liquid against crystallization is a main reason for the formation of bulk amorphous alloys. Consequently, it is important to search for a new Fe-, Co- or Ni-based amorphous alloy with a large supercooled liquid region which does not belong to the above-described two groups. More recently, we have reported that Ni-based bulk amorphous alloys are formed around Ni_{40}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6} and exhibit high tensile strength of 2900 MPa for the cast rod sample.\(^12\) Considering that no distinct supercooled liquid region is observed in a Ni_{70}P_{2}B_{6} alloy, the addition of Cr, Mo and Nb elements is concluded to be effective for the appearance of a large supercooled liquid region exceeding 50 K and the achievement of high glass-forming ability. The similar effectiveness of these additional elements is expected to be valid for Fe- and Co-based alloys. The aim of this paper is to present the composition range in which an amorphous phase with a supercooled liquid region above 60 K is formed in melt-spun (Fe, Co, Ni)_{50}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6} alloys, and thermal stability and crystallization behavior of the amorphous alloys as well as to examine the formation tendency and mechanical properties of the bulk amorphous alloys.

2. Experimental Procedure

Multicomponent Fe_{50–x–y}Co_{x}Ni_{3}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6} alloy ingots were prepared by induction melting the mixture of pure metals, Fe–P pre-alloyed ingot and pure crystal B in a flowing argon atmosphere. The alloy compositions represent the nominal atomic percentage. Amorphous alloy ribbons with a cross section of 0.02 × 1.2 mm\(^2\) were produced by melt spinning. Bulk amorphous alloy rods were also produced by copper mold casting. The amorphous structure was examined by X-ray diffraction, optical microscopy (OM) and transmission electron microscopy (TEM). The thermal stability was examined by differential scanning calorimetry (DSC) with a heating rate of 0.67 K/s. Mechanical properties were measured at a strain rate of 3.5 × 10\(^{-4}\) s\(^{-1}\) with an Instron tensile testing machine and the fracture surface was examined by scanning electron microscopy (SEM).

3. Results

We have confirmed that the melt-spun Fe_{50}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6}, Co_{50}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6} and Ni_{50}Cr_{5}Mo_{5}Nb_{3}P_{14}B_{6} alloys consist only of broad peaks in the X-ray diffraction patterns and no appreciable crystalline phase is seen in the bright-field TEM images. Figure 1 shows DSC curves of the three kinds of amorphous alloys. All the amorphous alloys exhibit a distinct glass transition, followed by a supercooled liquid region and then an exothermic peak due to crystalliza-

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The $T_g$ and the onset temperature of crystallization ($T_s$) are, respectively, 772 and 826 K for the Fe-based alloy, 775 and 843 K for the Co-based alloy, and 697 and 761 K for the Ni-based alloy. The $\Delta T_s$ is evaluated to be 54 K for the Fe-based alloy, 68 K for the Co-based alloy and 64 K for the Ni-based alloy. It is noticed that the three kinds of amorphous alloys have a large supercooled liquid region exceeding 50 K. For the understanding of the reason for the high thermal stability of the supercooled liquid of the three amorphous alloys, the crystallized structure was examined. The X-ray diffraction patterns of the $M$$_{15}$Cr$_5$Mo$_5$Nb$_5$P$_{14}$B$_6$ ($M$ = Fe, Co or Ni) amorphous alloys annealed for 3.6 ks at 953 K, which is much higher than the crystallization peak, were identified as mixed phases of $\alpha$-Fe, Fe$_3$P, Fe$_3$B, Cr$_2$B and Nb$_2$P for $M$ = Fe, $\alpha$-Co, Co$_2$B, Cr$_2$B, CoMoP and Co$_{12}$Nb$_2$P$_7$ for $M$ = Co, and Ni, Ni$_3$P, Ni$_2$B, Ni$_5$Mo$_2$P, Cr$_3$P and NiNbP for $M$ = Ni. The necessity of long-range rearrangements of the constituent elements leading to the nearly simultaneous precipitation of more than three kinds of crystalline phases seems to cause the high thermal stability of the supercooled liquid against crystallization.

With the aim of searching for a new amorphous alloy with a much larger supercooled liquid region before crystallization, the thermal stability of the supercooled liquid was examined in the (Fe, Co, Ni)$_{35}$Cr$_5$Mo$_5$Nb$_5$P$_{14}$B$_6$ alloys. Figure 2 shows the compositional dependence of $T_g$ for the Fe$_{65}$-$x$-$y$Co$_{x}$Ni$_{35-x}$Cr$_5$Mo$_5$Nb$_5$P$_{14}$B$_6$ amorphous alloys. The $T_g$ shows a minimum of 770 K around the Ni-rich alloy of Fe$_5$Co$_{20}$Ni$_{40}$, increases with increasing Fe and Co contents and shows a maximum of 833 K for the Co-rich Fe$_5$Co$_{45}$Ni$_{15}$ alloy. Similar compositional dependence is recognized for $T_s$. The $T_s$ shows a minimum of 770 K around Fe$_{15}$Co$_{10}$Ni$_{40}$ and a maximum of 830 K around Fe$_2$Co$_{20}$Ni$_{40}$. The $\Delta T_s$ shows a maximum value above 80 K around Fe$_5$Co$_{20}$Ni$_{40}$ and decreases with deviating from the alloy composition, as shown in Fig. 3. However, it is noticed that all the alloys in the (Fe, Co, Ni)$_{35}$Cr$_5$Mo$_5$Nb$_5$P$_{14}$B$_6$ system exhibit $\Delta T_s$ values above 40 K and the $\Delta T_s$ exceeds 60 K for
the Co- and Ni-rich alloys. Figure 4 shows DSC curves of the Ni-rich Fe<sub>5</sub>Co<sub>20</sub>Ni<sub>40</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub> and Co-rich Co<sub>43</sub>Ni<sub>28</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub> amorphous alloys with \( \Delta T_\text{x} \) of 82 and 69 K, respectively. The crystallization occurs through a mostly single-stage exothermic reaction from the supercooled liquid and the crystallized structure has been confirmed to consist of Ni<sub>3</sub>Cr<sub>2</sub>, Ni<sub>3</sub>P<sub>3</sub>, Cr<sub>3</sub>P<sub>3</sub>, Ni<sub>3</sub>Mo<sub>5</sub>P<sub>3</sub> and Co<sub>12</sub>Nb<sub>5</sub>P<sub>7</sub> phases for the former Ni-rich alloy and \( \alpha \)-Co, Co<sub>2</sub>B, Cr<sub>2</sub>B, Co<sub>12</sub>Nb<sub>5</sub>P<sub>7</sub>, Ni<sub>3</sub>Mo<sub>5</sub>P<sub>3</sub> and Ni<sub>12</sub>Nb<sub>5</sub>P<sub>3</sub> phases for the latter Co-rich alloy. The crystallization mode leading to the simultaneous precipitation of more than three kinds of phases plays an important role in the stabilization of the supercooled liquid against crystallization. Furthermore, we observed a single endothermic peak with an onset at 1162 K. This result indicates that the melting occurs through a single reaction and the deepest eutectic point in the multicomponent alloy system lies around Fe<sub>5</sub>Co<sub>20</sub>Ni<sub>40</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub>. It is noticed that the reduced glass transition temperature \( (T_g/T_m) \) is as high as 0.61.

It has generally been recognized that the ease of forming bulk amorphous alloys is closely related to \( T_g/T_m \) and the alloys with \( T_g/T_m \) above 0.60 can be rather easily made into a bulk amorphous form.\(^5\,13\) Thus, the previous data indicate the possibility that a bulk amorphous alloy is produced for the Fe<sub>5</sub>Co<sub>20</sub>Ni<sub>40</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub> alloy with \( T_g/T_m \) of 0.61. We examined the X-ray diffraction patterns of the Ni-rich alloy rods with diameters of 0.5, 1.0 and 2.0 mm prepared by copper mold casting. No distinct crystalline peak was seen in the diffraction patterns of the rods with diameters of 0.5 and 1.0 mm, but the rod of 2 mm in diameter consisted of amorphous and crystalline phases. The \( T_g \) and \( T_x \) of the 1 mm diameter rod are 717 and 792 K, respectively, and hence the resulting \( \Delta T_x \) is 75 K, in agreement with that for the melt-spun amorphous ribbon. The Young's modulus \((E)\), tensile fracture strength \((\sigma_f)\), fracture elongation including elastic elongation

![Fig. 4 DSC curves of Ni<sub>40</sub>Co<sub>20</sub>Fe<sub>5</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub> and Co<sub>43</sub>Ni<sub>28</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub> amorphous alloys.](image)

![Fig. 5 Tensile fracture surface of a bulk amorphous Ni<sub>40</sub>Co<sub>20</sub>Fe<sub>5</sub>Cr<sub>3</sub>Mo<sub>5</sub>Nb<sub>5</sub>P<sub>14</sub>B<sub>6</sub> rod with a diameter of 1 mm.](image)
(σf) and Vickers hardness (HV) of the 1 mm diameter rod were measured to be 110 GPa, 2800 MPa, 1.88% and 890, respectively. The ratios of 2σf/E and 9.8HV/3E are 0.025 and 0.026, respectively, being nearly the same as those for the Zr-, Pd–Cu- and Ni-based bulk amorphous alloys subjected to the same tensile testing. Figure 5 shows the tensile fracture surface of the Ni40Co20Fe5Cr5Mo5Nb3P14B6 bulk amorphous rod. The fracture appears to occur along the maximum shear plane which is inclined by about 45 degrees to the direction of tensile load and the fracture surface consists mainly of a vein-like pattern.

4. Discussion

Here, we discuss the reason why the Ni40Co20Fe5Cr5Mo5Nb3P14B6 amorphous alloy exhibits a large ΔTc of 82 K and a high Tg/Tm of 0.61. The endothermic reaction due to melting of the mixture of Ni, Ni3P, Ni3B, Cr3P, Ni6Mo2P3 and Co12Nb2P7 phases occurs through a single stage. It is therefore said that the alloy composition lies around the deepest eutectic point in the multicomponent alloy system. One can remind of the three empirical rules for the stabilization of supercooled liquid for metallic alloys, i.e., (1) multicomponent alloy systems consisting of more than three kinds of elements, (2) significant atomic size mismatch above 12% among the main three constituent elements, and (3) suitable negative heats of mixing among their main elements. When the three empirical rules are applied to the present alloy system, the alloys are also composed of three types of elements of late transition metal (LTM = Fe, Co, Ni), early transition metal (ETM = Cr, Mo, Nb) and metalloid (M = P, B). The atomic size ratios are evaluated to be in the range of 1.09 to 1.10 for Mo/LTM, 1.14 to 1.15 for Nb/LTM and 1.14 to 1.39 for LTM/M, indicating that the atomic size mismatch among the main LTM, Nb and M elements is larger than 12%. The heat of mixing is negative for all the atomic pairs of ETM-LTM, LTM-M and M-ETM and the negative values are in the range of 2 to 89 kJ/mol. It is regarded that the present alloy series also satisfy the three empirical rules for the stabilization of supercooled liquid. It has previously been reported that the alloy liquid with the three empirical rules can have a new liquid structure with highly dense random packed atomic configurations, new local atomic configurations and long-range homogeneous atomic configurations with strong interaction. In the new liquid structure, the atomic diffusivity is suppressed and the long-range atomic rearrangement from the new local atomic configuration is required for the simultaneous precipitation of more than three kinds of crystalline phases.

5. Summary

In conclusion, a large supercooled liquid region of 82 K before crystallization as well as a high Tg/Tm of 0.61 was observed for an amorphous Ni40Co20Fe5Cr5Mo5Nb3P14B6 alloy and bulk amorphous alloy rods with high tensile strength were synthesized by choosing the alloy with the large ΔTc and high Tg/Tm values. The synthesis of bulk amorphous alloys in the new Ni–Co–based system is significant for the future extension of bulk amorphous alloys to various engineering application fields.

REFERENCES