Improving permanent magnetic properties of rapidly solidified nanophase RE–TM–B alloys by compositional modification

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Article history:
Received 28 September 2008
Available online 11 February 2009

Keywords:
Permanent magnet
Rare-earth–transition metal–boron
Nanocrystalline
Magnetic property

ARTICLE INFO

Rapid solidification is one of the most important techniques to produce nanocrystalline rare-earth–transition metal–boron (RE–TM–B) hard magnetic materials. To achieve high performance on these NdFeB-based alloys, compositional modification and microstructure optimization have been frequently employed. In this short review, various substitutions and doping elements have been discussed regarding to their behaviors in adjusting the individual or combined hard magnetic properties as well as the microstructure based on our recent results. It has been demonstrated that Pr and Dy enhance coercivity $H_c$, whereas Sm reduces $H_c$ due to their effects on intrinsic properties. Co improves the thermal stability as well as the microstructure. Introducing Fe$_{65}$Co$_{35}$ is a possible approach to enhance the magnetization and maximum energy product $(BH)_{max}$. As a doping element, Ta was found to play an important role to obtain an appropriate combination of magnetic properties for this type of alloys.

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1. Introduction

Rapid solidification is one of the most important techniques to produce nanocrystalline hard magnetic rare-earth–transition metal–boron (RE–TM–B) powders. To achieve high performance for this type of alloys, two approaches have been frequently employed, i.e. microstructure optimization and compositional modification. The control of the nanostructures has been mainly realized by the synthesis methods of melt spinning and mechanical alloying. As for compositional modification, various substituent elements and dopants have been studied. The main difference between substitution and dopant is the solubility range within the Nd$_2$Fe$_{14}$B (2/14/1) phase. These elements are generally divided into four types as in (Nd–S1)–(Fe–S2)–B; (M1,M2) [1]: Substituent elements S1 (S1 = Pr, Dy, Tb, Sm, etc.) and S2 (S2 = Co, Ni, Cr) replace Nd and the Fe atoms, respectively, in the hard magnetic 2/14/1 phase and considerably change intrinsic properties, such as spontaneous polarization $(J_s)$, Curie temperature $(T_C)$ and magnetocrystalline anisotropy constant $(H_k)$. Dopant elements M1 or M2 can form new intergranular phases. Dopants M1 (Al, Cu, Zn, Ga, Ge, Sn, etc.) form binary M1–Nd or ternary M1–Fe–Nd phases, dopants M2 (Ti, Zr, V, Mo, Nb, W, etc.) form binary M2–B or ternary M2–Fe–B phases. M1 or M2 elements in some cases can increase the coercivity $(H_c)$ and improve the corrosion resistance. Since the substituent or dopant elements may have opposite effects on the $J_s$, $H_C$ and their temperature dependencies, multiple substitutions are sometimes required to improve the combination of magnetic properties or the magnet stability.

For nanocrystalline RE–TM–B alloys, enhanced remanence and energy product result from exchange coupling between hard grains and, for nanocomposite alloys, between hard and soft grains. The exchange coupling can also influence coercivity [2,3]. The exchange coupling only occurs over a characteristic distance, known as the exchange length $\lambda_{ex}$, which can be expressed as $\lambda_{ex} = \sqrt{A/K}$, where $A$ is the exchange stiffness and $K$ the magnetocrystalline anisotropy constant. For nanocomposite alloys, $A$ refers to the effective exchange stiffness and $K$ the effective exchange constant [4]. In the case of nanocomposite alloys, the optimum grain size of the soft phase is $d_{op} \approx 2\pi\sqrt{A/K}$, the calculated $d_{op}$ for Nd–Fe–B ternary alloys is around 10 nm. Substituent elements can affect exchange coupling by changing the exchange length. Dopant elements are generally employed to enhance exchange coupling and, thus the magnetic properties, these enhancements are accomplished by microstructural changes such as inhibiting grain growth and reducing grain size.

In this paper, the effects of various substitutions and doping elements on the hard magnetic properties as well as the microstructure are discussed. In particular, the effects of Pr, Dy
or Sm substituting Nd, Co substituting Fe and Ta doping are presented.

2. Experimental

In this review, all materials discussed were prepared by rapid solidification technique of melt spinning. The melt spinning wheel speed is optimized to achieve the uniform fine nanocrystallites. The magnetic properties of directly quenched ribbons are characterized using vibrating sample magnetometer (VSM) with a maximum field of 9 or 1.5 T. The phase constitution is obtained by an X-ray diffractometer (XRD). Transmission electron microscopy (TEM) has been employed to characterize the morphology and phase details.

3. Results and discussion

Nd–Fe–B-based hard magnetic nanocrystalline and nanocomposite alloy ribbons can be successfully produced by melt spinning. The melt spinning parameters for achieving fully nanocrystalline microstructure must be carefully controlled. It has been demonstrated that, using the optimized process, excellent hard magnetic properties and enhanced exchange coupling can be obtained in directly quenched ribbons. The latter is demonstrated by the excellent shape of hysteresis loop and high value (>0.5) of remanence ratio \(J_r/J_s\), as shown in Fig. 1a for NdPr–FeCo–B alloys with various compositions fabricated by melt spinning. Fig. 1b provides the typical microstructure of the nanocomposite. A grain size less than 30 nm is observed.

The three types of nanocrystalline NdFeB alloys, single phase alloy, nanocomposite and RE-rich alloy, are distinguished from their composition or phase constitution. Fig. 1a also shows the typical loops for these three types of alloys. Single phase alloy containing only Nd2Fe14B type (2/14/1) phases has the modest typical loops for these three types of alloys. Single phase alloy, nanocomposite and RE-rich alloy, are distinguished from their composition or phase constitution.

3.1. Substitutions for Nd

The RE2Fe14B structure forms for all the rare-earth elements, except Eu and Pm. For different RE2Fe14B compounds, high values of \(J_r\) are exhibited for RE = Pr, Nd and Sm, these high values make high \(J_r\) value feasible. The anisotropy field \(H_a\) also has large values for RE = Pr, Nd, Sm, Tb and Dy [5], the high \(H_a\) value also increases \(J_C\). The intrinsic properties of RE2Fe14B phases mentioned above are shown in Table 1. Although Tb has high \(T_C\) and the highest \(H_a\) value, the use of it has been restricted due to the high cost of Tb metal. Based on the above reasons, the effects of Pr, Sm and Dy, on the magnetic properties of melt spun NdFeB nanocrystalline and nanocomposite alloys were investigated.

In Nd–Fe–B alloys, substituting Pr for Nd has at least three advantages: (1) reduction or elimination of the spin reorientation, (2) increase of coercivity because Pr2Fe14B phase has higher anisotropy field \(H_a\) than Nd2Fe14B as shown in Table 1 and (3) low production cost because Nd and Pr co-exist in the natural ores and the work of separating them can be avoided. Fig. 2 shows the dependences of magnetic properties on the Pr concentration for the nanocrystalline single phase (Nd1−xPrx)12(Fe1−xCo)x2B6 alloys. Pr substitution indeed enhances the \(H_C\) without a reduction in \(J_r\) and maximum energy product (BH)max. This is very important for nanocomposites and for Co substituted alloys, since \(H_C\) is reduced by the exchange coupling or Co addition in these alloys.

For RE2Fe14B compounds, Dy2Fe14B also shows a higher value of \(H_a\) than that of Nd2Fe14B (Table 1). It is, therefore, expected that substituting Nd by Dy will also improve \(H_C\). Fig. 3 shows the demagnetization curves and magnetic properties for NdPr–FeCo–B alloys with various Dy substitutions. Excellent loop squareness can be realized in these alloys. The results clearly show that partial replacement of Nd by Dy indeed increases \(H_C\).
However, Dy substitution reduces $J_s$ and $J_r$ since the magnetic moment of Dy couples antiparallel to both Nd and Fe moments. To control the combined magnetic properties, the doping level of Dy should be controlled accordingly. As shown in Fig. 3b, for nanocomposite alloys, despite the reduced $J_s$, both the $H_C$ and the $(BH)_{max}$ can be improved by selecting the appropriate substitution level of Dy. Due to this advantage, Dy is generally employed with Co substitution to compensate the possible reduction in $H_C$ caused by Co addition.

Another 2/14/1 compound with high $H_a$ is Sm$_2$Fe$_{14}$B. However, Sm$_2$Fe$_{14}$B compound is not uniaxial and the magnetization is in the easy plane, which affects $H_a$. Fig. 4 shows the nanocomposite Nd$_{10}$Fe$_{85}$B$_5$ alloys with Co, Dy or Sm substitutions. The roles of various elements in adjusting the demagnetization curve are illustrated. The result indicates that Dy substitution can compensate $H_C$ loss due to Co addition. Although some researchers reported an improved $H_C$ with Sm substitution [6], our results indicate that Sm reduces $H_C$ of Nd–FeCo–B alloy. As pointed out by Chen et al. [7] and Zhang et al. [8], the decrease in $H_C$ can be attributed to the decrease of the magnetocrystalline anisotropy of the material. On the other hand, despite the lower values of Sm$_2$Fe$_{14}$B than Nd$_2$Fe$_{14}$B, 10% Sm addition did not greatly reduce $J_r$ and, indeed, a very good squareness of 2nd quadrant $J$–$H$ curves is obtained for Sm substituted alloy, which indicate excellent exchange coupling between hard and soft phase. Thus, the reduced $H_C$ may also be attributed to improved exchange coupling. Yang et al. [9] also noticed the enhanced exchange coupling interaction associated with a small amount of Sm substitution and obtained a reduced $H_C$ for Sm substituted Nd$_2$Fe$_{14}$B/α-Fe nanocomposite. The reason can be explained as follows: compared to the Nd$_2$Fe$_{14}$B phase, Sm$_2$Fe$_{14}$B has a negative value of $K$ [10]. If a small amount of Sm is substituted for Nd, the magnetocrystalline anisotropy constant $K$ of the hard 2:14:1 phase is reduced. The exchange length $L_x$ and critical grain size $d_{cr}$ exchange-coupled soft phase (as described in Introduction section) would be increased. This would enhance the exchange coupling interaction between the hard and soft phase.

3.2. Substitution for Fe

For RE–Fe–B alloys, the main element that can substitute Fe is Co. It is the only element which leads to significant changes in the magnetic ordering temperature. Co substitutions for Fe increase $T_C$ monotonically with $x$ in the stoichiometric RE$_2$Fe$_{14}$–Co$_x$B compounds. Concerning the extrinsic properties, Co additions have been reported as enhancing the $J_s$ and $(BH)_{max}$ values [11], but generally with decreasing $H_C$ [12–14]. The improvement of...
(BH)\text{max} by Co substitution is attributed to the enhancement of \( J_a \), presumably resulting from the increase in magnetization of both the 2/14/1 and \( \alpha \)-(Fe,Co) phases and exchange coupling between the soft and hard magnetic phases. Other results [15–17] also indicated that a small amount of Co does not decrease \( J_a \) and even improves both \( J_a \) and \( J_C \); the reason has been attributed to microstructural changes.

The effect of Co substitution on the room-temperature magnetic properties can be seen from Fig. 5, where 2nd quadrant demagnetization curves (J–H and B–H) are plotted for \((Nd_{0.25}Pr_{0.75})_8Fe_{86}B_6\) nanocomposites with various Co concentrations. Increasing Co substitution reduces \( J_C \), especially for more than 10% Co substitution. Co substitution also destroys the linearity of the second quadrant B–H curve for this nanocomposite. However, \( J_a \) is somewhat improved by 20% Co substitution. As a result, when Co is employed to improve the elevated temperature properties, it is possible to maintain (BH)\text{max} at a high level by controlling its concentration.

As we know, the binary phase Fe50Co50 has the highest \( M_s \) (2.4T) among all soft magnetic materials [18]. The idea of achieving high \( J_a \) in nanocomposite by employing Fe50Co50 phase is pursued. Fig. 6 shows the J–H hysteresis loops under a maximum applied field of 1.5T for nanocomposite Nd6Fe65B6 and Nd6(Fe0.65Co0.35)36B6 alloys. The combination of magnetic properties for the latter is \( J_a = 1.06T; J_{1,5,7} = 1.52T; J_C = 265 \text{kA/m} \) and (BH)\text{max} = 70 kJ/m3. The result indicated that, compared to the alloy without Co substitution, higher \( J_a \) and \( J_C \) have been achieved for 35% Co substituted alloy. Thus, it is expected that RE\textsubscript{2}(FeCo)\textsubscript{14}B+Fe50Co50-based nanocomposites would have higher maximum energy product compared to current RE2Fe14B+Fe alloy.

The so-called microstructural parameters \( a_k \), \( a_{ex} \) and \( N_{eff} \) are temperature-independent and which reflect the effect of microstructure on the coercivity. \( a_k \) describes the influence of the non-perfect grain surfaces on the crystal anisotropy. The effective demagnetization factor \( N_{eff} \) is due to enhanced stray fields at the edges and corners of the grains. The parameter \( a_{ex} \) takes into account the effect of exchange coupling between neighboring grains. \( a_{ex}^{min} \) is related to the grain orientation distribution in the magnet [22,23]; in an array of randomly oriented grains of RE2Fe14B it is equal to \( 1/2 \) [17]. \( a_{ex} \) is the anisotropy field of single crystal RE2Fe14B.

According to the above equation, a plot of the experimental values of \( \mu_0H_C(T)/\mu_0H_a(T)\) versus the theoretical values \( \mu_0H_a(T)/\mu_0H_C(T) \) should yield a straight line, having a slope 1/2\( a_k a_{ex} \) and an ordinate intersection (–\( N_{eff} \)). Fig. 7 shows this plot for the nanocomposite \((Nd_{0.25}Pr_{0.75})_8(Fe_{1-x}Co_x)_{36}B_6\) alloys with various Co contents. The microstructural parameters calculated from the straight lines are shown in the figure. Increasing Co concentration decreases the values of both \( a_k \) and \( N_{eff} \), showing that Co substitution improves the exchange coupling, and alters the microstructure. The improved exchange coupling can be qualitatively explained by the increased exchange length due to the decreased anisotropy constant resulting from Co substitution. The improved microstructure resulting from Co substitution is demonstrated by the enhanced \( J_a \) and (BH)\text{max} at room temperature [15]. It is possible that Co addition leads to more equiaxed grains and smoother grain boundary resulting in a reduction of local stray field.

### 3.3. Elemental doping

Doping elements such as Nb, Zr have been well studied, and the coercivity can be substantially increased by a small addition of these elements [24–26]. It is also reported that Nb and Zr can retard the formation of \( \alpha \)-Fe and enhance the formation of...
Nd$_2$Fe$_{14}$B. This is very useful for nanocomposites with relatively low coercivity and with large grains of the soft phase. Other transition metals such as Hf, Ti and V have also been investigated in detail. An optimum level of these elements are beneficial for $H_C$ and $(BH)_{\text{max}}$ due to the microstructural changes [27]. However, another transition metal, Ta has received little attention. Although Ta has been frequently employed in soft magnetic materials such as Fe or FeCo-based thin films or bulk metallic glass for improving thermal stability, high-frequency properties and glass formability [28–30], there have been very few reports on the effect of Ta doping on the structure and magnetic properties of RE–Fe–B nanocomposites.

Shown in Fig. 8a are the hysteresis loops for nanocomposite Nd$_{9}$Fe$_{86}$Ta$_x$B$_5$ alloys with various Ta doping measured under a magnetic field of 1.5 T. $H_C$ increases with introduction of 1% Ta and with increase of Ta concentration from 1% to 2%. Further increase of Ta to 3 at% reduces the coercivity. $J_s$ (at 1.5 T) and $J_r$ decrease linearly with increasing Ta content. The best squareness of the 2nd quadrant $J$–$H$ loop is obtained for 1% Ta-doped alloy whereas 3 at% Ta doping results in a deterioration in the squareness. The reason for the latter is attributed to the precipitated second phase, which decouples the nanograins and reduces the magnetization [31].

Fig. 8b shows the dependence of magnetic properties on the Ta concentration. The maximum $(BH)_{\text{max}}$ of 139 kJ/m$^3$ is obtained in a Ta concentration of 1 at%. This $(BH)_{\text{max}}$ value is quite high if one consider that the maximum applied field used here is only 1.5 T, which did not saturate the material. Except enhanced room-temperature coercivity, an improved thermal stability was also found in 2 at% Ta-doped (NdDy)–(FeCo)–B alloys [31]. The results indicate that Ta doping provide a possible compositional choice to adjust the combination of magnetic properties for nanocomposite NdFeB alloys.

The microstructure of Nd$_{9}$Fe$_{86}$B$_5$ alloys without and with 2 at% Ta doping are shown in Fig. 9. The results, however, do not show reduced grain size associated with Ta doping. Thus, as initially observed by Chin et al. [31], there is no evidence of grain refinement due to alloying with Ta. Large Ta-containing inclusions were also not found.

4. Conclusions

Compositional modification has been frequently employed to improve the magnetic properties of rapidly solidified nanocrystal-
line Nd–Fe–B hard magnetic alloys. The effects of Pr, Dy, or Sm substituting Nd, Co substituting Fe and Ta doping have been investigated in this review. It has been demonstrated that Pr and Dy enhance $H_C$, whereas Sm reduces $H_C$. Co improves the thermal stability as well as the microstructure. Introducing Fe$_{65}$Co$_{35}$ enhanced the magnetization and is a possible approach to improve $(BH)_{max}$. Ta acts as a doping transit metal and has been shown to play an important role in producing an appropriate combination of magnetic properties, though there is no evidence of grain size reduction caused by Ta doping.

Acknowledgements

This work is partly supported by SERC, Singapore through Grant no. 0621010032 and a gift grant from Applied Materials Inc. The authors thank X.D. Han and L.H. Chua from NTU for providing some relevant data. ZWL also thank the financial supports from Guangdong Natural Science Foundation through Grant no. 81510641000084, Guangdong Provincial Science & Technology Program through Grant no. 2008B010600005, and State Key Laboratory For Advanced Metals and Materials through Grant no. 2008F-01.

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