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Bulk Glassy Fe–Ga–P–C–B Alloys with High Saturation Magnetization and Good Soft Magnetic Properties Synthesized by Fluxing Treatment and Copper Mold Casting

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The effect of fluxing treatment on the glass-forming ability for the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy alloy was investigated. The fluxing treatment was found to be effective for the elimination of heterogeneous nucleation sites. The glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid region (ΔT_x) and reduced glass transition temperature (T_g/T_m) are all increased by fluxing treatment. The T_g, T_x, ΔT_x and T_g/T_m values for $Fe_{75}Ga_5P_{12}C_4B_4$ glassy alloy are 731 K, 768 K, 37 K and 0.610 respectively before fluxing treatment, increase to 749 K, 805 K, 56 K and 0.625 respectively after fluxing treatment. Bulk glassy $Fe_{75}Ga_5P_{12}C_4B_4$ alloy rods with high saturated magnetization (I_s) of 1.27 T and good soft magnetic properties of 1.6 A/m for coercive force (H_c) were prepared with diameters range up to 2.5 mm by the copper mold casting method of fluxed alloy melt. The glass synthesis consists of preparing the alloy ingot by induction melting, thermal cycling and purifying the melt in B_2O_3 flux inside a silica tube and then casting the purified alloy into a copper mold. The size of 2.5 mm in diameter of the rod is not an upper limit.

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1. Introduction

Amorphous ferromagnetic alloys have been investigated for the last three decades for potential use as electrical devices because of their good soft magnetic properties. However, the shape of amorphous ferromagnetic alloys has been usually limited to sheet, wire and film forms because of their low glass-forming ability, leading to the restriction of their application fields. For instance, the amorphous thin ribbons are difficult to handle and thus the transformers cannot be constructed by the ordinary method which has been used for conventional 0.3 mm thick crystalline Fe–Si laminas. In addition, the reduced thickness of the ribbons causes a decrease in the core packing density since air gaps are left between the large number of thin ribbons needed to build up the core, and this decreases the efficiency of the transformer. Therefore, it is very important to search an Fe-based bulk glassy alloy with high saturation magnetization and high glass-forming ability.

Since 1995, new Fe-based bulk glassy alloys with good soft magnetic properties in the Fe–(Al, Ga)–(P, C, B, Si), Fe–(Nb, Mo, Zr, W)–B and Fe–(Cr, Mo)–Ga–(P, C, B) alloy systems have been produced in a cylindrical form with diameters of 2 to 6 mm.[1–4] However, these bulk glassy alloys have a disadvantage of relatively lower Fe concentrations less than 73 at% leading to saturated magnetization (I_s) values below 1.1 T. More recently, a bulk glassy $Fe_{75}Ga_5P_{12}C_4B_4$ alloy of 1 mm in diameter with high saturation magnetization I_s of about 1.28 T has been synthesized by Inoue group.[5] This bulk glassy alloy has a large supercooled liquid region ΔT_x ($=T_x - T_g$) of 37 K and a high reduced glass transition temperature (T_g/T_m) of 0.61. It is noticed that high T_g/T_m value exceeds 0.60 which can be regarded as a critical value for the formation of a bulk glassy alloy. Within the author's knowledgement, little has been reported about Fe-based glassy alloys with T_g/T_m above 0.60,[6] and the $Fe_{75}Ga_5P_{12}C_4B_4$ alloy has the highest T_g/T_m value in all Fe-based glassy alloys reported up to date. Therefore, there is a high possibility of forming a glassy rod with a larger diameter by use of this alloy.

It is known that the main competition to undercooling is attributed to oxides and other inclusions in the melts which act as heterogeneous nucleation centers for crystallization.[7,8] Consequently, the elimination of heterogeneous nucleation sites in the molten alloy by using fluxing treatment is expected to lead to the formation of a bulk glassy alloy with a much larger thickness. Up to now, the main procedure in the fluxing technique to get a bulk glassy alloy consists of quenching the melt covered with flux in a silica tube into water after fluxing treatment.[4,9] However, this method is not suitable for large-scale commercial production for the electric device applications. This paper is intended to present the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods with diameters range up to 2.5 mm with high saturation magnetization and good soft magnetic properties synthesized by fluxing technique and copper mold casting. The effect of fluxing treatment on the glass-forming ability of the alloy is also discussed.

2. Experimental Procedure

An $Fe_{75}Ga_5P_{12}C_4B_4$ alloy ingot was prepared by induction melting the mixtures of pre-alloyed Fe–P and Fe–C ingots, pure Ga metal tip and pure B crystal in a purified argon atmosphere. The alloy ingot and dehydrated B_2O_3 were put together in a silica tube. The tube was heated to a temperature about 1273 K also by induction melting in the purified argon atmosphere and then cooled to a temperature above the glass transition temperature (T_g) of B_2O_3. After several thermal cycles, the system was cooled to room temperature. The flux-treated ingot was inserted into a silica nozzle and remelted in the purified argon atmosphere. Then, the glassy rod was prepared by injecting the melt into a copper mold. The glassy nature was identified by X-ray diffractometry and optical microscopy. The thermal stability associated with Curie temperature (T_c), glass transition temperature T_g, supercooled liquid region ΔT_x and crystallization temperature (T_x) was examined at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). The melting temperature (T_m) was measured by differential thermal analysis (DTA). Magnetic properties of saturation magnetization I_s and coercive force (H_c) were measured with a vibrating sample magnetometer (VSM) and a B-H loop tracer.

3. Results

Figure 1 shows the outer morphology of the bulk $Fe_{75}Ga_5P_{12}C_4B_4$ rods with a diameter of 2.5 mm synthesized by the fluxing treatment and then injecting the molten alloy into the copper mold. The samples have a smooth surface and metallic luster and no appreciable ruggedness corresponding to a crystalline phase can be seen on the outer surface confirmed by optical observation. In order to examine the formation of an amorphous phase and the absence of any crystalline phase in the rod samples, the rods were sectioned with a diamond saw and then the cross sectional structure observation was performed. No contrast typical to a crystalline phase can be observed over the whole cross section for all the samples with a diameter of 2.5 mm. Figure 2 shows the X-ray diffraction patterns taken from the transverse cross sections of the rod samples with diameters of 1.5, 2.0 and 2.5 mm. The diffraction patterns consist only of a broad peak around $2\theta = 45$ degrees and no diffraction peak corresponding to a crystalline phase is observed. These results indicate that the bulk alloys are composed only of a glassy phase.

Figure 3 shows the DSC curves of the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods with diameters of 1.5, 2.0 and 2.5 mm prepared by the fluxing treatment and copper mold casting technique. The data of the melt-spun glassy ribbon and the glassy rods in diameter of 0.5 and 1.0 mm without fluxing treatment are also shown for comparison. As a result of fluxing treatment, the crystallization temperature T_x of the glassy rod of 1.5 mm in diameter increases to 784 K, accompanying the increase in the supercooled liquid region ΔT_x ($=T_x - T_g$) to 47 K. Based on this encouraging result, we increased the number of thermal cycling to reduce the heterogeneous nuclei thoroughly as possible as we can, and then prepared the glassy rods in the diameters of 2.0 and 2.5 mm. As shown in the figure, the crystalline temperature T_x of the ϕ2.0 and 2.5 mm glassy rods increase to 805 K, and the supercooled liquid region ΔT_x also increases to 57 K. In addition, the internal equilibrium state in which the disordered structure can be fully relaxed during continuous heating at the rate of 0.67 K/s is maintained in the temperature interval of 30 K before crystallization for

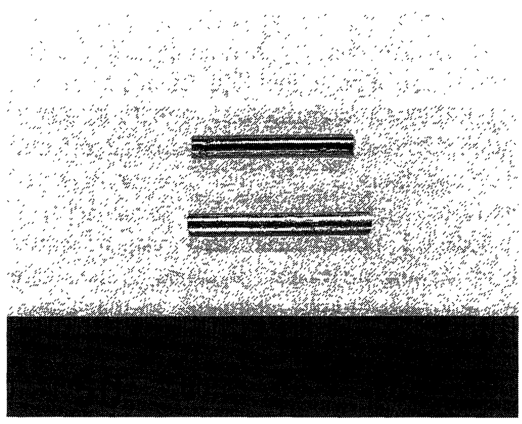

Fig. 1 Outer morphology and surface appearance of $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods with a diameter of 2.5 mm prepared by fluxing treatment and then copper mold casting.

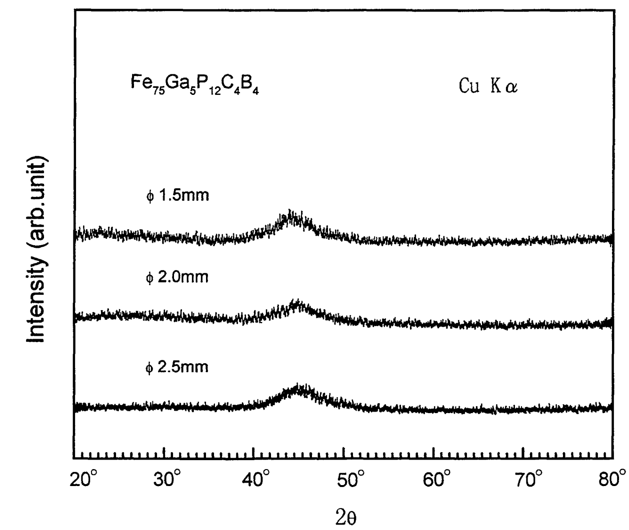

Fig. 2 X-ray diffraction patterns of $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods with diameters of 1.5, 2.0 and 2.5 mm prepared by fluxing treatment and then copper mold casting.

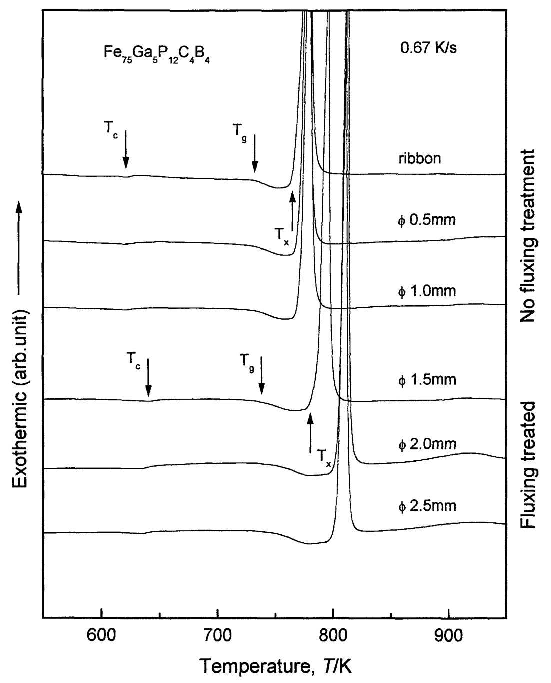

Fig. 3 DSC curves of the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods with different diameters up to 2.5 mm. The data of the melt-spun ribbon with a thickness of 20 μm are also shown for comparison.

these two glassy rods. This means that the supercolled liquid has high thermal stability. It is also found that the Curie temperature T_c and glass transition temperature T_g increase significantly.

The glassy rods also exhibit high saturation magnetization and good soft magnetic properties. As an example, the hysteresis I-H loop of the glassy rod in the diameter of 2.5 mm is shown in Fig. 4, where the hysteresis loop of the melt-spun glassy ribbon is also shown for comparison. The hysteresis I-H loops were measured only by VSM because the conventional B-H loop tracer could not be used for the cylindrical form of the bulk glassy alloys. As shown in the figure, the saturation magnetization I_s is about 1.27 T, and no distinct difference in the hysteresis I-H loops measured by VSM is seen between the bulk sample and the melt-spun ribbon. The saturation magnetization I_s and coercivity H_c of the melt-spun ribbon measured by B-H loop tracer are 1.28 T and 1.6 A/m. Here, it is reasonable to consider that the cast bulk glassy samples also have nearly the same soft magnetic properties from the similarity in the I-H loops between the melt-spun ribbons and the cast bulk samples measured by VSM.

Table 1 summarizes the diameter (d), T_g, T_x, ΔT_x, T_g/T_m, saturated magnetization I_s and coercive force H_c of the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods with diameters range up to 2.5 mm. The data of the melt-spun ribbon are also shown for comparison. It can be noted that the reduced glass transition temperature T_g/T_m increases from 0.610 to 0.625 and the supercooled liquid region ΔT_x increases from 37 to 56 K after fluxing treatment. Therefore, after fluxing treatment the glass forming ability increases as compared with that before fluxing treatment. The large glassy rod can be prepared even by ordinal copper mold casting and the quenching of the melt into water is not necessary. The size of 2.5 mm in diameter is not an upper limit in this alloy system. One can also see that these glassy rods exhibit high saturation magnetization as well as good soft magnetic properties, *i.e.*, high I_s of 1.28 T and low H_c of 1.6 A/m.

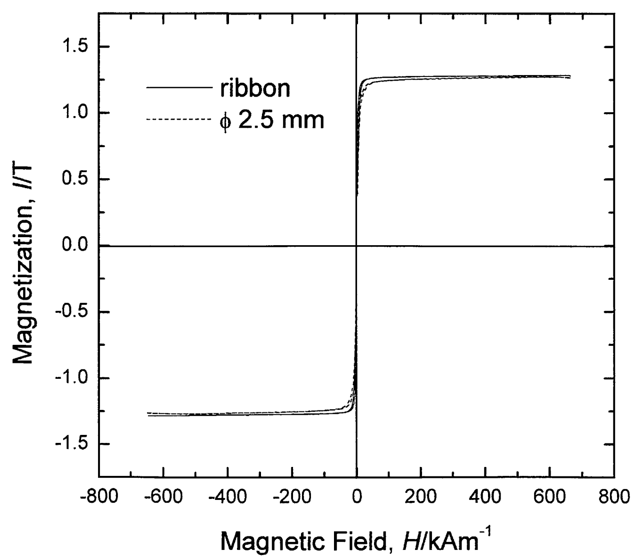

Fig. 4 Hysteresis I-H loops of the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy alloys in the rod form with a diameter of 2.5 mm and in a ribbon form with a thickness of 20 μm.

Table 1 Diameter, thermal stability and magnetic properties of the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods. The data of the melt-spun glassy ribbon are also shown for comparison.

d (mm)	T_g (K)	T_x (K)	ΔT_x (K)	T_g/T_m	T_c (K)	I_s (T)	H_c (A m^{-1})
ribbon	731	768	37	0.610	622	1.28	1.6
ϕ1.5	737	784	47	0.615	638	1.27	1.6
ϕ2.0	749	805	56	0.625	636	1.27	1.6
ϕ2.5	749	805	56	0.625	636	1.27	1.6

4. Discussion

Here, we discuss the reason why the effect of fluxing treatment on the glass-forming ability of the alloy is such distinct. Normally, high cooling rates ($\sim 10^6$ K/s) are required to quench a molten metallic alloy through its rapid crystallization regime to form a glass. If heterogeneous nucleation is avoided then the minimum cooling rate required for glass formation is determined by the homogeneous nucleation rate of the alloy. Besides, from classical nucleation theory, it is expected that alloy with high glass transition temperature T_g, relative to their equilibrium melting temperature T_m, will have relatively low homogeneous nucleation rate.[10] Another very important parameter is the supercooled liquid region ΔT_x which is defined by the difference between the glass transition temperature T_g and crystallization temperature T_x. The appearance of the wide supercooled liquid region also implies that the supercooled liquid has a high resistance against crystallization leading to large glass-forming ability. An alternate approach to the removal of nucleating heterogeneities, is to heat and cool the molten metal while it is immersed in a molten oxide flux. After gravity segregation to the oxide flux-metal interface, most heterophase impurities presumably are dissolved or deactivated (*e.g.*, by being wet) by the molten oxide flux. The effect of the fluxing treatment is evidenced by the success of preparing the glassy rods with diameters above 1.5 mm in this study. Figure 5 plots the data of T_g, T_x, ΔT_x, and T_g/T_m as a function of sample diameter for the $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods synthesized by fluxing treatment. The data of the 1.0 mm diameter sample which is not treated by fluxing are also plotted for comparison. As a result of eliminating the "pre-existing" nuclei such as oxides and other inclusions by thermal cycling the melt in the molten B_2O_3, the supercooled liquid tends to be very stable and is more difficult to crystallize, so that the crystallization temperature T_x increases for every sample. Besides, the glass transition temperature T_g also increases. It may be the first evidence of the increase of the glass transition temperature T_g. The reason is not so clear, but it may be considered to result from fluxing treatment. Because of the inclusions in glass are few after fluxing treatment, so that the degree of the topological short-range ordering and the internal energy of the glass become lower. As a result, the glass has higher thermal stability and the T_g shifts to higher temperature side. Therefore, the reduced glass transition temperature T_g/T_m increases as shown in the figure. It is therefore concluded that the larger bulk glass of this alloy can be formed at a lower

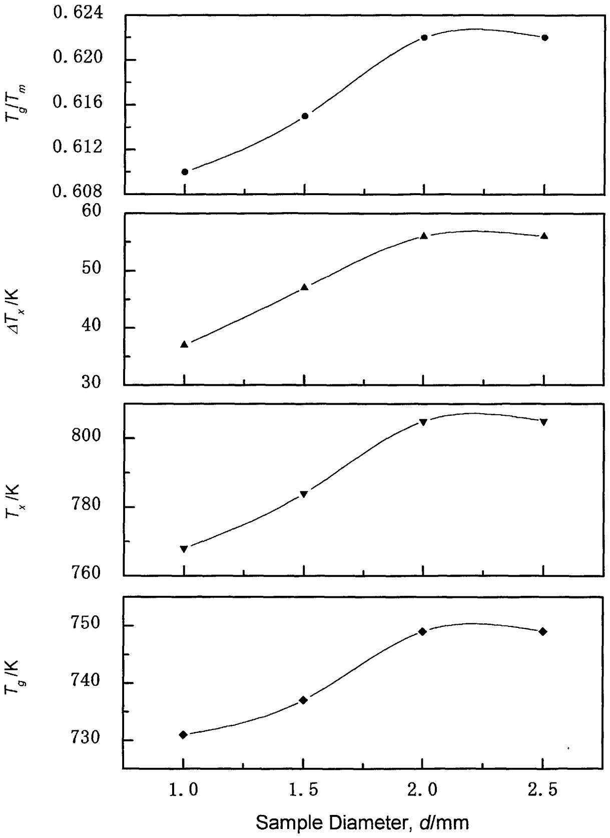

Fig. 5 Changes in T_g, T_x, ΔT_x and T_g/T_m as a function of sample diameter for $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods prepared by fluxing treatment and then copper mold casting. The date of the glassy rod of 1.0 mm in diameter not treated by fluxing are also shown for comparison.

cooling rate if the heterogeneous nucleation is eliminated or at least inhibited.

Otherwise, it is also found that the Curie temperature T_c increases as shown in Fig. 3. The increase of T_c is interpreted to result from the progress of structural relaxation[11] as the diameter of the glassy rod becomes larger. It is considered that the ferromagnetic properties of Fe will despair if its structure is the closed-packed lattice which has large coordination number of nearby atom.[12] The structure relaxation resulted in destroying of unrelaxed atomic configuration and decreased the coordination number of nearby atom, so that the Curie temperature T_c increased. This result is also consistent with the previous data for Fe-based glassy alloys.[13]

5. Summary

The effect of B_2O_3 flux treatment on the glass-forming ability and maximum sample thickness for glass formation was examined for the ferromagnetic $Fe_{75}Ga_5P_{12}C_4B_4$ alloy. The results obtained are summarized as follows.

(1) The heterogeneous nucleation, although not completely avoided, can be minimized by thermal cycling the alloy melt in the molten B_2O_3.

(2) The onset temperature of crystallization increases significantly for the fluxed sample, leading to the significant extension of the supercooled liquid region.

(3) It may be the first finding that the glass transition temperature also increases drastically leading to significant increasing of the reduced glass transition temperature.

(4) The large scale $Fe_{75}Ga_5P_{12}C_4B_4$ glassy rods in the diameter range up to 2.5 mm with high saturation magnetization I_s of 1.27 T, good soft magnetic properties of 1.6 A/m for coercive force H_c and high Curie temperature T_c of 636 K were synthesized by fluxing treatment and ordinary copper mold casting. It is very encouraging for engineering applications in electric devices.

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