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CORROSION BEHAVIOR AND MAGNETIC PROPERTIES OF MELT-SPUN Nd-(Fe,Co,Ni)-B-(Al,Ti) RIBBONS.

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The corrosion behaviors and magnetic properties of the melt-spun Nd-Fe-B alloy ribbons in which have replaced Fe with Co and Ni and added a small quantities of Al,Ti were investigated from the anodic corrosion point of view and using EDXS and AES analyses. Although the corrosion degraded the magnetic properties, the addition of Ni gave these melt-spun ribbons the superior corrosion resistance with increasing Ni content. The corrosion products of ribbons surface were consisted of Nd and Fe oxides in the ribbon samples which didn't contain Ni, but Nd oxide in corrosion products almost disappeared in the Ni-added samples and the degradation of magnetic properties was also suppressed.

From these results, it was thought that the improvement of corrosion resistance was due to the suppressed dissolution of Nd-rich phase in grain boudaries and the suppression of coercive force's degradation in Ni-added ribbons magnet could be explained by the pinning effect between the Nd-rich phase and domain wall.

1. Introduction

Since the Nd-Fe-B magnet alloys were developed, it has taken a growing interest in Nd-Fe-B based permanent magnetic materials because of their superior magnetic properties. However, in spite of their excellent magnetic properties, the commercial utilization of these magnets is considerably limited because they have a poor thermal stability[1)] and a weak corrosion resistance even under ordinary environments.

Presently, in order to improve the corrsion resistance of Nd-Fe-B magnet alloys, it has been studying in two ways. One is to apply the oxidation-proof coating to magnet alloys[2)] and the other is to add some elements to magnet alloy so as to produce better corrosion resistance[3)].

The aim of this study is to investigate the role of small quantities of Al, Ti, and Ni on the magnetic properties of Nd-(Fe,Co)-B melt-spun ribbons and bonded magnets, and the corrosion behavior of them from the viewpoint of microstructure and electrochemical kinetics.

2. Experimental procedures

The composition of alloy ingots was divided into 2 groups based on Nd-(Fe, Co)-B as a standard composition. One group included a small amount of Al and Ti without Ni addition and the other group involved not only Ni, but also Al and Ti. The compositional ratios of samples are shown in Table 1.

The base alloys were fabricated by vacuum induction melting furnace(VIM) under high pure Ar gas to prevent rare-earth elements from evaporating. After crushing the based alloys into pieces, the melt-spun ribbons were made of them and the surface velocity of Cu-wheel was about 20 m/sec at which the magnetic properties are expected to be optimum. The corrosion behavior of samples was electrochemically monitored by potentiostat. Saturated calomel electrode was used as reference electrode and Pt electrode as counter electrode.

After melt-spun ribbons have been magnetized up to the saturation point under the pulsed field of 60kOe,magnetic properties were measured after and before corrosion test using vibrating sample magnetometer.

Table 1 Chemical composition of base alloys.

at%	Nd	Fe	Co	Ni	B	Al	Ti
I	15.05	61.20	15.93	0	5.78	2.04	0
II	14.12	64.23	14.79	0	4.78	1.05	1.02
III	14.11	63.19	10.77	5.11	4.79	0	2.03
IV	14.13	63.27	5.66	10.09	4.73	1.06	1.02

The microstructure was observed by polarization microscope, transmission electron microscope, the chemical composition of samples and corrosion products were examined by Electron Probe Micro Analysis, Energy Dispersive X-ray Spectroscopy and Auger Electron Spectroscopy.

3. Resuts and discussion

3-1. The microstructure of melt-spun ribbons

The microstructure of melt-spun ribbons observed by TEM is shown in Fig. 1. The grain size of only Al-added sample was about 150~200nm which were much larger than that of only Ti-added (50~70nm). Fig.1-b) shows the microstructure near the grain boundary. $Nd_2Fe_{14}B$ grains were surrounded by the grain boundary phases whose shape is a membrane along the grain boundary. These grain boundary phases met one another at the triple junction and coarse grain boundary phases were formed. According to Pinkerton et al[4], the coercivity of Nd-Fe-B melt-spun ribbon magnets can be explained by the pinning mechanism where $Nd_2Fe_{14}B$ grains were enclosed noncrystalline phase in the grain boundary. Therefore, it was thought the above grain boundary phases were related to the coercivity of Nd-(Fe,Co,Ni)-B-(Al,Ti) melt- spun ribbons.

It was examined from our EPMA results that the grain boundary phase was Nd-rich phase, as reported elsewhere, but they have not verified thoroughly. That is, whereas it was reported by Croat, Mishra etc.[5] that the

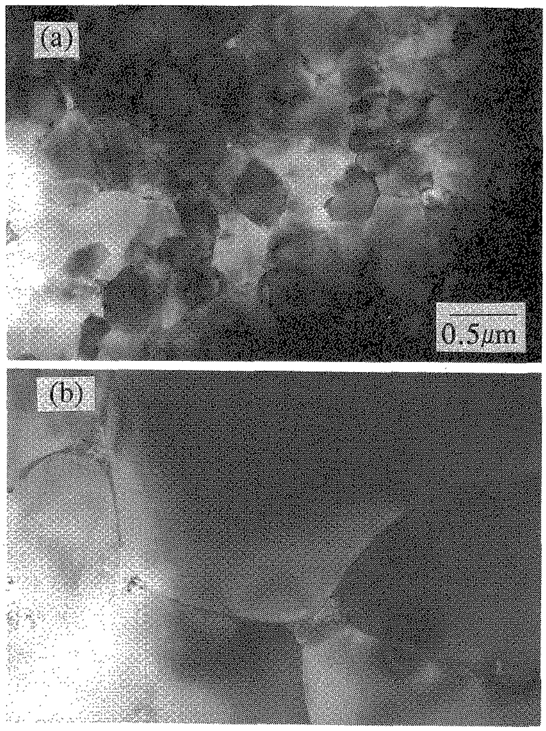

Fig. 1 TEM micrographs of $Nd_{15.05}(Fe_{61.20}Co_{15.93})B_{5.78}Al_{2.04}$ melt-spun ribbon.

ratio of Nd and Fe in grain boundary phase was 7:3, their ratio was 5:3 in this experiment. Meanwhile, one more inhomogeneous phase could be seen at the triple junction and it assumed to be B-rich phase. The ratio of Nd and Fe in this phase was about 2:7. It seemed that this phase was similar to the new grain boundary phase($Nd_{1+e}Fe_4B_4$ phase[6]) reported by Mishra which could be seen in the slowly cooled Nd-Fe-B melt-spun ribbons. However, because this phase could rarely be seen in other regions, we are now understanding the study for this phase.

3-2. Corrosion behavior

Fig. 2 shows the anodic polarization curves of melt-spun ribbons in neutral (NaCl), acid (H_3PO_4) and alkaline (NaOH) solutions respectively. As the potential increased, the corrosion current density increased in neutral and alkaline solutions. But, in acid solution, because the passive film layer was formed by corrosion products and it could prevent the solution from penetrating into the samples, oxidation/reduction reaction was suppressed.

And, Open circuit potentials(OCP) of Ni-added samples were higher than those of samples without Ni by 80~100mV. So, Ni-added samples are more stable than samples without Ni under all three corrosive solutions.

The corrosion mechanism in the Nd-Fe-B magnet was proposed by K.Sugimoto et al[7]. Nd-Fe-B-based magnet consisted of three phases with different compositions, i.e. $Nd_2Fe_{14}B$ phase, Nd-rich phase, and B-rich phase, and these phases were in contact one another to causes galvanic corrosion on the surface. That is, Nd-rich phase and B-rich phase acted as anode, $Nd_2Fe_{14}B$ phase as cathode, resulting in preferential corrosion in anode. As a result, both the B-rich phase and Nd-rich phase were corroded much rapidly, and the intergranular corrosion was proceeded.

In Ni-added samples, however, some of Fe in $Nd_2Fe_{14}B$ phase were replaced with some of Ni, and remaining Ni segregated into grain boundaries[3]. Since the segregated Ni made the potential of grain boundary phases higher and the difference in potential of anode and cathode reduced, the corrosion resistance of the grain boundary phases was improved, so the corrosion of these materials was suppressed.

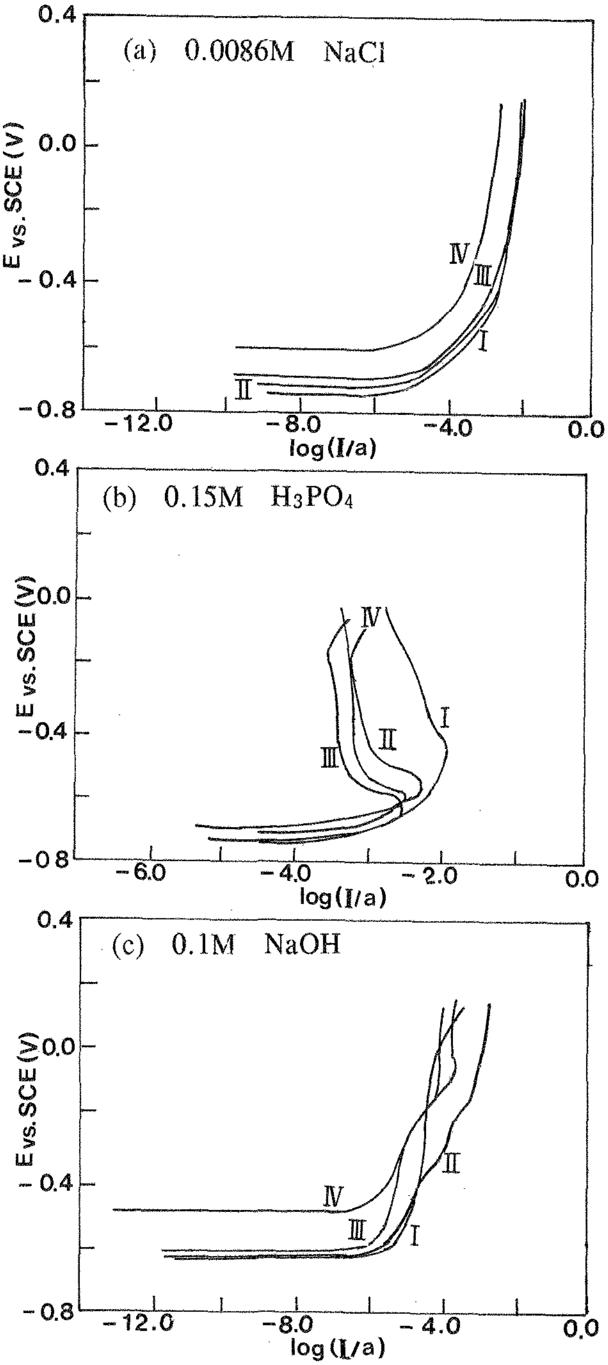

Fig. 2 Anodic polarization curves of melt-spun ribbons.

3-3. Magnetic Properties before and after the corrosion test

The magnetic properties of melt-spun ribbons were measured before and after the corrosion test. After corrosion test, as the corrosion resistance was improved, the degradation of magnetic properties was suppressed. That is, when the corrosion of ribbon was occurred by the previous galvanic corrosion, the Nd-rich phase at grain boundaries became depleted, and this might change the grain boundary composition, thereby the domain wall pinning becomes less and result in the degradation of coercive force.

However, in Ni-added sample, the dissolution of Nd-rich phase at grain boundaries are suppressed due to the Ni segregated into grain boundaries, so the magnetic properties are not degraded greatly. This fact also might be understood by the following discussion on the surface products of corrosion.

3-4. Surface Products of Corrosion

Fig.3 shows the appearance of corrosion products formed on the surface of Nd-(Fe,Co,Ni)-B-(Al,Ti) melt-spun ribbons after the corrosion in NaCl solution. In the case of Ni-added ribbons, the special differences in surface morphologies were not observed before and after the corrosion, but in Ni-free ribbon, there were considerable differences between them, showing that intense corrosion had occurred on the ribbon. In Fig. 3, white parts (actually, bright and blue color) show Nd-corrosion products such

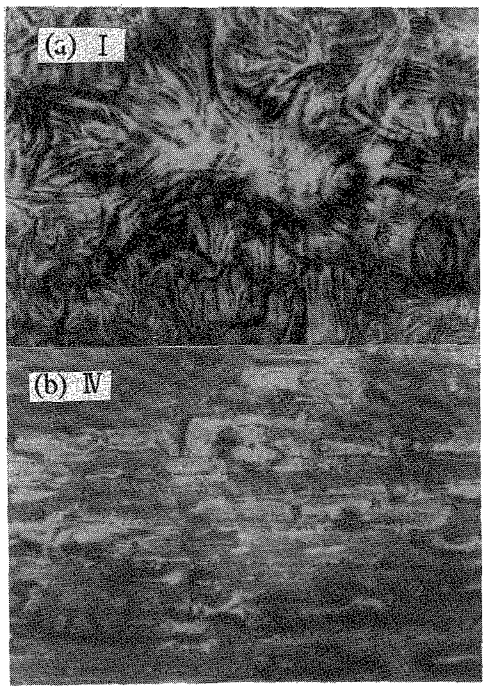

Fig. 3 Optical micrographs of melt-spun ribbon after corrosion test.(0.0086M NaCl)

as Nd_2O_3 and black parts (actually, dense brown color) Fe-corrosion products like Fe_2O_3. Therefore, resulting from these photograghs, whereas the considerable amount of Nd-corrosion products produced on the surface of Ni-free ribbons, the corrosion of grain boundary phases was suppressed highly in Ni-added ribbons, so that Nd-corrosion products were much disappeared.

While, we investigated the corrosion products of ribbons after the corrosion in H_3PO_4 solution using EDX and AES. Fig. 4 and 5 show EDX and Auger spectrum of melt-spun ribbons which were obtained after corrosion test. From EDXS and AES analyses, we also obtained the results that the amount of Nd element in the covered surface film was much more in Ni-free ribbons than in Ni-added ribbons. Such surface characteristics are consistent with that of corrosion products in NaCl solution.

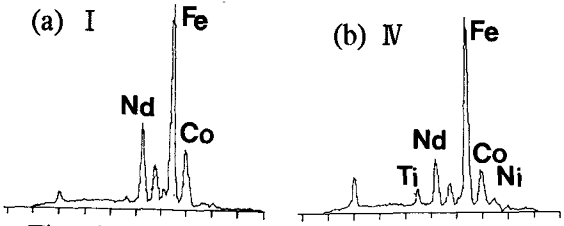

Fig. 4 Energy dispersive X-ray Spectrum of melt-spun ribbons after corrosion test. (0.15M H_3PO_4 solution)

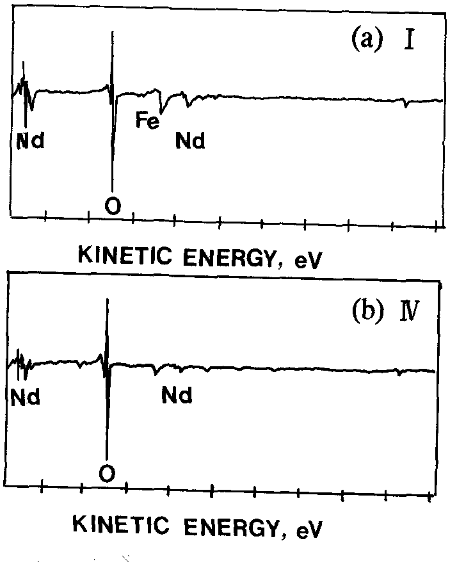

Fig. 5 Auger spetrum of melt-spun ribbons after corrosion test.(0.15M H_3PO_4 solution)

4. Conclusion

1) The addition of Ni decreased the coercive force of the melt-spun ribbons, and Al was more effective than Ti in improving coercive force, but the addition of both Ti and Al seemed to be very effective in improving the corrosion resistance as well as the coercive force before the corrosion test.

2) The addition of Ni improved the corrosion resistance of ribbons magnet through increasing the potential of the grain boundary phase and the more corrosion resistance, the more the degradation of magnetic properties were suppressed, which was believed to be due to the suppressed dissolution of Nd-rich phase in grain boundaries.

3) EDXS and AES analyses showed that the corrosion products of surface film were consisted of Nd and Fe oxides in the sample which didn't contain Ni, but the corrosion products of Nd oxide almost disappeared in the Ni added samples. Therefore, Ni addition not only improves the corrosion resistance,but also suppresses the degradation of magnetic properties by giving the Nd-rich phase more corrosion resistance.

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