Investigation of fabrication of Mn-Ga-Al/Fe-Co nanocomposite hard magnetic materials

Nguyen Mau Lam1,2, Do Thi Thuy2, Pham Ha Trang1, Nguyen Hoai Anh1, Nguyen Thi Luyen1, Nguyen Thi Hien1, Ngo Thi Truong1, Pham Thi Thanh3, Nguyen Hai Yen3, Nguyen Van Duong1, Nguyen Huy Ngoc4, Duong Dinh Thang1, Tran Minh Thi2 and Nguyen Huy Dan3

1 Hanoi Pedagogical University No 2, No 32 Nguyen Van Linh, Phuc Yen, Vinh Phuc, Vietnam
2 Hanoi National University of Education, No 136 Xuan Thuy, Cau Giay, Hanoi, Vietnam
3 Institute of Materials Science, Vietnam Academy of Science and Technology, No 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
4 VNU University of Engineering and Technology, No 144 Xuan Thuy, Cau Giay, Hanoi, Vietnam

E-mail: lamsp2@yahoo.com

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Abstract
Mn-Ga-Al/Fe-Co nanocomposite hard magnetic materials were combined from \( \text{Mn}_{65}\text{Ga}_{20}\text{Al}_{15} \) hard magnetic and \( \text{Fe}_{65}\text{Co}_{35} \) soft magnetic phases. The nanoparticles of hard and soft magnetic phases were fabricated by using high energy ball milling method with milling times of 8 h and 32 h to have size of about 50 nm and 70 nm, respectively. The hard and soft magnetic phases were then mixed together for 1 h with different weight fractions of \( \text{Fe}_{65}\text{Co}_{35} \) soft magnetic phase from 5 to 20%. The nanocomposites show quite good exchange-spring coupling of hard and soft magnetic phases. Saturation magnetization \( M_s \) and coercivity \( H_c \) of the nanocomposites strongly depend on the weight fraction of the soft magnetic phase. The \( M_s \) increases rapidly, while the \( H_c \) decreases with increasing the fraction of the soft magnetic phase. With appropriate fabrication conditions, the Mn-Ga-Al/Fe-Co nanocomposites can possess \( M_s > 50 \text{ emu g}^{-1} \) and \( H_c > 9 \text{ kOe} \). Maximum energy products, \( (BH)_{\text{max}} \), above 4 MGOe have been achieved for this kind of rare earth-free hard magnetic materials.

Keywords: nanocomposite hard magnetic material, exchange-spring magnet, rare earth-free magnet, high energy ball milling
Classification numbers: 5.02

1. Introduction

Hard magnetic materials known as permanent magnets were discovered and applied since BC. Nowadays, permanent magnets present everywhere in both the industry and social life such as motors, generators, computers, microwaves, loudspeakers, ore-sorters, magnetic resonance imaging, etc [1]. Currently, permanent magnets are divided into two groups, rare earth-free magnets and rare earth-containing ones. The group of rare earth-free magnets consists of Alnico, Ferrite, etc [2–7], which contain cheap components but their quality is not high. In contrast, the rare earth magnets such as Nd-Fe-B [8] and Sm-Co [9, 10] have good quality but high cost, due to content of rare earth elements, which are concentrated in only a few countries and restricted to exploitation as well as exportation. Therefore, many scientists have been constantly changing manufacture technology to improve the magnetic quantities of the traditional magnets. In addition, to change the manufacture technology, scientists are...
also focusing on reducing content of rare earth elements and finding new rare earth-free hard magnetic phases. Among rare earth-free magnets, the Mn-based compounds such as Mn-Bi, Mn-Ga are concentrated to study because they have high potential in practical applications [11–13]. The Mn-Bi system was discovered long time ago, but this system was not much concentrated because of the development of the rare earth magnets. The advantage of the Mn-Bi system is large amplitude and positive temperature coefficient of its coercivity. Recently, another Mn-based system, the Mn-Ga compounds have been found to reveal a strong hard magnetic phase, which have a relatively large coercivity of 20 kOe [14–16]. In terms of structure, the magnets are divided into micrometer-structure magnets and nanometer-structure magnets. The magnets with nanostructures have been more and more investigated and applied because of their interesting physical properties in nanometer scale. In 1993, the Nd$_2$Fe$_{14}$B/$\alpha$Fe nanocomposite material was found [17], which had superior magnetic properties compared to those of previous hard magnetic materials. According to theoretical calculations, nanocomposite hard magnetic materials might have a maximum energy product $(BH)_{\text{max}}$ more than 100 MGOe [18] based on a combination of strong coercivity of hard magnetic phases and high saturation magnetization of soft magnetic phases. Recently, the Mn-Ga based hard magnetic materials have been attracting research interests as a new hard magnetic phase for the nanocomposite materials [19–23]. By adding elements such as Cu, Fe, Al… the D0$_{22}$-type hard magnetic phase is formed more easily and its coercivity can exceed 10 kOe, high enough for coupling with the soft magnetic phase. As for the soft magnetic phase of the nanocomposites, Fe-Co alloys are commonly selected because of their high saturation magnetization up to 245 emu g$^{-1}$ [24, 25]. There are several methods to fabricate the nanocomposites including melt-spinning, high energy mechanical milling, spark-plasma sintering... In this report, we present the results of studying Mn$_{65}$Ga$_{20}$Al$_{15}$/Fe$_{65}$Co$_{35}$ nanocomposites prepared by high energy mechanical milling and subsequently annealing.

2. Experiment

The Mn$_{65}$Ga$_{20}$Al$_{15}$ hard magnetic and Fe$_{65}$Co$_{35}$ soft magnetic phases were prepared by high energy ball milling method from high-purity (99.9%) Mn, Ga, Al, Fe, and Co elements.
Before milling, the Mn$_{65}$Ga$_{20}$Al$_{15}$ ingots were fabricated by arc-melting method. The Mn$_{65}$Ga$_{20}$Al$_{15}$ and Fe$_{65}$Co$_{35}$ alloys were milled with the same ratio of ball/powder of 4/1 but different milling times of 8 and 32 h, respectively, in pure ethanol solvent to limit oxidation and clustering of particles. After milling, the alloy powders were dried in a vacuum chamber for a time period of 12 h. The Mn$_{65}$Ga$_{20}$Al$_{15}$ nanoparticle powder was annealed from 500°C to 700°C for various times from 2 to 45 min. The Mn$_{65}$Ga$_{20}$Al$_{15}$ hard magnetic nanoparticles were mixed into the Fe$_{65}$Co$_{35}$ soft magnetic ones with various weight fractions from 5 to 20%. The mixed powder was then pressed and annealed at 650°C for 15 min to obtain nano-composite magnets. The milling and mixing processes were carried out on a SPEX 8000D Mixer/Mill and the mixed powder was made into pellets under pressure of 3 ton cm$^{-1}$.

The structure and particle size of the samples were analyzed by x-ray diffraction (XRD) and scanning electron microscope (SEM) methods. The magnetic properties of the samples were investigated by magnetization measurements on pulsed field and vibrating sample magnetometers.

3. Results and discussions

Figure 1 shows the SEM images of the Mn$_{65}$Ga$_{20}$Al$_{15}$ and Fe$_{65}$Co$_{35}$ alloy powders after milling for 8 and 32 h, respectively. One can realize that particle size of the powder is fairly uniform for both the samples, in the range of 40–60 nm for Mn-Ga-Al particles and 60–80 nm for Fe-Co ones. The average size of the particles of Mn$_{65}$Ga$_{20}$Al$_{15}$ and Fe$_{65}$Co$_{35}$ was roughly determined to be 50 and 70 nm, respectively.

Figure 2(a) presents X-ray diffraction patterns of the as-milled Mn$_{65}$Ga$_{20}$Al$_{15}$ and Fe$_{65}$Co$_{35}$ samples. The XRD patterns of the Fe$_{65}$Co$_{35}$ alloy show two characteristic peaks of FeCo phase at $2\theta = 44.8^\circ$ and $65.3^\circ$. As for the XRD patterns of the Mn$_{65}$Ga$_{20}$Al$_{15}$ sample, there appear two crystalline phases of MnAl and Mn$_3$Ga with structural types of D0$_{19}$ and D0$_{22}$. The number of diffraction peaks of the MnAl phase is more than that of the Mn$_3$Ga phase. Besides, the intensity of the Mn$_3$Ga peaks is lower than that of the MnAl phase. From hysteresis loops in figure 2(b), one can see that the Fe$_{65}$Co$_{35}$ sample shows a soft magnetic behavior with a high saturation magnetization of 227 emu g$^{-1}$ and a low coercivity of 73 Oe. As for the Mn$_{65}$Ga$_{20}$Al$_{15}$ sample, its saturation magnetization and coercivity are less than 5 emu g$^{-1}$ and 10 Oe, respectively. Thus, the milling process does not produce a hard magnetic phase for the Mn-Ga-Al alloy.

In order to improve the Mn$_3$Ga hard magnetic phase, the Mn$_{65}$Ga$_{20}$Al$_{15}$ powder was annealed at different temperatures. Figure 3 shows the XRD patterns of the Mn$_{65}$Ga$_{20}$Al$_{15}$ powder annealed at different temperatures for 15 min. From the XRD patterns, one can see that the two crystalline phases of Mn$_3$Ga and Mn$_3$Al$_2$ were formed in the samples with the annealing temperatures of 600°C – 675°C. Intensity of XRD peak of the Mn$_3$Ga hard magnetic phase is higher than that of the Mn$_3$Al$_2$ phase and that of the peak at $2\theta = 41.5^\circ$ dramatically increases. Thus, the annealing process improved...
the D022-Mn3Ga hard magnetic phase. When the annealing temperature increases to 700 °C, the number and intensity of the D022-Mn3Ga peaks decrease. Along with the reduction of the D022-Mn3Ga phase, there appear some XRD peaks corresponding to MnAl phase. From the XRD patterns, we can realize that the optimal annealing temperature for the formation of the hard magnetic phase is from 650 °C to 675 °C.

Hysteresis loops at room temperature of the Mn65Ga20Al15 powder annealed in various conditions is presented in figure 4. Most of the hysteresis loops have quite large squareness and coercivity, indicating that the magnetocrystalline anisotropy in the samples is high. The results showed that the optimal annealing temperature for the best magnetic properties is 650 °C. The results are consistent with those obtained on the XRD patterns (figure 3). Figure 4(b) shows the hysteresis loops of the samples annealed at 650 °C for various times. The results of our hard magnetic properties obtained on these Mn-Ga-Al samples are similar to those of other research groups on the same material [20, 23, 26]. From the obtained results, we selected the annealing temperature of 650 °C and

Figure 6. Magnetic characteristic curves (a)–(e) and maximum energy product \((BH)_{\text{max}}\) (f) of the nanocomposites with various fractions of the soft magnetic phase.
time of 15 min for the hard magnetic phase. The $Mn_{65}Ga_{20}Al_{15}$ powder after annealing has a saturation magnetization of 34 emu g$^{-1}$ and a coercivity of 12 kOe.

To produce the $Mn$-Ga-Al/Fe-Co nanocomposite magnets, the $Mn_{65}Ga_{20}Al_{15}$ powder was mixed with the soft magnetic Fe$_{65}$Co$_{35}$ powder with various weight fractions. After pressing into pellets, the mixed powder was annealed at 650°C for 15 min.

Figure 5(a) shows hysteresis loops of the nanocomposite samples with 5, 10, 15 and 20 wt% of the Fe$_{65}$Co$_{35}$ soft magnetic phase. One can see that the saturation magnetization $M_s$ of the nanocomposites increases with increasing the weight fraction of the soft magnetic phases while their coercivity $H_c$ rapidly decreases. The hysteresis loops of the nanocomposites with high fraction of the soft magnetic phase are sunken. The sunken level of the hysteresis loops increases with increasing the fraction of the soft magnetic phase. This can be explained as follows. According to theoretical models, Skomski-Coey and Kneller-Hawig [17, 18], for nanocomposite materials, to have good interactions between the two hard/soft magnetic phases, the optimal particle size is about 10 nm. In this work, the particle size of the samples prepared by the high energy ball milling method is rather larger (50–70 nm). Thus, the particle size of the hard and soft magnetic phases is not optimal. Therefore, a part of the crystalline particles of the hard magnetic and soft magnetic phases has no interaction between them but exists independently.

Figure 6 presents the maximum energy product $(BH)_{max}$ of the nanocomposite samples with various weight fractions of the soft magnetic phase. Table 1 shows saturation magnetization, $M_s$, coercivity, $H_c$, and maximum energy product, $(BH)_{max}$, of the nanocomposites with various fractions of the soft magnetic phase. One can see that the saturation magnetization monotonously increases from 32 to 54 emu g$^{-1}$, while the coercivity fast decreases from 12 to 1.7 kOe with increasing the weight fraction of the soft magnetic phase of Fe$_{65}$Co$_{35}$. As for the maximum energy product, its value reaches a maximum of 4.3 MGOe at 15 wt% of the soft magnetic phase. To enhance $(BH)_{max}$, the optimal size of the magnetic nanoparticles should be found to make the best exchange-spring interaction for the material.

In comparison with other rare earth-free hard magnetic materials, our Mn-Ga-Al/Fe-Co nanocomposite magnets have moderate magnetic parameters. For examples, the Co-C based hard magnetic phases (Co$_2$C, Co$_3$C, …) have $H_c$ of about 3 kOe [27, 28], the Hf-Co based ones (HfCo$_7$, Hf$_2$Co$_{11}$B, …) have $H_c$ of about 4.5 kOe [29, 30]. The maximum energy product of these rare earth-free hard magnetic materials is commonly less than 5 MGOe.

4. Conclusions

We have successfully fabricated the $Mn_{65}Ga_{20}Al_{15}$ hard magnetic nanoparticles with coercivity of 12 kOe and the Fe$_{65}$Co$_{35}$ soft magnetic nanoparticles with a high saturation magnetization of 227 emu g$^{-1}$ by high energy mechanical milling method. The magnetic properties of the $Mn_{65}Ga_{20}Al_{15}$/Fe$_{65}$Co$_{35}$ nanocomposites were investigated with variation of the fraction of the soft magnetic phase from 5 to 20 wt%. The maximum energy product of 4.3 MGOe has been achieved for these rare earth-free nanocomposites.

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References

[1] Kramer M J, McCallum R W, Anderson I A and Constantinides S 2012 J. Miner. Met. Mater. Soc. 64 752
[2] Basubramanian B, Das B, Skomski R, Zhang W Y and Sellmyer D J 2013 Adv. Mater. 25 6090
[3] Yoshifuru M, Keichi K, Yuko N, Shin-ichi O and Watanabe K 2009 J. Japan Inst. Met. Mater. 73 40
[4] Yuan Z Z, Chen J M, Lu Y and Chen X D 2008 J. Alloys Compd. 450 245
[5] Sergeyev V and Bulygina T 1969 J. Appl. Phys. 40 1307
[6] Kamiino K, Kawaguchi T and Nagakura M 1966 IEEE Trans. Magn. 2 506
[7] Lynch C 1957 Sci. Program. 45 210
[8] Croat J J, Herbst J F, Lee R W and Pinkerton F E 1984 Appl. Phys. Lett. 44 148
[9] Herbst J F, Croat J J and Yelon W B 1985 J. Appl. Phys. 57 4086
[10] Zhang J, Takahashi Y K, Gopalan R and Honko K 2005 Appl. Phys. Lett. 86 122509
[11] Heikes R R 1955 Phys. Rev. 99 446
[12] Oikawa K, Mitsui Y, Koyama K and Anzai K 2011 Mater. Trans. 52 2032
[13] Cocy J M D 2014 J. Phys.: Condens. Matter 26 064211
[14] Saito T and Nishimura R 2012 J. Appl. Phys. 112 083901
[15] Ahmed A E and Hadjipanayis G C 2015 J. Phys. D: Appl. Phys. 48 125001
[16] Ahmed A E and Hadjipanayis G C 2015 J. Phys. Chem. C 119 8898
[17] Skomski R and Coey J M D 1993 Phys. Rev. B 48 15812
[18] Kneller E F and Hawig R 1991 IEEE Trans. Magn. 27 3588
[19] Skomski R and Coey J M D 2016 Scr. Mater. 112 3
[20] Saito T and Nishio-Hamane D 2016 AIP Adv. 6 075004

Table 1. Saturation magnetization, $M_s$, coercivity, $H_c$, and maximum energy product, $(BH)_{max}$, of the nanocomposites with various fractions of the soft magnetic phase.

| $Fe_{65}Co_{35}$ (wt%) | $M_s$ (emu g$^{-1}$) | $H_c$ (kOe) | $(BH)_{max}$ (MGOe) |
|------------------------|---------------------|-------------|---------------------|
| 0                      | 32                  | 12          | 1.7                 |
| 5                      | 38                  | 9.2         | 2.4                 |
| 10                     | 43                  | 7.4         | 3.3                 |
| 15                     | 48                  | 4.7         | 4.3                 |
| 20                     | 54                  | 1.7         | 2.7                 |
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[21] Daniel R B, Ke H, Theo S, Tiglet B and Niu R 2016 AIP Adv. 6 056012

[22] Akira K, Toshiyuki S and Doi A M 2016 Japan. J. Appl. Phys. 55 07MC04

[23] Saito T and Nishio-Hamane D 2015 J. Alloys Compd. 632 486

[24] Manh D H, Tung D K, Phong L T H, Thanh P T and Phuc N X 2014 JPS Conf. Proc. 1 012010

[25] Ogawa T, Takano H, Kura H and Takahashi M 2012 J. Appl. Phys. 111 07B553

[26] Buchelnikov V D, Taskaev S V, Zagrebin M A, Zayak A T and Entel P 2008 Mater. Sci. Eng. A 481–2 218

[27] Zamanpour M, Bennett S P, Majidi L, Chen Y and Harris V G 2015 J. Alloys Compd. 625 138

[28] Turgut Z, Lucas M S, Leontsev S, Semiatin S L and Horwath J 2016 J. Alloys Compd. 676 187

[29] Balamurugan B, Das B, Zhang W Y, Skomski R and Sellmyer D J 2014 J. Phys.: Condens. Matter 26 064204

[30] McGuire M A and Rios O 2015 J. Appl. Phys. 117 053912