Effects of B Doping on the Structure and Magnetic Properties of SmFe10Mo2 Alloy Postprint

Authors: Sun Naikun, Du Shengjie, Guo Jie

Date: 2023-03-18T00:00:00+00:00

Abstract

Master alloy ingots of SmFe10Mo2 and SmFe10Mo1.5B0.5 were prepared by arc melting. After homogenization annealing, SmFe10Mo1.5B0.5 nanocrystalline alloy powder was fabricated by ball milling. The effects of B doping on the phase structure and magnetic properties of SmFe10Mo2 bulk alloy and the influence of ball milling on SmFe10Mo1.5B0.5 nanocrystalline powder were investigated. The results show that after B doping, the ThMn12 phase structure of the alloy remains unchanged, while the Curie temperature increases from 270°C to 334°C; the compositional inhomogeneity of the alloy leads to two phase transition points in the thermomagnetic curve. After ball milling for 0.5 h, Mo precipitates significantly and the 1:12 phase decreases markedly in the SmFe10Mo1.5B0.5 alloy; with increasing ball milling time, α-Fe precipitates and forms a non-magnetic Mo2FeB2 phase, causing a significant decrease in intrinsic coercivity, and its saturation magnetization shows a trend of first increasing and then decreasing with ball milling time. The nanocrystalline alloy powder ball-milled for 0.5 h exhibits the optimal magnetic properties: Ms = 55 $\mathrm{A \cdot m^2/kg}$, iHc = 0.2 T.

Full Text

Preamble

Vol. 29 No. 1, *Chinese Journal of Materials Research*, January 2015
ChinaXiv Partner Journal

Effect of B-doping on the Structure and Magnetic Properties of SmFe10Mo2 Alloy

SUN Naikun, DU Shengjie, GUO Jie
School of Science, Shenyang Ligong University, Shenyang 110159, China

Supported by Liaoning Provincial Natural Science Foundation No. 2013020105 and Shenyang Science and Technology Foundation No. F13-316-1-39.

Manuscript received May 7, 2014; in revised form September 16, 2014.

To whom correspondence should be addressed
Tel: (024)24681253, E-mail: naikunsun@163.com

Abstract

Ingots of SmFe10Mo2 and SmFe10Mo1.5B0.5 master alloys were prepared by arc melting, homogenized through annealing, and then used to produce SmFe10Mo1.5B0.5 nanocrystalline alloy powders via ball milling. The effects of B doping on the phase structure and magnetic properties of bulk SmFe10Mo2 alloy, as well as the influence of ball milling on the nanocrystalline SmFe10Mo1.5B0.5 powder, were investigated. The results show that B doping does not alter the ThMn12-type phase structure of the alloy, but significantly increases the Curie temperature from 270°C to 334°C. Compositional inhomogeneity in the alloy leads to the appearance of two phase transition points in the thermomagnetic curve. After ball milling for 0.5 h, substantial Mo precipitation occurs in the SmFe10Mo1.5B0.5 alloy, accompanied by a marked reduction in the 1:12 phase. With increasing milling time, α-Fe precipitates and a non-magnetic Mo2FeB2 phase forms, causing a significant decrease in intrinsic coercivity. The saturation magnetization initially increases and then decreases with prolonged milling time. The nanocrystalline alloy powder milled for 0.5 h exhibits optimal permanent magnetic properties: Ms = 55 $\mathrm{A \cdot m^2/kg}$ and iHc = 0.2 T.

Keywords: metallic materials, ball milling, phase structure, permanent magnetic properties, Curie temperature

Classification: TM271

Article ID: 1005-3093(2015)01-0055-05

Introduction

Rare earth elements can form stable ThMn12-type rare earth compounds R(Fe, T)12 with transition elements such as Fe, Ti, V, and Mo [1]. These rare earth-iron intermetallic compounds have become another excellent permanent magnetic material following Nd2Fe14B [2-4]. Among them, SmFe11Ti exhibits the best performance with a maximum energy product (BH)max = 268 $\mathrm{kJ/m^3}$, remanence Br = 1.16 T, and Curie temperature TC = 312°C, showing promise for practical applications [5]. RFe10Mo2 compounds readily undergo spin reorientation at low temperatures [6], and SmFe12-xMox has attracted widespread attention due to its high magnetic anisotropy [7]. The crystal structure of this compound is the ThMn12-type symmetric structure with space group I4/mmm, containing two R(Fe, T)12 molecules (26 atoms) per unit cell [8]. Rare earth Sm atoms occupy the 2a crystallographic site, while Fe and Mo atoms can be distributed across three 3d sites (8i, 8j, and 8f), with Mo atoms preferentially occupying the 8i site [7].

The addition of trace interstitial atoms such as H, C, and N to R(Fe, T)12 compounds significantly improves magnetic performance [9]. Partial substitution of T elements in R(Fe, T)12Nx with V, B, Co, Mo, and other elements can also enhance magnetic properties [10]. Studies on Sm(Fe, Mo)12 interstitial nitrides [11] and hydrides [9] have shown that trace N and H atoms occupying interstitial lattice sites enhance the exchange interaction between Fe-Fe atoms and increase the Curie temperature of the compounds. Mo plays a dual role in 1:12 interstitial nitrides: on one hand, high Mo content tends to reduce the saturation magnetization and Curie temperature of R(Fe, T)Nx; on the other hand, substituting T elements with Mo in R(Fe, T)Nx can yield higher coercivity [7, 12]. Partial substitution of Fe with Mn leads to a decrease in the Curie temperature of SmFe10.5Mo1.5 alloy due to the combined effect of site occupation [13]. Y. B. Kim et al. [14] investigated the changes in intrinsic magnetic properties caused by B substitution for Ti in NdFeTi nitrides, finding that B addition increased the Curie temperature and saturation magnetization of the nitrides by 20% and 15%, respectively. In this work, SmFe10Mo2 master alloy ingots were prepared by arc melting, and SmFe10Mo1.5B0.5 alloy was synthesized. Nanocrystalline SmFe10Mo1.5B0.5 alloy powders were then prepared by high-energy ball milling to study the influence of milling time on phase structure and magnetic properties.

Experimental Methods

Rare earth element Sm with purity greater than 99.99%, and metallic Fe and Mo with purity greater than 99.5% were used as starting materials. The elements were weighed according to the desired chemical compositions and melted in a vacuum induction furnace or arc furnace under high-purity argon protection to prepare SmFe10Mo2 master alloy. FeB alloy (Fe: 80%, B: 20%) was added to produce SmFe10Mo1.5B0.5 alloy. Due to the high vapor pressure of rare earth element Sm, an extra 30 wt% of Sm was added during melting. The as-cast alloy ingots exhibited compositional inhomogeneity and required homogenization annealing to form the desired phase structure and reduce α-Fe content. The melted ingots were wrapped in molybdenum foil and homogenized at 950°C for 7 days under high-purity argon protection. The annealed samples were water-quenched, and surface oxide layers were removed for subsequent experiments.

The melted master alloys were coarsely crushed and then sealed in a ball mill jar with steel balls in a high-purity argon atmosphere glove box, with a ball-to-powder weight ratio of 20:1. SmFe10Mo1.5B0.5 alloy powders were prepared using a GN-2 high-energy ball mill at 100 V with a rotation speed of 600 r/min.

Phase composition and surface morphology were characterized using a Rigaku D/max-2500 X-ray diffractometer (XRD) (operating at 50 kV and 300 mA with Cu Kα radiation ($\lambda = 0.150456$ nm)) and an S-3400N scanning electron microscope (SEM). The Curie temperature of bulk alloys and room-temperature magnetic hysteresis loops of SmFe10Mo1.5B0.5 powders were measured using Lakeshore 7407 and VSM-220 vibrating sample magnetometers.

Results and Discussion

2.1 Phase Structure and Morphology Analysis

[Figure 1: see original paper] shows the X-ray diffraction patterns of bulk SmFe10Mo2 alloy and SmFe10Mo1.5B0.5 alloy powders milled for different durations. The master alloy bulk consists primarily of the 1:12 phase with ThMn12 structure. The 1:12 phase structure remains unchanged with B addition. However, Curie temperature measurements indicate that SmFe10Mo1.5B0.5 alloy exhibits two phase transition points, attributed to compositional inhomogeneity in the arc-melted bulk alloy. B enters the lattice of some SmFe10Mo2 compounds, forming Sm(Fe, Mo, B)12 phase that coexists with the SmFe10Mo2 phase. Our previous research found that ball milling significantly affects the phase composition of Sm2Co17 alloys [16]. Tang et al. [17] demonstrated that ball milling induces decomposition of the 1:12 phase in NdFe11Ti alloy, thereby improving magnetic properties. To investigate the influence of ball milling on the phase structure and magnetic properties of SmFe10Mo1.5B0.5 alloy, experiments with different milling durations were conducted. As shown in the figure, substantial Mo precipitation occurs after 0.5 h of milling. With further increase in milling time, α-Fe precipitation increases, and the main phase transforms to Mo2FeB2. After 2 h of milling, α-Fe precipitates extensively and becomes the dominant phase, while the phase composition remains essentially unchanged after 3 h. Meanwhile, diffraction peaks broaden significantly due to reduced grain size and increased internal stress during milling. The grain size calculated using the Scherrer formula is 21.7 nm for the 0.5 h milled sample and decreases to 7.4 nm for the 2 h milled sample.

[Figure 2: see original paper] presents SEM micrographs of SmFe10Mo1.5B0.5 alloy powders milled for 0.5 h and 2 h. The particle size distribution is non-uniform, with irregular shapes and typical agglomeration phenomena, similar to observations by T. Tao et al. in ball-milled tin dioxide powders [18]. After 2 h of milling, large particle clusters decrease noticeably, distinct boundaries become visible, and fine particles increase. Some large particles may result from agglomeration of overly fine powders with increased stickiness [8]. The particle sizes are 1–5 m and 0.5–5 m for samples milled for 0.5 h and 2 h, respectively.

2.2 Curie Temperature and Magnetic Properties

[Figure 3: see original paper] shows the thermomagnetic curves of SmFe10Mo2 and SmFe10Mo1.5B0.5 alloys, where curves (a) and (b) were measured at 0.01 T, and curve (c) at 0.05 T. The Curie temperature is defined as the temperature corresponding to the minimum of the first derivative of magnetization with respect to temperature on the thermomagnetic curve. As seen in Figures 3b and 3c, bulk SmFe10Mo2 alloy shows only one phase transition point corresponding to the 1:12 phase, whereas both bulk and 0.5 h milled nanocrystalline SmFe10Mo1.5B0.5 powders exhibit two phase transition points, corresponding to different compositions of the 1:12 phase. This result confirms that B-doped bulk alloys prepared by arc melting have compositional inhomogeneity. One transition temperature remains consistent with the master alloy bulk at approximately 270°C, confirming the presence of SmFe10Mo2 phase, while the other transition corresponding to Sm(Fe, Mo, B)12 phase increases substantially to 334°C, demonstrating that B doping significantly enhances the Curie temperature. This result is similar to the finding by C. S. Kim et al. [19] that B substitution for Ti increased the Curie temperature of NdFe10.7TiB0.3 by 17°C. The Curie temperature of R-T compounds depends primarily on T-T exchange interactions, which are strongly influenced by interatomic distances [8]. B substitution for partial Mo alters T-T interatomic distances, enhancing ferromagnetic exchange and thereby increasing the Curie temperature. Notably, compared with the bulk sample, the 0.5 h milled sample shows weakened Curie temperature peaks, with both transition temperatures decreasing from 272°C and 334°C to 250°C and 315°C, respectively. This is mainly attributed to changes in phase composition and reduced particle size induced by ball milling. X. C. Kou et al. [7] found that higher Fe content in SmFe12-xMox leads to higher Curie temperature of the 1:12 phase. As shown in the XRD patterns in Figure 1, extensive Mo precipitation and Mo2FeB2 phase formation in the 0.5 h milled sample alter the Fe/Mo composition ratio in the 1:12 phase, resulting in Curie temperature changes.

[Figure 4a: see original paper] shows the demagnetization curves of alloys before and after B doping. B addition decreases the saturation magnetization without significantly improving coercivity. The thermomagnetic curves in Figure 3 indicate that B introduction creates two distinct 1:12 phases in the alloy: SmFe10Mo2 phase and Sm(Fe, Mo, B)12 phase. Non-uniform B distribution leads to only modest coercivity improvement and reduced saturation magnetization in the bulk alloy. [Figure 4b: see original paper] presents demagnetization curves of samples milled for different durations. Coercivity increases significantly from 0.03 T to 0.2 T after 0.5 h of milling. The coercivity of magnets depends primarily on microstructural features (size, orientation, boundary defects) [20]. Ball milling refines grains and increases grain boundaries, enhancing domain wall pinning at grain boundaries and thereby increasing coercivity [21]. With increasing milling time, the 1:12 phase gradually decreases, α-Fe soft magnetic phase precipitates extensively, and grain refinement occurs. Severe lattice distortion within particles destroys intrinsic crystalline properties, weakening grain boundary pinning effects on domain walls [22], leading to a sharp decrease in coercivity and gradual increase in saturation magnetization of the nanocrystalline powders. After 2 h of milling, α-Fe precipitation saturates, reaching a maximum saturation magnetization of 78 $\mathrm{A \cdot m^2/kg}$. Further milling causes extensive Mo incorporation into the Mo2FeB2 phase, weakening Mo diffraction peaks, further reducing powder particle size, and promoting agglomeration and oxidation [23], which decreases saturation magnetization to 70 $\mathrm{A \cdot m^2/kg}$. The alloy powder milled for 0.5 h exhibits optimal magnetic properties: saturation magnetization Ms = 55 $\mathrm{A \cdot m^2/kg}$ and intrinsic coercivity iHc = 0.2 T.

Conclusions

1. B-doped SmFe10Mo2 alloy maintains the ThMn12-type phase structure, with Curie temperature significantly increased from 270°C to 334°C. Compositional inhomogeneity leads to two phase transition points in the thermomagnetic curve and reduces alloy saturation magnetization.
2. Ball milling of SmFe10Mo1.5B0.5 alloy significantly increases both coercivity and saturation magnetization. With increasing milling time, substantial Mo and α-Fe precipitation occurs, the main phase decreases markedly, and a non-magnetic Mo2FeB2 phase forms, causing a sharp decrease in nanocrystalline powder coercivity and a saturation magnetization trend that first increases then decreases.

References

[1] YANG Yingchang. Structural and magnetic properties of Y(Mn1-xFex)12. *Acta Metallurgica Sinica*, 17(3), 355 (1981).

[2] V. T. Hien, J. M. Le Breton, N. T. Hien, L. T. Tai, N. P. Thuy, N. H. Duc, N. P. Duong, J. Teillet. Magnetic and Mössbauer studies of the DyFe11Mo compound. *Journal of Magnetism and Magnetic Materials*, 237(1), 10 (2001).

[3] Study of RFe10.5Mo1.5Cx compounds. *Physica B: Condensed Matter*, 328(3-4), 363 (2003).

[4] SUN Guangai, CHEN Bo, WU Erdong, DU Honglin, SUN Kai. Structure and magnetic properties of DyFe10Si2Nx compounds. *Chinese Journal of Materials Research*, 20(3), 327 (2006).

[5] K. H. J. Buschow. New developments in hard magnetic materials. *Reports on Progress in Physics*, 54(9), 1123 (1991).

[6] X. C. Kou, R. Grössinger, G. Wiesinger, J. P. Liu, F. R. de Boer, I. Kleinschroth, H. Kronmüller. Intrinsic magnetic properties of RFe10Mo2 compounds (R=Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, or Tm). *Physical Review B*, 51(13), 8254 (1995).

[7] X. C. Kou, E. H. C. P. Sinnecker, R. Grossinger, G. Wiesinger, T. Zhao, J. P. Liu, F. R. de Boer. Magnetocrystalline anisotropy of SmFe12-xMox compounds with x=0.5, 1.0, 1.5, 2.0 or 3.0. *Journal of Magnetism and Magnetic Materials*, 140(2), 1025 (1995).

[8] ZHAO Xinguo. The Structure and Magnetic Properties of Sm2(Fe1-x, Tix)17Nδ Prepared by Hydrogenation Process. Shenyang: Institute of Metal Research, Chinese Academy of Sciences, 1999.

[9] O. Isnard, M. Guillot. Investigation of the magnetic properties of SmFe10Mo2 and SmFe10Mo2H in high magnetic field. *Journal of Applied Physics*, 85(8), 4681 (1991).

[10] ZHANG Shengen, ZHANG Jiuxing, LI Er, ZHOU Meiling. The study of R(Fe, M)12Nx new rare-earth permanent magnets. *Journal of Beijing Polytechnic University*, 23(4), 23 (1997).

[11] Structural and magnetic properties of RMo1.5Fe10.5Nx. *Journal of Applied Physics*, 74(6), 4066 (1993).

[12] M. Endoh, K. Nakamura, H. Mikami. Nd(Fe, Mo)Nx compound and magnets. *IEEE Transactions on Magnetics*, 28(2), 2560 (1992).

[13] YANG Suping, LIN Pinghua. Structure and magnetic properties of SmFe10.5-xMnxMo1.5 compounds. *Journal of Magnetic Materials and Devices*, 37(05), 0018 (2006).

[14] Y. B. Kim, H. T. Kim, C. S. Kim, T. K. Kim. Effects of B and Mo on the magnetic properties of NdFeTi-nitrides with ThMn12-type structure. *IEEE Transactions on Magnetics*, 29(6), 2848 (1993).

[15] C. S. Kim, Y. J. Lee, S. W. Lee, Y. B. Kim, C. S. Kim. Crystallographic and magnetic properties of NdFe10.7TiM0.3(M=B, Ti). *Journal of Applied Physics*, 79(8), 5516 (1996).

[16] SUN Naikun, DU Shengjie. Effect of Fe-doping and ball milling on the structure and magnetic properties of Sm2Co17 alloy. *Journal of Functional Materials* (supplement I), 45, 21001 (2014).

[17] S. L. Tang, C. H. Wu, B. W. Wang, X. M. Jin, G. S. Li, B. Z. Ding, Y. C. Chuang. Nonequilibrium phase transformation of NdFe11Ti compound during mechanical milling. *Journal of Magnetism and Magnetic Materials*, 188(3), 387 (1998).

[18] T. Tao, A. M. Glushenkov, H. P. Hu, Q. Y. Chen, Y. Chen. Ball milled SnO2: a modified vapor source for growing nanostructures. *Journal of Alloys and Compounds*, 504(S1), 315 (2010).

[19] C. S. Kim, Y. J. Lee, S. W. Lee, Y. B. Kim, C. S. Kim. Crystallographic and magnetic properties of NdFe10.7TiM0.3(M=B, Ti). *Journal of Applied Physics*, 79(8), 5516 (1996).

[20] CHEN Wei, GAO Ruwei, ZHU Minggang. Dependence of the coercivity of Nd-Fe(Co, Ga, Nb)-B nanocomposite on the grain size. *Chinese Journal of Materials Research*, 17(2), 151 (2003).

[21] LU Nianduan, SONG Xiaoyan, ZHANG Jiuxing. Preparation and characterization of Sm2Co17 nanocrystalline bulk. *Journal of Materials Engineering*, (10), 200 (2008).

[22] PENG Yuandong, YI Jianhong, LI Yunqing, LI Liya, LUO Shudong, TANG Xinwen. Effect of the powder’ s features on the magnetic properties of sintered Sm2(Co, Fe, Cu, Zr)17 alloys. *Powder Metallurgy Industry*, 11(5), 13 (2001).

[23] CHANG Ying, ZHAO Jian, LI Xiaodong, WEI Zhiyong. Preparation and analysis of anisotropic Sm2Co17 nanoflakes prepared by ball milling in magnetic field. *Journal of Functional Materials*, 22(43), 3123 (2012).

Note: Figure translations are in progress. See original paper for figures.