5-1-2000

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# Effects of Ga substitution for Fe on the structure and magnetic properties of $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ ($x=0-2.2$) alloys prepared by mechanical alloying

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The effects of a partial substitution of Ga for Fe on the structure and magnetic properties of mechanically alloyed $Nd_{8.4}Fe_{87.1}B_{4.5}$ were studied. With increasing Ga content, the magnetic properties of the nanocomposite magnets first improve, reach maxima at 1.1 at. % Ga, and then degrade. The addition of Ga helps to control the morphology, especially the grain sizes of both $\alpha$-Fe and $Nd_2Fe_{14}B$. © *2000 American Institute of Physics.* [S0021-8979(00)22308-6]

Ga is consistently used as an additive for improving the magnetic properties of conventional single-phase $Nd_2Fe_{14}B$ magnets.[1,2] In this article, the effects of a partial substitution of Ga for Fe on the structure and magnetic properties of the nanocomposite $Nd_{8.4}Fe_{87.1}B_{4.5}$ magnet are reported.

To prepare $Nd_{15}Fe_{77-x}Ga_xB_8$ ($x=0$, 1, 2, and 3) ingots, the starting materials with at least 99.9% purity were arc melted twice, under purified argon. The ingots were crushed to prepare the alloy powders, with particle sizes of less than 150 $\mu$m. Then, according to the nominal compositions $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ ($x=0$. 1.1, 1.6, and 2.2), the alloy powders were mixed with an appropriate amount of $\alpha$-Fe powders with particle sizes of less than 10 $\mu$m. The powder mixtures were then milled under argon for 5 h in a high-energy ball mill. The as-milled powders were annealed at temperatures ranging from 600 to 750 °C for 20 min in vacuum higher than $1\times10^{-3}$ Pa.

X-ray diffraction (XRD) analysis of the samples was conducted using Cu $K\alpha$ radiation. The average grain sizes of the samples were deduced from Scherrer's method of XRD, and $K\alpha$ spectral and instrument broadening were corrected by a computer implementation of Stokes. For the specimens with a given composition, the measurements of the average grain sizes were performed for each one from the same batch as those annealed at different temperatures. Ac initial susceptibility measurement was used to determine the Curie temperatures. The morphology was observed by transmission electron microscopy (TEM). The magnetic properties were measured at room temperature using a pulsed magnetometer in fields up to 8 T. The results of the magnetic measurements were corrected using an experimentally determined effective demagnetization factor of 0.28.

As indicated by XRD patterns, the as-milled alloys with nominal composition $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ ($x=0$. 1.1, 1.6, and 2.2) are composed of a mixture in which nanocrystalline $\alpha$-Fe is embedded in an amorphous matrix. In all the alloys annealed at 600 °C or above for 20 min, a mixture of nanostructured $\alpha$-Fe and $Nd_2Fe_{14}B$ is formed. The XRD patterns for all the alloys annealed at 650 °C for 20 min are shown in Fig. 1. Figure 2 shows the dark-field TEM micrograph of the sample corresponding to Fig. 1(a). It is observed that $\alpha$-Fe grains (white grains) are approximately spherical and randomly distributed.

The dependence of intrinsic coercivity $\mu_0 H_c$, remanence $J_r$, maximum magnetic energy product $(BH)_{\max}$, and reduced remanence $J_r/J_s$ on Ga content for all the magnets annealed at 650 °C for 20 min is shown in Fig. 3. It can be seen that with increasing Ga content $\mu_0 H_c$, $J_r$, and $(BH)_{\max}$ of the nanocomposite magnets first increase and reach a maximum at 1.1 at. % Ga content and then decrease. In the case of fully crystallized melt-spun nanocrystalline $Nd_{4.5}Fe_{73}B_{18.5}Co_3Ga_1$, three-dimensional atom probe and TEM observations revealed that a slight enrichment of Ga atoms partition at the $Nd_2Fe_{14}B/Fe_3B$ interface.[3] Likewise, in the present work, some of the Ga atoms or the Ga-rich phases may cluster at the $Nd_2Fe_{14}B/\alpha$-Fe intergranular re-

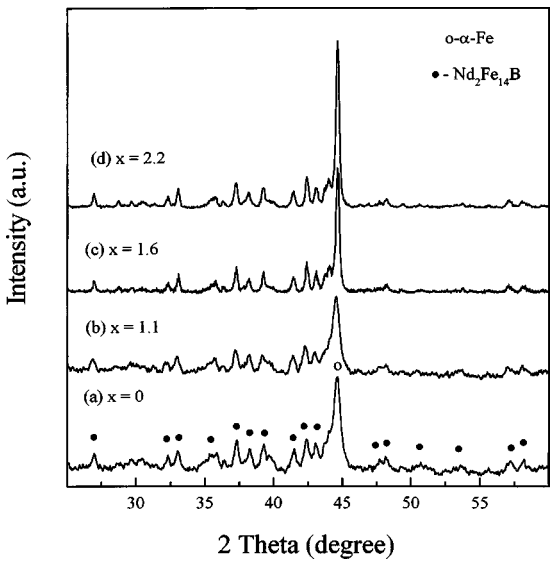


FIG. 1. XRD patterns for $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ alloys annealed at 650 °C for 20 min.

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FIG. 2. Dark-field TEM micrograph of $Nd_{8.4}Fe_{87.1}B_{4.5}$ annealed at 650 °C for 20 min.

gions, which can change the morphology of the nanocomposite magnets. In particular, the addition of 1.1 at. % Ga results in a notable refinement of both the soft and the hard grains (cf. Fig. 4). The appropriate refinement of the soft grains is favorable for the exchange fields from the hard-phase grains nearest in proximity to fully penetrate the soft grain embedded between the nearest hard grains and suppress the easy nucleation of inverse magnetization in the soft grains. On the other hand, the refinement of both the soft and hard grains leads to a significant increase in the ratio of interface area (or grain-boundary area) to volume of the grains. Therefore, the effective contact areas between the soft and hard grains are increased, the exchange coupling between a soft grain and its nearest-neighboring hard grains can be enhanced, and it will play an essential role in improving the magnetic properties of nanocomposite magnets. In addition, increased grain interfaces or grain boundaries will act as the obstacles to propagation of inverse magnetization. In this way, the magnetic properties of nanocomposite magnets are measurably improved. Compared with the 1.1 at. % Ga-containing alloy, for the alloys with the Ga content $x \geqslant 1.6$ at. %, the grain sizes of both the soft and hard phases are significantly bigger (as shown in Fig. 4). Correspondingly, $\mu_0 H_c$, $J_r$, and $(BH)_{\max}$ of the Ga-containing alloys are degraded. For example, the average grain size of the soft phase in the alloys with $x=1.6$ is always smaller than that of the alloys with $x=2.2$ under the same annealing conditions. But, the average grain sizes of the hard grains in these two alloys are not apparently different. Annealed below 650 °C, the average grain sizes of the hard grains in the alloys with $x=2.2$ are even smaller than those of 1.6 at. % Ga-containing alloys. However, the magnetic properties of the former are worse than those of the latter (as shown in Fig. 5). This indicates that the average grain size of $\alpha$-Fe plays a predominate role in determining the magnetic properties of

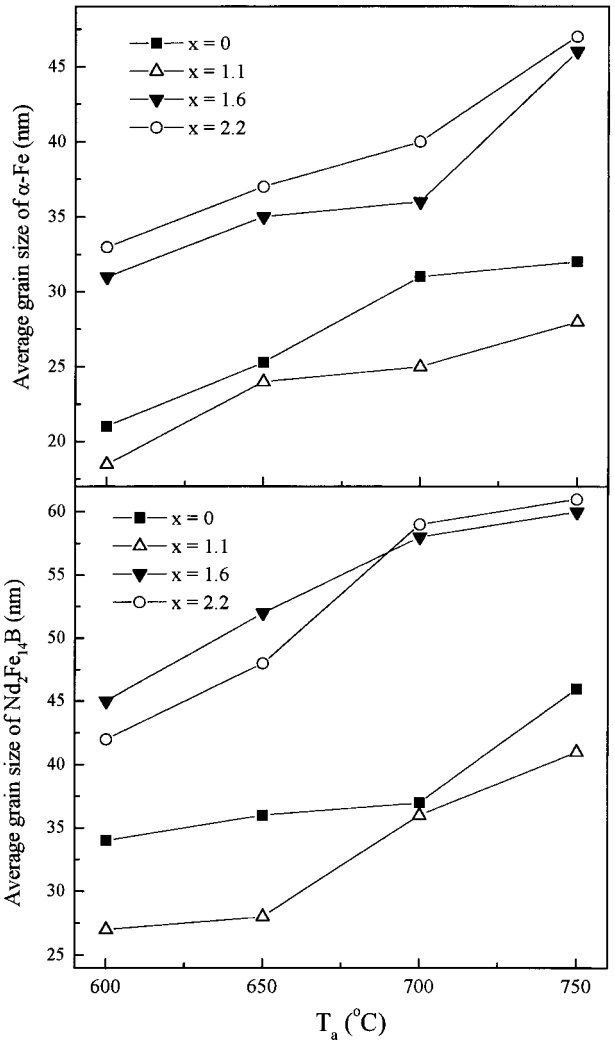


FIG. 4. Dependence of the average grain sizes of $\alpha$-Fe and $Nd_2Fe_{14}B$ on annealing temperature ($T_a$) for $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ alloys.

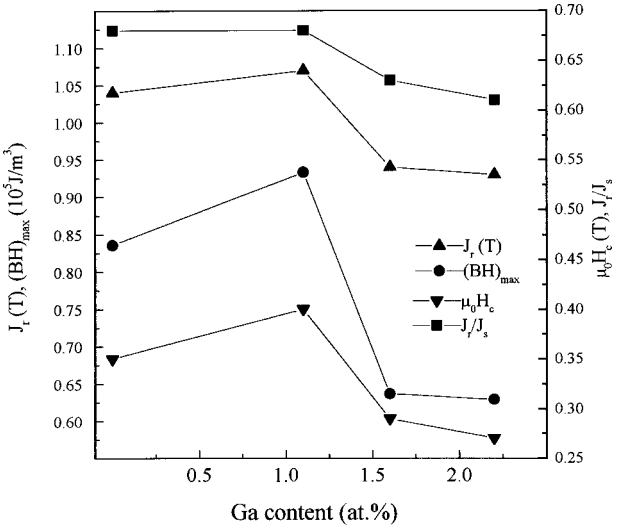


FIG. 3. Dependence of $\mu_0 H_c$, $J_r$, $(BH)_{\max}$, and $J_r/J_s$ on Ga content for $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ alloys annealed at 650 °C for 20 min.

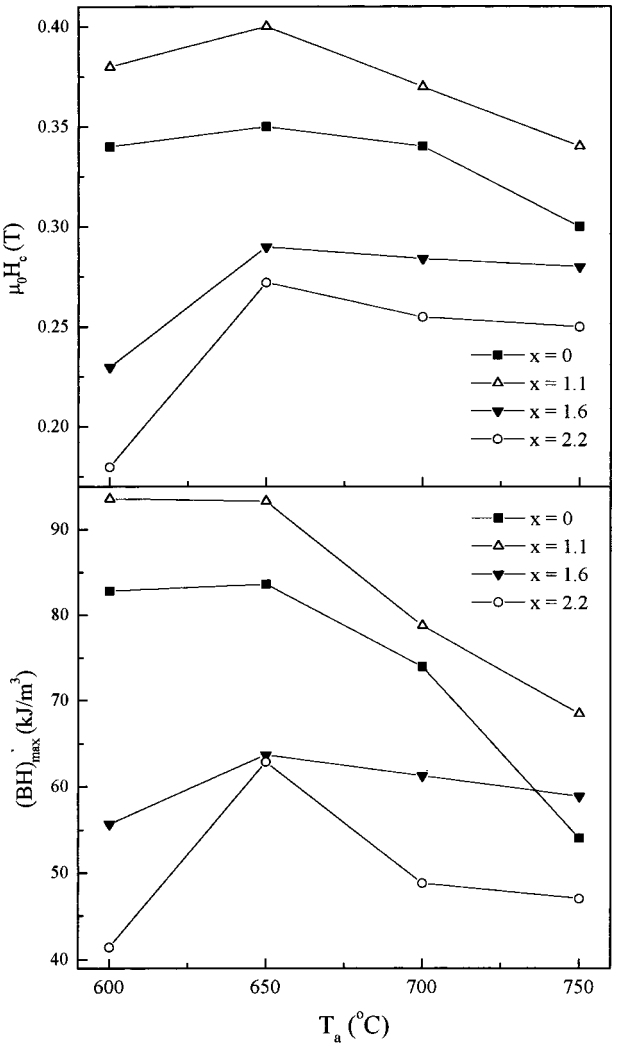


FIG. 5. Dependence of $\mu_0 H_c$ and $(BH)_{\max}$ on annealing temperature ($T_a$) for $Nd_{8.4}Fe_{87.1-x}Ga_xB_{4.5}$ alloys.

nanocomposite magnets under the condition that the average grain size of $Nd_2Fe_{14}B$ is almost identical.

As revealed by XRD (Fig. 1), with increasing Ga content, the relative intensities of the characteristic peaks of the $Nd_2Fe_{14}B$ phase decrease, while those of the $\alpha$-Fe phase increase. This suggests that the addition of excessive Ga will suppress the formation of the $Nd_2Fe_{14}B$ phase. More Ga-containing or Ga-rich phases may distribute in the $Nd_2Fe_{14}B/\alpha$-Fe intergranular regions. These intergranular phases may play a role of partially decreasing the exchange interaction between the soft and the hard grains. This would deteriorate the magnetic properties of such nanocomposite magnets. From the results of ac initial susceptibility measurements, the addition of Ga enhances slightly the Curie temperature of the hard phase. For $x=0$, 1.1, 1.6, and 2.2, the Curie temperatures of the hard phase are 312, 315, 325, and 325 °C, respectively. By slowly scanning the characteristic peaks of the $Nd_2Fe_{14}B$ phase for all samples, it can be seen that the characteristic XRD peaks of the $Nd_2Fe_{14}B$ phase in all the Ga-containing alloys move systematically towards lower angles, which shows that some of the Ga atoms enter into the lattice of the $Nd_2Fe_{14}B$. The Mössbauer study of $Nd_2Fe_{13}Ga_1B$ shows that the Ga atoms preferably occupy the $k_2$ sites and substitute for some of the iron atoms at the lattice sites.[1] Thus, the Fe–Fe exchange interaction in the $Nd_2Fe_{14}B$ phase is reinforced, increasing the Curie temperature of the hard phase.[1,4,5] However, more substitution of the nonmagnetic Ga for Fe leads to a decrease of the magnetic moment per formula unit of the hard phase. Therefore, it is found that $J_r$ of the alloys, except for the one containing 1.1 at. % Ga, slightly decreases (as shown in Fig. 3). The improvement of $J_r$ of 1.1 at. % Ga-containing alloy may result from the strong exchange interaction between nanograins, which in turn originates from the notable refinement of both soft grains and hard grains, as mentioned above. A small amount of substitution of Ga for Fe in the lattice of $Nd_2Fe_{14}B$ results in a slight increase of the magnetocrystalline anisotropy field $H_A$. Compared with that of the $Nd_2Fe_{14}B$, $H_A$ of $Nd_2Fe_{13}Ga_1B$ only increases by 3%.[1,2] Therefore, generally, the effect of the Ga addition on the magnetic properties of nanocomposite magnets is mainly realized by changing the morphology, especially the grain sizes of the soft and hard phases.

The Ga addition may affect the average grain size of $\alpha$-Fe in the following ways: (1) A Ga-containing or Ga-rich phase distributed at the grain-boundary regions may hinder the $\alpha$-Fe grains from growing. (2) Compared with the Ga-free alloy, the addition of too much Ga ($x=1.6-2.2$) will result in a higher volume fraction of $\alpha$-Fe. The higher the volume fraction of $\alpha$-Fe in the nanocomposite magnet, the larger the average grain size of $\alpha$-Fe.[6]

At relatively low annealing temperatures, though $\alpha$-Fe grains are small, the incomplete crystallization of the amorphous phase is obviously unfavorable for the magnetic properties of nanocomposite magnets. At relatively high annealing temperatures, the magnetic properties degrade due to an observable coarsening of both the soft grains and the hard grains (as shown in Fig. 5). Thus, the best magnetic properties are attained after annealing at 650 °C.

This work has been supported by the National Nature Science Foundation Committee of China (Grant Nos. 59725103 and 59831010), the U.S. NSF (Grant No. INT-9812082), and the Science and Technology Commissions of Shenyang and Liaoning. Two of the authors (J.P.L. and D.J.S.) are also supported by AFOSR (Grant No. F49126-98-1-0095).

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