Synthesis of NdFe$_{10}$Mo$_2$ by a Reduction−Diffusion Process

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Considerable interest has been stimulated for ternary intermetallic compounds with the ThMn$_{12}$ structure since the discovery of a dramatic increase of the Curie temperature and of a switch to the uniaxial magnetic anisotropy by nitrogenation, as found in NdFe$_{11}$TiN.[1,2] Although the remarkable intrinsic magnetic properties of these nitrides provide possibilities for their actual use as permanent magnetic materials, the extrinsic magnetic properties, such as remanence and coercivity, from the application point of view, need to be further modified. Among the many factors that may influence the extrinsic properties, the grain size of the magnetic materials is very important. In the conventional preparation methods, such as melting at high temperature, the control of the particle size is realized mostly by mechanical milling. However this will normally cause considerable degradation of the crystalline integrity and consequently affect the extrinsic magnetic properties.

On the other hand, there is a growing trend in materials chemistry to use, so called, soft chemistry routes to synthesize superfine materials,[3] especially oxides. With these preparation methods, different forms of materials, such as films, nanoscale powder, ceramics, and glasses, were obtained at relevant low temperature. We have carried out the synthesis of NdFe$_{10}$Mo$_2$ by using a reduction−diffusion process, in which the superfine rare-earth and transition-metal oxides obtained by soft chemistry were used as precursors.

Nd$_2$O$_3$, Fe(NO$_3$)$_3$·9H$_2$O, and (NH$_4$)$_2$MoO$_4$ were used as the starting materials for the synthesis of superfine rare-earth and transition-metal oxide precursors. Employing the polymer-network gel process,[4,5] a mixed rare-earth and transition-metal oxides gel was obtained with a stoichiometric ratio as in NdFe$_{10}$Mo$_2$. In a tube furnace the gel was 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 gel into the oxides. A prereduction treatment, at 700 °C under Ar−H$_2$ for 4 h, was further applied to the precursors to reduce the transition-metal oxides to their metallic state. In an
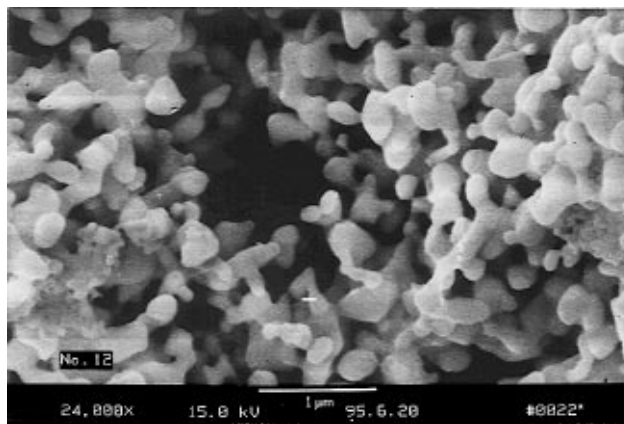

Figure 1. FESEM image of the oxide precursor prepared by polymer-network gel method.

argon-filled glovebox the sample was then mixed with excess calcium hydride and transferred into a stainless steel crucible. The reduction−diffusion reaction was carried out below 1010 °C for 4−8 h under purified argon. After quenching to room temperature the NdFe$_{10}$Mo$_2$, the alloy was recovered by washing the product with dilute acetic acid and subsequently with water. Chemical analysis of the product shows Nd 15.9 (16.12), Fe 61.7 (62.43), Mo 21.0 (21.45), and Ca 0.8 (in weight percent).

The microstructures of the oxide precursors and of the obtained alloy were 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 chemical analysis was carried out on a inductively coupled plasma atomic emission spectrometer (ICP).

The particle size of the oxide precursor is crucial in controlling the particle size of the final alloys. By varying the concentration of the rare-earth and transition-metal ions in the polymer-network gel, the particle size of the oxide precursor can be controlled in a wide range from about 10 nm to about several hundred nanometers. Figure 1 shows a morphological view of the oxide precursor prepared with the polymer-network gel method. One can see that the particle sizes of the oxide precursor are narrowly distributed with a mean value of about 200 nm. It was revealed by X-ray diffraction that this oxide precursor is not a single-phase precursor but instead a mixture of the binary and ternary oxides, namely, Fe$_2$O$_3$, NdFeO$_3$, and Fe$_2$(MoO$_4$)$_3$. Further treatment under Ar−H$_2$ at 700 °C leads to the reduction of the transition-metal oxides to their metallic state. In this particular case, the detectable known phases in X-ray diffraction pattern are α-Fe and Nd$_2$O$_3$. Another sharp peak and a broad band are located at about $2\theta = 37.88°$ and $40−46°$, respectively. We could not definitely identify these peaks, but they may relate to some binary Fe−Mo alloys. The reaction under Ar−H$_2$ atmosphere at 700 °C may be expressed as

$$23Fe_2O_3 + 6NdFeO_3 + 4Fe_2(MoO_4)_3 \xrightarrow[700\ °C]{Ar−H_2}$$
$$72Fe(Mo)\ alloys + 3Nd_2O_3 + 114H_2O$$
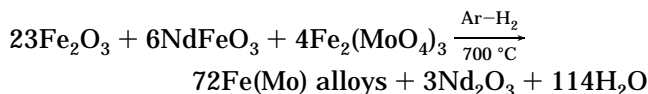
The particle size of the materials shows considerable

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2546 *Chem. Mater., Vol. 8, No. 11, 1996*

Communications
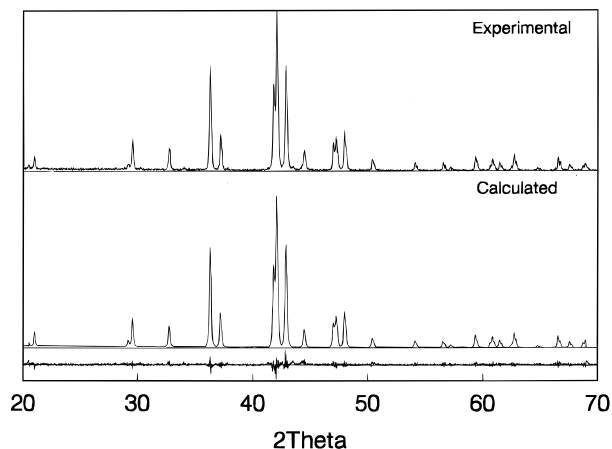
Figure 2. X-ray diffraction pattern of $NdFe_{10}Mo_2$ alloy.

Figure 3. FESEM image of $NdFe_{10}Mo_2$ alloy.

segregation during this treatment, from about 200 nm for the oxides to about 1 μm for the α-Fe.

The reduction of Nd_2O_3 and the formation of $NdFe_{10}Mo_2$ occur when the precursors were further treated with CaH_2 at 1010 °C for 4 h. We have examined the required reaction temperature to obtain $NdFe_{10}Mo_2$ alloy from the oxide precursors with different particle sizes. For the oxide precursors with a mean size of 200 nm, the reduction—diffusion reaction occurs and goes to completion at a temperature lower than 1010 °C. For the smaller particle size precursors (about 50 nm), the reduction—diffusion reaction may be carried out at a lower temperature (about 960 °C). In comparison with the conventional reduction—diffusion process, for instance for the $Nd_2Fe_{14}B$, the reaction has to be carried out at 1200 °C for a longer period of time. There are certainly many advantages in using a precursor of smaller particle size in the reduction—diffusion reaction, in term of acceleration of the reaction. Meanwhile, further reducing the particle size of the precursor may increase the difficulties of the later treatment. In particular, the corrosion of the alloy will be much more serious for the smaller particles when the product is washed with acetic acid. Presently, therefore, the oxide precursors we used, in most cases, are preferably in a submicron level.

The product of the reduction—diffusion reaction contains $NdFe_{10}Mo_2$, CaO, and a small amount of excess calcium metal. After removing CaO and calcium metal by dilute acetic acid and water, $NdFe_{10}Mo_2$ phase was obtained. In Figure 2 we show the X-ray powder diffraction patterns of the $NdFe_{10}Mo_2$ alloy. To verify the purity of the product, the whole diffraction pattern was refined with the Rietveld analysis starting from a structural parameter set of $YFe_{11}Ti$.[2] Although the residual of the refinement maintains at a comparatively high level ($R = 0.13$), the fitting of the reflections is fairly satisfactory, and furthermore no concrete evidence of the impurity phases were identified even from the difference pattern. The refinement of the lattice parameters leads to $a = 8.6173(2)$ Å and $c = 4.8188(2)$ Å, which are close to the $a = 8.618$ Å and $c = 4.807$ Å reported in ref 6. On the other hand, the chemical analysis seems to reveal the presence of a small amount of impurities (about 1.4%) in the product. Actually considerable caution should be taken in using this small
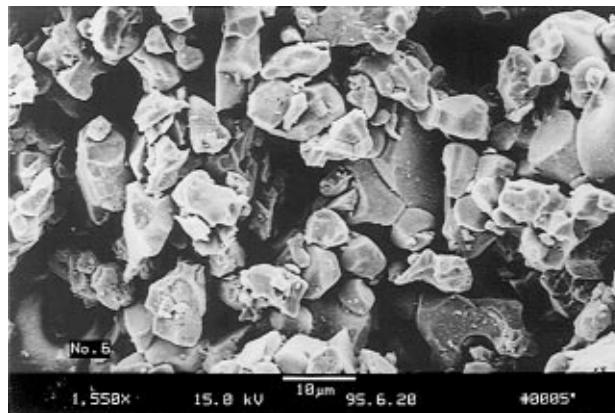
value, since it may probably reach to the limitation of the analytical method. However, the existence of about 0.8% of calcium in the product is an obvious indication that the impurity is mainly the unremoved calcium oxide or hydroxide. We have examined the existence of the oxygen in the $NdFe_{10}Mo_2$ alloy by X-ray photoelectron spectroscopy (XPS) and found that there certainly exists some amount of oxygen in the product. Nevertheless, from both X-ray diffraction and chemical analysis, it is certain that the impurity phases are contained at a very low level in the product.

It is known that α-Fe is a soft magnetic material and the suppression of α-Fe is very important in improving the extrinsic properties of the permanent magnetic alloys. There were many efforts to reduce the content of α-Fe in the rare-earth permanent magnetic alloys, including the use of excess rare-earth metal in the starting materials etc. In our case, however, a considerable pure $NdFe_{10}Mo_2$ product without α-Fe was obtained from the stoichiometric starting materials. The cleanness of this reaction may be related to the small particle size of the precursor and the low reaction temperature, at which the evaporative loss of the rare-earth metal is prevented.

Figure 3 shows a FESEM image of $NdFe_{10}Mo_2$ alloy. In comparison with the precursors, the particle size had increased, from about hundreds nanometers for the oxide precursor to about a few microns for the final alloy. This particle size can probably meet the needs of the technological applications for this magnetic materials. More importantly, since mechanical milling is no longer necessary, the crystalline integrity of the alloy is maintained. On the contrary, in some metallurgical methods reducing the particle size is realized mostly with mechanical milling. Under these circumstances, retaining both small particle size and crystalline integrity is quite difficult. Furthermore reasonable caution has to be exercised to prevent the alloys from oxidation in the whole process. In our preparation route, however, at most of the time we are dealing with stable materials such as oxides. The oxidation problem only needs to be considered at the last stage. Another advantage of the method is that the starting materials used are rare-earth and transition-metal oxides or salts instead of high-purity metals. This will definitely reduce the production cost and the consumption of energy.

A potential problem for this preparation process is the corrosion of the alloy during the washing. From our

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Communications

Chem. Mater., Vol. 8, No. 11, 1996 **2547**

experience, the neodymium alloys are quite resistant to dilute acid. For instance, with dilute acetic acid, no significant attack was observed for the $NdFe_{10}Mo_2$ when the particle size is about several microns. Corrosion of the smaller particles is a serious problem indeed, but it can still be handled with great care. But for the samarium alloys, such as Sm_2Fe_{17}, the corrosion becomes a real problem if acetic acid is employed during the washing. We observed the broadening of the reflection in the X-ray diffraction pattern after washing Sm_2Fe_{17} with dilute acetic acid. The decomposition into α-Fe and the samarium oxide is also evidenced by X-ray diffraction.

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