Preparation of Bulk Glassy Fe$_{76}$Si$_9$B$_{10}$P$_5$ as a Soft Magnetic Material by Spark Plasma Sintering

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Preparation of a soft magnetic Fe$_{76}$Si$_9$B$_{10}$P$_5$ glassy bulk material has been carried out by the spark plasma sintering (SPS) technique below the glass transition temperature. The glassy powders were consolidated into bulk forms with relative densities above 98.7% through sintering them at 740 K under a pressure of 600 MPa while the samples still keep a glassy state. These as-sintered samples with a diameter of 15 mm exhibited excellent soft magnetic characteristics, which is as good as that of the cast samples with a size of 2.5 mm.

Keywords: iron–silicon–boron–phosphorus alloy, metallic glass, spark-plasma sintering, soft magnetic properties

1. Introduction

Bulk glassy alloys (BGAs) are promising materials for structural application as they exhibit high mechanical strength, high hardness, good fracture toughness, superior corrosion resistance, and so on.$^{1,2}$ BGAs with excellent glasses forming ability were developed in the 1990s by conventional casting methods$^3$ where Fe- and Co-based glassy alloys were found to have good soft magnetism at room temperature.$^{3,4}$ Recent work reports that the Fe$_{76}$Si$_9$B$_{10}$P$_5$ bulk metallic glass has an unusual combination of high $B_T$ of 1.51 T due to high Fe content and high glass forming ability forming a glassy rod with a diameter of 2.5 mm without any glass-forming metal elements$^5$ where $B_T$ denotes the full magnetic induction.

The BGAs are usually low-dimensional, such as thin films, sheets, powders, wires and rods due to the necessity of high cooling rates, which limit the possible applications. Thus, the powders metallurgy technique is utilized to form bulk samples,$^6$ which however need extensive equipments. An alternative is SPS (spark plasma sintering) technique$^7$ where lower temperature and shorter time can be realized for the sintering. The technique thus can avoid any crystallization of BGAs and realized sintering for larger size samples.$^{8,9}$ Therefore, this technique has been applied for sintering of several Fe-base bulk glassy magnetic materials, such as Fe-Al-Ga-P-C-B-Si,$^{10}$ Fe-Co-Ga-P-C-B$^{11}$ and Fe-Co–Nd–Dy–B.$^{12}$

In this contribution, Fe$_{76}$Si$_9$B$_{10}$P$_5$ glassy bulk samples are sintered using SPS technique. It is found the sample can be as large as 15 mm while the corresponding magnetic properties remain. Thus, the technique is beneficial for possible applications.

2. Experimental Procedure

Master ingots of the Fe$_{76}$Si$_9$B$_{10}$P$_5$ were prepared by induction melting the mixture of pure metals of Fe (99.98 mass%), pre-melted Fe-P (99.9 mass%), and pure metalloid of crystal B (99.5 mass%) and Si (99.999 mass%) in an argon atmosphere. The Fe$_{76}$Si$_9$B$_{10}$P$_5$ glassy powders were produced by a high pressure argon gas atomization method where the atomic compositions denote that of adding percentages. The ingots were re-melted at 1473 K under atmosphere condition in a quartz tube using an induction heating coil, followed by injection through a nozzle with a diameter of 0.8 mm, and then atomized by high pressure argon gas with a dynamic pressure of about 9.3 MPa. The powders were classified and characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). The size of the used powders for the sintering experiment is smaller than 63 μm. The glassy powders were pre-compact, and then sintered in a vacuum using a SPS-1050 system. The sintering temperatures ($T_s$) selected below the glass transition temperature ($T_g$) is 680, 720, 740, 760 K. The heating rate is 100 K/min from room temperature to $T_s$ with the holding time of 6 min. A uniaxial pressuring method was conducted using top and bottom WC hard metal punches. The loading pressure used was 600 MPa. The sintered samples obtained have a cylindrical shape with a diameter of 15 mm and a height of about 3 mm. The density of the sintered samples was determined by the Archimedean method using tetrabromoethane. The structures were examined by XRD. The thermal stability was determined by DSC at a heating rate of 0.67 K/s. Microstructures of the sintered samples were observed with a SEM. The $B_T$ was measured under an applied field of 800 kA/m with a vibrating sample magnetometer. The coercivity ($H_c$) of the magnetic core, which was abraded after cut from the sintered disc by an electrical discharge machine, was measured with a DC B-H loop tracer in the applied field of 1.6 kA/m.

3. Results and Discussions

Figure 1 shows the surface morphology of the powders gas-atomized with a smaller size than 63 μm. No appreciable contrast revealing the formation of a crystalline phase is observed on the surface of any particles.

The DSC curve of the compact sintered at $T_s = 720$ K is shown in Fig. 2, together with the result of the original Fe$_{76}$Si$_9$B$_{10}$P$_5$ glassy powders. Typical endothermic reaction due to glass transition and two exothermic peaks due to crystallization are observed in the DSC curve of the glassy powders, which denote a Curie transition peak, a glass
transition peak and two crystallization peaks. $T_g$ and the crystallization temperature ($T_x$) of the Fe$_{76}$Si$_{9}$B$_{10}$P$_5$ powders are 780 K and 832 K, respectively. The largest $\Delta T_x$ is 52 K for Fe$_{76}$Si$_{9}$B$_{10}$P$_5$ powders where $\Delta T_x = T_x - T_g$, which is in agreement with that of the casting samples with a diameter ($D_{cr}$) of 2.5 mm$^3$ where $T_g$ and $T_x$ are almost the same. The endothermic and exothermic reactions are also observed in the DSC curve of the sample sintered at 720 K although the intensity of endothermic peak of the sintered samples is slightly lower than that of the powders. Curie temperature of the sintered sample also shifts to higher temperature.

Figure 3 shows the XRD patterns of these as-sintered compacts together with the pattern of the glassy powders for comparison. The diffraction patterns of the samples sintered at the of 720 K and 740 K consist of a halo pattern while no detectable diffraction peaks of crystalline phases is found, being in agreement with that of the original glassy powders. However, when $T_s = 760$ K, crystallization is present with the formation of Fe$_3$B and $\alpha$-Fe phases identified by the XRD patterns.

Figure 4 shows the relative densities of the sintered samples at different $T_s$. The relative densities are expressed in percentage against the glassy ribbon density. The relative density of the compacts increases with increasing $T_s$. The relative density is 98.5% at $T_s = 720$ K, 98.7% at $T_s = 740$ K and reached 99.5% at $T_s = 760$ K which is just below $T_g$. Since the hot-pressing technique needs a much higher temperature, SPS technique should be the unique one to compact powers at $T_s < T_g$ while in our case $T_s = 740$ K < $T_g = 780$ K. It is reported that the imposition
of the pressure of 500 MPa reduces the glass transition temperature by 40 K. We used in the present study the pressure of 600 MPa. Although this value is slightly larger than Ref. 13), we consider that the highest value of $T_s$ was within observed $T_g$.

Figure 5 shows a micrograph of polished Fe$_{76}$Si$_9$B$_{10}$P$_5$ sample sintered at 720 K. Only a few small pores are observed and raw powders are consolidated precisely. The increase of the relative density of in sintered Fe$_{76}$Si$_9$B$_{10}$P$_5$ alloy is due to the pressing of undercooled liquid at the sample surface into the pore zones due to plunging the powder with the surface in supercooled liquid state into the pores zones14,15) which was caused by the rise of temperature during SPS operation.16)

Figure 6 shows $dc$ $B$-$H$ hysteresis loop curve of the bulk Fe$_{76}$Si$_9$B$_{10}$P$_5$ alloy sintered at 720 K. The data of the powders is also shown for comparison.

**4. Conclusions**

We have fabricated bulk Fe$_{76}$Si$_9$B$_{10}$P$_5$ glassy alloys with a diameter of 15 mm using SPS technique just below $T_g$ with excellent soft magnetic properties. Under the conditions of pressure of 600 MPa, holding time of 6 min and $T_s = 740$ K, the relative densities reach 98.7% while the glassy state remains. $B_{800}$, $\mu_{max}$ and $H_c$ with $T_s = 720$ K are 1.45 T, 3471 and 17.6 A/m, respectively.

**Acknowledgements**

The financial supports of NNSFC under Grant No. 50771023 and Natural Science Foundation of Jilin Province under Grant No. 20060502 are acknowledged.

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