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Effect of Al and Al/Mo addition on microstructure and magnetic properties of sintered $Nd_{22}Fe_{71}B_7$ magnets①

YANG Sen(杨 森), SONG Xiao-ping(宋晓平), WANG Xian-hui(王献辉), SUN Zhan-bo(孙占波), SUN Jun(孙 军)
(School of Materials Science and Engineering, Xi′an Jiaotong University, Xi′an 710049, P.R.China)

[Abstract] The alloying elements Al and Al/Mo were added into the intergranular regions of sintered NdFeB magnets and their effects on microstructure and magnetic properties were investigated. Results show that a small amount of Al and Al/Mo additives can largely enhance the coercivity with a little loss of the remanence of NdFeB magnets. Apart from the improvement of Nd-rich phase wetting ability arising from the individual pure Al addition, the improvement of coercivity can be attributed to the occurrence of a net-shaped $Nd(FeAl)_2$ phase in the intergranular region of the Al-doped and Al/Mo-doped magnets and the segregation of Mo on the surface of the main phase grains, which reduces the magnetic coupling of the $Nd_2Fe_{14}B$ grains and impedes effectively the propagation of the domain walls. Compared with the single element alloying method, the combined alloying of different elements to the intergranular region is more efficient to modify the properties of NdFeB magnets.

[Key words] NdFeB magnets; alloying; coercivity
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1 INTRODUCTION

It is well known that the intergranular microstructure of sintered Nd-Fe-B magnets plays a key role in developing their coercivity[1,2]. Earlier studies showed that the intergranular microstructure is composed of a Nd-rich phase and a small amount of B-rich phase[3]. It has been shown that the Nd-rich phase is beneficial to the coercivity, whereas the B-rich phase is detrimental to the coercivity and should be avoided[3,4]. Recently, we have found a new additional Fe-Nd-O intergranular phase in the magnets which has a strong effect on the coercivity and the temperature dependence of the coercivity[5]. Kim also reported that a small amount of Cu addition to the intergranular region leads to an improvement in both the coercivity and remanence[6]. Our recent results further showed that additions of pure W, Mo, Nb and V can largely enhance the coercivity of sintered Nd-Fe-B magnets and some certain different elements co-addition is more efficient to improve the coercivity than individual pure element addition[7~9]. These results suggested that it is possible to improve both the coercivity and the thermal stability of Nd-Fe-B magnets by an appropriate modification of the intergranular microstructure. In the present work, the elements Al and Al/Mo are separately added into the intergranular regions of sintered Nd-Fe-B magnets and their effects on microstructure and magnetic properties are investigated.

2 EXPERIMENTAL

On the basis of our recent works[8,9] and for studying the intergranular microstructure more conveniently, we used a Nd-richer composition $Nd_{22}Fe_{71}B_7$ in this study to obtain a larger volume fraction of the intergranular phase. Samples were prepared by a conventional powder metallurgical process from melting raw materials of 99% Nd, 99.99%Fe and 20% B-Fe in the vacuum induction furnace. Ingots were crushed in the vibratom. A jet mill was used to produce a fine powder of approximately 3 μm in average diameter, which was pressed under a magnetic field of 1.6 MA·m^{-1}. Sintering and annealing were performed in a vacuum furnace at 1 273 K and 873 K for 1 h, respectively. Fine powders of chosen alloying elements were added to the Nd-Fe-B powder prior to the jet milling. In the case of Al/Mo co-addition, 0.8%(mass fraction) Al was chosen and fixed, whereas Mo content was varied from 0.2% to 2.0%. In order to study the segregation of alloying elements on the surface of magnetic phase grains, corrosion experiments were conducted. Samples were electrolyticly corroded in 5%~8% chlorhydric acid for 1 h, and then the samples were cleaned in alcohol and examined using SEM.

Magnetic properties were measured with a DGY-2 hysteresigraph. The microstructure of magnets was investigated by an S-2700 scanning electron microscope equipped with an energy-dispersive X-ray analy-

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sis (EDX) unit and a Neophot-21 optical microscope.

3 RESULTS

Fig.1 shows the coercivity ${}_iH_c$ and remanence B_r variations of $Nd_{22}Fe_{71}B_7$ magnets with the alloying additive contents. In the case of individual pure Al addition, the coercivity increases gradually with Al content increasing and reaches a maximum value 1.30 MA/m at 1.2 % Al. In the Al and Mo co-added magnet (Al content is fixed at 0.8 %), the coercivity also increases gradually with Mo content increasing and reaches a maximum value 1.56 MA/m at 1.6 % Mo content. With the further increasing of Mo content above 1.6 %, the coercivity does not increase any more. It is noticed that the coercivity increases by about 37 % in the individual pure Al addition magnet, but it increases by 64 % in the Al and Mo co-added magnet. However, the curve of remanence is different from that of coercivity. It decreases gradually with the increasing of Al or Mo content in both Al and Al/Mo addition magnets.

Fig.2 shows the optical micrographs for the Nd-Fe-B magnets. It can be seen that the magnets of individual addition and co-addition have different microstructures. In the individual pure Al-added magnets, the morphology of magnetic phase grains becomes more spherical, but accompanying the increasing of grains size with the increasing of Al content. At the same time, the volume of intergranular phase increases gradually and a new gray net-shaped phase appears in the intergranular regions. In the Al and Mo co-addition magnets, the size of magnetic phase has no distinct change. But the quantities of gray net-shaped phases in the intergranular region increase obviously.

Fig.3 shows the SEM micrographs for the Nd-Fe-B magnets electrolyticly corroded and Table 1 lists the composition analysis results from the intergranular phase and from the surface of magnetic phase, which is determined by EDX. Before electrolytic corrosion,

Table 1 Results of EDX analysis of Al and Mo-doped $Nd_{22}Fe_{71}B_7$ magnets

Region	x(Fe)/%	x(Nd)/%	x(Al)/%	x(Mo)/%
A	65.0	32.0	3.0	0
B	87.2	12.5	0.3	0
C	63.6	33.5	2.5	0.4
D	57.5	12.5	1.6	28.4

SEM observation and EDX analysis show that the composition of the gray net-shaped phase in the intergranular region is 32Nd-65Fe-3Al (Fig.3(a) and (c)). So this net-shaped phase is a $Nd(FeAl)_2$ phase. After electrolytic corrosion, the Nd-rich phase of the surface was eroded off from the surface of magnetic grains. In the individual pure Al-added magnets, the composition of the surface of magnetic phase is the same as that of magnetic phase, and no element Al can be detected in the magnetic phase (Fig.3(b)). So it could be concluded that element Al is dissolved into the Nd-rich phase in the intergranular region during the sintering, resulting in the net-shaped $Nd(FeAl)_2$ formation thereafter cooling process. But in the Al and Mo co-added magnets (Fig.3(d)), about 28.4 %(mole fraction) element Mo is detected on the surface of the magnetic phase and 0.4 % Mo is found in the net-shaped $Nd(FeAl)_2$ phase. This suggests that element Mo mainly segregates on the surface of magnetic phase and a little of element Mo is dissolved into the $Nd(FeAl)_2$ phase.

4 DISCUSSION

The above microstructure studies and composition analysis reveal that element Al is dissolved into the Nd-rich phase in the intergranular region during the sintering and a net-shaped $Nd(FeAl)_2$ phase is formed after sintering in both individual pure Al-added and Al/Mo co-added magnets. The much more spherical of magnetic grain illustrates that wettability between the Nd-rich phase and the magnetic phase is

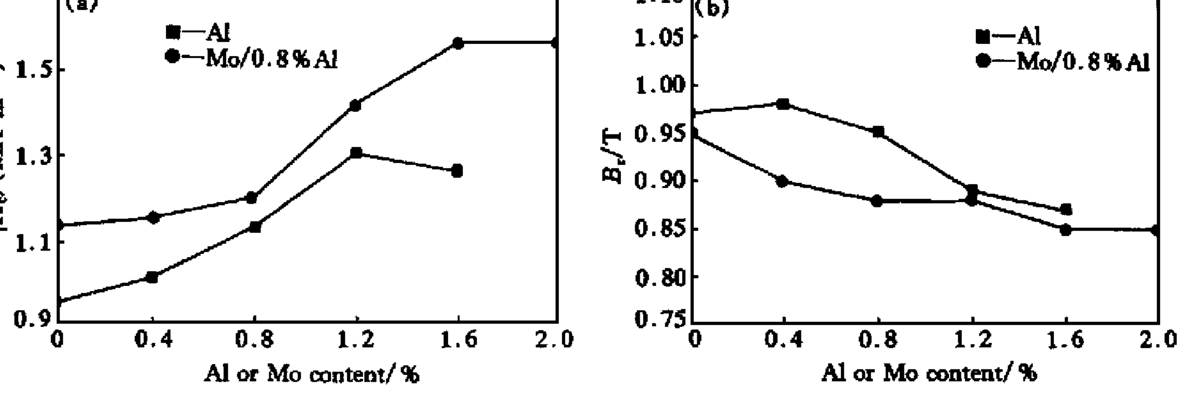

Fig.1 Content of alloying element additives dependence of coercivity (a) and remanence (b) for $Nd_{22}Fe_{71}B_7$ magnets

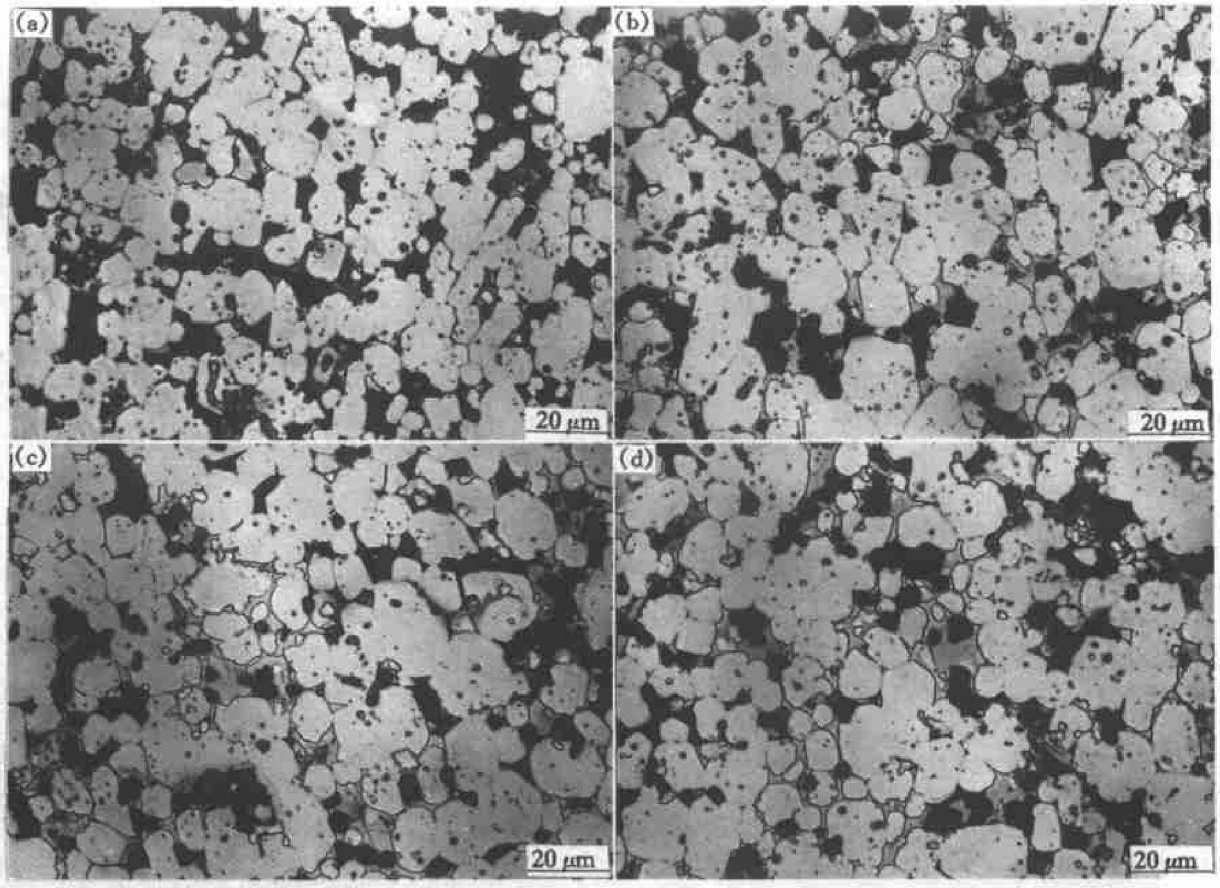

Fig.2 Optical micrographs for $Nd_{22}Fe_{71}B_7$ magnets with Al and Mo additions

(a) —0.8 % Al; (b) —0.8 % Mo; (c) —0.8 % Mo + 0.8 % Al; (d) —1.6 % Mo + 0.8 % Al

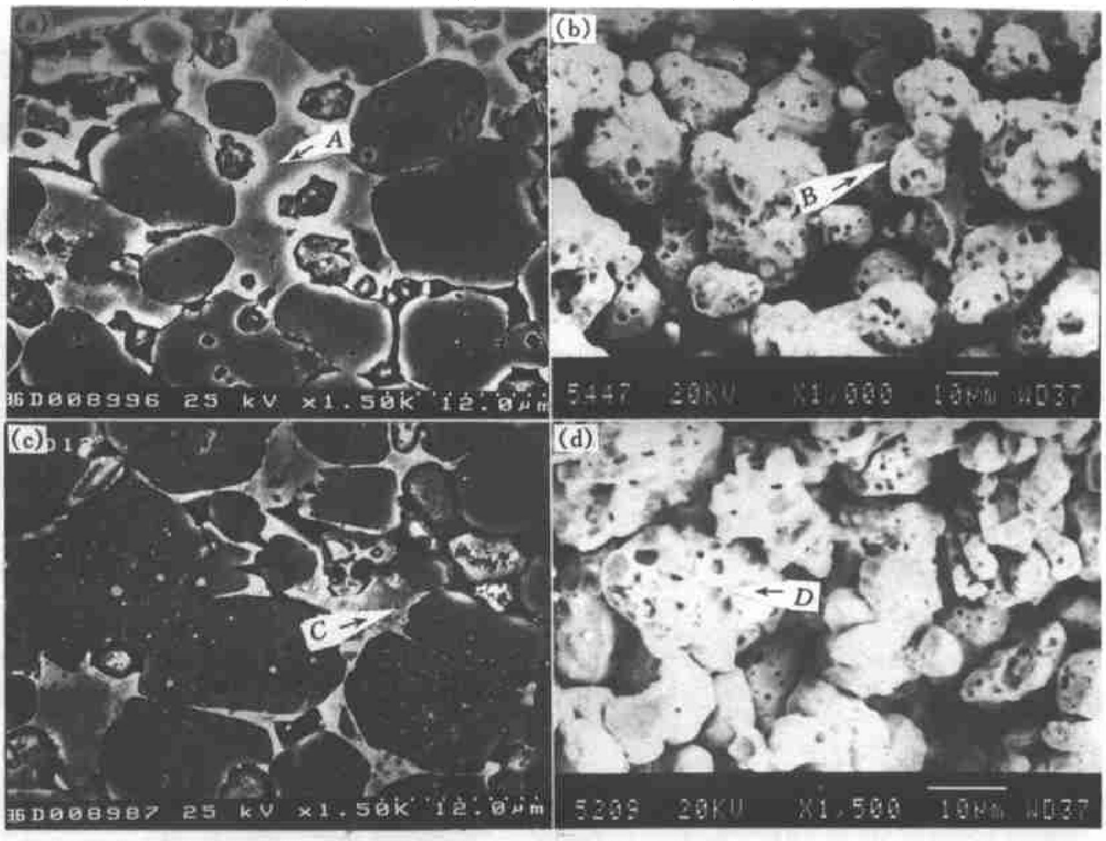

Fig.3 SEM micrographs for $Nd_{22}Fe_{71}B_7$ magnets with Al and Mo additions

(a) —1.6 % Al; (b) —1.6 % Al, etched; (c) —0.8 % Al + 2.0 % Mo; (d) —0.8 % Al + 2.0 % Mo, etched improved, which has been reported by Knoch[10]. The appearance of $Nd(FeAl)_2$ phase may reduce the magnetic coupling of $Nd_2Fe_{14}B$ grains. These would enhance the coercivity of Nd-Fe-B magnets. But there is an evident difference for microstructure in the Al and Mo co-addition magnets. Element Mo segregates on the surface of the magnetic phase, which can reduce the magnetic coupling of $Nd_2Fe_{14}B$ grains and impede effectively the propagation of reversed domain walls through the magnetic phase grain. The better separation and decoupling of hard magnetic grains also contribute to the enhancement of coercivity of Nd-Fe-B magnets. At the same time, a little of element Mo is dissolved into $Nd(FeAl)_2$ phase and facilitates forming more $Nd(FeAl)_2$ phase. So the coercivity of the Nd-Fe-B magnets is dramatically increased. Because the volume of the magnetic phase decreases for both additions, the remanence monotonically decreases. It is noticed that the coercivity increases by about 37 % in the individual pure Al addition magnet, but it increases by 64 % in the Al and Mo co-added magnet. So, Al and Mo co-addition can improve the coercivity more efficiently than individual pure Al addition.

5 CONCLUSIONS

1) The coercivity of sintered Nd-Fe-B magnets can be enhanced in the individual pure Al-added magnets. The improvement of the coercivity can be attributed to the improvement of wettability of the Nd-rich phase and the occurrence of a net-shaped $Nd(FeAl)_2$ phase.

2) The coercivity of sintered Nd-Fe-B magnets can be largely enhanced in the Al and Mo co-added magnets. The improvement of the coercivity can be attributed to the segregation of Mo on the surface of $Nd_2Fe_{14}B$ phase and the occurrence of more net-shaped $Nd(FeAl)_2$ phases.

3) The coercivity increases by about 37 % in the individual pure Al addition magnets, but it increases by 64 % in the Al and Mo co-added magnets. So, Al and Mo co-addition can improve the coercivity more efficiently than individual pure Al addition.

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