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Electrochemical behavior of aluminum-coated Nd–Fe–B alloy

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Abstract

The Al thin film of about 10 μm was coated on the surface of the sintered $Nd_{11.0}Dy_{2.5}Fe_{79.5}Co_1B_6$ magnetic alloy, hereinafter described as the Nd–Fe–B specimen, and the effect of the Al thin film coating on the corrosion resistance of Nd–Fe–B permanent magnets has been investigated through the electrochemical measurements and XPS analysis. The glass peening on the Al thin film was also carried out, and its effect on the corrosion resistance was studied. Both of the Al-coated and Al-coated + glass-peened specimens showed the natural electrode potentials of −1.00 and −0.97 V which were slightly lower than −0.94 V of the Nd–Fe–B specimen. Comparing the natural electrode potentials of these three specimens, that of pure Al was remarkably low of −0.13 V. It was therefore considered that the corrosion solution penetrated to the surface of the Nd–Fe–B specimen through the Al-coated film formed on it. The XPS analysis showed that Si existed on the surface of the Al-coated + glass-peened specimen, which indicated that the glass peening treatment deteriorated the Al-coated film for the corrosion resistance.

Keywords: Nd–Fe–B permanent magnet; Potentiodynamic polarization curve; Corrosion resistance; Thin film Al coating; Glass peening

1. Introduction

Permanent magnets based on intermetallic compounds composed of rare earth elements and transition metals show exceptionally excellent magnetic properties. Therefore, they have been in practical use for numerous applications such as the devices in consumer electronics, computer peripherals, acoustics, magnetic resonance, biomedical and automation. Among these magnets, particularly Nd–Fe–B magnets on the basis of $Nd_2Fe_{14}B$ [1] has been investigated extensively due to its outstanding magnetic properties; for example, a commercially available magnet exhibits a maximum energy product, $(BH)_{max}$ of higher than 350 kJ/m^3, and hence, it occupies a leading position today. However, it is at the same time notorious for its poor corrosion resistance. According to Sugimoto et al. [2], the corrosion rates of these phases increase as follows: $Nd_2Fe_{14}B$ phase < $Nd_{1.1}Fe_4B_4$ phase < Nd-rich phase.

Therefore, under electrochemical conditions, the Nd-rich phase located around the $Nd_2Fe_{14}B$ phase becomes anodic against the $Nd_2Fe_{14}B$ phase. This occurs due to the formation of a galvanic couple between the $Nd_2Fe_{14}B$ phase and the Nd-rich phase. The reason for forming galvanic couple between these phases is ascribed to the fact that Nd is extremely active element against matrix phase of $Nd_2Fe_{14}B$. In addition, there is a great difference in volume between the $Nd_2Fe_{14}B$ phase and the Nd-rich phase. This means a small amount of anode metal composed mainly of Nd connects to a large amount of cathodic matrix of $Nd_2Fe_{14}B$; as a result, the corrosion rate of the Nd-rich phase is extremely accelerated. In order to improve the corrosion resistance, the effect of small additions of alloying elements on the corrosion behavior has been studied from the view point that the alloying elements should not only improve the corrosion resistance but also should not deteriorate the magnetic properties [3]. Ohashi et al. reported that Co is one of the most promising elements to improve the corrosion resistance [4]. However, it was reported that Co decreases the coercive force though it increases the Curie temperature [5–7]. It was also reported that this unfavourable

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influence of Co on the coercive force is effectively eliminated by the addition of Dy, Tb, etc. [8–10]. Besides the method of the addition of metal elements in order to improve the corrosion resistance of Nd–Fe–B magnets, the coating method with metals has been investigated. Among the metals, Al is reported to be one of promising metals. In this experiment, three specimens: the Nd–Fe–B, the Al-coated Nd–Fe–B, the Al-coated + glass-peened Nd–Fe–B and pure Al specimens were prepared, and their corrosion behavior was investigated by the potentiodynamic polarization and exposure methods.

2. Experimental

In this study, using neodymium metal (99.5% of purity), dysprosium metal (99.5% of purity), electrolytic iron (99.9% of purity), cobalt (99.9% of purity) and boron (99.9% of purity), the magnetic alloys corresponding to $Nd_{11.0}Dy_{2.5}Fe_{79.5}Co_1B_6$ (Nd–Fe–B specimen) were prepared by sintering process. Al coating was conducted by vacuum evaporation method, and the thickness of the Al-coated film formed on the specimen was about 10 μm. The glass peening was also carried out on some of the Al-coated specimens in order to make the Al film denser. Electrochemical methods were conducted as follows. The specimen with the dimension of 50 mm in length, 15 mm in width and 2 mm in thickness was polished with No. 2000 grit waterproofed abrasive paper followed by washing in alcohol and subsequent ultrasonic rinsing in acetone. The specimen electrode was coated with silicon rubber leaving uncoated area of 15 mm × 5 mm. Testing solution should be prepared considering that the specimen described above has poor corrosion resistance. In this experiment, therefore, 2.5% Na_2SO_4 aqueous solution of pH 6.4 was used, in which the solution was adjusted by deionized water whose specific electrical conductivity was less than 2.0×10^{-5} S m. The schematic diagram of apparatus for the measurement of the potentiodynamic polarization curve is shown in Fig. 1. It consists of a thermostatic bath, H-type electrolytic cell with anodic and cathodic chambers of $2 \times 10^{-4}\,m^{-3}$ in volume, an intermediate cell of Ag–AgCl (3.33 kmol/m^3 KCl) as a reference electrode, a potentiostat, and a personal computer for the measurement control. All of the potential values were shown based on the Ag–AgCl reference electrode. The exposure test was conducted under the condition of 383 K × 70%$_{RH}$ for 80 h, and the natural electrode potential was measured every 8 h. The corrosion product formed on the specimen surface was analyzed by XPS.

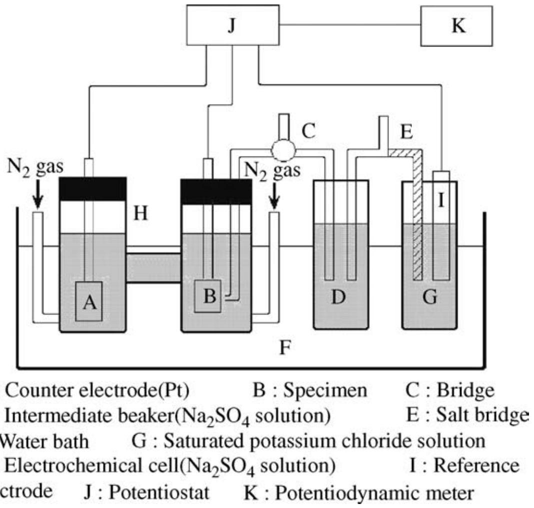

Fig. 1. Schematic diagram of apparatus for impedance measurement.

3. Results and discussion

Fig. 2 shows potentiodynamic polarization curves of four different specimens, i.e. (1) the Nd–Fe–B specimen, (2) Al-coated Nd–Fe–B specimen, (3) Al-coated + glass-peened Nd–Fe–B specimen, (4) pure Al specimen. The Nd–Fe–B specimen presented the typical hydrogen evolution type polarization curve in the cathodic region lower than the natural electrode potential of −0.94 V. The anodic current density was retarded between −0.90 and to −0.60 V, while above −0.60 V it increased abruptly. The diffusion-controlled anodic current density behavior was observed in the higher potential region than −0.50 V. Both of the Al-coated and the Al-coated + glass-peened specimens show the natural electrode potentials of −1.00 indicated by dotted line and −0.97 V indicated by broken line which are 0.06 V and 0.03 V lower than −0.94 V of the Ne–Fe–B specimen. This result means that the latter has a slightly poorer corrosion resistance than the former in spite of glass peening treatment. Though there exists the natural electrode potential differences among these three specimens, these differences are very small. Comparing the natural electrode potentials of these three specimens, that of pure Al was remarkably low of −0.13 V. It is therefore supposed that the corrosion solution penetrates to the surface of the Nd–Fe–B specimen through the Al-coated film formed on it.

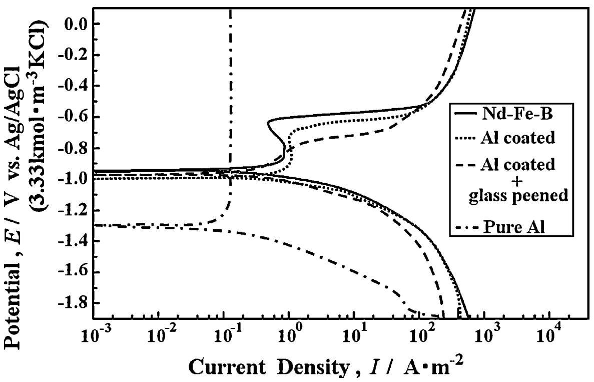

Fig. 2. Potentiodynamic polarization curves of the Nd–Fe–B specimen, Al-coated Nd–Fe–B specimen, Al-coated + glass-peened Nd–Fe–B specimen and pure Al in 0.176 kmol/m^3 Na_2SO_4 at 298 K.

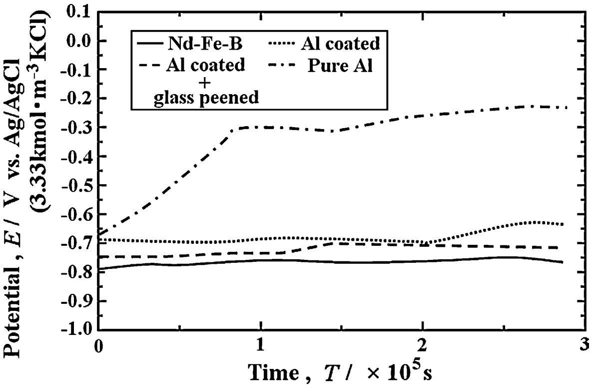

Fig. 3. The time dependence of the natural electrode potential during exposure test.

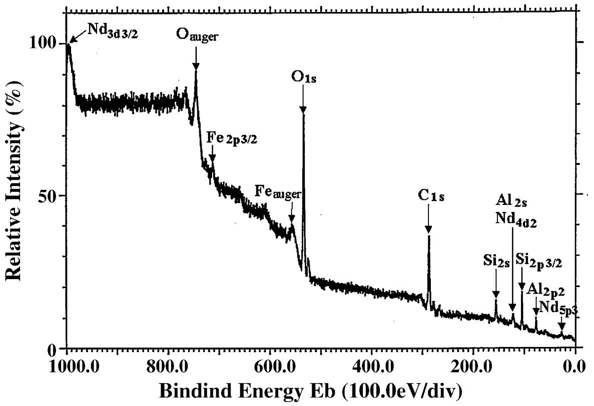

Fig. 4. XPS spectrum on the surface of the Al-coated + glass-peened specimen after exposure test for 80 h.

Fig. 3 shows the time dependence of the natural electrode potential during exposure test. The natural electrode potential was measured every 8 h. If the surface of the Nd–Fe–B specimen is perfectly covered with aluminum by Al-coating, the Al-coated Nd–Fe–B specimen should show the similar natural electrode potential change against time to that of pure Al specimen. The Al-coated Nd–Fe–B specimen however showed the similar behavior to the Nd–Fe–B specimen. It is therefore considered that Al-coating does not form the film with enough protection. In addition, comparing to the Al-coated specimen curve without glass peening indicated by dotted line the location of the Al-coated specimen curve with glass peening indicated by broken line is closer to that of the Nd–Fe–B specimen curve. This indicates that the film formed by Al coating is damaged by the glass peening.

Fig. 4 shows XPS analysis result on the surface of the Al-coated Nd–Fe–B specimen with glass peening after exposure test for 80 h. Judging from the fact that both Si_{2s} and Si_{2p} spectra exist in Fig. 4, it is confirmed that glass enters and remains in the Al-coated film with glass peening. It is supposed that the glass in the film causes cracking and makes it easy for the corrosion solution to enter into the film and reach the surface of the Nd–Fe–B specimen. Consequently it is concluded that the glass peening treatment did the Al-coated film more harm than good for the corrosion resistance. Therefore, the other method to make the Al-coated film smoother and denser should be investigated in the future, e.g. the method using ice or dry ice ball instead of glass ball.

4. Conclusion

In this study, four specimens: the Nd–Fe–B, the Al-coated Nd–Fe–B, the Al-coated + glass-peened Nd–Fe–B and pure Al specimens, were prepared, and their corrosion behavior were investigated by the electrochemical method. Both of the Al-coated specimen and the Al-coated + glass-peened specimen showed the much more similar potentiodynamic polarization curves to that of the Nd–Fe–B than that of the pure Al specimen. This means that both of the Al coating and the Al coating + glass peening treatment were not effective to improve the corrosion resistance of the Nd–Fe–B specimen. The XPS analysis indicated that Si existed on the surface of the Al-coated + glass-peened Nd–Fe–B specimen, which suggested that glass peening treatment deteriorated the Al-coated film.

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