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On the synthesis of intermetallic compounds containing a volatile component: $Ln_2Fe_{17-x}Sb_x$ (Ln=Nd, Sm)

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Abstract

Sb-substituted $Nd_2Fe_{17-x}Sb_x$ and $Sm_2Fe_{17-x}Sb_x$ materials were synthesized using a modified reduction-diffusion process with superfine Fe metal powder as starting material. Sb is a volatile element at high temperature and Sb-substituted intermetallic materials cannot be prepared using a conventional metallurgical method. The substitution of Sb in Nd_2Fe_{17} and Sm_2Fe_{17} enhances significantly the magnetic interaction between Fe atoms and improves their chemical stability, particularly for Sm_2Fe_{17}-related materials. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The discovery [1,2] of the rare earth permanent magnet $Nd_2Fe_{14}B$ stimulated great efforts to search for new rare earth–iron intermetallic compounds with promising magnetic properties. It is known that the Curie temperatures of rare earth iron binary phases are normally low so they cannot be used as permanent magnetic materials. The reason for the low Curie temperature originates from that part of the Fe moments in the compound interacting antiferromagnetically. To enhance the ferromagnetic interaction between Fe atoms, one could modify the Fe–Fe bond distances to optimized values, and this can be realized by introducing other elements into the interstitial sites or by partial substitution of other elements for iron. Significance progress in this respect is to introduce nitrogen or carbon atoms into the interstitial sites for Ln_2Fe_{17} materials, which improves their magnetic performance significantly [3,4]. A parallel effort is to partially replace the iron atoms by main group elements or other transition metal elements. Many elements, such as Al, Si, Ga, Ti, Zr, V, Cr, Mo and W, have been used to replace the Fe atoms in Ln_2Fe_{17} [5–7], and this has indeed been shown to have a considerable influence on the magnetic property of these materials. Nevertheless, as far as the substitution effect is concerned, it is interesting to study the substitution of other main group elements, such as Sn, Sb, Pb and Bi. These elements, however, have seldom been studied largely due to their low melting points and high volatility at high temperature. Conventional metallurgical synthesis, in general, requires a high temperature, so it cannot be used in the synthesis of materials containing volatile components. Recently, we developed a modified reduction-diffusion process in which superfine starting materials were employed, so that the reaction can proceed at relatively low temperatures [8–10]. In this paper, we report the synthesis of Sb-substituted $Ln_2Fe_{17-x}Sb_x$ (Ln=Nd and Sm) and the influence of the substitution on the magnetic properties.

2. Experimental

Starting from $Fe(NO_3)_3 \cdot 9H_2O$, superfine iron oxide powders were obtained using a polymer-network gel method [6–8]. The polymer-network gels were first treated at 120°C in vacuum for 3 to 5 h and then heated to 600°C in an oxygen atmosphere to convert the gels into superfine powders of iron oxides. A preliminary H_2 reduction treatment at 700°C was applied to reduce the iron oxides to

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the metallic state. The starting materials, i.e. Fe, rare earth oxides (2 atm% excess), Sb powder (50 atm% excess) and CaH_2 (50% excess), were thoroughly mixed in an argon-filled glove box and transferred into stainless steel crucibles. The reduction-diffusion reactions were carried out at 950°C for 3 h under purified argon. After air quenching, the alloys were obtained by washing the product several times with distilled water and acetone.

Chemical analysis of the product was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The morphology of the samples was examined with an AMRAY-1910FE field emission scanning electron microscope (FESEM). X-ray powder diffraction patterns were recorded with a Rigaku D/Max-2000 diffractometer with Cu Kα radiation. The Curie temperatures were measured with a Faraday balance.

3. Results and discussion

To synthesize highly volatile element substituted intermetallic compounds successfully, one has to reduce the reaction temperature. For a reduction-diffusion reaction, it is known that the free energy change ($-\Delta G$) is larger at lower temperature. This means that the reaction has a larger driving force at lower temperature [11]. However, the reduction-diffusion reaction has to be carried out at high temperature because the diffusion of the species is slow. One way of reducing the kinetic barrier is to use small particulate starting materials. To ensure effective reduction at low temperature, we employed superfine iron metal powders as starting material. In our experience, the particle size of rare earth oxides and antimony does not influence the reaction and, therefore, commercial reagents were used in the reaction. By using these starting materials, the reduction-diffusion reaction can proceed at relatively low temperature (950°C) in a short time (3 h). Although many efforts have been made to optimize the reaction process, a considerable amount of antimony was lost during the reaction. The compositions of the products were, therefore, established using chemical analysis.

The polymer-gel method is a suitable way to prepare superfine iron powders, in which the particle size of the iron powder can be controlled by chemical processes, i.e. the concentration of the solution and the temperature of the treatment. Starting from superfine iron powders, we successfully prepared two systems, $Nd_2Fe_{17-x}Sb_x$ and $Sm_2Fe_{17-x}Sb_x$, at 950°C. Fig. 1 shows FESEM images of the iron metal powder and the two typical products, $Nd_2Fe_{16.5}Sb_{0.5}$ and $Sm_2Fe_{16}Sb$. The particle size of the iron metal powder is about 300 nm and, after the reaction, the particle size increased to about 5 μm for both $Nd_2Fe_{16.5}Sb_{0.5}$ and $Sm_2Fe_{16}Sb$.

Fig. 2 shows the X-ray powder diffraction patterns of the samples in the $Nd_2Fe_{17-x}Sb_x$ system, where the marked peak at about 44.5° originates from α-Fe and the

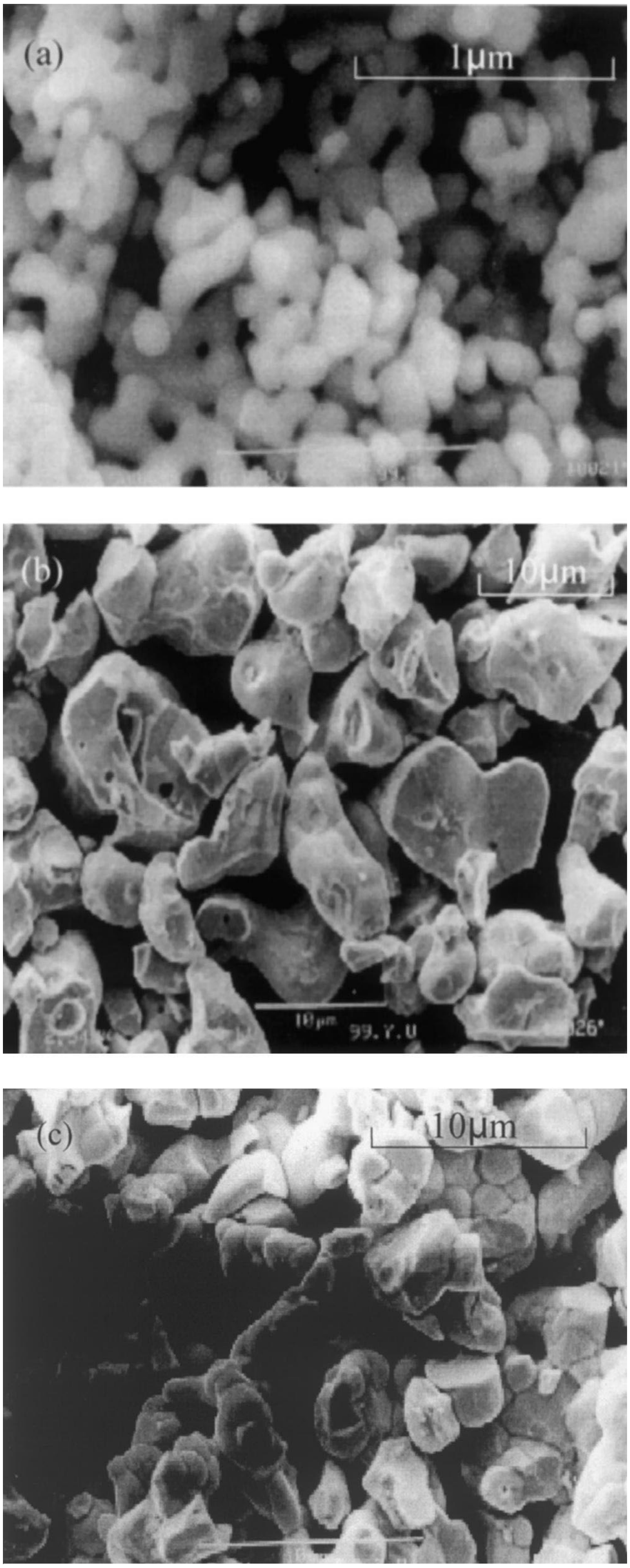

Fig. 1. FESEM images of (a) superfine Fe metal powder, (b) $Nd_2Fe_{16.5}Sb_{0.5}$ and (c) $Sm_2Fe_{16}Sb$.

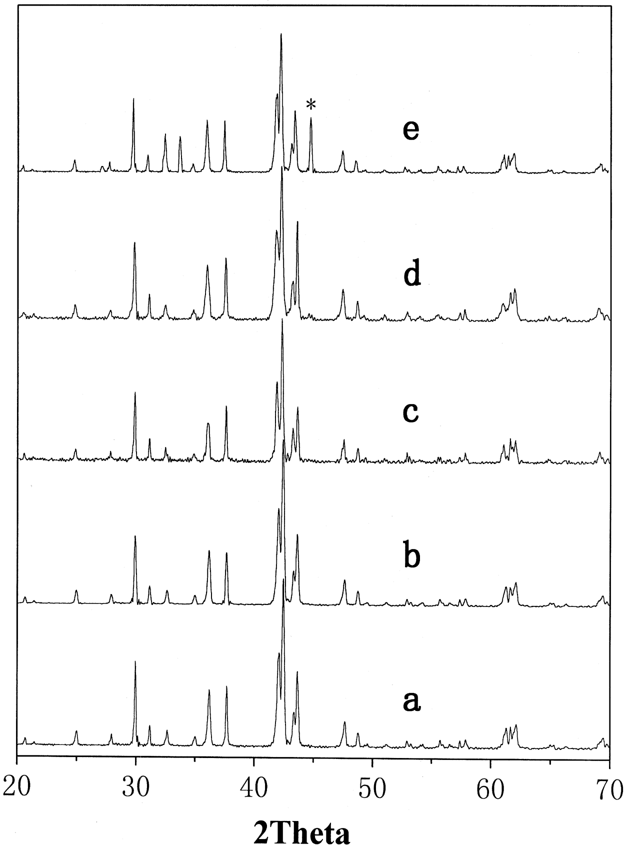

Fig. 2. X-ray powder diffraction pattern of $Nd_2Fe_{17-x}Sb_x$: (a) $x=0$, (b) $x=0.25$, (c) $x=0.5$, (d) $x=0.75$ and (e) $x=1.0$; the marked reflection originates from α-Fe.

rest of the reflections are all from the trigonal $Nd_2Fe_{17-x}Sb_x$ phase. A systematic synthetic study reveals that the maximum substitution of Sb in $Nd_2Fe_{17-x}Sb_x$ is about $x=0.75$. Further increase of the Sb content results in the appearance of α-Fe in the products and, below this value ($x=0.75$), single-phase products can be obtained. Presently, we do not know the reason for the appearance of α-Fe in the high-Sb-substituted samples, but it indicates that the reaction did not proceed appropriately. Therefore, this can be used as an indication of the substitution limit of these systems. It was also found that excess Nd_2O_3 is of importance in compensating for the possible evaporation loss of neodymium; it actually suppresses α-Fe and other impurity phases in the products. The X-ray powder diffraction peaks of the products are sharp and well defined, indicating that the products have satisfactory crystalline integrity.

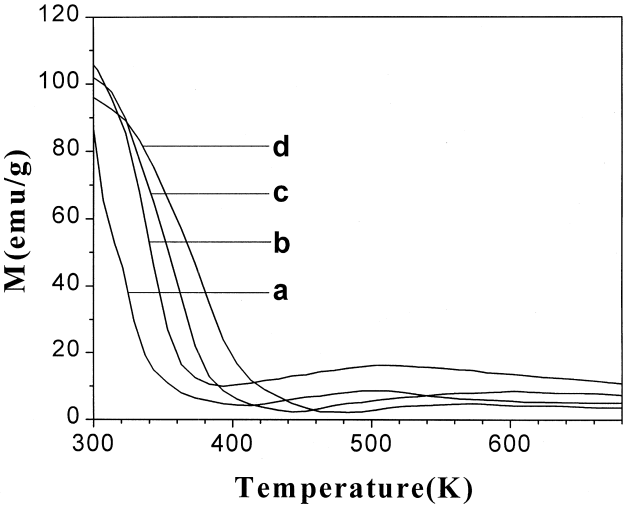

Fig. 3. Temperature dependence of the magnetization of $Nd_2Fe_{17-x}Sb_x$: (a) $x=0$, (b) $x=0.25$, (c) $x=0.5$ and (d) $x=0.75$.

As shown in Table 1, the cell volume of the $Nd_2Fe_{17-x}Sb_x$ system increases gradually with Sb content. Owing to the narrow solid solution range in this system, the change of the unit cell is small and the largest volume expansion is only about 1.35% for $Nd_2Fe_{16.25}Sb_{0.75}$. However, a significant increase of the Curie temperature was observed. Fig. 3 shows the temperature dependence of the magnetization for the $Nd_2Fe_{17-x}Sb_x$ system. It can be seen that the Curie temperature increases from 348 K for Nd_2Fe_{17} to about 421 K for $Nd_2Fe_{16.25}Sb_{0.75}$ and, at the same time, the saturation magnetization of the materials is reduced slightly.

Sm_2Fe_{17} is a very reactive material and can easily be oxidized to Sm_2O_3 and α-Fe in the presence of oxygen or water. In addition, Sm is one of the most volatile elements in the series of rare earth elements. The preparation of a single-phase product of Sm_2Fe_{17} was, therefore, a challenge for both metallurgical and chemical synthesis. In the

Table 1
Structural and magnetic parameters of $Nd_2Fe_{17-x}Sb_x$ and $Sm_2Fe_{17-x}Sb_x$

Sample	a (nm)	c (nm)	V (nm^3)	$\Delta V/V$ (%)	T_C (K)	M_s (emu/g)
Nd_2Fe_{17}	0.8586(9)	1.2452(1)	0.7950		348	116.9
$Nd_2Fe_{16.75}Sb_{0.25}$	0.8604(1)	1.2452(1)	0.7983	0.42	365	111.8
$Nd_2Fe_{16.5}Sb_{0.5}$	0.8624(8)	1.2453(7)	0.8021	0.89	391	105.9
$Nd_2Fe_{16.25}Sb_{0.75}$	0.8644(4)	1.2456(1)	0.8058	1.36	421	100.4
Sm_2Fe_{17}	0.8605(5)	1.2378(1)	0.7937		389	110.6
$Sm_2Fe_{16.7}Sb_{0.3}$	0.8616(8)	1.2407(4)	0.7976	0.49	439	108.7
$Sm_2Fe_{16.5}Sb_{0.5}$	0.8626(8)	1.2419(5)	0.8003	0.83	472	104.8
$Sm_2Fe_{16}Sb$	0.8640(6)	1.2436(2)	0.8040	1.30	499	98.9

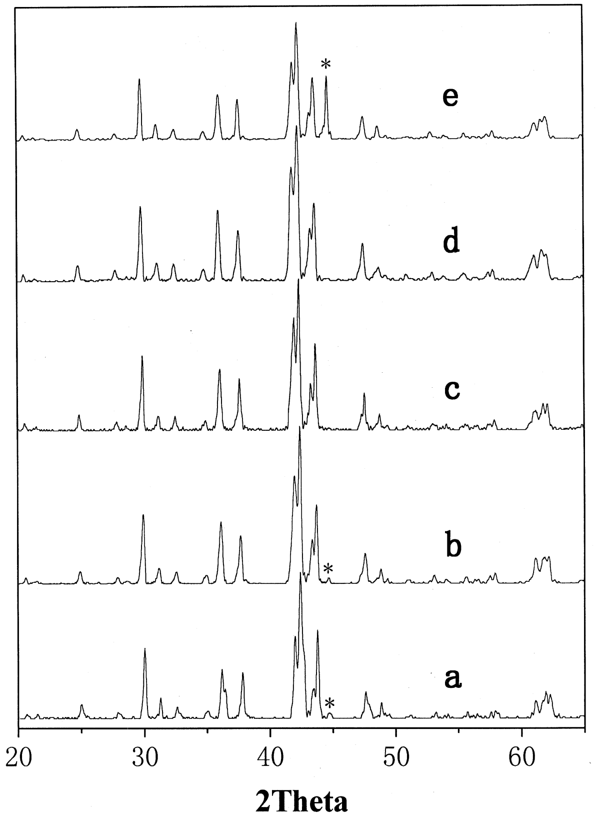

Fig. 4. X-ray powder diffraction pattern of $Sm_2Fe_{17-x}Sb_x$: (a) $x=0$, (b) $x=0.3$, (c) $x=0.5$, (d) $x=1.0$ and (e) $x=1.5$; the marked reflection originates from α-Fe.

metallurgical synthesis, all processes are carried out under an inert atmosphere and the major difficulty is to reduce the evaporation loss of Sm during the reaction. In the chemical synthesis, however, one has to remove the residual Ca and CaO in the products by water. So the Sm_2Fe_{17} samples obtained using the reduction-diffusion process often contain considerable amounts of α-Fe. In Fig. 4 we show the X-ray diffraction patterns for the $Sm_2Fe_{17-x}Sb_x$ system prepared with the reduction-diffusion reaction. A small amount of α-Fe is indeed present in Sm_2Fe_{17} and the low-Sb-substituted sample $Sm_2Fe_{16.7}Sb_{0.3}$. To our surprise, the $Sm_2Fe_{17-x}Sb_x$ samples containing a high Sb content form single-phase products and no α-Fe was detected in these materials. Furthermore, these samples show high chemical stability. They could be treated with water extensively without significant yield loss and remained almost unchanged after being exposed to air for several months. It is obvious that the substitution of Sb in Sm_2Fe_{17} improves the stability. This observation is remarkable since the handling of Sm_2Fe_{17} used to be a problem in the manufacturing process due to its high reactivity. A further increase of the Sb content ($x>1$) results in the reappearance of α-Fe (Fig. 4e), so we believe that the solubility of Sb in the $Sm_2Fe_{17-x}Sb_x$ solid solution range is also small.

Fig. 5 shows the temperature dependence of the magnetization of $Sm_2Fe_{17-x}Sb_x$. It can be seen that the magnetic interaction is greatly enhanced by Sb substitution, although the substitution level is very limited. The Curie temperature increases significantly from about 390 K for the binary compound Sm_2Fe_{17} to about 500 K for $Sm_2Fe_{16}Sb$. The saturated magnetization remains almost unchanged by Sb substitution.

Assuming that the Sb atoms mainly occupy the Fe sites, Sb substitution may influence the distances between the Fe atoms in Ln_2Fe_{17} materials. As far as the atomic radius is concerned, Sb substitution should lead to expansion of the unit cell, since the atomic radius of Sb (1.61 Å) is larger than that of Fe (1.28 Å). This is in agreement with the $\Delta V/V$ data listed in Table 1.

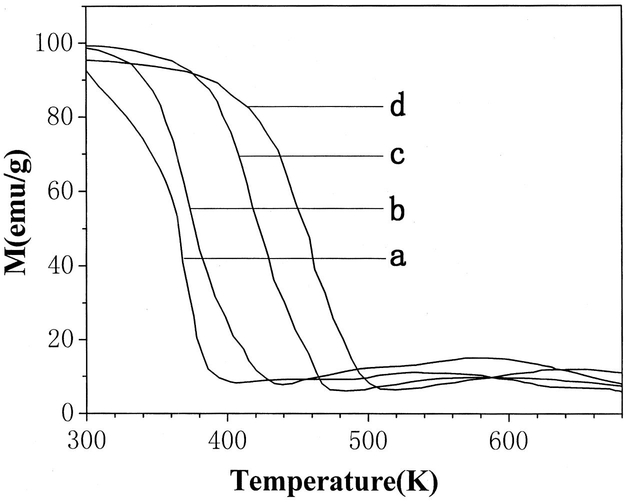

Fig. 5. Temperature dependence of the magnetization of $Sm_2Fe_{17-x}Sb_x$: (a) $x=0$, (b) $x=0.3$, (c) $x=0.5$ and (d) $x=1.0$.

Acknowledgements

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