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High magnetic performance $NdFe_{10.5}Mo_{1.5}N_x$ prepared by mechanical alloying

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Spherical or nearly regular hexagonal Nd powders with the size of 20–150 nm, Fe powders with the size of 20–150 nm and Mo powders with the size of 80–100 nm were prepared by Argon and Hydrogen arc plasma. The nanostructural $NdFe_{10.5}Mo_{1.5}$ compound with $ThMn_{12}$-type structure have been formed after having been mechanically alloyed for 6–12 hours and crystallized at 700–850 °C under high purified Argon atmosphere. After having been nitrided at 400–500 °C for 2 hours, $NdFe_{10.5}Mo_{1.5}N_x$ nanopowders with $ThMn_{12}$-type structure can be obtained, which have excellent permanent magnetic properties such as iH_c within range of 360.4–716.2 kA/m (4528–8997 Oe), B_r within range of 0.6363–0.9831 T (6363–9831 Gs), $(BH)_{max}$ within range of 42.87–166.2 kJ/m^3 (5.386–20.88 MGOe).

1. Introduction

$NdFe_{10.5}Mo_{1.5}N_x$ with M = Ti, V, Mo, Si, Cr etc., have been recognized as suitable candidates for permanent magnet applications since their discovery in 1990 [1]. It has been reported the formation of a fine crystalline microstructure that shows high coercivities can be achieved using the mechanical alloying technique and solid state reaction by heat treatment [2, 3]. In this study, we report the $NdFe_{10.5}Mo_{1.5}N_x$ obtained by mechanical alloying, crystallizing and nitriding using element nanopowders.

2. Experiment

Nd, Fe and Mo Nanopowders were prepared by evaporation-concentration method using Argon and Hydrogen arc plasma. Mechanical alloying of $NdFe_{10.5}Mo_{1.5}$ powders was performed in a high-energy ball miller under a high-purified Argon atmosphere using these nanopowders. The mechanically alloyed powders were annealed at 700–850 °C for 30 min to form $ThMn_{12}$-type structure. After having been nitrided at 400–500 °C for 2 hours, $NdFe_{10.5}Mo_{1.5}N_x$ with the $ThMn_{12}$-type structure was obtained.

3. Results and discussions

Transmission electron microscope (TEM) images show the shapes of nanopowders (Fig. 1). Nd nanopowders are almost regular hexagons that are about 50 nm. Fe nanopowders are spherical with diameter ranging from 20 nm to 150 nm, mostly about 50 nm. Mo nanopowders are spherical also, with diameter ranging from 50 nm to 200 nm, mostly between 80 nm and 100 nm. High-resolution transmission electron microscope (HRTEM) image shows that Fe nanopowders have many twins that are 2–4 nm (Fig. 2). X-ray diffraction (XRD) patterns show that all the nanopowders appear the shape diffraction peaks, which show the characteristic of crystalline (Fig. 3).

Fig. 4 is XRD patterns of $NdFe_{10.5}Mo_{1.5}$ mixtures mechanically alloyed for different periods under a high-purified Argon atmosphere. No Brag peak can be seen except for the (110) peak of α-Fe. XRD patterns show the mechanically alloyed $NdFe_{10.5}Mo_{1.5}$ powders are composed of amorphous phase and nanostructural α-Fe. The width of the (110) peak of α-Fe is widened as the milling time is prolonged. The average grain size is estimated using Scherrer formula [4] (Table I). When the milling time is longer, the average grain size of α-Fe is finer. After mechanically alloyed for 12 hours, the average grain size of α-Fe is 3.7 nm, which is equal to the width of the twins (Fig. 2). This is so probably because when the nanopowders are milled and broken along the weak twin boundaries. As the grains become finer and finer, it becomes more difficult to break the α-Fe grains.

The relation between amorphous phase formation and milling time was investigated using HRTEM (Fig. 5). There is amorphous phase area with 1–2 nm width among nanopowders which have been mechanically alloyed for 1 hour. After having been mechanically alloyed for 3 hours, amorphous phase area with 2–4 nm width can be formed and the boundaries among nanopowders are indistinct. The width of amorphous

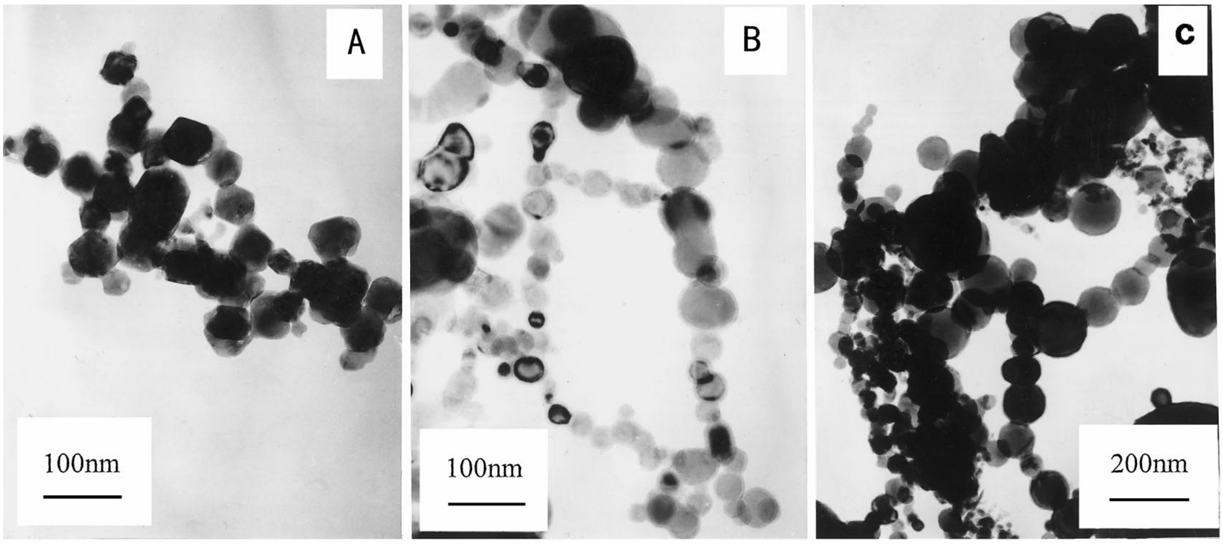


Figure 1 Micrographs of nanopowders (TEM). (a) Nd; (b) Fe; (c) Mo.

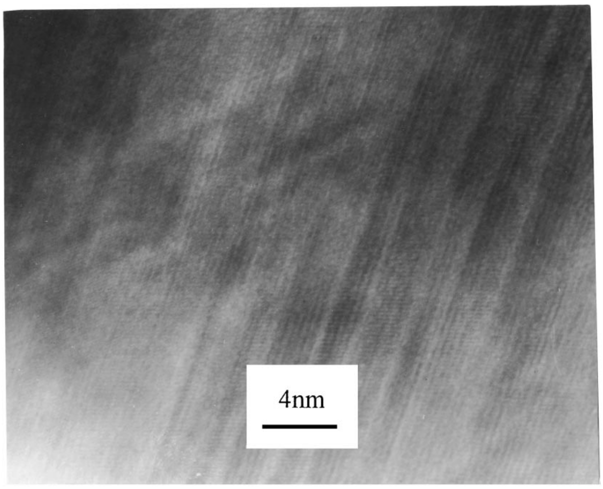


Figure 2 Twins of Fe nanopowders (HRTEM).

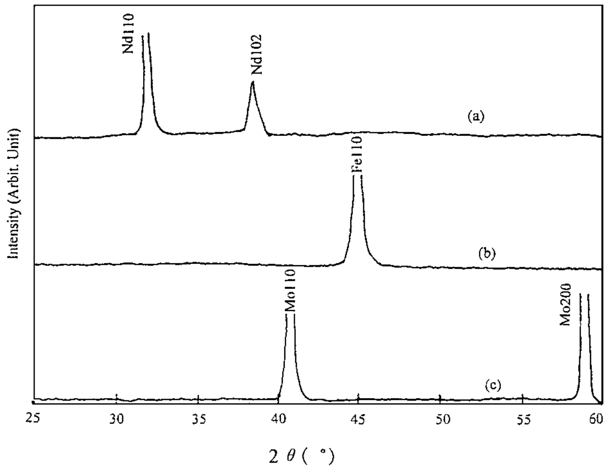


Figure 3 XRD patterns of nanopowders. (a) Nd nanopowders; (b) Fe nanopowders; (c) Mo nanopowders.

TABLE I The average grain size of α-Fe of mechanically alloyed $NdFe_{10.5}Mo_{1.5}$ alloys

Milling Time (hrs)	Average grain size (nm)
1	16.6
3	10.0
6	5.0
9	4.2
12	3.7

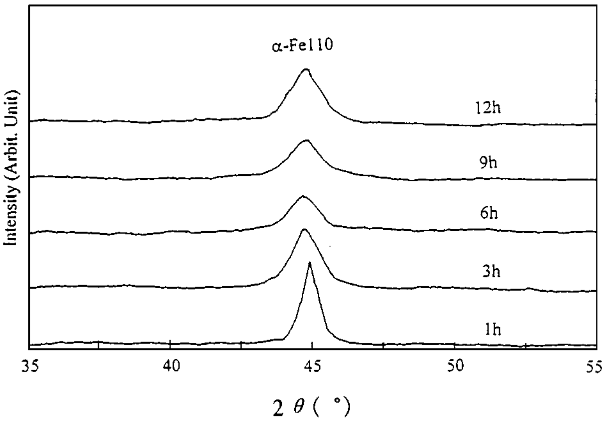
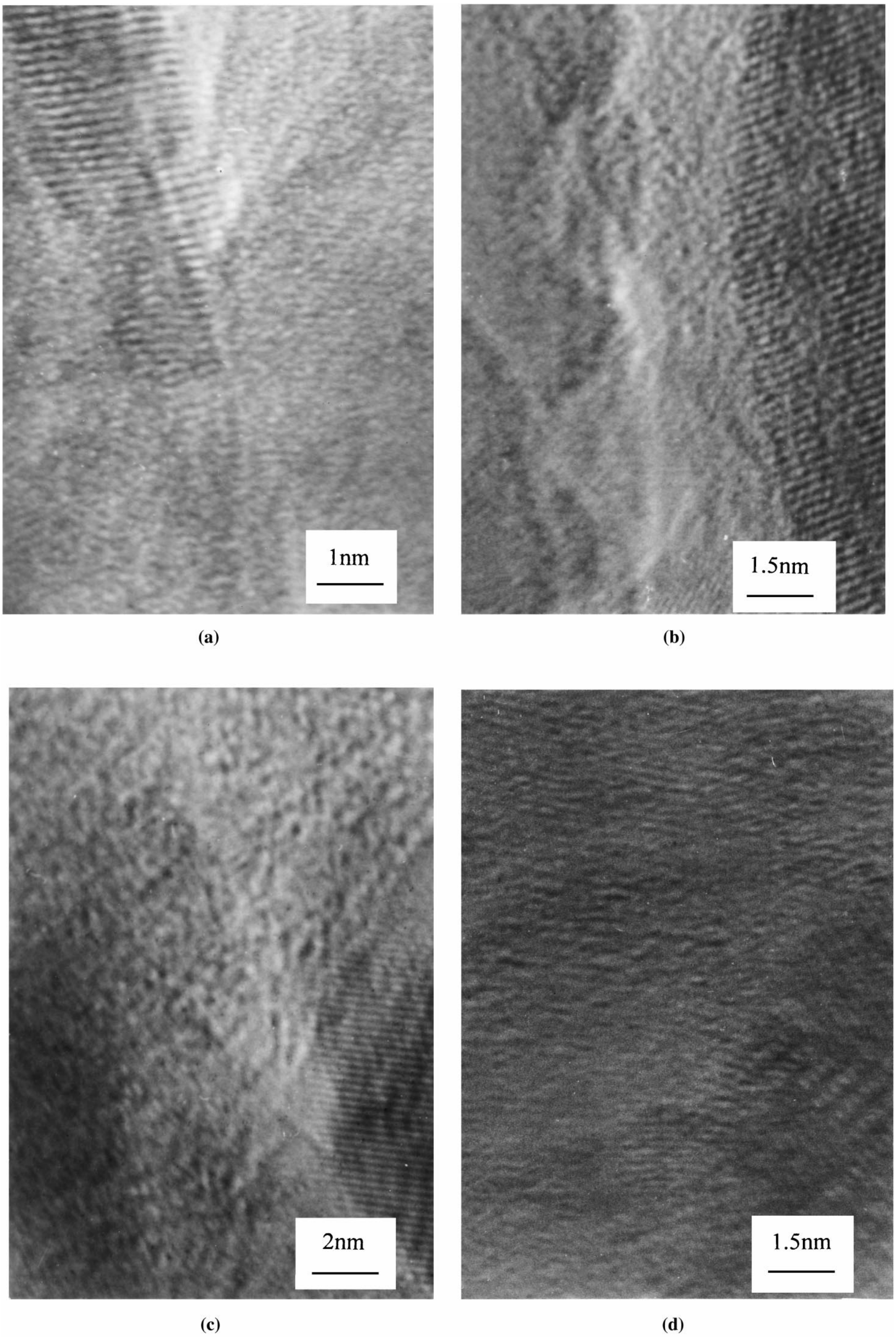


Figure 4 XRD patterns of mechanically alloyed $NdFe_{10.5}Mo_{1.5}$.

phase area reaches 10 nm and the boundaries among nanopowders disappear after having been mechanically alloyed for 6 hours. After having been mechanically alloyed for 12 hours, the samples are composed of amorphous phase and nanostructural α-Fe with 2–5 nm width, which have well distributed.

Nanopowders exhibit special thermodynamic characteristic, such as its low melting point. The temperature of nanopowders go up when milling. The nanopowders are melted and alloyed with each other. Then the heat energy of alloyed molten drops are absorbed and conducted by huge steel balls. The alloyed molten drops are rapidly solidified and formed fragile amorphous phase in the surface of nanopowders. As the mill is prolonged, the amorphous phase become more and more. The samples are composed of amorphous phase and nanocrystalline α-Fe in the end. So the mechanism of amorphous phase formation is melting-rapid solidification.



(a) (b) (c) (d)

Figure 5 High-resolution images of mechanically alloyed $NdFe_{10.5}Mo_{1.5}$ (HRTEM). (a) MA1h; (b) MA3h; (c) MA6h; (d) MA12h.

Fig. 6 is a differential thermal analysis (DTA) curve that is measured under an high purified Argon atmosphere with heat rate of 10 °C min^{-1}. At 237.14 °C there is an exothermic peak which is caused by structural relaxation in amorphous phase. At 270.53 °C there is an endothermic peak which is caused by the incubation period of crystallization of amorphous phase. At 331.43 °C and 419.19 °C, there are two exothermic peaks, which are caused by crystallization of amorphous phase. In crystallization stage, the Nd and Mo atoms solubilize in nanostructural α-Fe, then form nanostructural α-Fe supersaturated solid solution. Solid state reaction happens between 419.19 °C and 958.72 °C. In solid state reaction stage, nanostructural α-Fe supersaturated solid solution transforms into $Nd(Fe,Mo)_{12}$ with $ThMn_{12}$-type structure. Surpassing 958.72 °C, there is a new base line. At 1312.50 °C there is an endothermic peak, which is caused by melting of

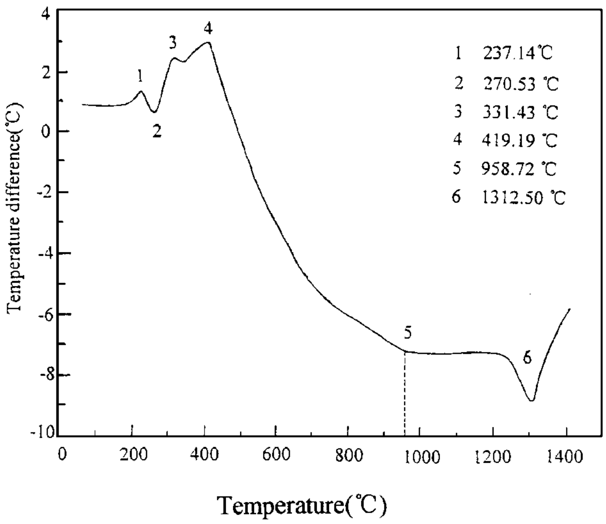


Figure 6 DTA curve of mechanically alloyed $NdFe_{10.5}Mo_{1.5}$.

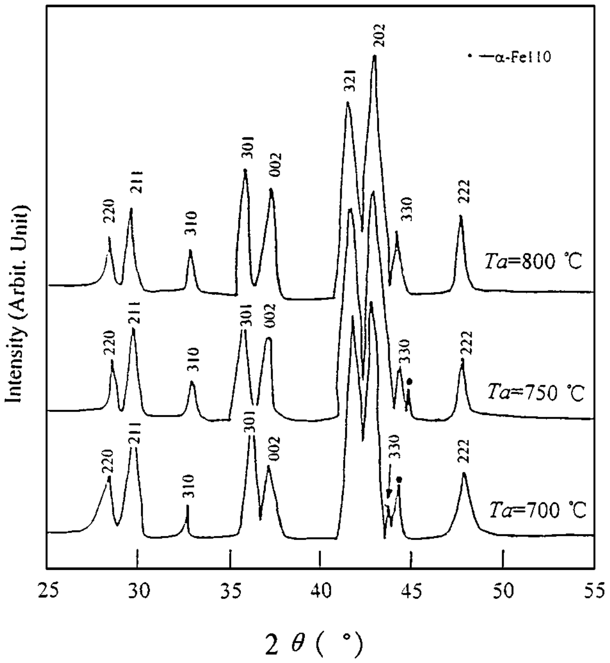


Figure 7 XRD patterns of $NdFe_{10.5}Mo_{1.5}$ alloy mechanically alloyed for 6 hours and annealed at different temperature for 30 min.

$Nd(Fe,Mo)_{12}$. Fig. 7 shows the XRD patterns of the mechanically alloyed $NdFe_{10.5}Mo_{1.5}$ annealed at different temperature for 30 min. $NdFe_{10.5}Mo_{1.5}$ is composed of $Nd(Fe,Mo)_{12}$ and an amount of α-Fe. The amount of α-Fe decreases as increasing the annealing temperature. α-Fe Brag peak disappears when the samples have been annealed at 800 °C for 30 min. The average grain size of $Nd(Fe,Mo)_{12}$ is estimated using Scherrer formula [4] (Table II). The average grain size of $Nd(Fe,Mo)_{12}$ coarsen quickly with raising annealing temperature.

The $NdFe_{10.5}Mo_{1.5}N_x$ can be obtained after having been nitrided at temperature from 400 °C to 500 °C for 2 hours. The magnetic properties of $NdFe_{10.5}Mo_{1.5}N_x$ are listed in Table III. The intrinsic coercivity iH_c tend to increase with increasing nitriding temperature. Fig. 8 is a typical hysteresis loop of $NdFe_{10.5}Mo_{1.5}N_x$ mechanically alloyed for 9 hours, annealed at 750 °C for 30 min and nitrided at 500 °C for 2 hours. The permanent magnetic properties are intrinsic coercivity $iH_c = 677.4$ kA/m (8.51 kOe), remanence $B_r = 0.9831$ T (9.83 kGs), maximum energy product $(BH)_{max} = 166.2$ kJ/m^3 (20.88 GMOe). The good magnetic properties are contributed by the nanostructural $Nd(Fe,Mo)_{12}N_x$.

TABLE II The Average grain size of $Nd(Fe,Mo)_{12}$ (Mechanically alloyed for 6 hrs and crystallized at different temperature for 30 min)

Crystallizing temperature (°C)	Average grain size (nm)
700	18.7
750	23.5
800	32.3

TABLE III The magnetic properties of $Nd(Fe,Mo)_{12}N_x$ mechanically alloyed for 9 hours, annealed at 750 °C for 30 min and nitrided at different temperature for 2 hours

Nitriding	B_r		iH_c		$(BH)_{max}$	
temperature (°C)	T	Gs	kA/m	Oe	kJ/m^3	MGOe
400	0.6363	6363	360.4	4528	42.87	5.386
450	0.8982	8982	704.0	8844	153.1	19.23
500	0.9831	9831	677.1	8506	166.2	20.88

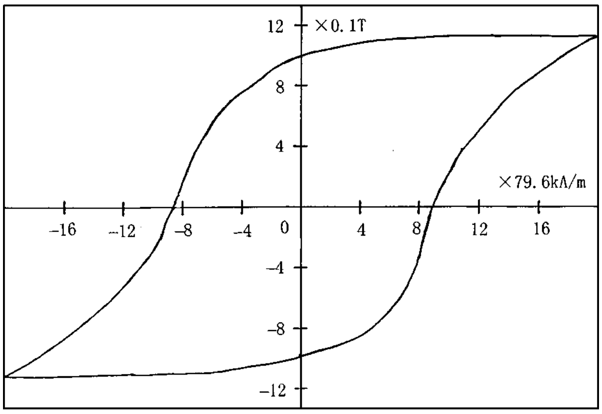


Figure 8 The hysteresis loop $Nd(Fe,Mo)_{12}N_x$ at room temperature.

4. Conclusions

1. Nd, Fe and Mo nanopowders, prepared by argon and hydrogen arc plasma, are nearly regular hexagonal or spherical. There are many 2–4 nm twins in Fe nanopowders.

2. $NdFe_{10.5}Mo_{1.5}$ mechanically alloyed for 12 h, is composed of amorphous phase and nanocrystalline α-Fe. The average size of nanocrystalline α-Fe is 3.7 nm.

3. The mechanism of amorphous phase formation is melting-rapid solidification.

4. DTA shows that amorphous phase structure relaxation, amorphous crystallization and solid stage reaction occur in heating.

5. The amount α-Fe of samples is controlled by annealing temperature. The annealing temperature is higher, the amount of α-Fe is lower. But too high annealing temperature results in the coarseness of $Nd(Fe,Mo)_{12}$.

6. High magnetic performance Nd(Fe,Mo)$_{12}$N$_x$ Powders can be obtained by mechanically alloyed using Nd, Fe and Mo nanopowders.

References

1. Y. C. YANG, X. D. ZHANG and S. L. GE, *et al.*, in Proc. 6th Int. Magnetic Anisotropy and Coercivity in RE-TM Alloys., Pittsburgh, 1990, p. 190.
2. WEI GONG and G. C. HADJIPANAYIS, *IEEE Trans. Magn.* **28**(5) (1992) 2563.
3. T. ITSUKAICHI, M. UMEMOTO and I. OKAME, *et al.*, *J. Alloys and Compounds* **193** (1993) 262.
4. B. D. CULLITY, “Elements of X-ray Diffraction,” 2nd ed., (Addison-Wesley Publishing Company, Inc., Reading, 1978) p. 102.

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