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Structure and magnetic properties of $Nd_{1.5}Fe_{10.5}Mo_{1.5}N_x$ prepared by mechanical milling①

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Abstract: Mechanical milling has been applied to prepare Nd-Fe-Mo magnetic powders. For preparing the single-phase $Nd_{1.5}Fe_{10.5}Mo_{1.5}$ compounds with $ThMn_{12}$-type structure, a mixture of amorphous phase and α-Fe was obtained by ball milling for 4~ 18 h. In the process of ball milling, the powders went through breaking and recombining, which were closely related to amorphous formation. The powders of nanostructured 1: 12 phase was formed after annealing at 700~ 850 ℃ for 10~ 40 min. The optimum magnetic properties were obtained with the following nitriding treatment at 500~ 550 ℃ for 1~ 2 h.

Key words: ball milling; amorphous powders; multi-particles **Document code: A**

1 INTRODUCTION

In 1990, interstitial nitrogen atoms were introduced into intermetallic compounds $RFe_{12-x}T_x$ (R= rare earth, T= transition metal or metalloid) with a $ThMn_{12}$-type structure to greatly improve the permanent magnetic properties. Thus, the RE-Fe nitrides having the $ThMn_{12}$-type structure have become new potential permanent materials[1~3]. In the recent years, the $R(Fe, T)_{12}$ (M= Ti, V, Cr, Mn) and their nitrides have been studied intensively. It has been found that the $NdFe_{12-x}Mo_xN_{1-\delta}$ compounds are the most promising candidates for permanent magnet due to the easy attainment of higher coercivity[4~8]. Mechanical milling is an effective method to prepare permanent magnet materials with higher coercivity, having advantages of simple in equipment, easy in operation and being capable of big scale production[9,10]. In this paper, we present detailed information of the structure variation in the process of ball milling and give the optimal permanent magnetic properties of $Nd_{1.5}Fe_{10.5}Mo_{1.5}N_x$ powders.

2 EXPRIMENTAL

Alloy with stoichiometric composition of $Nd_{1.5}Fe_{10.5}Mo_{1.5}$ was prepared by arc melting 99.5% purity metals under argon protection. Then, the ingots were sealed into a quartz tube full of argon, and annealed at 850~ 950 ℃ for 24~ 168 h. The ingots were pulverized into powders with a size of less than 80 mesh. Mechanical milling was conducted in a GN-2-type high energy ball-mill under the protection of argon. The ratio of powders to steel balls is 1: 20. All handling of the starting and milled powders was conducted in a glove box filled with argon gas. The milling of 6~ 12 h leaded to a mixture of amorphous and α-Fe phases. The milled powders were heat-treated at 700~ 850 ℃ for 10~ 40 min to form 1: 12 phase. These samples were then nitrided at 500~ 550 ℃ for 2~ 4 h. A small amount of powders was drawn at different milling times to conduct X-ray diffraction with CuK_α radiation and DTA analyses. The morphology of the ball milled powders were examined by scanning electron microscopy (SEM) and the magnetic properties were measured by a vibrating sample magnetometer (VSM) with a maximum applied field of 1 592 kA/m.

3 RESULTS AND DISCUSSION

The X-ray diffraction patterns for $Nd_{1.5}Fe_{10.5}Mo_{1.5}$ alloy after annealing at 850 ℃ for 120 h were given in Fig. 1, from which it can be seen that a good single phase with a $ThMn_{12}$-type structure has been formed. Fig. 2 shows the X-ray diffraction patterns of milling process up to 4.5 h, from which it is found that the diffraction peaks of $Nd_{1.5}Fe_{10.5}Mo_{1.5}$ gradually broadened in the milling process, and the peaks almost disappear at 2.5 h, and a broadened amorphous peak appears instead. The intensity of the amorphous peaks gradually increased in the following milling process, and the maximum intensity of the peaks gradually shifted to high angles. The maximum intensity keeps nearly constant around 43° after 4.5 h. At this time it is thought the ball milling may end,

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and the X-ray peaks show an overlapping of amorphous and α-Fe peaks, which identifies the prepared powder is a mixture of amorphous and α-Fe phases. In the final stages, the intensity of broadened peaks increased due to the appearance of partial α-Fe phase.

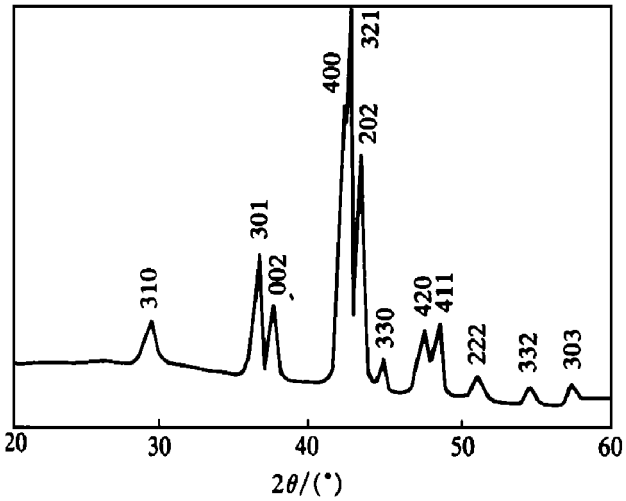

Fig. 1 XRD pattern of ingot after homogenization at 850 ℃ for 120 h

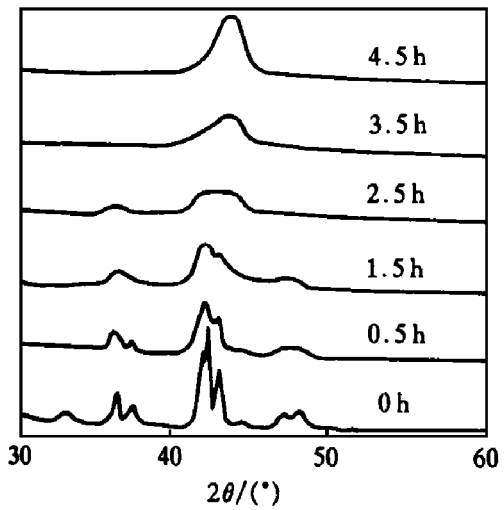

Fig. 2 XRD diffraction patterns in milling process up to 4.5 h

The milling time was prolonged to 18 h in order to investigate whether single amorphous phase could be obtained. The X-ray diffraction patterns of the powders ball-milled for up to 18 h are given in Fig. 3. It is seen that the X-ray diffraction patterns remain unchanged after ball milling for 9 h, which shows that the phase of the powders was stable after ball milling for 9 h. Therefore, it is confirmed that single amorphous phase was not obtained by milling single-phase Nd-Fe-Mo powders. Scherrer's formula was used to calculate the average size of grains and short-range order size of amorphous phase. Fig. 4 gives the variation of the average size of grains with milling time. In the later stages of ball milling, the powders were a mixture of α-Fe and amorphous phase, so the calculating value is an average value of α-Fe grains and the short-range distant size of amorphous phase, and this average size has been expressed as equivalent grain size in Fig. 4. From Fig. 4 it is seen that the size of grains decreased drastically in the initial ball milling stage, and then a nearly stable value is attained, in which the amorphous phase is the main phase. From Fig. 4 it is also seen that the size of grains does not change up to 9 h.

Fig. 5 shows the DTA curve of $Nd_{1.5}Fe_{10.5}Mo_{1.5}$ compounds milled for 18 h. The powders were heated

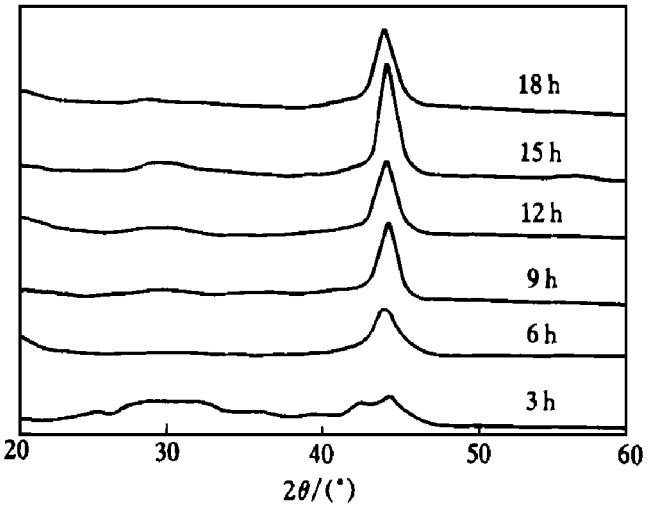

Fig. 3 XRD patterns in milling process up to 18 h

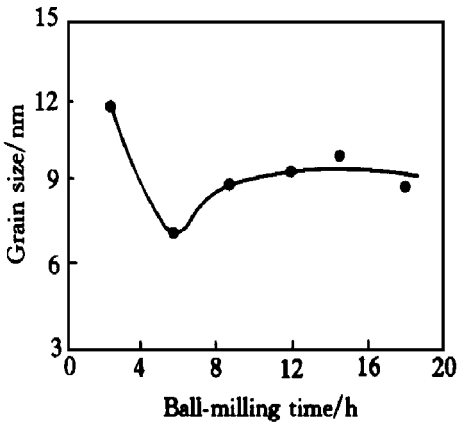

Fig. 4 Relation between powder grain size and milling time

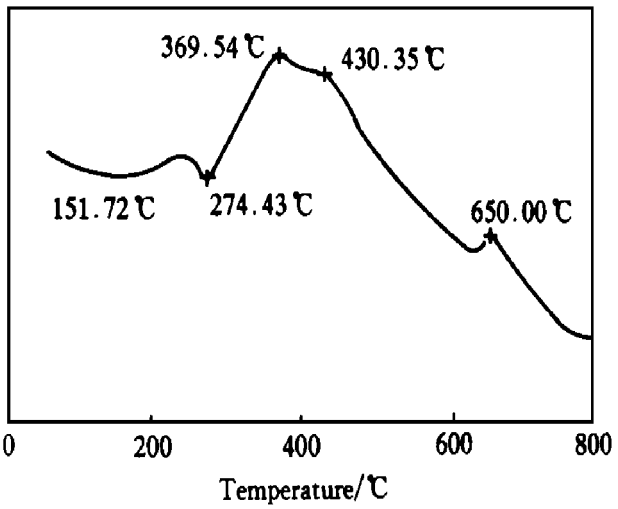

Fig. 5 DAT curve of $Nd_{1.5}Fe_{10.5}Mo_{1.5}$ compounds milled for 18 h

at the temperatures ranging from room temperature to 800 ℃ with protection of argon and a heating rate of 10 ℃/min. It is clearly seen that a crystallization peak appears at 369.54 ℃. Therefore, it is apparent that the amorphous phase is predominant in the final milling product.

Fig. 6 shows the morphologies of the powders at initial and different milling times. Fig. 6(a) shows the morphology of the initial powders before milling, and the different shapes and sizes of the particles can be observed, which corresponds to a sharp diffraction pattern as shown in Fig. 1. Fig. 6(b) shows the morphology of the powders milled for 0.5 h, the powders were refined immediately and became equiaxial particles gradually. Fig. 6(c) shows the morphology of the powders milled for 1.5 h, at this time the powders are fine and even, and exhibit equiaxial. As milling continued, the equiaxial particles were deformed remarkably, at the same time the deformed particles gathered together and became multi-particles due to overlapping and cold-welding. Fig. 6(d) shows the morphology of the powders milled for 2.5 h, the following milling made the size of powders decrease rapidly. It is found that the formation of multi-particles by overlapping or cold-welding appears in the middle and later periods of ball milling, which is just the periods of amorphous transition. Therefore, the amorphous transition of compounds is closely connected with the formation of multi-particles. The "fresh" surface of the particles contact each other by breaking or grinding, so the diffusion of atoms of different

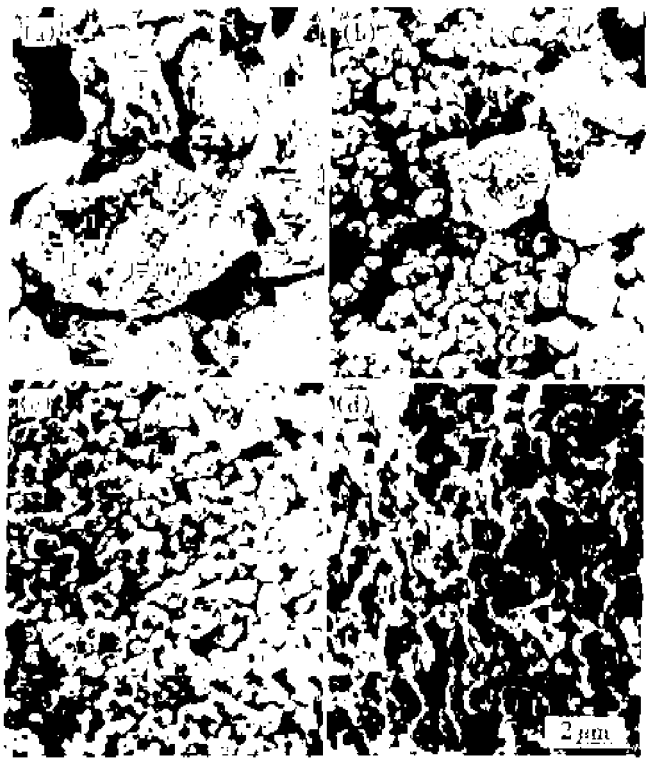

Fig. 6 Morphologies of powders milled for different times

atoms of different particles is enhanced intensively, which offers the possibility of the formation of amorphous phase.

The powders prepared by milling for 6 h was annealed at 810 ℃ for 30 min with the following nitriding treatment at 500 ℃ for 2 h, the optimum magnetic properties were obtained, $_iH_c$ = 462 kA/m, M_r = 0.478 T, $(BH)_{max}$ = 4.2 MGOe.

4 CONCLUSIONS

1) A mixture of amorphous phase and α-Fe was obtained by mechanical milling single-phase Nd-Fe-Mo compounds with $ThMn_{12}$-type structure.

2) For the Nd-Fe-Mo compounds, mechanical milling was composed of two basic processes, breaking and recombining. Amorphous transformation of the compounds was closely connected with cold-welding and recombining.

3) The optimum magnetic properties were obtained by controlling ball milling technology and selecting a suitable heat treatment.

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