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Preparation of Nd–Fe–B based magnetic materials by soft chemistry and reduction-diffusion process

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Abstract

Starting from superfine precursors, Nd–Fe–B based magnetic materials, $Nd_2Fe_{14}B$ and $Nd_2Fe_{12}Co_2B$, have been prepared by reduction-diffusion reaction at relative low temperature. The boride precursors used in the reactions, i.e., $Co_{2.0}B_{1.2}$ and $Fe_{1.0}B_{0.25}$, were obtained from the reduction of $CoCl_2$ and $FeSO_4$ with $NaBH_4$ in aqueous solution at room temperature. The other precursors, Nd_2O_3 and Fe_2O_3 were obtained by a polymer network gel process. The obtained $Nd_2Fe_{14}B$ and $Nd_2Fe_{12}Co_2B$ materials are fine crystalline powders which show quite strong magnetic anisotropy. The particle sizes of these materials can be controlled to about a few microns without using mechanical milling processes.

Keywords: Nd–Fe–B based magnetic materials; Reduction-diffusion process

1. Introduction

Recently we have been developing a novel route to prepare rare earth and transition metal alloys by utilizing both soft chemistry and reduction-diffusion (R-D) processes. The basic idea of this preparation strategy is that, to avoid the use of mechanical milling, superfine precursors, such as rare earth oxides and transition metals, were used in the reduction-diffusion reactions. Employment of the superfine precursors in R-D reaction can significantly reduce the reaction temperature and the reaction time, which in turn prevent the growth of the crystalline particles of the final alloys. This approach has been proved quite successful in producing R_2Fe_{17} [1] and $RFe_{10}M_2$ [2], where the R is the rare earth metal and M is the early transition metal. Small particulate crystalline powders (~6 μm in diameter) of these alloys were obtained with this method without use of mechanical milling. To further verify the generality of this preparation method, we report here the synthesis of Nd–Fe–B based alloys with this process.

For synthesis of Nd–Fe–B based alloys with this process, superfine Co–B and Fe-B precursors are needed. These transition metal borides can be prepared by melting the elemental materials at high temperature [3]. It has been known that some special preparation routes can lead to the amorphous alloys, such as liquid–quench technique [5]. Another approach to these borides is to reduce the transition metal ions by alkali-metal borohydride [4–8] in aqueous solution. This process leads directly to small particulate alloys and, in some cases, to amorphous alloys.

2. Experimental

The chemical reduction of transition-metal ions by use of alkali-metal borohydride in aqueous solution have recently been studied extensively [4–8]. Although the reaction mechanism has not yet been fully understood, the amorphous nature of the alloys has been established by X-ray diffraction and Mössbauer spectroscopy. Following up the process in Refs. [5–8], an aqueous solution of 3.0 g (0.023 mol) $CoCl_2$ was added slowly into a 500 ml round flask which contains 1.75 g $NaBH_4$ (0.046 mol) and 300 ml H_2O with vigorous stirring under nitrogen atmosphere. With addition of $COCl_2$, black precipitation was formed together with evolution of hydrogen gas. After standing for a few hours, the black powder was filtered and washed in water and then in acetone. Chemical analysis carried out with inductively coupled plasma atomic emission spectroscopy (ICP) shows that the composition of alloy is $Co_{2.0}B_{1.2}$.

Superfine Fe–B alloy was obtained with a similar process as $Co_{2.0}B_{1.2}$, from the reaction of $FeSO_4$ and $NaBH_4$ in aqueous solution. The produced Fe–B alloy is an air sensitive black powder. It turns reddish after a few

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minutes exposure to air. The composition of the alloy, obtained by ICP chemical analysis, is $Fe_{1.0}B_{0.25}$.

Nd_2O_3 and $Fe(NO_3)_3 \cdot 9H_2O$ were used as the starting materials for the synthesis of superfine neodymium oxide and iron oxide with a polymer-network gel method [1,9,10]. The gels obtained were first treated at 250 °C for 3 h in an oxygen atmosphere to remove all of the organic and other volatile components. The temperature was, then, increased to 500 °C to convert the gels into oxides. A preliminary reduction treatment at 700 °C under $Ar–H_2$ for 2 h, was applied to reduce Fe_2O_3 to the metallic states.

$Co_2B_{1.2}$, $Fe_{1.0}B_{0.25}$ and iron metal with the stoichiometric ratios as in $Nd_2Fe_{12}Co_2B$ and $Nd_2Fe_{14}B$ were used in the reactions. For compensating possible evaporating loss of neodymium metal during the reactions, 2 at% excess neodymium oxide was employed in the starting materials. In an argon filled glove box the precursors were mixed with excess calcium hydride and transferred into a stainless steel crucible. The reduction-diffusion reaction was carried out at 930 °C for 2 to 4 h under purified argon. After quenching to room temperature the small particulate alloys of $Nd_2Fe_{12}Co_2B$ and $Nd_2Fe_{14}B$ were recovered by washing the product with dilute acetic acid and subsequently with water.

The Curie temperatures were determined with a thermomagnetic balance. Magnetization curves were measured with a vibrating sample magnetometer on the alloys which had been oriented in epoxy resin by applying a magnetic field of 10 kOe. Microstructure of the oxide precursors and of the obtained alloy were examined with an AMRAY-1910FE field emission scanning electron microscope (FESEM) and a CX200 transmission electron microscope (TEM). X-ray powder diffraction patterns were recorded with a Rigaku D/Max-2000 diffractometer with CuKα radiation.

3. Results and discussion

Reduction of transition metal ions in aqueous solution by use of alkali-metal borohydride was described by Schlesinger [11] many years ago and extensively studied recently [4–8]. Borohydride ion in aqueous solution is a good reductant. It acts as a source of hydride ions which reduce the transition metal ions to their lower oxidation states or to the metallic states. If this reduction reaction is carried out at a temperature below the glass transition temperature (T_g) of the forming alloys, amorphous materials are produced. By using KBH_4 as a reductant, Wonterghem [4] has examined the reduction reactions of mixed ions of iron and cobalt, of iron and nickel and of iron along. They found that, to stabilize amorphous iron alloys, another element, such as cobalt or nickel, must be present. More recent studies [5–8] indicated that the composition of the obtained products depended strongly on the reaction conditions and on how the reaction was proceeded. Nevertheless, the amorphous Fe–B alloys with boron content in the 32-37-at% have been obtained by addition of an iron-salt solution to borohydride solution [5].

We have re-examined the reaction of $CoCl_2$ and of $FeSO_4$ by $NaBH_4$ in aqueous solution. For the cobalt case, the X-ray diffraction pattern of the product appears as a broad band peaking at about $2\theta=46°$, indicating the amorphous nature of the alloy (Fig. 1a). After annealing at 400 °C for 4 h, the crystalline Co_2B alloy is formed (Fig. 1b). As for the iron case, the boron content of the prepared alloy is lower than that was reported in Ref. [4], although the phases, identified in both cases identically crystallize with the α-Fe structure (Fig. 1c). The reason of this composition difference is not clear at the moment.

The amorphous nature of the Co_2B alloy can be also visualized from the TEM image in Fig. 2a. The particles are small and highly dispersed, which makes this alloy a very reactive precursor. Fig. 2b shows a FESEM image of the iron powder prepared from the polymer network gel process. The particles are uniformly distributed with a mean size of about 0.5 μm. The Nd_2O_3 precursor, obtained with a similar process, shows a similar size distribution with a mean size of about 100 nm. By using these superfine precursors, the reduction-diffusion reaction can occur and proceed to completion at relatively low temperature. For both $Nd_2Fe_{12}Co_2B$ and $Nd_2Fe_{14}B$, the reactions were carried out at 930 °C for 2 h. As a comparison, for synthesis of $Nd_2Fe_{14}B$ from coarser starting materials, the reaction must be carried out at 1200 °C [12].

The products obtained from the reactions are mixtures containing the produced Nd–Fe–B based alloys, CaO, unreacted calcium metal and small amount of a boron rich alloy $NdFe_4B_4$. Leaching process with dilute acetic acid

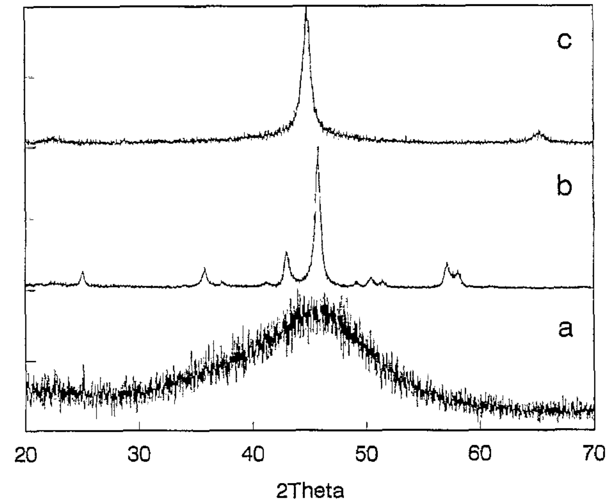

Fig. 1. X-ray diffraction patterns of (a) the amorphous $Co_{2.0}B_{1.2}$ alloy obtained from $NaBH_4$ reduction, (b) the $Co_{2.0}B_{1.2}$ alloy after annealing at 400 °C for 4 h and (c) the $Fe_{1.0}B_{0.25}$ alloy obtained from $NaBH_4$ reduction.

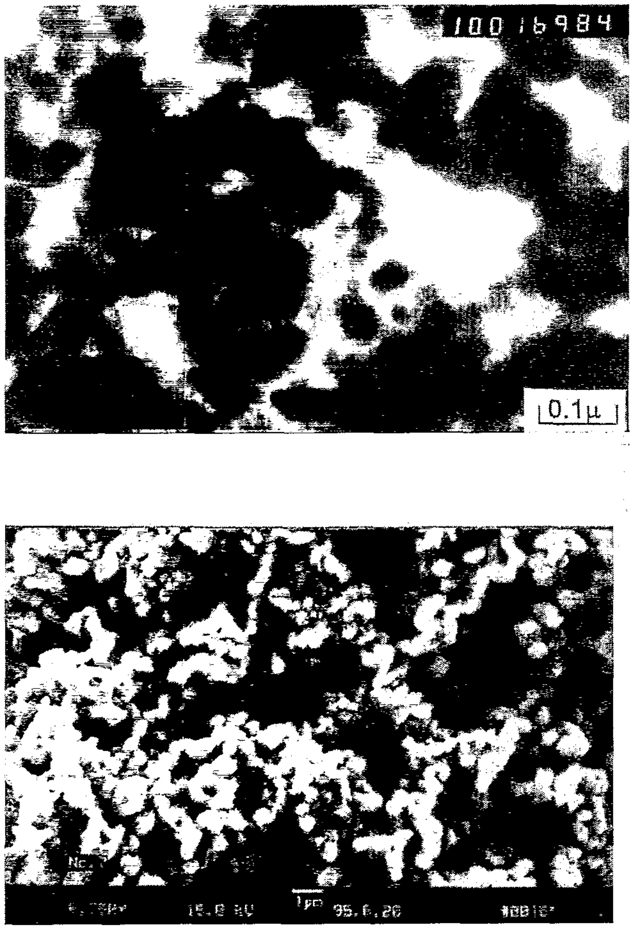

Fig. 2. (a) TEM image of the amorphous $Co_{2.0}B_{1.2}$ alloy, (b) FESEM image of the Fe obtained by using the polymer–network gel process.

and water can remove calcium oxide and calcium metal in the product, resulting in the relatively pure alloys $Nd_2Fe_{12}Co_2B$ and $Nd_2Fe_{14}B$. Fig. 3 shows the X-ray diffraction patterns of the prepared alloys. A simulated pattern of $Nd_2Fe_{14}B$ is also included. In comparison with the simulated pattern, small amount of $NdFe_4B_4$ can be identified from the diffraction pattern of $Nd_2Fe_{12}Co_2B$. It is known that the existence of this boron-rich alloy and a neodymium rich phase are of importance in producing high-performance Nd–Fe–B based magnets [13]. We have not identified the presence of the neodymium rich phase in the products. It is known that the neodymium rich phase is not stable in acid and water and may possibly be removed during the leaching process. The $Nd_2Fe_{14}B$ alloy, in this particular case, is a single phase and neither $Nd_2Fe_4B_4$ nor neodymium rich phase is identified in the x-ray diffraction pattern (Fig. 3d). The lattice parameters of $Nd_2Fe_{12}Co_2B$ was refined to $a=8.800(3)$ Å and $c=12.180(5)$ Å which is compatible to the values reported the Ref. [14] for $Nd_2Fe_{14}B$.

Fig. 3c presents the diffraction pattern of $Nd_2Fe_{12}Co_2B$ in a magnetic field. $Nd_2Fe_{12}Co_2B$ has uniaxial magnetic anisotropy along c-axis, which should be aligned along the magnetic field. This alignment gives rise to a strong preferred orientation in the diffraction pattern. As compared with the diffraction pattern in absence of magnetic field (Fig. 3b), the preferred orientation is significant in the magnetic field. Many reflections with small l-index are absent or present with very weak intensities. This phenomenon implies that particles of the alloy are singly crystallized and are not present in the aggregated state, so they can rotate freely in the magnetic field.

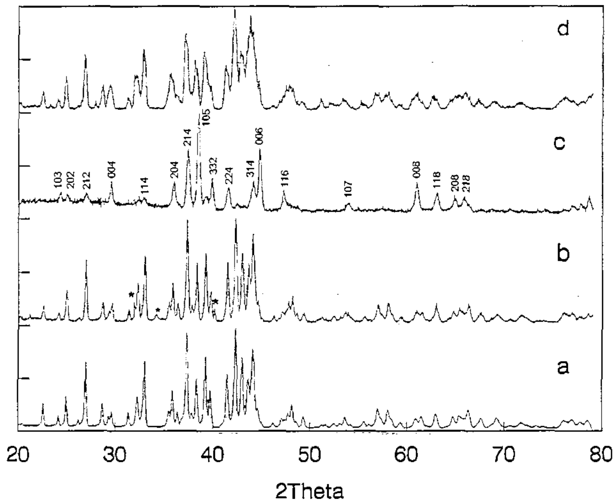

Fig. 3. X-ray diffraction patterns of the Nd–Fe–B based alloys, (a) simulated diffraction pattern for $Nd_2Fe_{14}B$, (b) diffraction pattern of $Nd_2Fe_{12}Co_2B$, the * indicates the reflections from $NdFe_4B_4$, (c) diffraction pattern of $Nd_2Fe_{12}Co_2B$ in magnetic field and (d) diffraction pattern of $Nd_2Fe_{14}B$.

Single crystallization of particles in these alloys was further confirmed by TEM images. Fig. 4 shows a TEM image of $Nd_2Fe_{12}Co_2B$ alloy. The particles of this alloy are formed as small and square-shaped single crystals. Furthermore, it was observed that, in most cases, the particle sizes of the final alloys are similar to those of the iron precursor (Fig. 2a). This observation may reveal that the alloys are formed through diffusion of rare earth atoms

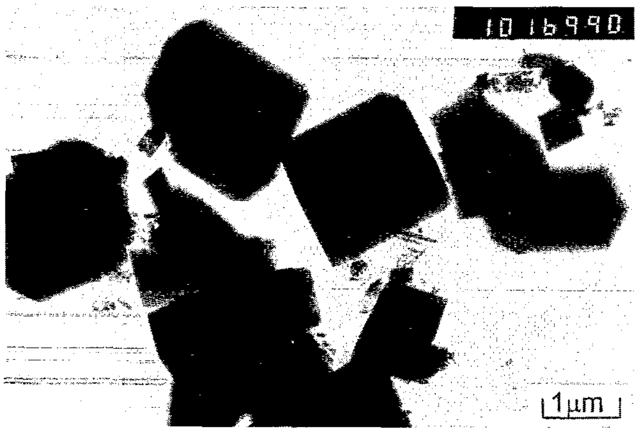

Fig. 4. TEM image of the $Nd_2Fe_{12}Co_2B$ alloy.

into iron particles, i.e., the particle sizes of the alloys is, therefore, controlled mainly by the iron precursor instead of the rare earth oxides. Moreover the singly-crystalline particles only exist in the samples prepared at relative low temperature. If the reaction is carried out at higher temperature, aggregation of the particles appears. This leads to the isotropic magnetic property of the materials. In fact we did observe an isotropic magnetic behavior for the $NdFe_{10}Mo_2N$ alloy prepared above 1100 °C. But this isotropic magnetic behavior can be removed by gentle hand-milling treatment.

The singly-crystalline particles can be obtained by an extensively mechanical milling for the samples prepared by the melting process. Meanwhile, extensive milling may lead to degradation of the crystalline integrity, which in turn degrades the magnetic property of the materials. With mechanical alloying method, very small crystalline particles can be obtained from annealing the amorphous alloys at low temperatures. Within these small crystalline particles, multiple twins or domains are present, resulting in an isotropic magnetic behavior. However, by using the soft chemistry and the reduction-diffusion process proposed above, well crystalline, anisotropic particles with small particle sizes can be obtained without use of mechanical milling.

A preliminary study of the magnetic properties has been carried out for the $Nd_2Fe_{12}Co_2B$ and $Nd_2Fe_{14}B$ alloys. Fig. 5 shows the temperature dependence of the magnetization for these two alloys. The Curie temperature is about 300 °C for the $Nd_2Fe_{14}B$ and about 400 °C for the $Nd_2Fe_{12}Co_2B$. It has been known that the substitution of Fe by Co can significantly increase the Curie temperature of Nd-Fe-B materials. A 100 °C increase has been obtained in our case by the replacement of two Fe atoms with Co per formula unit. This agrees well with a similar alloy prepared by another metallurgy method [15]. A typical hysteresis loop of a cylindrical shaped sample of $Nd_2Fe_{14}B$ is shown in Fig. 6. The coercivity is about 6.0 kOe for this sample. Most of the samples obtained with our method appeared to have the coercivity between 3.0 to 6.0 kOe. It should be noted that the permanent magnetic properties, such as coercivity and remanence, depend on many processing factors, which in this case have not yet been optimized.

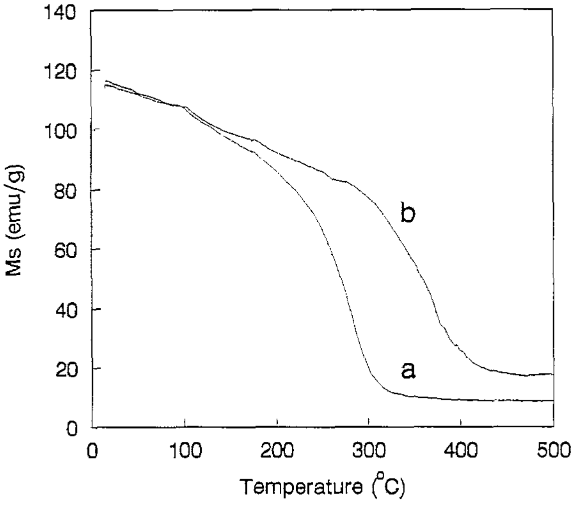

Fig. 5. The temperature dependence of the magnetization for (a) $Nd_2Fe_{14}B$ and (b) $Nd_2Fe_{12}Co_2B$ alloys.

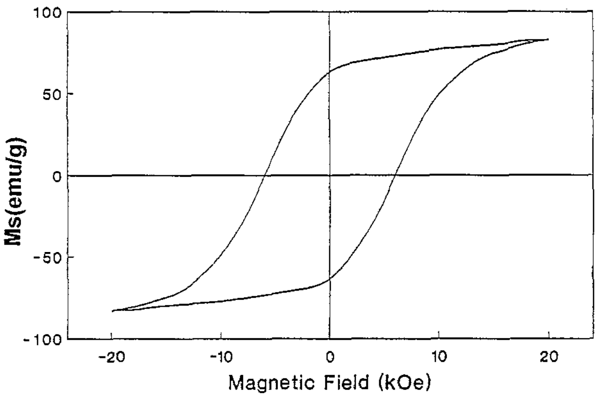

Fig. 6. Hysteresis loop of $Nd_2Fe_{14}B$ alloy.

In conclusion, the magnetic alloys of $Nd_2Fe_{12}Co_2B$ and $Nd_2Fe_{14}B$ have been synthesized by reduction-diffusion processes with superfine Fe–B and Co–B, iron metal and Nd_2O_3 as the starting materials. The produced alloys are crystalline powders with small particle sizes and with anisotropic magnetic properties. This preparation route may have potential application in the synthesis of permanent magnetic materials.

Acknowledgments

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