RAPID PUBLICATION

Fe-Based Ferromagnetic Glassy Alloys with Wide Supercooled Liquid Region

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A multicomponent $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy was found to form a glassy phase with a wide supercooled liquid region before crystallization and of ferromagnetism at room temperature. The glass transition temperature (T_g), crystallization temperature (T_x) and temperature intervals of supercooled liquid, $\Delta T_x (= T_x - T_g)$ for the glassy alloy are 732, 793 and 61 K, respectively. It is to be noticed that the supercooled liquid region exceeds 60 K which is about 3 times larger than the largest ΔT_x value for the Fe-based glassy alloys reported up to date. The amorphous alloy also exhibits good bending ductility and rather good soft ferromagnetic properties at room temperature. The soft magnetic properties are improved by annealing at temperatures above the Curie temperature (T_c). The magnetic properties at room temperature for the glassy alloy annealed for 600 s at 723 K are 605 K for T_c , 1.07 T for saturation magnetization, 5.1 A/m for coercivity, 9000 for permeability at 1 kHz and 2.0×10^{-6} for magnetostriction. The finding of the ductile Fe-based glassy alloy exhibiting simultaneously the wide supercooled liquid region and good soft ferromagnetic properties is expected to create a new ferromagnetic bulk material with good deformability.

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I. Introduction

It has recently been found that glassy alloys in a number of metal-metal systems such as Ln-Al-TM⁽¹⁾⁽²⁾, Mg-Ln-TM⁽³⁾⁽⁴⁾, Zr-Al-TM⁽⁵⁾⁽⁶⁾, Hf-Al-TM⁽⁷⁾, Ti-Zr-TM⁽⁸⁾ and, Ti-Zr-Be-TM⁽⁹⁾. (Ln=lanthanide metal, TM=transition metal) have a wide supercooled liquid region before crystallization and the temperature interval between T_g and T_x , $\Delta T_x (= T_x - T_g)$ reaches as large as 127 K⁽¹⁰⁾. The appearance of the wide supercooled liquid region implies that the supercooled liquid has high resistance against crystallization. As a result, these glassy alloys with large ΔT_x values have been confirmed to have an extremely large glass-forming ability which enables the production of bulk glassy alloys with a maximum thickness of about 20 mm⁽¹¹⁾. Furthermore, the critical cooling rate for glass formation has been measured to be of the order 1 to 10² K/s from the experimental data on the continuous-cooling-transformation (C.C.T.) curves from the supercooled liquid to the crystalline or the amorphous phase⁽¹²⁾.

However, these glassy alloys with the wide supercooled liquid region exceeding 60 K and the critical cooling rates less than 100 K/s have been limited to Ln⁽¹⁾⁽²⁾, Mg⁽³⁾⁽⁴⁾, Zr⁽⁵⁾⁽⁶⁾, Hf⁽⁷⁾ and Ti⁽⁸⁾⁽⁹⁾-based alloys without ferromag-

netism at room temperature. There is no report on a ferromagnetic glassy alloy with a wide supercooled liquid region exceeding 60 K. The finding of a ferromagnetic glassy alloy with large glass-forming ability is expected to increase significantly the engineering importance of glassy alloys. An empirical atomic size rule for the achievement of glassy alloys with large glass-forming ability has been derived⁽¹³⁾⁻⁽¹⁵⁾ from a number of data on the glass formation in the above-described alloy systems. Based on the atomic size rule, we have recently searched a ferromagnetic glassy alloy with large glass-forming ability in the Fe- and Co-based alloy systems and succeeded in finding a new ferromagnetic glassy alloy with a wide supercooled liquid region exceeding 60 K in the Fe-Al-Ga-P-C-B system. This paper is intended to present the alloy composition, thermal stability, crystallization behavior and magnetic properties of the new Fe-based glassy alloy.

II. Experimental Procedure

A multicomponent $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy was used in the present study. The ingot was prepared by induction melting a mixture of pure Fe, Al and Ga metals, pre-alloyed Fe-C and Fe-P ingots and pure B crystal in a purified argon atmosphere. The composition is nominally expressed in units of atomic percent. From the master alloy ingot, a ribbon with a cross section of about $0.02 \times 1.5 \text{ mm}^2$ was prepared by a single roller melt-spinning technique in an argon atmosphere. The glassy

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nature of the melt-spun ribbon was examined by X-ray diffractometry and transmission electron microscopy (TEM).

The specific heat (C_p) associated with structural relaxation, glass transition and crystallization was measured with a differential scanning calorimeter (DSC). The accuracy of the data was about ± 0.4 J/mol·K for absolute C_p values and better than ± 0.1 J/mol·K for the relative C_p or ΔC_p measurements. The samples were first scanned at 0.67 K/s to the temperature of the supercooled liquid to obtain in the as-quenched state ($C_{p,q}$), and then cooled to room temperature. The $C_p(T)$ measurement was immediately repeated in situ to obtain data on the relaxed reference sample ($C_{p,s}$). The crystallization behavior was also examined by DSC, X-ray diffractometry and TEM. The melting temperature of the alloy was measured at a scanning rate of 0.33 K/s with a differential thermal analyzer (DTA). The magnetization under an applied field of 800 kA/m was measured at room temperature with a vibrating sample magnetometer. Hysteresis B - H loops under an applied field of 1.59 kA/m were measured at room temperature with a B - H loop tracer. The effective permeability at 1 kHz under 0.8 A/m was evaluated with a vector impedance analyzer. In addition, the magnetostriction was measured in an applied field up to 8 kA/m by a three-terminal capacitance method.

III. Results and Discussion

Figures 1(a), (b) and (c) show a bright-field electron micrograph, selected-area electron diffraction pattern and X-ray diffraction pattern, respectively, for the rapidly solidified $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy. The bright-field

Fig. 1 (a) Bright-field electron micrograph, (b) selected-area electron diffraction pattern and (c) X-ray diffraction pattern of a rapidly solidified $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy.

Fig. 2 DSC curve of a glassy $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy.

image consists of only a featureless contrast typical for a glassy single phase and no contrast revealing the precipitation of a crystalline phase is seen. The electron and X-ray diffraction patterns consist of halo rings and halo peaks, respectively, indicating that the as-quenched phase is composed only of a glassy phase. The formation of the glassy phase in the present multicomponent alloy is consistent with the previous result⁽¹⁶⁾ that a glassy phase is obtained in the rapidly solidified ternary alloys of the Fe-P-C, Fe-P-B, Fe-B-C and Fe-Al-B systems containing the metalloids (P, C and B) of about 20 at%. Furthermore, it is important to point out that the Fe-Al-Ga-P-C-B glassy alloy has good bending ductility which is shown by bending through 180 degrees without fracture.

Figure 2 shows the DSC curve of the glassy Fe-Al-Ga-P-C-B alloy. A sharp exothermic peak is seen in the temperature range of 793 to 816 K, indicating that the crystallization of the glassy phase takes place through a single stage leading to simultaneous precipitation of more than two kinds of crystalline phases. In addition to the exothermic peak, one can see an endothermic reaction due to the glass transition, followed by the achievement of a supercooled liquid state in a wide temperature range below the onset temperature of crystallization. It should be noticed that the supercooled liquid region defined by the temperature difference between T_g and T_x , $\Delta T_x (= T_x - T_g)$ reaches as large as 61 K. Although no supercooled liquid state is observed for Fe-based glassy alloys reported up to date, we can scarcely observe the glass transition for some limited glassy alloys in the Fe-P-C, Fe-P-B and Fe-Ni-Si-B systems. The ΔT_x values for these ternary Fe-based glassy alloys are as small as below 25 K⁽¹⁷⁾ because of the absence of the supercooled liquid state after the glass transition. Consequently, the appearance of the wide supercooled liquid region exceeding 60 K is believed to be the first evidence for Fe-based glassy alloys. The melting temperature (T_m) of the Fe-Al-Ga-P-C-B alloy is measured to be 1271 K and hence the reduced glass transition temperature (T_g/T_m) is evaluated to be 0.58 which is consistent with the expected value from the previous empirical relation between ΔT_x

Fig. 3 Temperature dependence of apparent specific heat C_p for a glassy $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy. The $C_{p,q}$ and $C_{p,s}$ represent the specific heat of the samples in as-quenched state and heated once for 60 s at 760 K.

and $T_g/T_m^{(13)-(15)}$. With the aim of confirming the appearance of the glass transition and subsequent supercooled liquid state for the Fe-Al-Ga-P-C-B glassy alloy, the thermograms in as-quenched and heated once to the supercooled liquid at 760 K are shown in Fig. 3. The apparent specific heat of the as-quenched sample $C_{p,q}$ begins to deviate from the $C_{p,s}$ curve at about 400 K, decreases gradually in the temperature range of 400 to 630 K, shows a minimum value at about 645 K and then increases rapidly in the higher temperature range. The rapid increase in C_p is due to the glass transition and the C_p values remains nearly constant in the supercooled liquid ranging from 768 to 790 K before the onset of crystallization. The difference in specific heat between the glassy solid and the supercooled liquid is measured to be about $15 \text{ J mol}^{-1} \text{ K}^{-1}$. Also, the difference between $C_{p,q}$ and $C_{p,s}$ is due to the structural relaxation by heating and the heat of structural relaxation can be evaluated by the relation $\int \Delta C_p (=C_{p,s}-C_{p,q}) dT$ ($\Delta C_p > 0$). The $C_p(T)$ curves shown in Fig. 3 demonstrate clearly that the present Fe-based glassy alloy has a distinct supercooled liquid state in the wide temperature interval of 22 K. It is to be noticed that the temperature interval of the supercooled liquid is comparable to those⁽¹⁶⁾ for noble metal base amorphous alloys such as the Pt-Ni-P and Pd-Ni-P systems, though Ln-Al-TM, Mg-Ln-TM and Zr-Al-TM glassy alloys have a much wider supercooled liquid region⁽¹⁾⁻⁽⁶⁾. In addition, one can see a small λ -type endothermic peak around 600 K due to the transition from ferromagnetism to paramagnetism. The $C_p(T)$ data indicates that the Curie temperature (T_c) is 596 K for the as-quenched sample and 608 K for the sample annealed for 60 s at 760 K. The increase in T_c by annealing is consistent with the previous data⁽¹⁶⁾ for ferromagnetic Fe-based amorphous alloys.

The crystallization structure was examined for the Fe-Al-Ga-P-C-B glassy alloy annealed for 600 s at 873 K which is 67 K higher than the peak temperature of the

exothermic reaction due to crystallization. The X-ray diffraction patterns taken from the crystallized sample was identified to consist of the bcc-Fe(Al, Ga), orthorhombic Fe_3P , orthorhombic Fe_3C and bct- Fe_3B phases. It is therefore concluded that the crystallization takes place through the simultaneous precipitation of more than two kinds of constituent phases. The single-stage crystallization process agrees with that⁽¹³⁾⁻⁽¹⁵⁾ for almost all other glassy alloys in the Ln-, Mg- and Zr-based systems with a wide supercooled liquid region exceeding 60 K, suggesting that the progress of the crystallization for the present Fe-based glassy alloys requires atomic rearrangement of the constituent elements on a long-range scale. The necessity is thought to cause the increase in the thermal stability of the supercooled liquid which enables the appearance of the wide supercooled liquid region.

Figure 4 shows the hysteresis B - H loops of the Fe-Al-Ga-P-C-B glassy samples which are in as-quenched state and annealed for 600 s at 723 K higher than T_c . The saturation magnetization (B_s) and coercivity (H_c) are 1.07 T and 12.7 A/m, respectively, for the as-quenched sample and 1.07 T and 5.1 A/m, respectively, for the annealed

Fig. 4 (a) Hysteresis B - H loops of a glassy $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy in as-quenched and annealed (723 K $\times$ 600 s) states, and (b) enlarged B - H loops in the low magnetic field and magnetization ranges for the hysteresis B - H loops shown in (a).

sample. Furthermore, it is measured that the magnetostriction (λ_s) of the as-quenched sample is 2.0×10^{-6} and remains unchanged in the annealed state, while the effective permeability at 1 kHz (μ_e) is 3600 for the as-quenched sample and increases to 9000 for the annealed sample. The T_c also increases from 596 K for the as-quenched sample to 605 K for the annealed sample. Thus, the present Fe-based glassy alloy possesses the following unique advantages: (1) The direct preparation of a bulk glassy alloy from liquid due to the large glass-forming ability, (2) the ease of deformation and working in the wide supercooled liquid region, (3) the good soft ferromagnetic properties, and (4) high mechanical strength and high electrical resistivity inherent to amorphous alloys. These advantages allow us to expect that the present Fe-based glassy alloy is used as magnetic head materials with high reliability for industrial applications such as telephone and prepaid cards.

IV. Summary

In conclusion, the $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ glassy alloy was found to have a wide supercooled liquid region reaching 61 K before crystallization and to exhibit rather good soft ferromagnetic properties at room temperature, i.e., 1.07 T for B_s , 12.7 A/m for H_c , 3600 for μ_e at 1 kHz and 2.0×10^{-6} for λ_s in the as-quenched state. The annealing treatment for 600 s at the temperature (723 K) above T_c caused the improvement of the soft magnetic properties to 605 K for T_c , 1.07 T for B_s , 5.1 A/m for H_c and 9000 for μ_e , though no appreciable change in λ_s is seen. The finding of the Fe-based glassy alloy exhibiting simultaneously the wide supercooled liquid region before crystallization and the soft ferromagnetism at room temperature will greatly contribute to the future development of a

new glassy ferromagnetic bulk alloy.

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