The analysis of adhesion failure between Ni-coating and sintered NdFeB substrate

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Abstract. Ni-coating was widely used to protect the sintered NdFeB magnet from corrosion by Watt electro-deposition solution. However, the protection failure always occurs due to poor adhesion strength between Ni-coating and NdFeB substrate. In present work, the adhesion strength of the Ni-coating on NdFeB substrate was measured by vertical tensile method to strip Ni-coating from NdFeB substrate. The results revealed that the adhesion failure was occurred in the side of the NdFeB substrate due to a weak zone sometimes shown cracks located inside of NdFeB substrate, rather than in the interface between Ni-coating and NdFeB substrate. Comparing with cross section morphology of NdFeB magnet after pretreatment, it is concluded that the crack could be formed during the electro-deposition process. The effect of the pH value of bath on adhesion strength indicated that the crack could be induced due to electrochemical hydrogenation of NdFeB substrate during electro-deposition.

1. Introduction
NdFeB permanent magnets have been widely used for their excellent magnetic performance [1]. However, the corrosion resistance of the NdFeB permanent magnets is poor due to its multiphase microstructure consisting of matrix phase Nd₅Fe₁₄B, Nd-rich phase, and B-rich phase [2-6]. Protective coatings had to be deposited on the NdFeB substrate surface to isolate the substrate from the environment [7, 8]. Ni-coating was widely used in industry by Watt electro-deposition solution. Adhesion strength of the Ni-coating on the NdFeB substrate is one of the most important crucial factors to protect the NdFeB magnet form corrosion. However, the failure of protection always occurs due to poor adhesion strength between the Ni coating and the NdFeB substrate. The mechanism of the adherence evaluation between electro-deposited Ni-coating and NdFeB permanent magnet was reported by a thermal shock method in previous paper [9]. In present report, the adhesion strength of Ni-coating on NdFeB substrate was evaluated by a vertical tensile method, the effect of pH on adhesion strength was researched and the adhesion failure mechanism between electro-deposition Ni-coating and sintered NdFeB substrate was discussed.

2. Experiment
The specimens of the sintered NdFeB magnets were shaped in dimension of 25×20×3mm. The NdFeB magnet is composed of matrix phase, Nd-rich phase, and B-rich phase. The matrix phase, a tetragonal
compound of Nd$_2$Fe$_{14}$B, is the most significant of the ferromagnetic phase. The Nd-rich phase was located at the grain boundary surrounding the matrix phase. B-rich phase disperses randomly inside the Nd-rich phase.

Before electro-deposition, pretreatment was performed as follows: degreasing the surfaces of the specimens in an alkaline solution for 2 minutes, pickling in a 3% nitric acid solution for 3 minutes, activated in a 3% sodium citrate solution for 2 minutes, and finally, rinsing with de-ionized water. The Ni-coating was deposited on NdFeB substrate by electro-deposition in watt solution, and the composition of bath as follows: NiSO$_4$ 1.8mol/L, NiCl$_2$ 0.35mol/L, HBO$_3$ 45g/L. The density of the deposition current was 0.3A/dm$^2$, with deposition time 100 minutes and bath temperature 323K. The Ni-coating was deposited in different pH value of bath, and the pH value as following: 4.75, 4.5, 4.16, 3.8.

The adhesion strength of electro-deposition Ni-coating on NdFeB substrate was tested by vertical tensile method, during test, the coating was stripped out from substrate by tensile load. The schematic diagram of test mount was shown in fig.1. A stainless steel rod with 18 mm diameter was glued onto the Ni-coating surface and dried at room temperature for 72 hours before tests. During adhesion strength test, with increasing tensile load, the load-displacement curve was recorded until the Ni-coating was stripped out from NdFeB substrate. After adhesion strength test, the NdFeB specimen was stripped into two parts: the stripped layer and the remained NdFeB substrate as its model was shown in fig.2. The cross section morphologies were observed by scanning electron microscopy (SEM).

3. Results and Discussion
For the tensile load applied on the coating, the NdFeB specimen was stripped into two parts: the stripped layer and the remained NdFeB substrate. Fig.3 shows the cross section morphology of the stripped layer, and its Ni-coating was deposited with the bath pH value of 4.16. Both the Ni-coating and NdFeB substrate can be seen from fig.3. It can be found that the fracture did not happen at the interface between the Ni coating and the substrate. The stripped plane was located inside of NdFeB substrate close to the interface between the Ni-coating and the NdFeB substrate. It indicated that the adhesion failure was happen at inside of NdFeB substrate.

Fig.4a shows the cross section morphology of the Ni-coated NdFeB substrate, and the Ni-coating was deposited with the bath pH value of 4.16. There is an excellent interface bonding between the Ni-coating and NdFeB substrate. However, a crack was found in the NdFeB substrate close to the interface between the Ni-coating and NdFeB substrate. As a weak zone, the crack of the substrate could lead to material fracture while a tensile load was applied to the as-deposited NdFeB specimens. The existence of the crack could induce the stripped plane occurred in the NdFeB substrate close to the interface between the Ni-coating and NdFeB substrate, and the NdFeB substrate was divided into surface layer and inner layer due to the crack. The adhesion strength was measured by vertical tensile
method reflected only the adhesion property between the surface layer and inner layer of the NdFeB substrate. The adhesion strength could depend intensively on the crack shape, and the wider or longer crack can lead to the lower adhesion strength. Therefore, the formation reason of the crack is a crucial factor to influence the adhesion strength. It is obvious that the crack can be formed during the whole Ni-coating preparation process including pretreatment and electro-deposition process. However, no crack was found in the cross section morphology of NdFeB substrate after pretreatment in Fig 4b and this indicated that the crack should be formed in the course of electro-deposition.

Figure 3. The cross-section morphology of the stripped layer.

Figure 4. a: The cross section morphology of Ni-coated NdFeB substrate; b: The cross section morphology of NdFeB substrate after pretreatment

Fig.5 shows adhesion strength of the NdFeB specimens deposited with the Ni-coating at different pH value of bath. The adhesion strength was increased gradually with the increase of pH value of bath. During electro-deposition in Watt solution, a small amount of hydrogen ions were reduced to atomic hydrogen on the electrode surface is inevitable. Generally, the decrease of pH value of bath can make more hydrogen atoms reduce on the substrate surface during electro-deposition, thereby the more hydrogen enter into the coating. This leads to the increase in the brittleness and decrease in the plasticity of the coating, and it could deteriorate the interface bonding and decrease the adhesion strength between the coating and substrate. However, for the Ni-coated NdFeB, the adhesion failure did not happen in the interface between the Ni-coating and NdFeB substrate, and the adhesion strength could depend intensively on the width and length of crack. The change of adhesion strength indicated that the pH value of bath had a strong influence on the crack and the reduced hydrogen atoms could diffuse into the NdFeB substrate and induced the formation of crack. W. Bloch had reported that hydrogen embrittlement could happen in the NdFeB substrate during electro-deposition of the Ni-
coating [10]. It was well known that the hydrogen can be absorbed forcefully into the sintered NdFeB magnet [11, 12]. The affinity of hydrogen with the Nd-rich phase is stronger than that of the Nd$_2$Fe$_{14}$B matrix phase [13], and in the case of electrochemical hydrogen charging, the hydrogen absorption process is rather slow and hydrogen is mainly located in intergranular regions surrounding the grains from all sides [14]. Therefore, for the electro-deposition of Ni-coating on NdFeB substrate, most of reduced hydrogen atoms could be absorbed into the Nd-rich phase and diffused into inside of the NdFeB substrate. Those hydrogen atoms could finally concentrate in the defects (pore, cavity etc) of the grain boundary. Subsequently hydrogen can react with Nd-rich grain boundary phase to produce Nd hydride, which can cause tremendous crystal lattices expansion of the Nd-rich phase and generate local stresses. The mechanical effect of the expansion is the disadhesion of the Nd$_2$Fe$_{14}$B matrix grains, and finally resulted in the crack formation. When tensile load was applied to the NdFeB specimen, the adhesion failure should be occurred in the weakest location, thus, the NdFeB specimen could be stripped along the crack. Even without load was applied to the NdFeB specimen, the bubbling and peeling of the Ni-coating could happen due to the existence of the inner crack.

![Graph](image.png)

**Figure 5.** Adhesion strength of NdFeB specimens deposited with Ni-coating at different pH value of bath.

4. Conclusion
Adhesion failure of the Ni-coated NdFeB substrate was occurred in the NdFeB substrate close to the interface between the Ni-coating and NdFeB substrate due to the existence of the crack. The crack formation was attributed to the electrochemical hydrogenation of the Nd-rich grain boundary phase during electro-deposition.

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