Consolidation of Fe–Co–Nd–Dy–B Glassy Powders by Spark-Plasma Sintering and Magnetic Properties of the Consolidated Alloys

Satoru Ishihara¹, Wei Zhang¹, Hisamichi Kimura², Mamoru Omori² and Akihisa Inoue²

¹Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation, Sendai 982-0807, Japan
²Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Consolidation of Fe₃Co₅Nd₄Dy₀.₅B₂₀ glassy powders has been tried by spark-plasma sintering (SPS) at around the glass transition temperature in order to synthesize a hard magnetic bulk material with a nanocomposite structure. The glassy powders were consolidated into bulk forms with relative densities above 97% by the sintering at 788 K and over. The sample sintered for 420 s at 788 K had a nearly full density of 99.1% and still kept a glassy single phase. The increase in the sintering temperature and time caused crystallization and the formation of Fe₂B phase. These as-sintered samples exhibited soft magnetic characteristics, but the soft magnetism changed to a hard type by annealing to form Nd₃Fe₄B, Fe₂B and α-Fe phases. The remanence, coercivity and maximum energy product for the bulk compact sintered for 420 s at 788 K, followed by annealing for 600 s at 913 K were 1.03 T, 277 kA/m and 83.1 kJ/m³, respectively.

(Received July 8, 2002; Accepted November 12, 2002)

Keywords: iron–cobalt–neodymium–dysprosium–boron alloy, metallic glass, crystallization, supercooled liquid, powder processing, magnetic properties

1. Introduction

Nanocomposite Fe–Nd–B magnets consisting of nanoscale hard magnetic Nd₃Fe₁₄B and soft magnetic α-Fe and/or Fe₂B phases are known to exhibit attractive hard magnetic properties.¹⁻⁹) Superior hard magnetic properties in these alloys are caused by an exchange-coupled effect between the hard and soft magnetic phases. In the nanocomposite magnets in the Fe–Nd–B system, two types of Fe-rich compositions around Fe₅₀Nd₃₀B₂₀ and B-rich compositions around Fe₇₈Nd₄B₁₈ have been widely studied. As reported in the respective references, the structure consists mainly of Nd₃Fe₁₄B+α-Fe for the former type, and Nd₃Fe₁₄B+Fe₂B+α-Fe for the latter type.¹⁻⁹) The B-rich type alloys have some advantages in comparison with the Fe-rich type: (1) lower Nd contents, (2) lower melting points, and (3) higher glass-forming ability.

The nanocomposite structure has been obtained by crystallization of an amorphous phase and/or by controlling cooling rate during melt-spinning, since the formation of nanoscale structures with highly homogeneous distribution of the constituent phases is necessary for good hard magnetic properties, as is the case for a number of other nanocrystalline materials. However, these processing methods are not always useful to produce a bulk nanocomposite with a full density. A number of studies have previously been carried out on the consolidation of amorphous alloy powders using various techniques: warm extrusion,¹⁰,¹¹ static high pressure compaction,¹²⁻¹⁶ explosive compaction,¹⁷,¹⁸ and dynamic compaction.¹⁹,²₀ In order to synthesize an Fe-rich type nanocomposite magnet, dynamic compaction of amorphous Fe₇₇Nd₁₈B₅₃ powders has been tried and an amorphous bulk of 93% density could be obtained.²¹) For a B-rich type nanocomposite magnet with the content of Fe₇₇.₅Nd₁₈.₅, similar dynamic compaction has been tried as well. However, the density of resultant amorphous bulk was 85%.²²) In spite of these great efforts, little has been reported about successful results on the formation of amorphous bulk forms exhibiting useful properties. Main difficulty lies in easy crystallization of amorphous alloys during consolidation.

On the other hand, glassy alloys with a large supercooled liquid region before crystallization have been found in many multicomponent systems.²³) Bulk samples of glassy alloys have also been obtained by various casting processes in addition to ribbon and powder forms. Some Fe- and Co-based bulk glassy alloys have been reported to exhibit good soft ferromagnetic properties.²⁴⁻²⁰) Recently, it has been found that some rapidly solidified Fe–Co–Nd–B alloys have a large supercooled liquid region and good hard magnetic properties after crystallization.²¹) Further improvements in thermal stability and hard magnetic properties have been achieved by addition of a small amount of Dy.²⁸) The representative alloy of Fe₇Co₉Nd₄Dy₀.₅B₂₀ among the alloy systems has a large supercooled liquid region of over 40 K before crystallization.²⁹,³₀) Its high thermal stability of the supercooled liquid has enabled us to form a bulk glassy alloy by various casting processes.³¹) Thick ribbon and bulk rod alloys formed above exhibit good hard magnetic properties after optimum heat treatments.³₀⁻³¹) The hard magnetic properties originate from a typical nanocomposite structure consisting of nanoscale hard magnetic Nd₃Fe₁₄B and soft magnetic α-Fe and Fe₂B phases. Therefore the Fe₇Co₉Nd₄Dy₀.₅B₂₀ alloy can be concluded to have the further advantage point of much higher glass forming ability so that glass transition and supercooled liquid region can be observed, as well as that of another B-rich type nanocomposite magnet alloys. However, the maximum thickness of the bulk metallic glasses has been limited to less than 0.5 mm even for the Fe₇Co₉Nd₄Dy₀.₅B₂₀ alloy.

Typical superiority for glassy alloys to amorphous alloys is superplasticity in the supercooled liquid state due to the Newtonian viscous flow which has been reported in some metallic glasses.³²⁻³⁴) High diffusivity accompanied by viscous flow in supercooled liquid state is also useful for fabrication of large-scaled bulk samples by consolidation of glassy powders using hot working techniques. It has been reported that Zr-based bulk metallic glasses with high
density, ≥99% and similar strength to the cast samples are fabricated by powder consolidation in the supercooled liquid state. Very recently, a soft magnetic bulk material has also been synthesized by hot-pressing of Fe75Co9Nd3Dy0.5B20 glassy powders in the supercooled liquid region. Further successful data of synthesizing soft magnetic bulk materials have been reported for Fe70Al3Ga2Fe0.65C5.75B4.6Si3 and Fe75Co9Nd3Fe15B6 glassy powders consolidated by spark-plasma sintering (SPS). The consolidation by SPS has also been reported for Fe75Nd10Co7V1B6 amorphous powders to synthesize an Fe-rich type bulk nanocomposite magnet. Consolidation by SPS has some merits in comparison with hot-pressing: shorter processing cycle time and good temperature controlling. We have previously examined and reported the consolidation behavior of the Fe75Co9Nd3Dy0.5B20 glassy powders by hot-pressing to synthesize bulk materials with good hard magnetic properties. In this study, we have tried consolidation of the same glassy powder by SPS. This paper presents the consolidation behavior of the glassy powders by SPS at around the glass transition temperature and magnetic properties of the consolidated bulk alloys.

2. Experimental procedure

Multi-component Fe76Co95Nd3Dy0.5B20 glassy powders were produced by mechanical crushing of melt-spun glassy alloy ribbons and used for consolidation experiments. The above alloy composition is nominal in mixture. Its master alloy ingot was first prepared by arc melting the mixture of pure metals and boron in an argon atmosphere. The glassy alloy ribbon with a thickness of about 0.02 mm was produced by the melt-spinning technique under an argon gas atmosphere. The glassy alloy ribbon was mechanically crushed using a rotor-milling machine under a nitrogen gas atmosphere. The powders sieved to 45–90 μm were used for the subsequent sintering experiment. Consolidation of the Fe76Co95Nd3Dy0.5B20 glassy powder was performed using a spark-plasma sintering system. The powders were pressed under a pressure of 300 MPa in a WC die (sintered with about 9 wt% Co as the sintering aid) with inner diameter of 20 mm. Graphite sheets were used for sealing of the powders to prevent reactions between the WC hard metal and powder. The die set under application of the pressure was heated by the pulsating current under vacuum and kept at each sintering temperature.

The density of the sintered compacts was measured by the Archimedean method using toluene. The density of the ribbon was determined as 7.58 Mg/m3 for the Fe76Co95Nd3Dy0.5B20 glassy alloy. The glassy and crystallized structures were examined by X-ray diffraction (XRD). The thermal stability associated with glass transition and crystallization was examined by differential scanning calorimetry (DSC) at the heating rate of 0.67 K/s. The annealing treatment was made in evacuated quartz tubes for 600 s at various temperatures. Magnetic properties of remanence and coercive force were measured using a vibrating sample magnetometer (VSM) in a maximum applied field of 1256 kA/m at room temperature.

3. Results

The Fe76Co95Nd3Dy0.5B20 glassy powders were sintered for 60 s at 763, 788 and 813 K, since the glass transition of the Fe76Co95Nd3Dy0.5B20 glassy alloy is about 800 K. At the sintering temperature of 788 K, experiments with different sintering times were performed. A sintering experiment for 420 s at 800 K was also performed. Figure 1 shows the relative densities of the compacts sintered at various conditions. The relative densities are expressed in percentage against the glassy ribbon density. The relative density of the compacts held for 60 s at each sintering temperature increased with increasing sintering temperature and reached a nearly full density at 813 K. The relative densities of the compacts sintered for 420 and 900 s at the sintering temperature of 788 K were higher than that for 60 s. That is, the density of the compacts increases with increasing sintering temperature and time. Optical micrographs (OM) of the cross sections of these as-sintered samples are shown in Fig. 2. The compact sintered for 60 s at 763 K has large pores as shown by black contrast in this figure. The size and fraction of the remaining pores in the compacts sintered for 60 s decreases with increasing sintering temperature (Fig. 2a, b, and d).

Figure 3 shows the XRD patterns of these as-sintered compacts together with pattern of the glassy powder for comparison. The diffraction patterns of the samples sintered at the conditions of 763 K-60 s, 788 K-60 s and 788 K-420 s consist of a halo pattern, and no detectable diffraction peak of crystalline phase is seen, in agreement with the original glassy powder. However, the increase in the sintering time to 900 s at 788 K results in additional appearance of crystalline peaks which are identified as Fe3B phase. The diffraction pattern of the samples sintered at higher temperatures of 813 K-60 s consists of crystalline peaks of Fe3B phase. The DSC curves of these compacts sintered for 60 s at various temperatures are shown in Fig. 4, together with the result of the glassy powder. Typical endothermic reaction due to glass

![Figure 1](image-url)
transition as well as large exothermic peak due to crystallization are observed in the DSC curve of the glassy powder. The endothermic and exothermic reactions are also observed in the DSC curves of the samples sintered at 763 and 788 K. The heats of crystallization ($\Delta H_c$) of the samples sintered at 763 and 788 K are about 4.1 kJ/mol and nearly the same as that of the glassy powder. However, no exothermic peak corresponding to crystallization is observed in the DSC curve of the sample sintered at 813 K. The DSC curves of the compacts sintered at 788 K for various sintering times are shown in Fig. 5. The endothermic and exothermic reactions are also observed in the DSC curves of the samples sintered for 420 s, though the glass transition temperature, $T_g$, increases slightly and the crystallization temperature, $T_x$, decreases as compared with the case of 60 s. The $\Delta H_c$ of the samples sintered for 420 s is nearly the same as that for 60 s. In the case of the sample sintered for 900 s, the endothermic reaction was not observed clearly and the first exothermic peak occurs at a lower temperature in the DSC curve. The $\Delta H_e$ of the exothermic reaction is 2.8 kJ/mol and about 70% of the samples sintered for 60 s and 420 s. The first exothermic peak with the small $\Delta H_e$ is thought to result from crystallization of the remaining glassy phase.

The hysteresis $J$-$H$ loop of the Fe$_{67}$Co$_{9}$Nd$_{3}$Dy$_{0.5}$B$_{20}$ bulk sample sintered for 420 s at 788 K is shown in Fig. 6. The soft magnetic behavior is recognized for the as-sintered sample. In contrast, the hysteresis loop of the sample annealed for 600 s at 913 K indicates a hard magnetic characteristic. The similar change in magnetism from soft to hard type by annealing at 913 K was also recognized for the samples sintered at the other conditions. Magnetic properties of the samples sintered for 420 s at 788 K, followed by annealing at...
different temperatures are shown in Fig. 7. These magnetic properties were measured both in parallel and perpendicular to the pressing direction. The properties measured in the direction perpendicular to the pressing direction are slightly better as compared with those of parallel direction. The difference between the measurement directions was observed for the samples sintered at the other temperatures as well. The remanence, $B_r$, the coercivity, $H_c$, and the maximum energy product, $(BH)_{\text{max}}$ of the sample increase gradually with annealing temperature up to 913K and then decrease with a further increase in annealing temperature, although the changes in respective properties are not so significant. Magnetic properties of the samples sintered at different conditions, followed by annealing for 600 s at 913 K are listed in Table 1. These properties are measured in the direction perpendicular to the press direction. The highest values of $B_r$, $H_c$ and $(BH)_{\text{max}}$ were obtained in the case of 788K-420s among the sintering conditions in the present

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>$B_r/T$</th>
<th>$H_c/kAm^{-1}$</th>
<th>$(BH)_{\text{max}}$/kJm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>763 K-60s</td>
<td>0.95</td>
<td>263</td>
<td>72.7</td>
</tr>
<tr>
<td>788 K-60s</td>
<td>0.99</td>
<td>277</td>
<td>79.1</td>
</tr>
<tr>
<td>788 K-420s</td>
<td>1.03</td>
<td>277</td>
<td>83.1</td>
</tr>
<tr>
<td>788 K-900s</td>
<td>0.97</td>
<td>246</td>
<td>66.8</td>
</tr>
<tr>
<td>800 K-420s</td>
<td>1.01</td>
<td>225</td>
<td>63.4</td>
</tr>
<tr>
<td>813 K-60s</td>
<td>0.97</td>
<td>229</td>
<td>61.5</td>
</tr>
</tbody>
</table>

(Annealing temperature: 913 K, time: 600 s)
study. The XRD pattern of the sample sintered at 788 K, followed by annealing for 600 s at 913 K is shown in Fig. 8. The XRD pattern indicates many crystalline peaks and these are identified as α-Fe, Fe₇B and Nd₂Fe₁₄B phases.

4. Discussion

The density of the sintered compact increased with increasing sintering temperature and reached a nearly full value at around the glass transition temperature. This tendency is similar to the previously reported result on the consolidation of glassy alloy powders by SPS.38,39) However, glassy bulk with the highest density was obtained at around the crystallization temperature for the consolidation by hot-pressing.16,41) The comparison indicates that the efficient densification by SPS can be obtained at lower temperature than that by hot-pressing. The densification by hot-pressing results from the additional thermal history due to the consolidation of the glassy alloy powders by hot-pressing.41) It is therefore required that the consolidation of the glassy alloy powder is performed without crystallization.

The magnetic properties of the best sample in the present study are 1.03 T for \( B_r \), 277 kA/m for \( iH_c \), and 83.1 kJ/m\(^3\) for \( (BH)_{max} \) respectively. These values are almost the same as that of the hot-pressed compact.41) On the other hand, the magnetic properties of the cast glassy Fe₆₇Co₉.₅Nd₅Dy₀.₅B₂₀ rod annealed at 913 K were reported to be 1.19 T for \( B_r \), 244 kA/m for \( iH_c \), and 92.7 kJ/m\(^3\) for \( (BH)_{max} \) respectively.41) While the \( B_r \) and \( (BH)_{max} \) of the consolidated sample are lower than those of the cast rod, it is noticed that the \( iH_c \) is higher. The difference in the magnetic properties between the consolidated compact and the cast rod results from the additional thermal history due to the consolidation, in addition to some defects such as pores and powder interfaces in the structures which are formed by the powder consolidation processing. Although the tendency of magnetic properties in the consolidated compacts is different from that of the cast rods, the magnetic properties sintered for 420 s at 788 K appear to approach the level of the cast rods.

The magnetic properties is compared with that of commercial Nd₂Fe₁₄B type products with isotropic properties42) in Table 2. The \( B_r \) of the present sample is higher than

<table>
<thead>
<tr>
<th>Materials</th>
<th>Remanence, ( B_r / T )</th>
<th>Coercivity, ( iH_c / kA/m )</th>
<th>Maximum energy product, ( (BH)_{max} / kJ/m^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>1.03</td>
<td>277</td>
<td>83.1</td>
</tr>
<tr>
<td>Fe₆₇Co₉.₅Nd₅Dy₀.₅B₂₀ Sintering</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>788 K-420 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealing: 913 K-600 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commercial products</td>
<td>Bonded</td>
<td>0.61–0.71</td>
<td>570–1310</td>
</tr>
<tr>
<td>Nd₂Fe₁₄B type</td>
<td>Hot-pressed</td>
<td>0.80–0.83</td>
<td>1393–1433</td>
</tr>
</tbody>
</table>

While the soft magnetic behavior was recognized for the as-sintered samples, the annealed samples indicated a hard magnetic characteristic. The crystalline peaks in the XRD pattern of the annealed sample were identified as α-Fe, Fe₇B and Nd₂Fe₁₄B phases as shown in Fig. 8. Since the result is as the same as that of the melt-spun ribbon and cast rod samples, the change of the magnetism from soft to hard type in the consolidated samples can be explained by the same behavior as the ribbon samples.

The hard magnetic properties measured in perpendicular to the pressing direction were slightly higher as compared with those of the parallel direction. This difference may be caused by the shape factor of powders, since the glassy powders used for the consolidation were produced by mechanical crushing of melt-spun glassy alloy ribbons and hence had flaky shape. However, the difference in direction is small, and hence the magnetic properties of the samples should be concluded as rather isotropic.

The maximum value of \( (BH)_{max} \) in the present study was obtained for the sample sintered for 420 s at 788 K, followed by annealing at 913 K. This sample had the highest density among compacts keeping the glassy state. This result agrees with that of the bulk samples consolidated by the hot-pressing.41)
that of commercial products, while the $H_c$ is lower. This reason is considered to be due to the lower content of Nd and higher B in the present sample. The $(BH)_{\text{max}}$ of the present sample is lower than that of hot-pressed commercial products. However, it should be noticed that the sintering temperature of the present SPS sample is much lower due to the glass transition than those hot-pressing temperatures above 1000 K. The $(BH)_{\text{max}}$ of the present sample is situated at the highest level in bonded commercial products. Although the sintering temperature of the present SPS sample is much lower than that of hot-pressed commercial products, the present sample can be consolidated without bonding materials, which is also the significant advantage of glassy alloy powders.

5. Conclusions

We have tried to consolidate the Fe$_{57}$Co$_{9.5}$Nd$_{3}$Dy$_{0.5}$B$_{30}$ glassy powders using the SPS technique at around the glass transition temperature for the production of hard magnetic bulk materials with a nanocomposite structure. The results obtained in this study are summarized as follows.

1) The glassy powders can be consolidated into bulk forms with the relative densities above 97% by the sintering at 788 K and over.

2) The sample sintered for 720 s at 788 K still keeps a glassy single phase. The increase in the sintering temperature and time causes crystallization and the formation of Fe$_3$B phase.

3) The as-pressed samples exhibit soft magnetic characteristics. The soft magnetism is changed to hard type by annealing. Fe$_3$B, $\alpha$-Fe and Nd$_2$Fe$_{14}$B phases are formed in the annealed sample.

4) The remanence, coercivity and maximum energy product for the compact sintered for 420 s at 788 K, followed by annealing for 600 s at 913 K are 1.03 T, 277 kA/m and 83.1 kJ/m$^3$, respectively.

REFERENCES