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Effect of B to P concentration ratio on glass-forming ability and soft-magnetic properties in $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ glassy alloys

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The effect of B to P concentration ratio on the glass-forming ability (GFA) and soft-magnetic properties of $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ ($x = 0.01$, 0.03, 0.05, 0.07 and 0.09) glassy alloys was investigated. By adjusting the concentration ratio of B to P, GFA and soft-magnetic properties are effectively improved. Bulk glassy alloys (BGAs) with diameters up to 1.5 mm were synthesized in the composition range of $x = 0.03–0.07$. In addition to high GFA, the FeNi-based glassy alloys exhibit excellent soft-magnetic properties, i.e., rather low H_c of 0.7–0.95 A/m, high μ_e of 17,200–24,300 and high saturation magnetization of 0.63–0.82 T. The $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.17}P_{0.05}]_{97}Nb_3$ BGA exhibits high hardness of 890 kg/mm^2. The improvement of GFA and soft-magnetic properties are derived from the enhanced atomic bonding nature and phase competing process in conjugation with precipitation of $(Fe, Ni)_{23}B_6$ phase with complex structure.

1. Introduction

Since the finding of a melt-spun FePC glassy alloy with ferromagnetism at room temperature in 1967 [1], soft-magnetic glassy alloys based on the ferromagnetic elements Fe, Co, Ni and their combination have attracted increasing interests. Compared with their crystalline counterparts, glassy alloys used as soft-magnetic materials exhibit high performances such as low coercivity (H_c), low core losses and high effective permeability (μ_e) even in a high frequency range. FeNi-based glassy alloys with high ferromagnetic elements under the trade mark of METGLAS2826, METGLAS2826 MB, VITROVAC4040 F and so forth have been used as soft-magnetic materials to substitute permalloys in sensors, magnetic shielding, read–write head of digital devices, switching and power transformers etc [2–5]. In addition to the excellent soft-magnetic properties, they exhibit higher anticorrosion properties, better mechanical prosperities and higher resistance than permalloys because of the amorphous structure [6]. However, the application is limited because the thickness of these thin ferromagnetic ribbons prepared by quenching the melt at rates on the order of 10^6 K/s are typically only 25–50 μm owing to the low glass-forming ability (GFA). The thin glassy ribbons are difficult to handle and thus the transformer cannot be fabricated by the traditional methods used with conventional 0.3 mm thick permalloys [3]. In addition, the reduced thickness of the foils causes a decrease in the core packing density, which decreases the efficiency of the apparatus and blocks miniature. Therefore, enhancement of the GFA and preparation of bulk glassy alloys (BGAs) would be of tremendous benefit [6]. Great deals of endeavors have been devoted by many research groups and some FeNi-based soft-magnetic BGAs were developed by employing two different strategies [3,7–9], i.e., (1) by introducing the flux melting and water-quenching technique; (2) by adding new glass-forming elements. In particular, 1 mm $Fe_{40}Ni_{40}P_{14}B_6$ BGA rods were prepared by Shen and Schwarz for the first time by using the first strategy in 2001 [3]. Gan et al. made $(Fe_{0.4}Ni_{0.4}P_{0.14}B_{0.06})_{96}Ga_4$ BGA with diameter of 3 mm using combination of Ga addition and flux purifying melting [7]. However, the flux purifying melting and water-quenching process are complicated and energy wasteful. In addition, as a noble element, Ga addition increases the cost greatly. They all restrict the mass industrial production and commercial application.

Recently, we synthesized a high ferromagnetic elements content $(Fe_{0.5}Ni_{0.5})_{75.5}B_{14.5}P_7Nb_3$ BGA with good soft-magnetic properties by copper mold casting [10]. In this paper, we investigated the effect of B and P concentration ratio on GFA and soft-magnetic properties as

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well as optimized the component of $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ glassy alloy with the aim of increasing the GFA. The relation between crystallization behavior and GFA are also studied. In addition, hardness is measured for the resistance to wear is an important factor to be considered as using in read–write head material of digital devices.

2. Experiment procedure

Multicomponent alloy ingots with nominal compositions of $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ ($x = 0.01$, 0.03, 0.05, 0.07 and 0.09) were premelt by induction melting the mixtures of pure Fe (99.99 mass%), Ni (99.9 mass%), Nb (99.9 mass%), and crystalline B (99.5 mass%), and pre-alloyed Fe–P ingots under a high-purity argon atmosphere. Ribbons with thickness of about 20 μm and width of 1.2 mm were prepared by the single copper roller melt-spinning method. Cylindrical alloy rods with diameters up to 2 mm were produced by copper mold casting in an argon atmosphere. The amorphous structure and crystalline phase were identified by X-ray diffraction (XRD) with Cu Kα radiation. Thermal stability associated with glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T_x = T_x - T_g$) were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus temperature (T_l) was measured with a DSC by cooling the molten alloy samples at a cooling rate of 0.067 K/s. As the magnetic properties depend on the sample size, in the interest of clarification the intrinsic soft-magnetic properties of this glassy alloy system, ribbon samples with similar size mentioned above were used for measurement. Magnetic properties of saturation magnetization (I_s) under an maximum applied field of 800 kA/m was measured with a vibrating sample magnetometer (VSM). H_c was measured with DC B–H loop tracer (model BHS-40, Riken) with high sensitivity under a field of 800 A/m. μ_e at 1 kHz was measured with an impedance analyzer under a field of 1 A/m and the length of the sample for μ_e measurement is 55 mm which is long enough to reduce the influence of the demagnetizing field. All of the ribbon samples for magnetic property measurements were annealed at the temperature of $T_g - 50$ K for 600 s for improving soft-magnetic properties though structural relaxation. Vickers hardness was measured with a Vickers hardness tester under different loads. Transverse cross-section of the as-cast glassy alloy rod and indents generated by hardness tester were examined by scanning electron microscopy (SEM).

3. Results

All of the melt-spun ribbons used for thermal and magnetic tests confirmed in the X-ray diffraction patterns are composed of a full glassy phase without crystallization. Fig. 1 shows DSC curves of the melt-spun $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ ($x = 0.01$, 0.03, 0.05, 0.07 and 0.09) glassy ribbons. All of the glassy alloys exhibit glass transition, followed by a large supercooled liquid region and then crystallization. With the increasing of P to B concentration ratio, the glassy transition temperature (T_g) decreases gradually from 732 K to 706 K, on the other hand, the onset temperature of crystallization (T_x) increases inchmeal from 771 to 781 K. As a result, the temperature interval of the supercooled liquid region (ΔT_x) increases remarkably from 39 to 75 K with increasing P content to 0.09. In addition, the obvious increase of the difference of specific heat (ΔC_p) at the glass transition region indicates that the structure of alloys with higher P content goes through larger changes [11]. Thus, it is suggested that the thermal stability of the supercooled liquid is effectively enhanced with increasing P content. As shown in the DSC figure, only one distinct crystallization exothermic peak indicates that the supercooled liquid phase is stabilized with respect to competing crystalline phases and the precipitation of the crystalline phases is suppressed [12].

As shown in Fig. 2, DSC curves of the $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ ($x = 0.01$, 0.03, 0.05, 0.07 and 0.09) alloys exhibit the cooling behavior of this glassy alloy system. It is clearly seen that T_l decreases gradually from 1285 K to 1240 K with increasing x up to 0.05, and then increases slightly to 1244 K at $x = 0.09$. In addition, the temperature interval of exothermic peaks decrease markedly and reached a minimum with P content of $x = 0.05$, indicating that the alloy with the P content of $x = 0.05$ is the closest to the eutectic point in this alloy system [13]. Accordingly, the reduced glass transition temperature T_{rg} (T_g/T_l) lies in the range of 0.568–0.576. All of these changes imply that the P content of $x = 0.03$, 0.05 and 0.07 are close to a eutectic point.

Based on the results of the thermal stability of supercooled liquid obtained by DSC in addition to the T_{rg} analyses, it is expected that the GFA of this alloy system is effectively enhanced, especially for the alloy with P content of $x = 0.05$. We tried to form cylindrical glassy rods with different diameters up to 2 mm by the copper mold casting method. As shown in Fig. 3, only broad peaks without an obvious crystalline peak can be seen for these rods, indicating that bulk sample with critical diameters of 1, 1.5, and 1 mm were

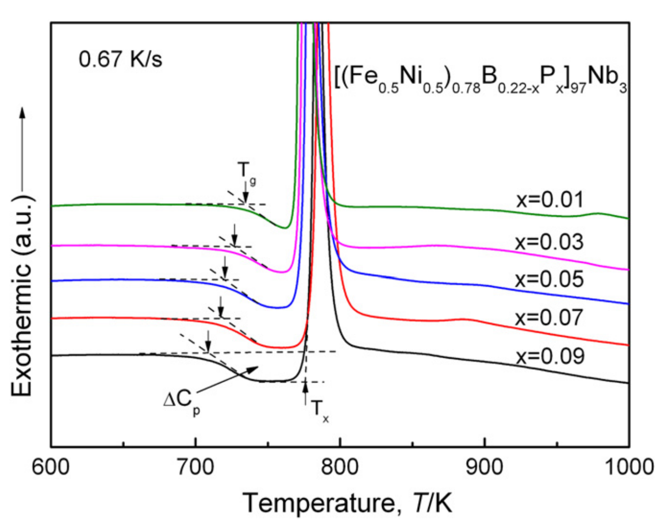

Fig. 1. DSC curves of melt-spun $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ ($x = 0.01$, 0.03, 0.05, 0.07 and 0.09) glassy alloys.

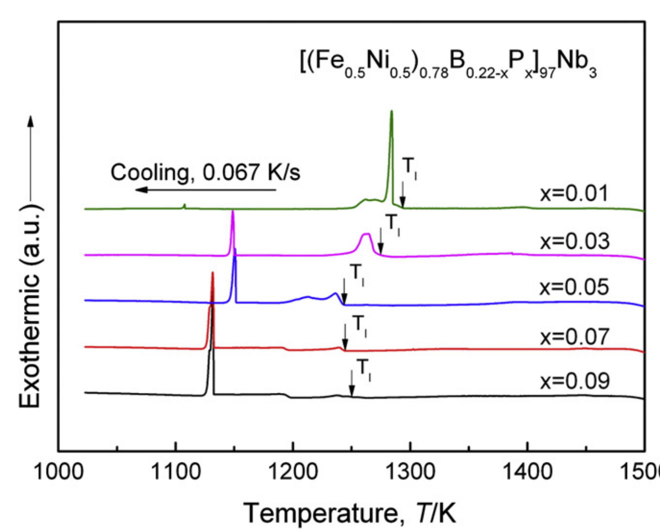

Fig. 2. DSC curves of molten $[(Fe_{0.5}Ni_{0.5})_{0.78}B_{0.22-x}P_x]_{97}Nb_3$ ($x = 0.01$, 0.03, 0.05, 0.07 and 0.09) alloys showing the cooling behavior.