



Nitrogenation effect of Nd(Fe,Mo)₁₂ alloys prepared by strip casting technique

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ABSTRACT

Nd_{1.1}Fe_{10.5}Mo_{1.5} alloys are prepared by strip casting technique and their nitrides are synthesized using the cast strips. It is found that the NdFe_{10.5}Mo_{1.5} strips can be directly nitrated to obtain interstitial NdFe_{10.5}Mo_{1.5}N_x compounds without pre-crushing. A phenomenon of spontaneous pulverization in the strips induced by nitrogenation is found for the first time. This kind of pulverization may result from the inter-granular failure along the grain boundary of Nd-rich phase as well as trans-granular failure of primary phase NdFe_{10.5}Mo_{1.5}, which is different from mechanical crushing of the strips where trans-granular failure is dominant. The nitrated strips are used to prepare anisotropic NdFe_{10.5}Mo_{1.5}N_x powders, and the anisotropic powders with a remanence (*B_r*) of 1.08 T, a coercive force (*H_c*) of 400 kA/m, and an energy product ((BH)_{max}) of 144 kJ/m³ are obtained. The results show that high performance NdFe_{10.5}Mo_{1.5}N_x nitrides can be prepared by a new and simpler technical route without pre-crushing.

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1. Introduction

Nd(Fe,M)₁₂N_x (M = Mo, V, Ti, ...) nitrides with the ThMn₁₂-type structure show very good intrinsic magnetic properties with high Curie temperature, moderately high saturation magnetization and large magneto-crystalline anisotropy, and have been considered as one of the good candidates for permanent magnet applications [1–4]. At present, a lot of efforts are made to study crystal structure and intrinsic magnetic properties of other compounds with the ThMn₁₂-type structure [5–8]. However, the work on the preparation process of anisotropic Nd(Fe,M)₁₂N_x powders is very little. Generally, in order to prepare anisotropic Nd(Fe,M)₁₂N_x powders, the Nd(Fe,M)₁₂ ingots have to be crushed into fine particles of about 200 μm to facilitate the subsequent nitrogenation in the conventional preparation process [9]. However, this crushing process may increase the oxygen content in the Nd(Fe,M)₁₂ alloys and make the preparation process more complex. The thickness of the Nd(Fe,Mo)₁₂-type strips prepared by strip casting technique is about 0.2–0.4 mm [9], which is close to the size (about 200 μm) of the Nd(Fe,Mo)₁₂ fine particles obtained by mechanical crushing method for nitrogenation. Therefore, it is possible to perform direct nitrogenation with the strips without pre-crushing. In this paper, we have tried to investigate the nitrogenation effect on the Nd(Fe,Mo)₁₂ strips, and spontaneous pulverization induced by nitrogenation is found for the first time in the nitrated

strips. The anisotropic Nd(Fe,Mo)₁₂N_x powders with high magnetic performance are obtained using a new technical route without pre-crushing.

2. Experimental procedures

The strips with the nominal composition of Nd_{1.1}Fe_{10.5}Mo_{1.5} were prepared by strip casting technique. The cooling roller speed was fixed at 3 m/s to obtain the strips with same microstructure as our previous result that the primary phase NdFe_{10.5}Mo_{1.5} with the mean size of about 4 μm and a few of grain boundary Nd-rich phases were observed [9]. Thermopiezic analysis (TPA) equipment was used to investigate the nitrogen absorption of the strips under the nitrogen atmosphere of 1.0 × 10⁵ Pa. The strips were nitrated for 3–8 h without pre-crushing around the chosen nitrogenation temperature, and then were kept at the room temperature in the argon atmosphere. This differs from the nitrogenation treatment of conventional preparation process in which the ingots were firstly mechanically crushed into fine powders and then nitrogenation process was executed [9]. X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) were used to study the microstructure and composition of nitrated strips and particles. The nitrogen content (*X*) of Nd(Fe,Mo)₁₂N_x was determined by weight increment upon nitrogenation. The particles obtained from spontaneous pulverization of nitrated strips were further crushed into fine powders by a ball mill technique. The powder sample of cylindrical shape was aligned with a magnetic field of 15 kOe in epoxy resin. Magnetic measurements were performed using a vibrating sample magnetometer. No demagnetization correction for the geometry of the sample was made and a density of 8.0 g/cm³ was used for the nitrated samples.

3. Results and discussion

In order to choose an appropriate nitrogenation temperature for the intact NdFe_{10.5}Mo_{1.5} strips, TPA equipment is employed to investigate their nitrogenation conditions. As a comparison, the results of nitrogenation of the crushed strips with the particle size of

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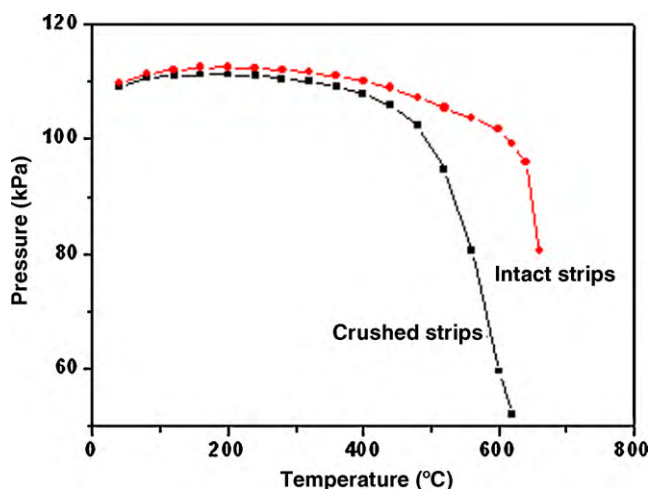


Fig. 1. TPA traces for the intact strips and crushed strips with the particle size of about 200 μm obtained by mechanical crushing of the same strips under nitrogen of 1.0×10^5 Pa.

about 200 μm obtained by mechanical crushing of the same strips is also listed. Fig. 1 shows the TPA results of intact strips and crushed strips under the nitrogen of 1.0×10^5 Pa. Both materials begin to absorb nitrogen at nearly the same temperature, but the maximum pressure drop temperature of the intact strips is observed at about 620 $^\circ\text{C}$ significantly higher than that (560 $^\circ\text{C}$) of the crushed strips, due to the fact that the reaction interface area between nitrogen and particles in the intact strips is significantly less than that in the case of the crushed strips. Increasing nitrogenation temperature may help the intact strips to achieve nitrogen saturation in a reasonable time by increasing the nitrogen diffusion rate [10].

Fig. 2 shows the XRD patterns of $\text{NdFe}_{10.5}\text{Mo}_{1.5}$ strips before and after nitrogenation at 620 $^\circ\text{C}$. The $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ compounds are found to maintain the same crystallographic structure as that before their nitrogenation, and single-phase $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ compounds are obtained. All diffraction peaks are shifted to lower angles due to volume expansion, indicating that the nitrogen atoms enter the interstitial sites of the $\text{NdFe}_{10.5}\text{Mo}_{1.5}$ phase. This suggests that the strips can be directly nitrided to obtain interstitial $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ compounds without pre-crushing.

It is noted that the nitrided $\text{NdFe}_{10.5}\text{Mo}_{1.5}$ strips are found to spontaneously pulverize into particles, as shown in Fig. 3. The possibility of the spontaneous pulverization in the $\text{NdFe}_{10.5}\text{Mo}_{1.5}$

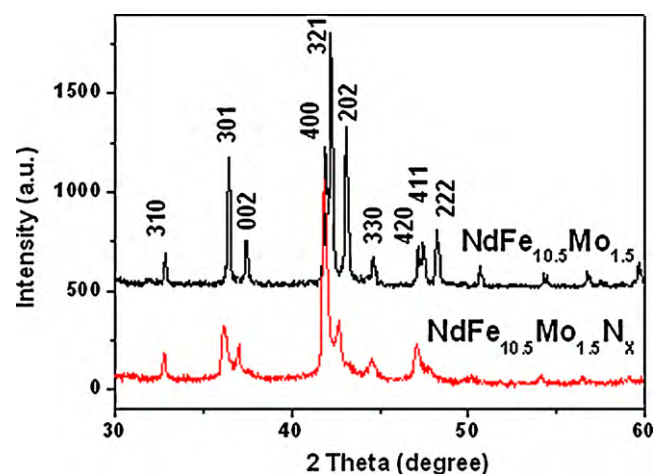


Fig. 2. X-ray diffraction patterns of $\text{NdFe}_{10.5}\text{Mo}_{1.5}$ strips before and after nitrogenation at 620 $^\circ\text{C}$.

ingots induced by nitrogenation is also investigated. Some cracks are found on the surface of the ingots with the sizes such as 10 mm \times 10 mm \times 10 mm and 5 mm \times 5 mm \times 5 mm, respectively, and the quantity of the cracks will increase with the decreasing size of the ingots. However, the obvious phenomenon of complete spontaneous pulverization is not observed. The reason maybe related to smaller surface–volume-ratio of the ingots than that of the strips, and the difference makes nitrogenation of the ingots more difficult. It suggests that the nitrogen-induced spontaneous pulverization maybe only true of the strips with the thickness of about 200 μm or smaller size. This spontaneous pulverization phenomenon is very similar to the hydrogen decrepitation observed in the Sm–Co and Nd–Fe–B alloys induced by hydrogenation [11,12], but the hydrogen decrepitation is also true of the ingots.

Fig. 3 shows the pulverization progress of the strips nitrided for 5 h at 620 $^\circ\text{C}$. It is seen that some visible cracks appear on the surface of the strips whose nitrogenation is just finished, and the strips become particles with the size ranging from 3 μm to 1 mm after 24 h. The nitrogenation processes of the $\text{Nd}(\text{Fe},\text{Mo})_{12}\text{N}_x$ -type and $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type interstitial nitrides are very similar [2], so spontaneous pulverization phenomenon is also expected in the nitrided $\text{Sm}_2\text{Fe}_{17}$ -type strips. Further work on the direct nitrogenation of the $\text{Sm}_2\text{Fe}_{17}$ -type strips is in progress.

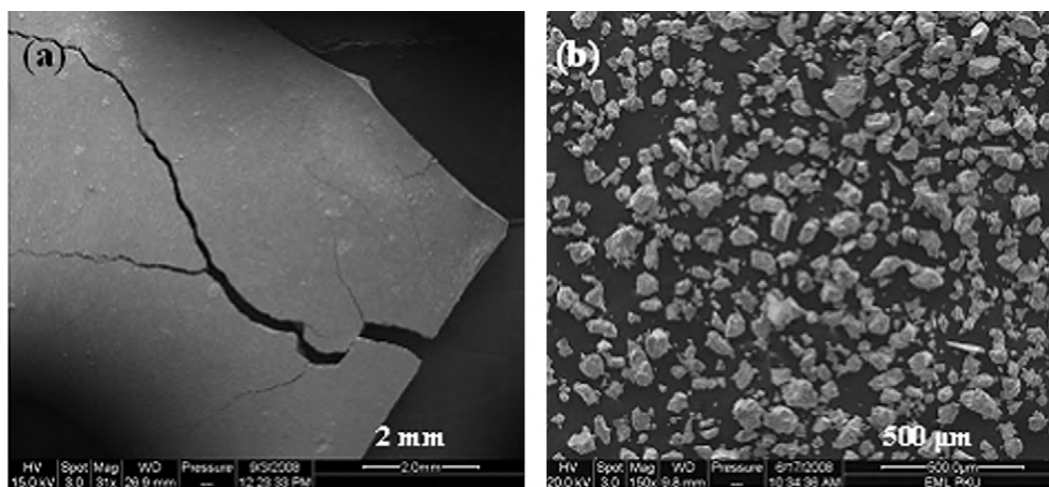


Fig. 3. The pulverization progress of the nitrided strips: (a) SEM of strips whose nitrogenation process is just finished; (b) SEM of the particles from nitrided strips after 24 h, and the particles are lightly sieved to be convenient for observation.

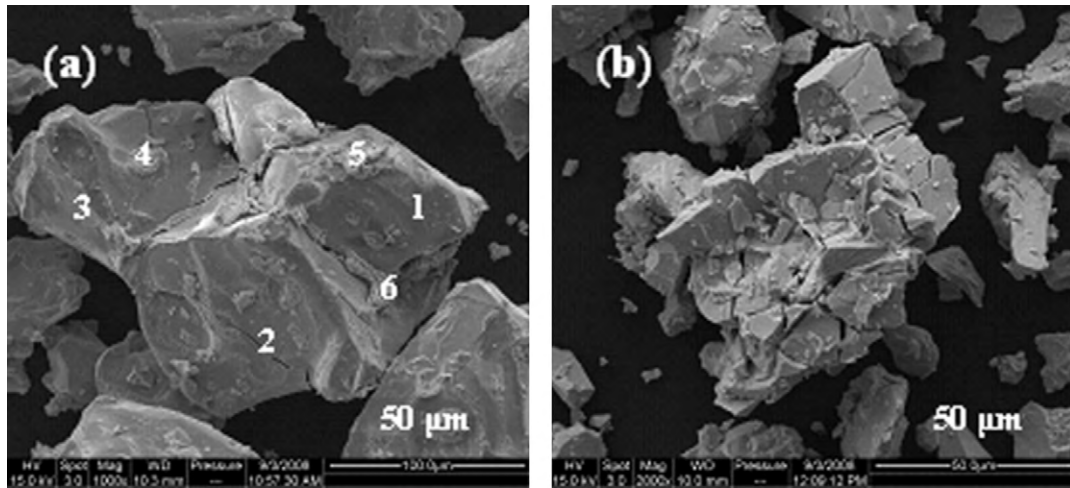


Fig. 4. Scanning electron micrographs of typical particles from (a) the spontaneous pulverization of the nitrated strips, and (b) the mechanical crushing of the strips.

The detailed morphology of the particles is shown in Fig. 4(a). There are a lot of micro-cracks in the individual particle, and much tiny debris is observed on the surface of the particles. And, the particles can be readily crushed into finer particles by agitating or lightly smearing. This suggests that the nitrogeneration process can be also utilized to pulverize the cast strips of $\text{Nd}(\text{Fe},\text{Mo})_{12}$ alloys besides preparing interstitial $\text{Nd}(\text{Fe},\text{Mo})_{12}\text{N}_x$ compounds, and mechanical crushing before nitrogeneration can be skipped in the preparation process.

The above particles are found to have lower oxygen content (0.2 wt%) compared with the particles (with the oxygen content 0.38 wt%) obtained by the mechanical crushing method. This indicates that the spontaneous pulverization of the strips induced by nitrogeneration is helpful for decreasing the oxygen content in the materials.

To study the mechanism of the pulverization induced by the nitrogeneration process, energy dispersive X-ray (EDX) spectrometry has been used to investigate the composition of the above particles (Fig. 4). The chemical composition of the typical particle as a whole indicates that the Nd/Fe/Mo atomic ratio is almost equal to the nominal composition 1.1/10.5/1.5 of the strips. Slightly less neodymium concentration is observed from spot analysis on the particle denoted by (1), (2) and (3), and these values are very close to the composition of the primary phase $\text{NdFe}_{10.5}\text{Mo}_{1.5}$. A very high Nd concentration is found in these tiny debris denoted by (4), (5) and (6) on the surface of the particle, indicating that they may result from the grain boundary of Nd-rich phase. Fig. 4(b) shows the morphology of the particles obtained from the mechanical crushing of the same strips. The composition of each particle is very close to that of the primary phase, and little debris with high Nd content is found, as compared to those particles obtained by spontaneous pulverization of nitrated strips. Thus, we suppose that spontaneous pulverization of nitrated strips may be caused by the inter-granular failure along the grain boundary of Nd-rich phase as well as trans-granular failure of primary phase $\text{NdFe}_{10.5}\text{Mo}_{1.5}$, while trans-granular failure is dominant in the mechanically crushed strips.

The particles from spontaneous pulverization of nitrated strips are ball milled into the fine powders to prepare anisotropic $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ magnetic powders. Fig. 5 shows the hysteresis loop of the above anisotropic powders. The magnetic properties are $B_r = 1.08$ T, $iH_c = 400$ kA/m, and $(\text{BH})_{\text{max}} = 144$ kJ/m³, comparable to those of anisotropic $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ powders obtained by the conventional preparation process [9]. Thus a new and simpler technical route to prepare high performance $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ nitrides is developed by making use of nitrogen-induced pulverization instead of mechanical crushing method.

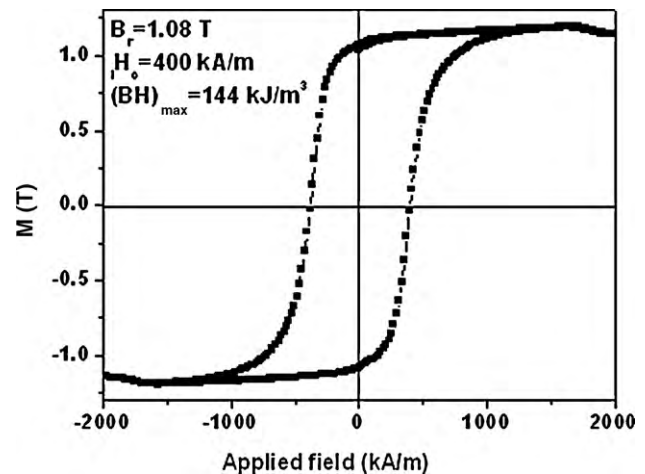


Fig. 5. Hysteresis loop of anisotropic $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ magnetic powders obtained from the nitrated strips.

4. Conclusions

Direct nitrogeneration of the cast $\text{Nd}(\text{Fe},\text{Mo})_{12}$ strips is feasible for preparing the interstitial $\text{Nd}(\text{Fe},\text{Mo})_{12}\text{N}_x$ nitrides with high magnetic performance. A phenomenon of spontaneous pulverization in the nitrated strips is observed, and the nitrogen-induced pulverization may result from the inter-granular failure along the grain boundary of Nd-rich phase as well as trans-granular failure of primary phase $\text{NdFe}_{10.5}\text{Mo}_{1.5}$. The results indicate that direct nitrogeneration of the strips can be used to prepare interstitial $\text{Nd}(\text{Fe},\text{Mo})_{12}\text{N}_x$ compounds and pulverize the strips into particles, so mechanical crushing process can be omitted. Based on this, a new technical route without pre-crushing process is established.

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