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Effects of Ti and(or) Cu on microstructures and magnetic properties of sintered Nd-Fe-B magnets①

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[Abstract] The alloying elements Ti and(or) Cu were added into the intergranular regions of sintered Nd-Fe-B magnets and their effects on microstructures and magnetic properties of the magnets were investigated. The results showed that a small amount of Ti and(or) Cu additions can enhance the coercivity and have little effect on the remanence of Nd-Fe-B magnets. Compared with individual addition of pure Ti or Cu elements, Ti and Cu co-addition of intergranular region is more efficient to improve the coercivity of the magnets. The improvement of the coercivity can be attributed to the segregation of Cu element on the surface of the magnetic phase ($Nd_2Fe_{14}B$) and the occurrence of fine Nd-Fe-Ti particles near grain boundaries. The former can prevent the magnetic coupling of $Nd_2Fe_{14}B$ grains to a certain degree and impede effectively the propagation of reversed domain walls through the magnetic phase grains. The latter can inhibit the growth of magnetic phase grains during the sintering process, resulting in a finer grain size. Both are beneficial to the coercivity enhancement. With increasing Ti content above 0.8 %, a strip Ti-rich phase appears in the intergranular region, resulting in the dramatic reduction of the remanence of Nd-Fe-B magnets.

[Key words] NdFeB magnets; microstructure; 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. 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, It was found that a new additional Fe-Nd-O intergranular phase exists in the magnets which has a strong effect on the coercivity and the temperature dependence of the coercivity[5]. These results suggest 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. Sasaki[4] reported that a small amount of $DyGa_2$ addied to the intergranular region is helpful to enhance the coercivity and thermal stability without remanence reduction. Kim[6] also reported that a small amount of Cu addied to the intergranular region leads to an improvement in both the coercivity and remanence. Our recent results[7~10] further showed that additions of pure Nb, Mo, V and W could 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. In the present work, the elements Ti and(or) Cu are separately added into the intergranular regions of sintered Nd-Fe-B magnets and their effects on microstructures and magnetic properties are investigated.

2 EXPERIMENTAL

On the basis of our recent works[8] and for studying the intergranular microstructure more conveniently, a Nd-richer $Nd_{22}Fe_{71}B_7$ was used 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 a vibratom. A jet milling 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. 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 Ti and Cu co-addition, 0.8 % Cu was chosen and fixed, whereas Ti 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 by using SEM.

Magnetic properties were measured in a DGY-2

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hysteresigraph. The microstructure of magnets was investigated by an S-2700 scanning electron microscope equipped with an energy-dispersive X-ray analysis (EDXA) 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 as a function of Ti or Cu content. In the case of pure Ti or Cu addition, the coercivity increases slowly and reaches a maximum value 0.98 MA/m in the Cu-doped magnet at 0.8% Cu, whereas the remanence remains almost unchanged for both addition. In the Ti and Cu co-added magnet (Cu content is fixed at 0.8%), the coercivity increases slowly when Ti content is below 0.4%, but begins to increase rapidly when Ti content exceeds 0.4% and reaches a maximum value of 1.56 MA/m at the content of 0.8% Ti. With further increasing Ti content over 0.8%, the coercivity decreases slightly. However, the curve of remanence is different from that of coercivity, it changes a little when Ti content is less than 0.8%, but it sharply decreases when Ti content is greater than 0.8%.

Fig.2 shows the optical micrographs for the Nd-Fe-B magnets. It can be seen that the magnets with individual additive and co-additives have different microstructures:

1) Compared with pure NdFeB magnets, the grain sizes of Ti-doped magnets have no observable change. But a strip Ti-rich phase is detected in the intergranular region of the magnets with Ti content greater than 0.8%.

2) The magnetic phase grain of Cu-doped magnets has a straight boundary. This shows that magnetic phase grains grow along a certain direction during the sintering. Examined from a direction perpendicular to the easy magnetic axis ([001] direction), the magnetic phase grains exhibit square morphology. However, examined from a direction parallel to the easy magnetic axis, they show rectangular morphology. (Fig.2(b), an arrow shows the easy magnetic axis direction). These results suggest that the magnetic phase grains grow along [100] or [010] direction during sintering.

3) The Ti and Cu co-doped magnet has a smaller grain size than that Ti-doped and Cu-doped magnets have. In addition, it is noticed that the magnetic phase grain also has a straight boundary as in the case of individual Cu addition (Fig.2(c)). However, it is found that the magnet has a larger grain size when Ti content exceeds 1.2% and a strip Ti-rich phase appears in the intergranular region (Fig.2(d)).

Fig.3 shows SEM micrographs for the Nd-Fe-B magnets electrolyticly corroded and Table 1 lists the composition analysis resulted from the intergranular phase and from the surface of main phase, which is determined by EDXA. Before electrolytic corrosion, SEM observation and EDXA show that little Cu and Ti element exist in the intergranular region in the Cu-doped and Ti and Cu-doped magnets. However, after electrolytic corrosion, about 30% Cu (mole fraction) is detected on the surface of the $Nd_2Fe_{14}B$ phase. Further SEM observation and EDXA show that a lot of fine particles of Nd-Fe-Ti phase occurred near the grain boundary of $Nd_2Fe_{14}B$ phase in the Ti and Cu-doped magnet (Fig.3(d)). The composition of strip Ti-rich phase is also listed in Table 1.

Table 1 Results of EDXA of Ti and Cu-doped $Nd_{22}Fe_{71}B_7$ magnets (%, mole fraction)

Region	w(Fe)	w(Nd)	w(Cu)	w(Ti)
A	3.5	0	93.3	
B	86.0	14.4	0	0
C	22.5	50.3	27.2	0
D	24.9	46.1	29.0	0
E	43.3	21.5	0.3	35.9

4 DISCUSSION

The above microstructure studies reveal that a

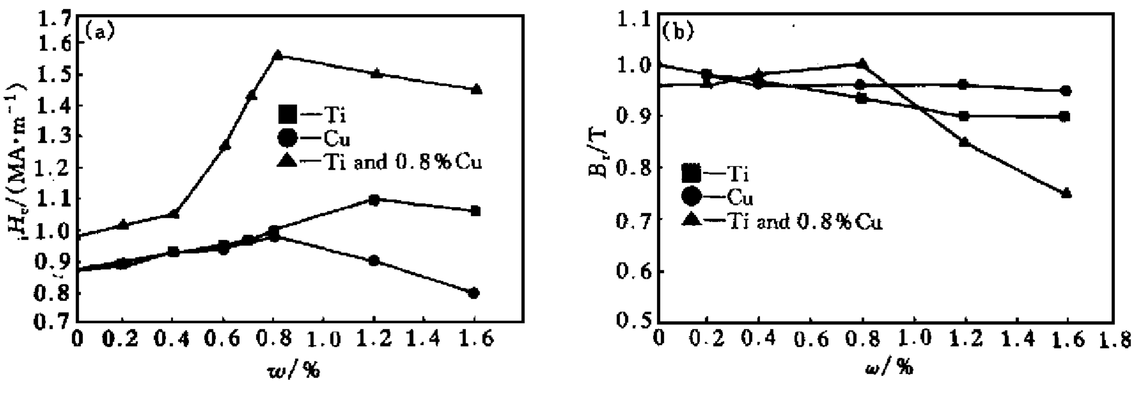

Fig.1 Content of alloying elements dependence of (a) coercivity (b) remanence for $Nb_{22}Fe_{71}B_7$ magnets

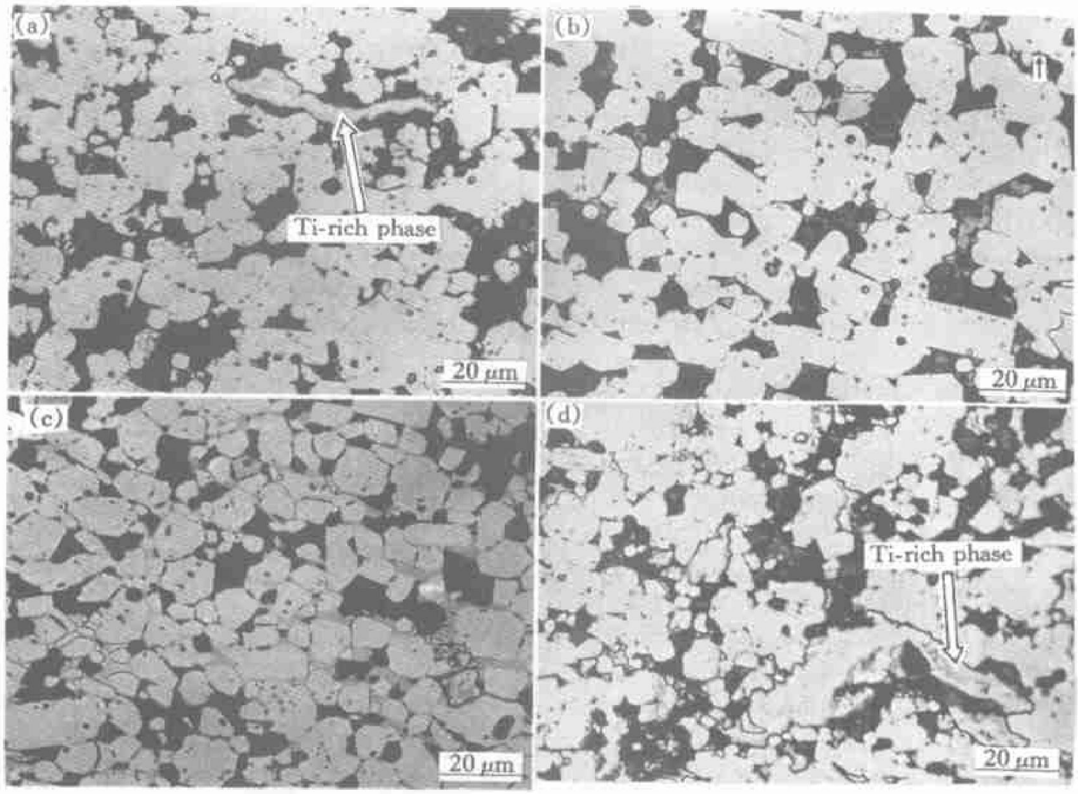

Fig.2 Optical micrographs for $Nd_{22}Fe_{71}B_7$ magnets with Ti and Cu additions
(a) —0.8 %Ti; (b) —0.8 %Cu; (c) —0.8 %Ti + 0.8 %Cu; (d) —1.6 %Ti + 0.8 %Cu

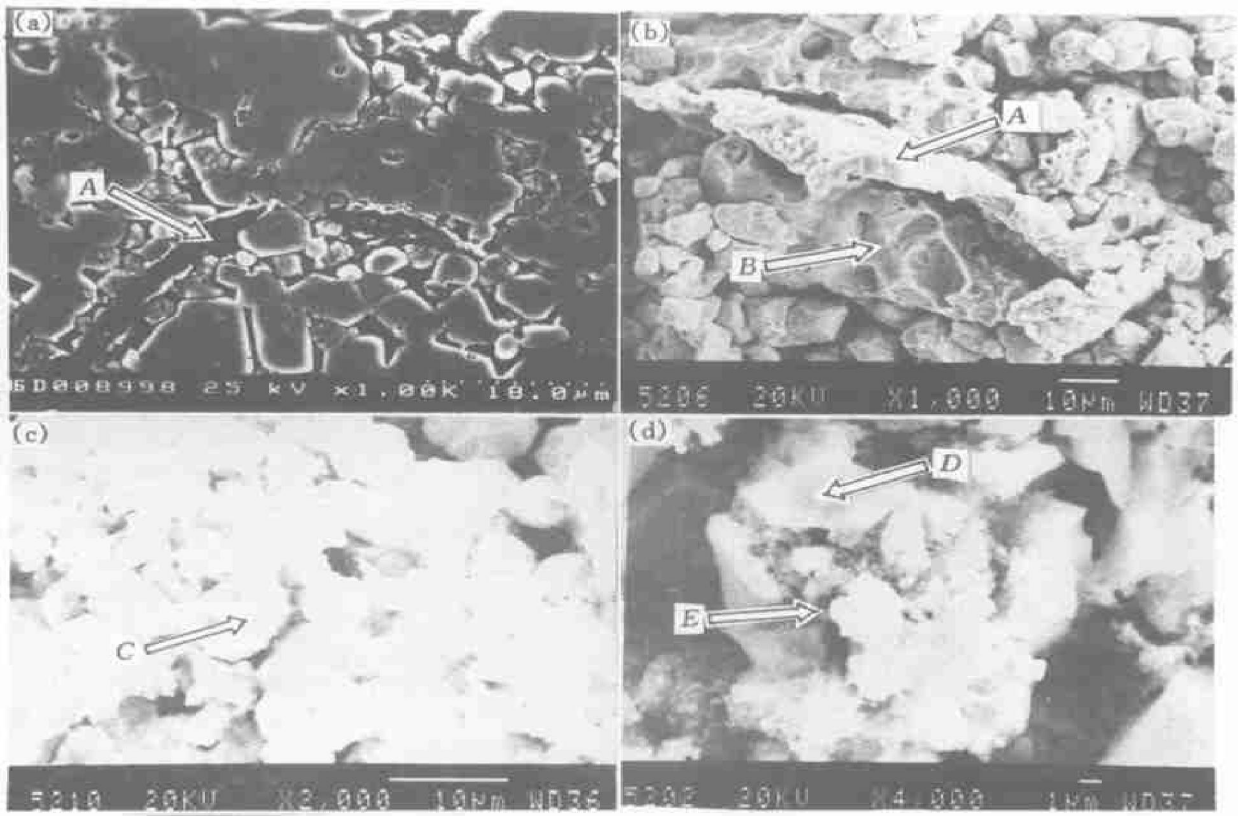

Fig.3 SEM micrographs for $Nd_{22}Fe_{71}B_7$ magnets with Ti and Cu additions
(a) —1.2 %Ti; (b) —1.2 %Ti, corroded; (c) —0.8 %Cu, corroded; (d) —1.2 %Ti + 0.8 %Cu, corroded

small amount of Ti addition has little effect on the microstructure of the $Nd_{22}Fe_{71}B_7$ magnet, so the coercivity changes slightly. If the Ti content is further increased over 0.8 %, a strip Ti-rich phase is formed in the intergranular region, resulting in the remanence decreasing sharply. In the Cu-doped magnet, element Cu segregates near the grain boundary of the magnetic $Nd_2Fe_{14}B$ phase and reduces the surface energy of the grain, so the grains of $Nd_2Fe_{14}B$ phase grow preferentially along a direction perpendicular to the easy magnetic axis during sintering. Though the segregation of Cu element on the surface of main phase reduces the magnetic coupling of the $Nd_2Fe_{14}B$ grains which is beneficial to the improvement of the coercivity, but the large $Nd_2Fe_{14}B$ grains is detrimental to the coercivity. So the coercivity improvement is limited to certain degree. In the Ti and Cu-doped magnets, element Cu also segregates on the surface of the magnetic phase, but interacts with element Ti to form a lot of fine Nd-Fe-Ti particles near the magnetic grain boundaries. The Nd-Fe-Ti particles can inhibit the growth of $Nd_2Fe_{14}B$ grains during the sintering, leading to a finer grains. So the coercivity of the Nd-Fe-B magnets is dramaticly increased. At the same time, the segregation of Cu and Ti elements on the surface of the main phase may 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. Because Ti cannot be completely dissolved in the Nd-phase of intergranular region when sintering with Ti of content over 0.8 %, a strip Ti-phase occurs in the intergranular region, which is the same as that in the individual Ti-doped magnet, resulting in the reduction of remanence. It is noticed that the coercivity increases by about 15 % in the individual pure Ti or Cu addition magnet, but it increases 73 % in the Ti and Cu co-added magnet. So, Ti and Cu co-addition can improve the coercivity more efficiently than individual pure Ti or Cu addition.

5 CONCLUSIONS

1) The coercivity of sintered Nd-Fe-B magnets can be slightly enhanced by individual pure Ti or Cu additives with little loss of remanence.

2) The coercivity of sintered Nd-Fe-B magnets can be largely enhanced by Ti and Cu co-addition. The improvement of the coercivity can be attributed to the segregation of Cu on the surface of $Nd_2Fe_{14}B$ phase and the occurrence of a lot of Nd-Fe-Ti particles near the $Nd_2Fe_{14}B$ phase grain boundaries. But the remanence sharply decreases at high Ti content due to the appearance of a strip Ti-rich phase in the intergranular region.

3) The coercivity increases about 15 % in the individual pure Ti or Cu addition magnet, but it increases by 73 % in the Ti and Cu co-added magnet. So, Ti and Cu co-addition can improve the coercivity more efficiently than individual pure Ti or Cu addition.

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