Magnetic Properties of α -Fe-Nd₂Fe₁₄B Exchange Spring Magnets Synthesized by Mechanical Alloying

Krishnamurthy Raviprasad^{☆1}, Satoru Kakoo^{☆2}, Ken Makita^{☆3} and Minoru Umemoto^{☆1}

^{☆1} Fac. of Eng., Dept. of Production Systems Eng., Toyohashi University of Technology, 1-1 Tempaku-cho, Toyohashi 441. ^{☆2} Graduate School, Dept. of Production Systems Eng., Toyohashi University of Technology, 1-1 Tempaku-cho, Toyohashi 441. ^{☆3} Sumitomo Special Metals Co., Ltd., 2-15-17 Egawa Shimamoto-cho Mishima-gun, Osaka.

Received January 16, 1996

SYNOPSIS

The possibility of producing isotropic permanent magnets with enhanced energy product has drawn lot of attention recently. The synthesis of two phase (hard and soft) nanocrystalline exchange coupled magnets by many research groups using different techniques and the various combination of two phases is an indication to the level of research interest in this area. The nitrogenated or carburized rare earth compounds with 2:17 or 1:12 structure as the hard phase was the focal point of many groups. However, the choice of Nd₂Fe₁₄B as the hard phase with the attractive advantages of single stage heat treatment, no drawbacks of incomplete nitrogenation or carburization and the possibility of higher sintering temperature has tilted the scale in its favor. The present article reports on the results of the synthesis of exchange spring magnets of Nd₂Fe₁₄B and α -Fe and their magnetic properties by mechanically alloying the powder mixture of Nd₂Fe₁₄B and iron. The magnets exhibit a spring back greater than 80% and a maximum energy product of 45 kJ/m³. The observed large spring back is an indication of the good coupling between the hard and the soft phases. The low energy product is attributed to the low coercivity of the starting Nd₂Fe₁₄B powder and requires further improvement.

KEY WORDS

mechanical alloying, exchange spring magnet, coercivity, remanence, spring back.

1 Introduction

The discovery of remanence enhanced isotropic permanent magnets by Coehoorn et al.^{1,2)} spurred lot of interest in the synthesis of two phase magnetic materials. Such an interest led to the development of exchange spring magnets³⁻⁶⁾. These are a new class of permanent magnets with nanostructured exchange coupled hard and soft phases. Though, two magnetically distinct phases constitute an exchange spring magnet the hysteresis loop is characteristic of a single phase material. The observed unusual behavior is attributed to the intergranular exchange coupling which also brings about the remanence enhancement⁷⁾. The concept of remanence enhanced isotropic two phase permanent magnet was introduced to increase the energy product of isotropic magnetic materials. The advantage of these materials are that one can avoid the

special processing techniques required to enhance the energy product and at the same time make them economically more viable, as the inexpensive soft phase (usually α -Fe) replaces the hard phase containing expensive rare earths. Thoughts along these lines has led to the search for suitable combination of the hard and the soft phases and the application of various synthesizing techniques. The pioneering work of Schultz and co-workers has demonstrated the versatility of the mechanical alloying technique for the synthesis of permanent magnetic materials⁸⁻¹²⁾. The observation¹³⁻¹⁶⁾ that the nitrogenated or carburized rare earth transition metal compounds with 2:17 structure (Th₂Zn₁₇ type or Th₂Ni₁₇ type) or 1:12 structure (ThMn₁₂ type) exhibit good hard magnetic properties suggested their incorporation into producing exchange

spring magnets. In fact, exchange spring magnets with these hard phases were synthesized¹⁷⁻²⁰⁾. However, the basic problem associated with the choice of these hard phases is the limitation imposed by the nitroge-nation or carburization temperature. The choice of Nd₂Fe₁₄B as the hard phase can in principle eliminate the restriction on sintering and provide a way out of the impasse. In addition to this the synthesis of the exchange spring magnets with Nd₂Fe₁₄B as the hard phase will involve single stage heat treatment compared to the nitroge-nated or carburized 2:17 or 1:12 hard phases. Also, the problem of inferior properties due to the incomplete nitroge-nation or carburiza-tion does not exist when Nd₂Fe₁₄B is used as the hard phase. The advantages of using Nd₂Fe₁₄B as a hard phase has influenced many research groups to synthesize exchange spring magnets by various techniques²¹⁻²⁴⁾. In the present article we delineate in detail the synthesis and magnetic properties of α -Fe-Nd₂Fe₁₄B exchange spring magnets by mechanical alloying.

2 Experimental procedure

Nd₂Fe₁₄B was prepared by induction melting. The ingot was pulverized to form fine Powders. For the synthesis of Nd₂Fe₁₄B, the constituent elements with more than 99.9% purity were used. The powdered Nd₂Fe₁₄B and elemental Fe powder were taken in a stainless steel vial (SUS 304) with balls of the same material having a diameter of 9.6 mm. The vial containing balls and powder in the ratio of 100:1 respectively were milled at a milling speed of 95 rpm. The total weight of powder was 36 g and the samples were milled for a maximum duration of 360 ks. The sealing of the vial and its opening after the completion of milling was carried out in a glove box maintained under argon atmosphere with oxygen content less than 1 ppm. The milled powders were taken in a quartz tube and annealed to produce a mixture of two phase. The as milled and annealed powders were characterized by X-ray diffraction. The magnetic properties of the samples were measured in a vibrating sample magnetometer operated with

a maximum field strength of 1200 kAm⁻¹ (15 kOe). The magnetization of the powder was calculated assuming the full density of 7.5 Mg/m³. The correction for demagnetization fields was performed using the demagnetization factor $N=0.18$ obtained from the demagnetization curve of Ni powder measured by the same method.

3 Results and discussion

Fig.1 shows the X-ray diffraction pattern of the Nd₂Fe₁₄B powder (induction melted and pulverized), milled for 100h and annealed at 973K for 1.8ks in vacuum. The pulverized material shows sharp peaks corresponding to the Nd₂Fe₁₄B phase. The milled state represents a mixture of amorphous and α -Fe phases. Upon annealing the milled powder at 973K for 1.8ks in vacuum one can retrieve the hard phase Nd₂Fe₁₄B. The diffraction pattern of the annealed and starting powders are similar. However, a close look at the diffraction pattern of the annealed powder indicates the possible existence of a minute fraction of α -Fe. The

Fig.1 X-ray diffraction pattern showing the peaks of Nd₂Fe₁₄B starting powder, after milling and annealing. Note the similarities in the peaks of starting and annealed powders.

Fig.2 Demagnetization curves of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder before milling (a) and after milling and annealing the same (b). The coercivity and energy product has improved after milling and annealing.

demagnetization curves of the starting $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder and the same after milling and annealing are shown in Fig.2. The powder from the induction melted ingot has a smaller coercivity and energy product. However, both the quantities improve considerably after milling and annealing, an indication that the grain size has refined considerably during milling. The dip in the demagnetization curve of the milled

and annealed powder confirms the presence of a small amount of $\alpha\text{-Fe}$. As magnetic measurements are sensitive at atomic level, the signature of $\alpha\text{-Fe}$ is clearer in the demagnetization curve than in the X-ray diffraction pattern.

The results of milling and annealing the $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder clearly confirmed that it is possible to retrieve the hard phase. Whether this situation changes or remains the same after milling and annealing with $\alpha\text{-Fe}$ (50 vol.%) is reported in Fig.3 and Fig.4 respectively. In Fig.3 the X-ray diffraction pattern corresponding to the milled state of the mixture of powders for various times is shown. The 1h milled sample show peaks corresponding to both the phases indicating that $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure is stable up to this time. However, milling for longer durations result in amorphous and $\alpha\text{-Fe}$ two phase mixture. The X-ray diffraction pattern of the annealed powders corresponding to various milling times are all similar (Fig.4) clearly showing the existence of similar phases. The coexistence of two phases suggest the possibility of synthesizing exchange spring magnets.

Fig.3 X-ray diffraction pattern of the mixture of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\alpha\text{-Fe}$ powders after milling for various times.

Fig.4 X-ray diffraction pattern of the mixture of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and α -Fe powders after milling for various times and annealing in vacuum at 973 K for 1.8 ks.

The demagnetization curves of the two phase mixture is shown in Fig.5. The demagnetization curves are characteristic of a single phase material suggesting a good coupling between the hard and the soft phases. With the addition of α -Fe, the remanence has increased compared to the pure hard phase material (see Fig.3). A comparison of the coercivity of the starting powder and the 1h milled and annealed sample shows clearly that the coercivity of the latter is smaller, which is to be expected with the addition of α -Fe. However, improvement in the coercivity of the two phase mixture has been observed for longer milling times and the energy product is also enhanced. Though, the observed energy product is not high enough, the same can be improved further by starting with $\text{Nd}_2\text{Fe}_{14}\text{B}$ having higher coercivity, like that of the milled and annealed $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder. Studies on such a possibility is being carried out.

Fig.6 shows the minor loops corresponding to the milled and annealed $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder

and the two phase mixture milled for 50 h and annealed at 973 K for 1.8 ks. It is clear that the spring back and the remanence of the two phase material is much higher compared to the single phase material. The observed small spring back effect in the latter can be attributed to the fraction of α -Fe present.

Fig.5 Demagnetization curves of the mixture of 50 vol.% $\text{Nd}_2\text{Fe}_{14}\text{B}$ and 50 vol.% α -Fe after milling and annealing. (a) Milled for 1 h and (b) milled for 50 h. Both the samples are annealed in vacuum at 973 K for 1.8 ks.

Fig.6 Minor loop after milling and annealing of (a) pure $\text{Nd}_2\text{Fe}_{14}\text{B}$ (360 ks, 973 K for 1.8 ks) and (b) mixture of 50 vol.% $\text{Nd}_2\text{Fe}_{14}\text{B}$ and 50 vol.% $\alpha\text{-Fe}$ (180 ks, 973 K for 1.8 ks).

Conclusions

1. Exchange spring magnets of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\alpha\text{-Fe}$ were prepared by annealing the milled mixture of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and iron powders.
2. The magnet exhibits large spring back effect and this reflects the strong exchange coupling

between the hard and soft phases.

3. The coercivity of two phase magnet requires improvement. Starting with a higher coercive $\text{Nd}_2\text{Fe}_{14}\text{B}$ can enhance the coercivity.

References

- 1) R.Coehoorn, D.B.de Mooij, J.P.W.B.Duchateau and K.H.J.Buschow, *J. de Phys.Colloq* **8**, (1988) C-669.
- 2) R.Coehoorn, D.B.de Mooij and C.de Waard, *J.Magn.Magn.Mater.*, **80** (1989) 101.
- 3) R.W.McCallum and A.M.Kadim, G.B.Clemente and J.E.Keem, *J. Appl. Phys.*, **64** (1988) 5299.
- 4) A.Manaf, M.Leonowitz, H.A.Davis and R.A.Buckley, *Proc. 12th Int. Workshop on Rare-earth Magnets and Their Applications*, Canberra (1992) 1.
- 5) S.Hirosawa, H.Kanekiyo and M.Uehara, *J. Appl.Phys.*, **73** (1993) 6488.
- 6) P.G.McCormick, J.Ding, Y.Liu and R.Street, *Proc. 2nd Int. Conf. on Structural Applications of Mechanical Alloying*, Vancouver (1993) 349.
- 7) Y.Otani, H.S.Li and J.M.D.Coey, *IEEE Trans. Magn.* **MAG-26** (1990) 2658.
- 8) L.Schultz, *Mater. Forum*, **88-90** (1992) 687.
- 9) L.Schultz, J.Wecker and E.Hellstern, *J. Appl. Phys.*, **61** (1987) 3583.
- 10) K.Schnitzke, L.Schultz, J.Wecker and M.Katter, *Appl.Phys.Lett.*, **57** (1990) 2853.
- 11) J.Wecker, M.Katter and L.Schultz, *J. Appl. Phys.*, **69** (1991) 6058.
- 12) L.Schultz, K.Schnitzke, J.Wecker and M.Katter, *Mat.Sci.Engr.*, **A133** (1991) 143.
- 13) J.M.D. Coey and H.Sun, *J.Mag.Mag. Mater.*, **87** (1990) L251.
- 14) X.P.Zhong, R.J.Radwanski, F.R.de Boer, T.H.Jacobs and K.H.J.Buschow, *J.Mag.Mag. Mater.*, **86** (1990) 333.
- 15) M.Katter, J.Wecker, L.Schultz and R.Gossinger, *J.Mag.Mag.Mater.*, **92** (1990) L14.
- 16) Y.Z.Wang and G.C.Hadjipanayis, *J.Appl. Phys.*, **70** (1991) 6009.
- 17) J.Ding, Y.Liu, P.G.McCormick and R.Street, *J.Mag. Mag. Mater.*, **123** (1993) L239.

- 18) J.Ding, P.G.McCormick and R.Street, *J.Mag. Mag. Mater.*, **124** (1993) 1.
- 19) J.Ding, Y.Liu, R.Street and P.G. McCormick, *J.Appl.Phys.*, **75** (1994) 1032.
- 20) K.Raviprasad, S.Kakoo, K.Makita and M. Umemoto, *J.Japan Soc. Powder and Powder Metallurgy*, **42** (1995) 1308.
- 21) A.Manaf, R.A.Buckley and H.A.Davies, *J. Magn.Magn.Mater.*, **128** (1993) 302.
- 22) L.Withanawasam, G.C.Hadjipanayis and R. F.Krause, *J.Appl.Phys.*, **75** (1994) 6646.
- 23) L.Withanawasam, A.S.Murthy and G.C. Hadjipanayis, *IEEE Trans. Magn.*, **MAG-31** (1995) 3608.
- 24) J.Yao and T.Chin, *IEEE Trans. Magn.*, **MAG-31** (1995) 3611.