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Preparation of $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ Bulk Glassy Alloy with Good Soft Magnetic Properties by Spark-Plasma Sintering of Glassy Powder

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With the aim of developing a large size bulk glassy Fe-based alloy with good soft magnetic properties by the powder metallurgy technique, we have applied the spark-plasma sintering technique to a $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ glassy alloy powder with a large supercooled liquid region of 50 K before crystallization. The existence of the supercooled liquid region enabled us to form a large size bulk glassy alloy of 20 mm in diameter and 5 mm in thickness with a high relative density of 99%. The resulting bulk glassy alloy exhibits good soft magnetic properties, *i.e.*, 1.20 T for saturation magnetization, 14 A/m for coercive force and 6000 for maximum permeability. The good soft magnetic properties for the multicomponent Fe-based bulk alloy are attributed to the combination of the high relative density and the maintenance of the single glassy structure. The success of forming the large size bulk glassy alloy with good soft magnetic properties by the powder metallurgy techniques is promising for future use as practical soft magnetic materials.

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Keywords: *iron-based alloy, large supercooled liquid region, glassy alloy powder, spark-plasma-sintering, large size bulk glassy alloy*

1. Introduction

Since amorphous alloys in Fe-metalloid system were found to exhibit good soft magnetic properties because of the absence of crystal magnetic anisotropy and grain boundaries in 1974,[1–3] a large number of studies on the development of soft magnetic amorphous alloys have been carried out for the subsequent ten years. It is well known that Fe–Si–B and Co–Fe–Si–B base amorphous alloys have been used as practical soft magnetic materials of high saturated magnetization-type and high-permeability-type, respectively.[4] However, the shape and dimension of the soft magnetic alloys have been limited to thin sheet with a thickness less than about 50 μm and fine wire with a diameter less than 150 μm, because of the necessity of high cooling rates for formation of an amorphous phase.[4,5] It is strongly expected that the elimination of the limitation of the sample shape and dimension causes a more wide extension of application fields.

Since 1995, various types of Fe-based glassy alloys with high glass-forming ability were found in Fe–(Al, Ga)–(P, C, B),[6] Fe–(Nb, Cr, Mo)–(Al, Ga)–(P, C, B),[7] Fe–Ga–(P, C, B),[8] Fe–(Nb, Cr, Mo)–Ga–(P, C, B),[9,10] Fe–(Zr, Hf, Nb)–B,[11] Fe–(Zr, Nb, Ta)–(Cr, Mo, W)–B,[12] Fe–Co–Ga–(P–C–B),[13] Fe–(Cr, Mo, Nb)–(B, C),[14] Co–Fe–Nb–Ta,[15] Fe–Si–B–Nb[16] and Fe–Ga–(P, C, B, Si)[17] systems. The use of these new Fe- and Co-based alloy compositions has enabled us to produce bulk glassy alloys with diameters up to 2 mm for Fe–(Al, Ga)–(P, C, B, Si),[18] Co–Fe–Nb–Ta[15] and Fe–Co–Ga–(P–C–B),[19] 3 mm for Fe–Ga–(P, C, B)[20] and Fe–Ga–(P, C, B, Si)[17] and 5 mm for Fe–(Zr, Nb, Ta)–(Cr, Mo, W)–B.[21] It is characterized that all these Fe-based bulk glassy alloys exhibit a large supercooled liquid region above 50 K before crystallization. The extension of the supercooled liquid region allows us to expect the synthesis of a bulk glassy alloy by the consolidation method in the supercooled liquid with significant viscous flowability.[22] The establishment of the process for producing a Fe-based bulk glassy alloy is expected to cause a much relaxation of sample shape and dimension. We have succeeded in forming a Fe–Al–Ga–P–C–B–Si bulk glassy alloy with a size of 18 mm in diameter and 1 mm in thickness by the powder metallurgy technique.[23] More recently, we also tried to form a $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy with a large size of 20 mm in diameter and even 5 mm in thickness by spark-plasma sintering of the Fe-based glassy alloy powder[24] because this alloy exhibited high glass-forming ability.[19] However, soft magnetic properties of the resulting sintered bulk alloy are inferior to those of the corresponding melt-spun glassy alloy ribbon because of its lower relative density resulting from the low applied pressure. Therefore, in this study, to get a bulk sample with high relative density, high pressure of 200 MPa were applied during compacting powder by using high strength mold and punches. This paper intends to present the improved results on the synthesis of the large size $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy with nearly full density and its good soft magnetic properties.

2. Experimental Procedure

Multi-component $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ alloy ingot was prepared by induction melting a mixture of pure Fe, Co and Ga metals, prealloyed Fe–C and Fe–P ingots, and pure B crystal in a purified argon atmosphere. Metallic glassy alloy powder was prepared by the high-pressure gas-atomization method.[25] The ingot was remelted under vacuum in a quartz tube using an induction-heating coil firstly, injected through a nozzle with a diameter of 0.8 mm and then atomized by high-pressure argon gas with a dynamic pressure of 9.8 MPa.

The glassy alloy powder sieved to below 53 μm was used for the subsequent sintering experiment. The bulk glassy sample in a disc shape of 20 mm in diameter and of 5 mm in thickness was produced from the powder by using a spark-plasma sintering equipment. The sintering was performed under an applied pressure of 200 MPa at the glass transition temperature (T_g) of 723 K for 600 s in a WC hard metal mold with two WC hard metal punches. To prevent the reaction between the WC hard metal and powder, the contact of mold and

punches with powder was avoided by using graphite sheets. The structure of the powder and sintered disc was examined by X-ray diffratometry with Cu–Kα radiation and optical microscopy (OM). The specific heat associated with glass transition, supercooled liquid region and crystallization was measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). The density of the sintered disc was measured by Archimedian method. Saturation magnetization was measured by using a vibrating sample magnetometer (VSM) in a maximum applied field of 800 kA/m at room temperature. Coercive force was measured with a D. C. *B*-*H* loop tracer in the maximum applied field of 800 A/m for magnetic core which was cut from the sintered disc by an electrical discharge machine.

3. Results

We have previously reported that the soft magnetic properties of the $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ sintered compact are much inferior to those of the cast bulk glassy alloy because of the lower relative density of about 96%.[24] In the previous study, the mold and punch made of graphite were used, and hence the applied pressure was limited to less than 80 MPa. In the present study, the mold and punch made of WC hard metal were used to prepare the disc-shaped compact under a much higher applied pressure of 200 MPa. Figure 1 shows the surface morphology of the gas-atomized $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ glassy powder with a size fraction smaller than 53 µm. No appreciable contrast revealing the formation of a crystalline phase is seen on the surface of any particles. Figure 2 shows the outer morphology of the sintered $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ disc core of 20 mm in outer diameter, 10 mm in inner diameter and 5 mm in thickness. The core was prepared by electrical discharging from the bulk sample sintered at 723 K which was the optimum sintering temperature for this glassy alloy.[24] The optimum sintering temperature agrees with the T_g (723 K) of the present alloy. The sintered sample has smooth surface and good metallic luster. Figure 3 shows the X-ray diffraction patterns of the sintered $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ alloy, together with the data of the glassy alloy powder below 53 µm in size. The X-ray diffraction pattern of the as-sintered sample consists only of a halo peak, in agreement with the original alloy powder. It is therefore concluded that the bulk glassy alloy without crystallinity is prepared by plasma sintering at 723 K. We further examined the thermal stability of the sintered bulk alloy. Figure 4 shows the DSC curve of the sintered bulk sample. The data of the original powder are also shown for comparison. No appreciable difference in the heat of exothermic reaction due to crystallization is seen, though the T_c, T_g and T_x values increased by about 10 K. Besides, the heat of relaxation-induced endothermic reaction decreased by about 130 J/mol for the sintered bulk sample. It is thus noted that the sintering process at appropriate sintering temperature and applied pressure leads to the large size bulk amorphous sample.

The sintered bulk sample exhibited a high relative density of 99% in the maintenance of a glassy single phase, being much higher than that (96%) of the bulk alloy with the same composition sintered under 80 MPa.[24] In order to confirm the formation of the nearly fully densified structure without crystalline phase, an optical micrograph (OM) of the bulk

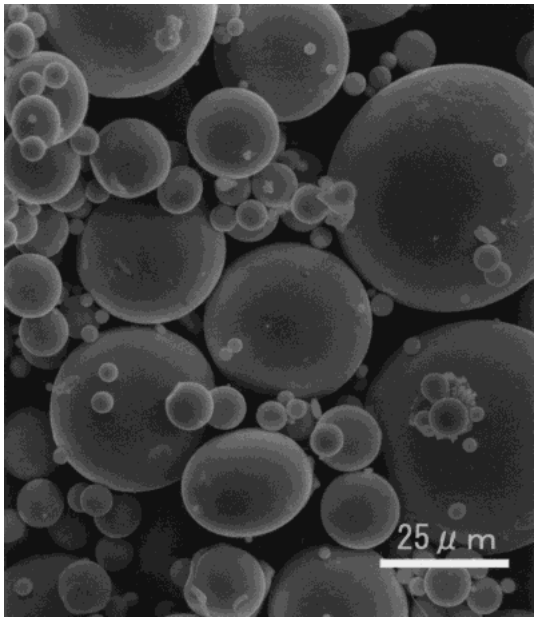

Fig. 1 Scanning electron micrograph of gas-atomized $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ powder with particle size fraction below 53 µm.

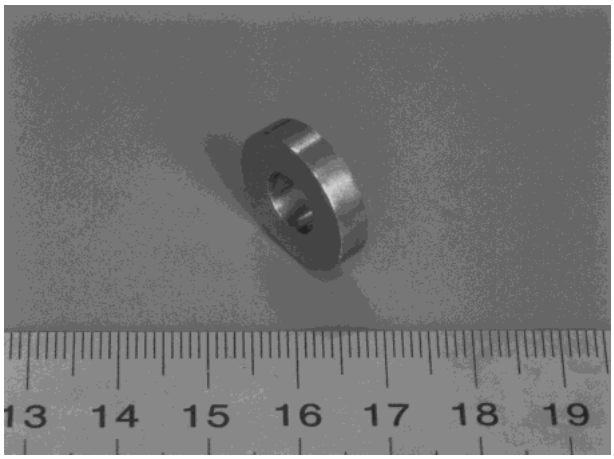

Fig. 2 Outer morphology of the $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ magnetic core with the size of 20 mm in outer diameter, 10 mm in inner diameter and 5 mm in thickness. The core was prepared by electrical discharging from the bulk sample sintered by spark-plasma sintering.

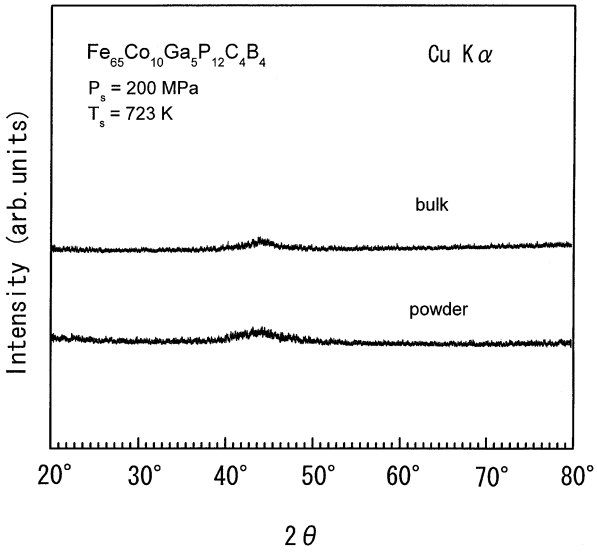

Fig. 3 X-ray diffraction patterns of $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy with a disc shape of 20 mm in diameter and 5 mm in thickness prepared by spark-plasma sintering. The data of the glassy powder are also shown for comparison.

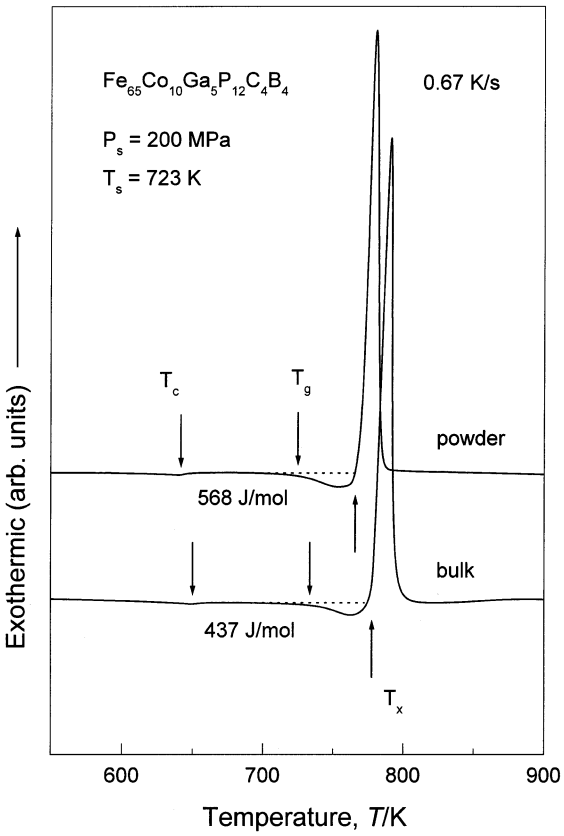

Fig. 4 DSC curve of $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy prepared by spark-plasma sintering at 723 K under 200 MPa. The data of the glassy powder are also shown for comparison.

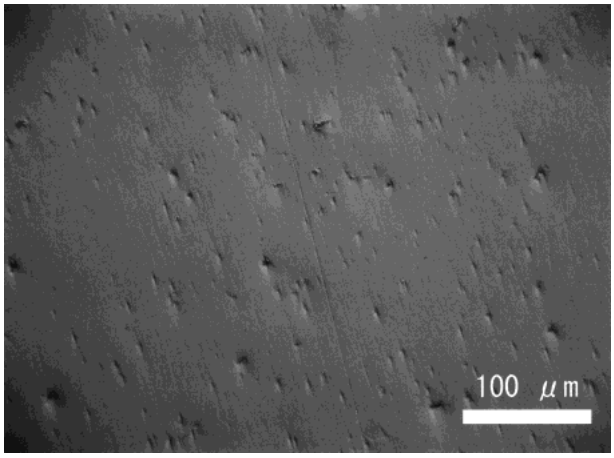

Fig. 5 Optical micrograph of $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy prepared by spark-plasma sintering at 723 K under 200 MPa.

$Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ alloy obtained by sintering at 723 K is shown in Fig. 5. Although some stretching traces caused by mechanical polishing are seen, one cannot see distinct pores as well as the trace of the powder, in addition to the absence of typical crystalline phases. The OM result is consistent with the data of X-ray diffraction, DSC and density.

Figure 6 shows the hysteresis I-H curve in the as-sintered state for the bulk glassy $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ sample prepared at sintering temperature of 723 K, together with the data of the powder for comparison. It is clear that the $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ sintered bulk sample exhibits the saturation magnetization (I_s) of 1.19 T, which is the same as that

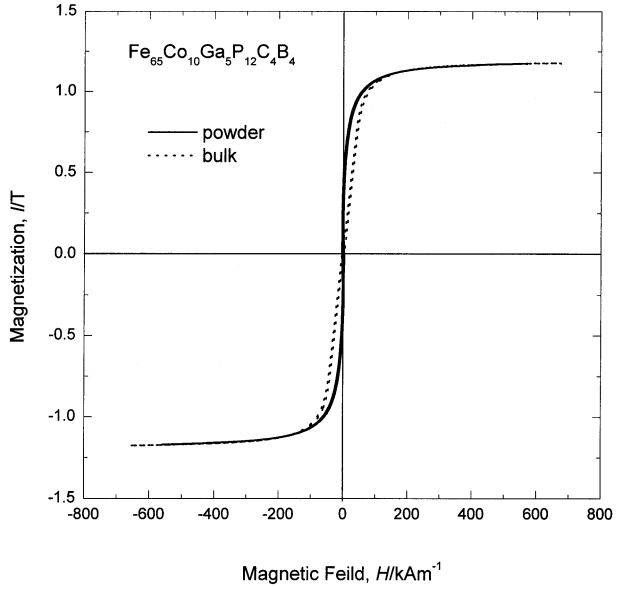

Fig. 6 Hysteresis I-H loop of $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy prepared by spark-plasma sintering at 723 K under 200 MPa. The data of the glassy powder are also shown for comparison.

for the powder. The coercive force (H_c) and maximum permeability (μ_{max}) were also measured by using the magnetic core as shown in Fig. 2. The H_c and μ_{max} of the as-sintered sample are 19 A/m and 3800, respectively, being much better than those (115 A/m and 230) of the same composition sample with lower relative density (96%) reported before.[24] However, its soft magnetic properties are not enough for application. It is well known that the soft magnetic properties of Fe- and Co-based amorphous alloys are significantly enhanced by annealing in the temperature range between T_c and T_x. Therefore, the sample was annealed for 3.6 ks at 708 K which is 25 K lower than the T_g (733 K) of the as-sintered sample, followed by gradual cooling in a furnace to eliminate the internal stress induced by sintering. After annealing, the I_s increased from 1.19 T to 1.20 T and, the H_c decreased from 19 A/m to 14 A/m, while the μ_{max} increased from 3800 to 6000. It is thus concluded that the $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy of 20 mm in diameter and 5 mm in thickness prepared by spark-plasma sintering exhibits good soft magnetic properties. The formation of the bulk glassy alloy with nearly full density is important for future development as soft magnetic bulk materials. This result also implies the importance of the selection of the glassy type Fe-based alloy with glass transition leading to the easy consolidation tendency into a bulk form with nearly full density.

4. Discussion

As described above, the T_c, T_g and T_x values increased by about 10 K for the sintered bulk sample, and the soft magnetic properties were improved by appropriate anneal leading to elimination of internal stress. Here we discuss the reason for these changes. It is well known that the structural relaxation occurs when the amorphous phase is heated. Inoue *et al.*[26] pointed out that the structural relaxation of $Pd_{48}Ni_{32}P_{20}$ glassy alloy was inhibited under application of high pressure. The same result was also obtained as shown

in Fig. 4. Although the supercooled liquid region of the powder was the same as that for the consolidated bulk, the heat of relaxation-induced endothermic reaction decreased from 568 to 437 J/mol under application of high pressure of 200 MPa. This means that the structural relaxation is also inhibited under high pressure for Fe-based glassy alloy. It is known that the rearrangement of constituent atoms in supercooled liquid phase is determined by diffusion through free volumes.[5] Under high pressure, in addition to the decrease in mobility of atom itself, the diffusion is reduced because of the decrease in free volumes. Consequently, the redistribution of atoms from unequilibrium state to equilibrium state, *i.e.*, structural relaxation is inhibited. As a result, the glass transition is suppressed. Thus, the T_g and T_x increased by about 10 K as seen in this study. The real sintering temperature in accordance with the T_g (723 K) of the powder is lower than that (733 K) of the compacted disc. The difference causes the generation of residual internal stress in the as-sintered sample because the sintering temperature is lower than the T_g of the compacted disc. That may be the reason why the soft magnetic properties can be improved by appropriate annealing. The reason for the increase in T_c under the present high pressure is not so clear, but may be also considered to result from the lower cooling rate because of the large heat capacity of the WC hard metal mold and punches.[5]

The good soft magnetic properties of the large size $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ bulk glassy alloy were obtained by spark-plasma sintering and appropriate annealing. Great efforts had been devoted to fabricate a bulk amorphous alloy with full density in Fe–Si–B system by using various kinds of consolidation techniques such as warm-pressing, explosive consolidation and warm extrusion *etc*.[27] However, there have been no successful data on the formation of a fully dense bulk amorphous Fe–Si–B alloy. The unsuccessful result has been thought to result from the absence of the supercooled liquid region before crystallization. As is evident from the present results, the application of the plasma sintering technique to the new Fe-based glassy alloy with a supercooled liquid region of 50 K before crystallization was found to be useful for the formation of the fully dense bulk glassy alloy. The formation of the fully dense bulk glassy phase is the major reason for the achievement of the good soft magnetic properties. In addition, it has been reported[23] that the new Fe-based glassy alloy has a unique glassy structure with the features of (1) a more highly dense random packed atomic configuration, (2) new local atomic configurations and (3) long-range homogeneity with attractive atomic interaction. The new structure typical for the bulk glassy alloys with a large supercooled liquid region has been pointed out[28] to exhibit a lower coercive force and a higher maximum permeability because of the more homogeneous glassy structure which leads to more easy movement of magnetic domain wall. The unique glassy structure in the present Fe-based alloy may be another important factor for the achievement of the good soft magnetic properties in the sintered bulk samples. The success in forming the bulk glassy alloy with good soft magnetic properties by the combination of the large supercooled liquid region before crystallization and the unique new glassy structure is encouraging for future application as a new type of soft magnetic bulk material.

5. Summary

We have tried to form a bulk glassy alloy core with full density and good soft magnetic properties by spark-plasma sintering of $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ glassy alloy powder exhibiting a large supercooled liquid region before crystallization. The results obtained are summarized as follows.

(1) The application of the spark-plasma sintering method to $Fe_{65}Co_{10}Ga_5P_{12}C_4B_4$ glassy alloy enabled us to form a large scale bulk glassy alloy with a high relative density of 99% in the case of sintering condition at 723 K under an applied pressure of 200 MPa.

(2) The coercive force of the as-sintered bulk glassy alloy is 19 A/m. After annealing to eliminate the internal stress, the bulk glassy alloy exhibits good soft magnetic properties, *i.e.*, saturation magnetization of 1.20 T, coercive force of 14 A/m and maximum permeability of 6000.

(3) The good soft magnetic properties are attributed to the combination of the higher relative density and the unique glassy structure which has been characterized by higher packing density, new local atomic configuration and long-range homogeneity with attractive bonding nature.

(4) The success in forming the large size bulk glassy Fe-based alloy of 20 mm in diameter and 5 mm in thickness with good soft magnetic properties indicates the possibility of extending application fields as soft magnetic materials.

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