

# Multi-layered electroless Ni–P coatings on powder-sintered Nd–Fe–B permanent magnet

Zhong Chen<sup>a,\*</sup>, Alice Ng<sup>a</sup>, Jianzhang Yi<sup>b</sup>, Xingfu Chen<sup>b</sup>

<sup>a</sup>*School of Materials Science & Engineering, Nanyang technological University, Singapore 639798, Singapore*

<sup>b</sup>*Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore*

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## Abstract

This paper has shown a successful protective coating scheme for powder-sintered Nd–Fe–B permanent magnet using multi-layered electroless nickel (EN) deposition. A low-phosphorus nickel layer is plated with an alkaline EN solution first, followed by a high-phosphorus nickel layer plated with an acidic solution. An additional topcoat by medium-phosphorus nickel on the high-phosphorus coating is also explored. It is shown that the high-phosphorus nickel layer coated in acidic solution provides the best corrosion protection because of its dense amorphous structure. The medium phosphorus topcoat is also dense and is able to provide reasonable corrosion resistance. The low-phosphorus layer itself does not have enough corrosion resistance; its main role is to provide an intermediate coating on the powder-sintered magnet. X-ray diffraction measurement shows that the low-phosphorus coating consists of nano-crystallites, and the high- and the medium-phosphorus coatings are dominated by amorphous structure. Microscopic observation and scratch test on these composite coatings demonstrate good adhesion between the magnet and the coatings. Remanence and coercivity of the plated magnet decrease with the applied coatings, but measured values are still very attractive for practical applications among known hard magnets.

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## 1. Introduction

Nd–Fe–B permanent magnet was developed in the 1980s [1] with excellent magnetic properties such as high remanence, high coercivity, and large maximum energy product. The major drawback that has prevented its wide spread application is its low corrosion resistance in humid and chloride environment. To overcome this problem, a lot of research work on the protective coating on Nd–Fe–B magnet has been carried out [2–8]. The coating material can be generally categorized into two groups: polymers, including epoxy resin [2,3] and bismaleimide (BMI) resin [4], and metals [2,5–8]. Generally epoxy coating is easy to apply and less costly. However, level of corrosion protection provided by polymeric resin is relatively low compared with metallic coatings. This is because polymers are, in

general, prone to moisture attack and mechanical scratch, which will weaken the adhesion between the coating and the base material. Among polymeric coatings, BMI seemed to be able to provide the best protection [4] but the material itself is brittle and difficult to prepare. Its adhesion has to be improved by an extra layer of undercoat [4], so the advantage of simplicity and low cost of polymer resin coating is, to a certain degree, lost. Generally polymeric coatings are considered more suitable for applications in less stringent conditions such as low temperature and low humidity environment.

Metallic protection is mainly achieved by two types of techniques: vapour deposition and electrochemical plating [5]. Post-deposition heat treatment may be necessary after coating is carried out to improve the adhesion between the coating and the magnet. The advantage of metallic coatings is that they are capable of providing better protection in harsher working environment. On the other hand, the disadvantage is the higher cost due to materials,

\*Corresponding author. Tel.: +65 67904256; fax: +65 67909081.

E-mail address: [aszchen@ntu.edu.sg](mailto:aszchen@ntu.edu.sg) (Z. Chen).

processes, and equipment involved. Despite the cost concern, so far the majority research work of magnet protection is still centred on metallic coatings because of the excellent protection they can provide. Coated metals that have been studied include Ni, Cr, Al, Zn, Cu, and various composite coatings such as Ti/Al, Ni/Al, Ni/Cr, and Al/Fe [2,5–10]. Successful protection has been achieved in spite of some disagreement on the superiority among some reports [2,5]. Among these metallic coatings, electrolytic Ni coating is one of the most promising candidates because of its good performance and relatively low processing cost.

This work explores the possibility of using electroless Ni–P (EN) plating for the protection of powder-sintered Nd–Fe–B permanent magnet. Electroless plating is a self-catalytic process, and, because of this uniqueness, the coatings are very uniform regardless the shape of coated parts. Electroless Ni–P plating requires less equipment set-up cost, and is most suitable for components of complex shape. Its excellent resistance to corrosion and wear has been proven by numerous other engineering applications. There has been little investigation on EN application on Nd–Fe–B magnet. Part of the reason is EN plating, especially the ones with medium- and high-phosphorus content for corrosion protection, is usually achieved in acidic solutions of pH around 4.8 [11]. However Nd–Fe–B reacts quickly with  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in acidic solutions. Unless a layer of coating can be quickly applied, strong reaction will prevent coating from being applied despite that Fe is a catalyst for Ni reduction. The problem is extremely serious with powder-sintered magnet; the chemical reaction precedes the Ni plating reaction, resulting in complete disintegration of the sintered magnet.

The approach adopted in the current study is to coat an intermediate layer of Ni–P in an alkaline solution first. This intermediate layer itself is not enough to provide the needed corrosion protection, since it is not dense enough and only contains a low percentage of phosphorus. The role of this layer is to provide a platable surface for the corrosion-resistant Ni–P coatings plated in the conventional acidic solutions.

After the coatings were successfully applied, their cross-sectional structure, adhesion to the magnet, corrosion resistance, and effect on magnetic properties were analyzed and discussed.

## 2. Experiment

Commercially available powder-sintered Nd–Fe–B permanent magnet samples were used in the experiment. They were in disk form with diameter and thickness of 8.0 and 1.5 mm, respectively. Samples were first degreased in an alkaline solution at 70–80 °C for 90 s, and then immersed in 5%  $\text{HNO}_3$  for 30 s at room temperature for oxide removal. Finally they were placed in 5%  $\text{H}_2\text{O}_2$  + 10% acetate solution for micro-etching the surface before the Ni–P coatings were applied.

Preliminary experiment had shown that this sintered magnet reacted strongly with acidic electroless nickel solution once being placed in the bath, causing plating out of the solution and disintegration of the sintered magnet itself. Therefore, it is necessary for an intermediate layer to be plated in an alkaline nickel solution first, followed by an acidic coating. Three types of sample were prepared for the study. Sample A was coated in the alkaline solution with a low-phosphorus Ni–P layer to 20  $\mu\text{m}$  thickness. Sample B was coated to 5  $\mu\text{m}$  thickness with the same low-phosphorus Ni–P in the alkaline solution, followed by 15  $\mu\text{m}$ -thick high-phosphorus Ni–P in an acidic solution. Sample C began with the same coatings as sample B and was further plated by 5  $\mu\text{m}$  topcoat of medium-phosphorus Ni–P in acidic solution. Table 1 gives a summary of the three types of coatings employed in this study.

The morphology of coatings was observed under a scanning electron microscope (SEM). Compositions of various layers of coating were analyzed by energy dispersive X-ray spectroscopy (EDX) installed in SEM. X-ray diffraction (XRD) was carried out to determine the degree of crystallinity of the coatings.

The adhesion between the coating and the magnet was examined by the observation on cross-section under microscope and a mechanical scratch test. The scratch test was carried out in a CSEM microscratch tester. Vertical load was progressively applied so that the depth was increased linearly with time during scratching. This test also serves the purpose of qualitatively probing the mechanical properties of coatings. For example, brittle films may fracture during a scratch test, and a weakly adhered film may delaminate from the substrate.

Corrosion resistance of the above three coatings was investigated by accelerated test in 50% HCl (by volume)

Table 1  
Summary of the structure and P content of the Ni–P coatings

Samples	Intermediate layer (alkaline solution)	High-P coating (Acidic solution)	Medium-P topcoat (acidic solution)
A	20 $\mu\text{m}$	No	No
B	5 $\mu\text{m}$	15 $\mu\text{m}$	No
C	5 $\mu\text{m}$	15 $\mu\text{m}$	5 $\mu\text{m}$
P content (wt%)	2.5–3.0	11.1	6.7

solution. Weight loss was monitored at every 5 min interval for up to 130 min.

Magnetic measurement was carried out before and after plating in a vibrating scanning meter (VSM). From the hysteresis curve, remanence,  $B_r$ , and coercivity,  $H_c$ , were determined.

### 3. Results and analysis

#### 3.1. The coating composition and microstructures

As discussed above, since the Nd–Fe–B reaction with acidic electroless Ni–P solution caused disintegration of the magnet, alkaline electroless solutions had to be employed first to provide an intermediate layer. Usually only low-phosphorus coating can be achieved in alkaline solutions [11]. The current study found no exception. Out of four types of solution that had been experimented with, only one proprietary recipe was able to achieve a uniform, well-adhered layer on the magnet. The successful solution consisted of 25 g/L nickel sulphate, 25 g/L sodium hypophosphite, and other necessary ingredients such as complexers, accelerators and stabilizers, working in the pH range 8.5–9 and temperature range 85–90 °C. The deposition rate was 8–10  $\mu\text{m/h}$ .

The phosphorus content of the low-, medium-, and high-P layers was found to be 2.5–3.0, 6.7, and 11.1 wt%, respectively by EDX. The surface morphology of the three samples is shown in Fig. 1. Sample A consists of much smaller nodules than B and C. Microscopic pores are visible in sample A (Fig. 1a). XRD examination in Fig. 2a reveals its structure to be mainly crystalline. Dense, much larger nodules microstructure was observed in samples B and C (Figs. 1b and c). XRD results in Figs. 2b and c reveal that both the high-phosphorus and medium-phosphorus coatings are mainly amorphous. Between the two, the peak in the high-phosphorus curve is broader, indicating a total dominance of amorphous structure.

#### 3.2. Adhesion assessment

The adhesion between the coatings and the magnet was examined by observing the cross section and the mechanical scratch test. As shown in Fig. 3, intermediate coating adheres well to the magnet. Despite that Nd–Fe–B powders were not densely packed in the surface layer, the Ni–P coating has successfully filled into the gaps between the magnet particles. The coating also conforms to the surface morphology of sintered magnet.

Fig. 4 shows the scratching marks on the coated sample. In all three samples, the diamond indenter tip ploughed into the coatings, leaving a clear trace of plastic flow of the coating materials. In sample A (Fig. 4a), a few micro-cracks/openings are observed in the low-P coating. This is due to the existence of pores in the coating acted as the initiation sites for cracking. Scratch marks in samples B and C (Figs. 4b and c) are smooth. In all three types of

samples, there was no sign of delamination of the coating from the substrate. Nor was there any sign of brittle fracture of coatings. These results indicate that (1) coatings are ductile, and (2) adhesion between the coatings and the magnet is strong enough to survive the shear action by scratch test.

#### 3.3. Corrosion performance

The result for weight loss in the HCl solution is shown in Fig. 5. Sample A exhibited the poorest corrosion resistance; coating broke off at 20 min. There were two reasons that contributed to the failure. First, low-P coating itself reacted with the HCl solution at very fast speed. Second, the coating was not dense enough to prevent the solution from reaching the magnet through pores. As a result, the solution penetrated through the coating and reacted with the magnet directly, causing the coating spall off quickly. Sample C showed a gradual increase in weight loss by the medium-phosphorus nickel coating but there was no spallation of the coating. There was a linear relation between weight loss and soaking time for the initial 110 min. Sample B maintained its integrity through out the test without any appreciable loss in weight. This result verifies what has been well known that high-P content, amorphous Ni–P coating provides the best corrosion resistance.

#### 3.4. Magnetic properties

There was little difference in the hysteresis curve among the three types of coated samples. On average, there was a loss of coercivity ( $H_c$ ) by 24% and of remanence ( $B_r$ ) by 16%. Fig. 6 shows the comparison between a coated and a uncoated sample. Possible cause of degradation will be discussed later. Values of  $B_r$  and  $H_c$  of coated sample are still very attractive among all known hard magnet materials.

### 4. Discussion

The exact cause for loss of coercivity and remanence remains to be further investigated. A possible cause could be the galvanic corrosion of the magnet during the series of pre-coating treatment and during intermediate coating. Nd–Fe–B magnet consists of three phases: B-rich phase, Nd-rich phase and  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phases [2]. In a galvanic corrosion, B-rich and Nd-rich phases along the grain boundary of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase will become an anode and can be corroded. In addition, since the volume of the two anode phases is much smaller than the cathode  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase, the corrosion of anode phases happens very fast. The Nd-rich phase plays the role of damping the nucleation of reverse domains. Therefore, corrosion of this phase results in the degradation of coercivity [12].

The series of pre-treatment is crucial to ensure a good adhesion between the coating and the base material.

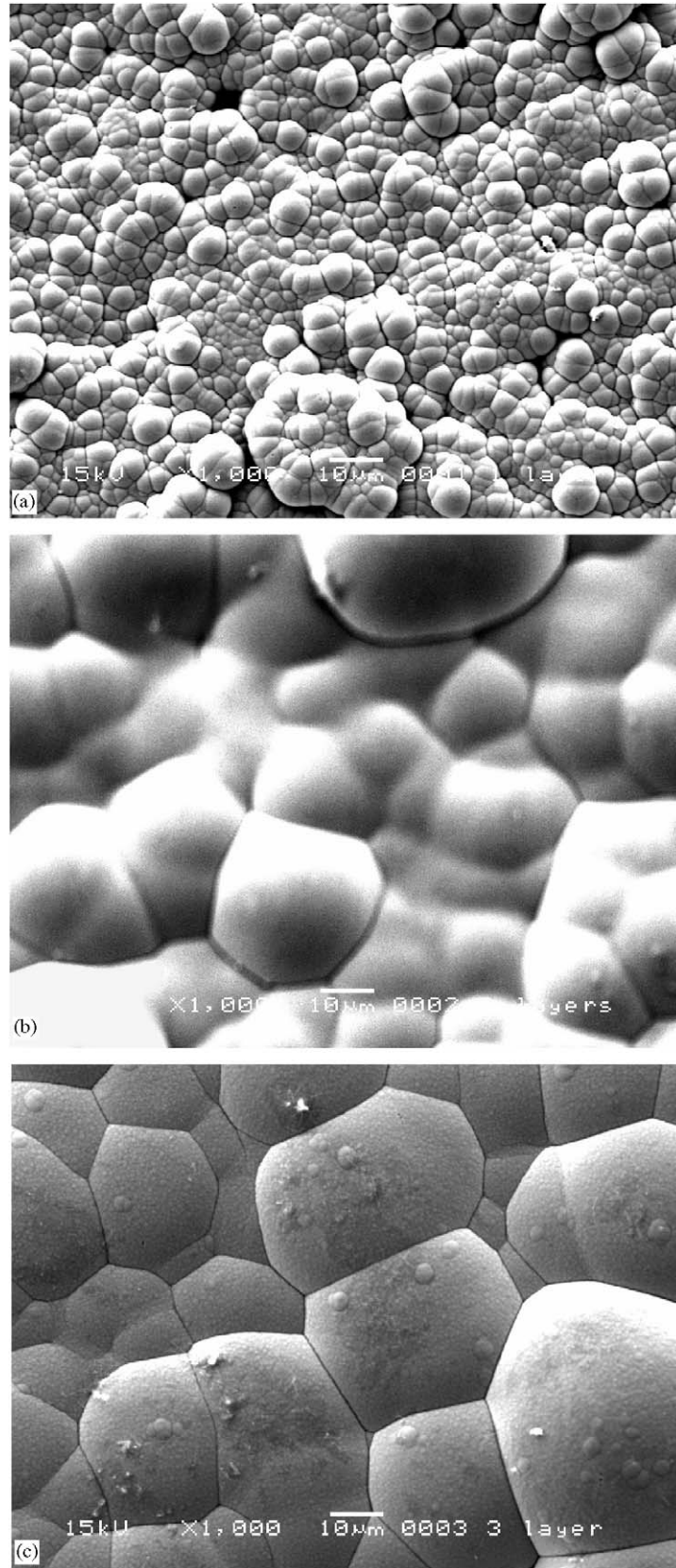


Fig. 1. Surface morphology of the three samples: (a) Sample A, (b) sample B and (c) sample C.

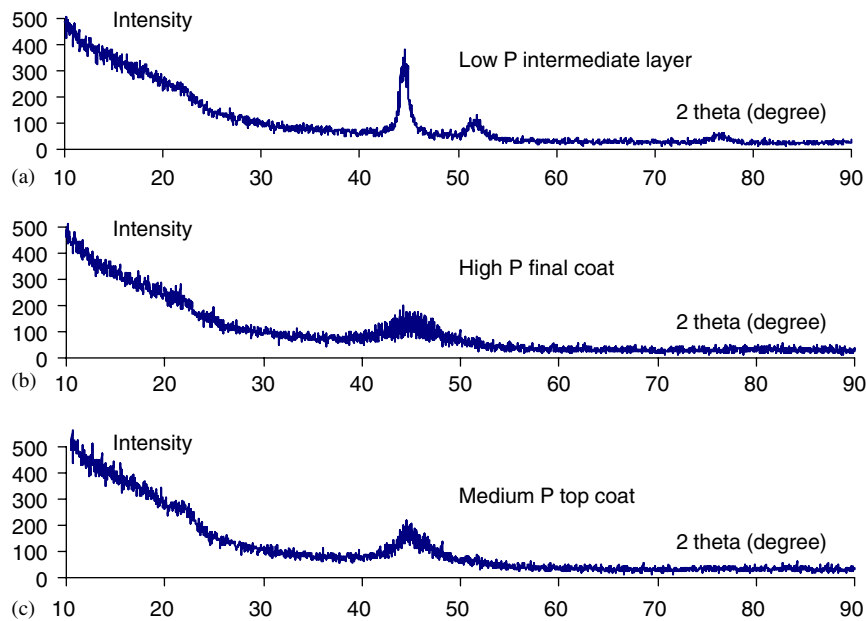


Fig. 2. XRD patterns of (a) sample A, (b) sample B and (c) sample C.

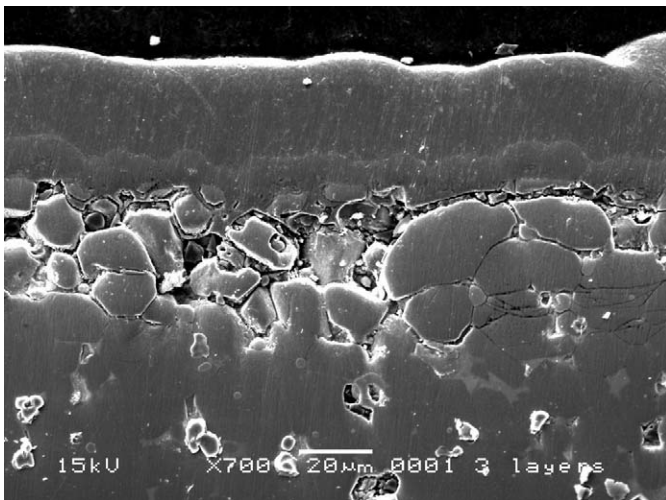


Fig. 3. Cross-section SEM of sample C. The three layers are clearly visible. The intermediate Ni–P coating fills up the gap between neighbouring Nd–Fe–B powders on the surface. Note that in its surface layer, the magnet powders are loosely packed.

Despite the loss after coating, values of  $B_r$  and  $H_c$  of the coated specimens are still very high compared with reported values of other hard magnets [13]. In applications that reliability/durability is of the most concern, the unavoidable sacrifice in magnet properties is well justifiable.

The purpose for a topcoat of medium-P coating in sample C is not to seek better corrosion protection than what the high-P coating can provide. In fact it is known to be inferior as far as corrosion resistance is concerned. The medium-P layer is to act as a sacrificial layer in case a mechanical scratch has penetrated through the top coating. Should this happen, the topcoat has a lower electrode

potential than the underneath high-P layer so that it will corrode first in such a galvanic corrosion.

Besides surface coating on the magnet, corrosion resistance could also be improved by alloying elements such as Al, Co, Cr, and Ni into the magnet [12,14]. Inevitably magnetic properties have to be sacrificed as the results of such an alloying process. Besides the inevitable processing cost increase, the increase of corrosion resistance is at the cost of magnet properties. Therefore, a balance between corrosion and magnetic properties has to be reached depending on the requirement for a specific application. Recently, Liu et al. [15] reported that the modified organic silicon (MOS) cladding and the dichromate passivation reducing (DPR) cladding of Nd–Fe–B powders showed improved compressive strength and corrosion resistance, and the DPR Sn-bonded Nd–Fe–B suffered more loss in magnetic properties. The current study shows that electroless Ni–P coating is a viable and reliable method for the protection of powder-sintered Nd–Fe–B magnet. We have shown good corrosion protection by EN plating of up to 25  $\mu\text{m}$  thick, which stands as an attractive candidate for low-cost, highly reliable alternative coating method.

## 5. Conclusions

Protection of power-sintered Nd–Fe–B magnet was successfully achieved by an intermediate coating in alkaline solution followed by high- or high-/medium-phosphorus coatings in acidic solutions. The phosphorus content for low-, medium- and high-phosphorus coatings are 2.5–3.0, 6.7, and 11.1 wt%, respectively. Microstructural and mechanical examinations show that good adhesion is achieved by the intermediate coat. All three coatings show

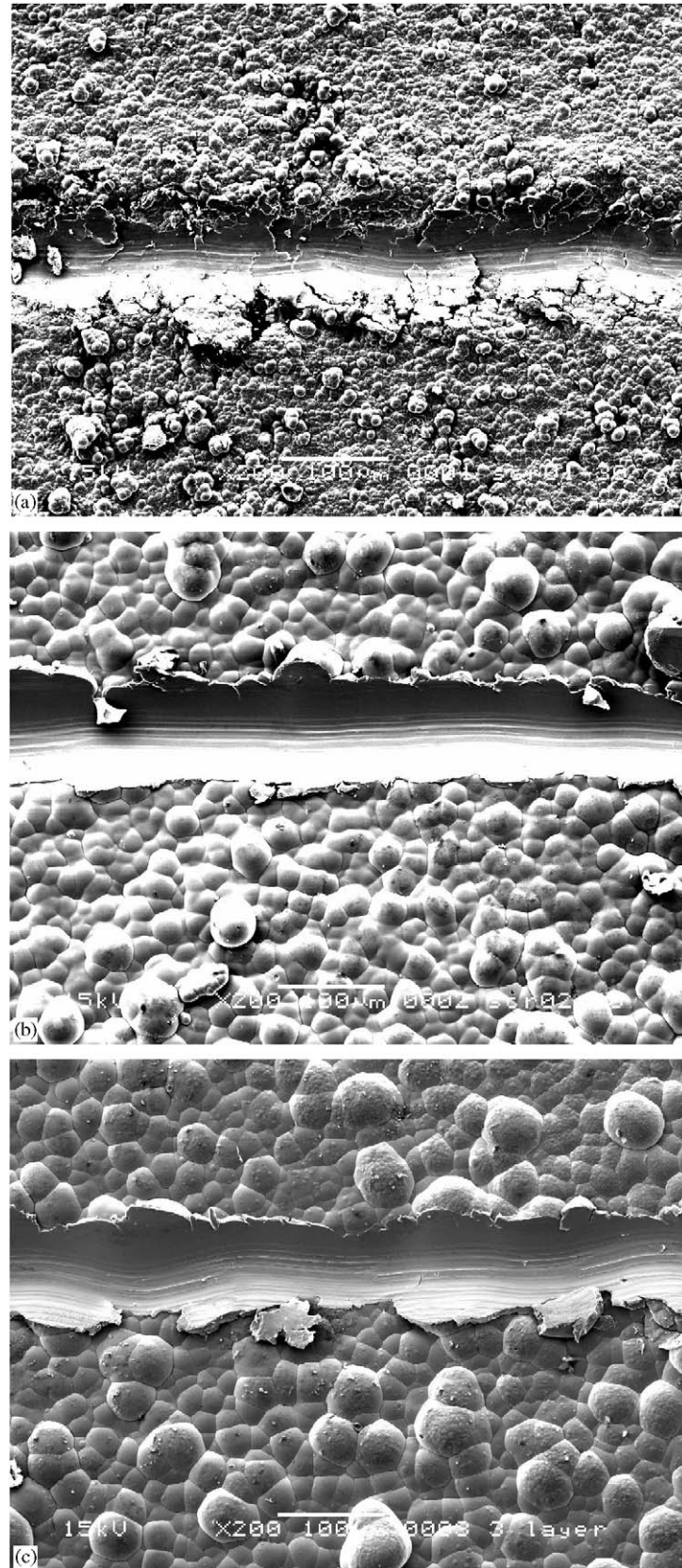


Fig. 4. Top surfaces after the scratch test. The diamond tip ploughs into the coatings. There is no sign of coating delamination. (a) Sample A; (b) sample B; (c) sample C.

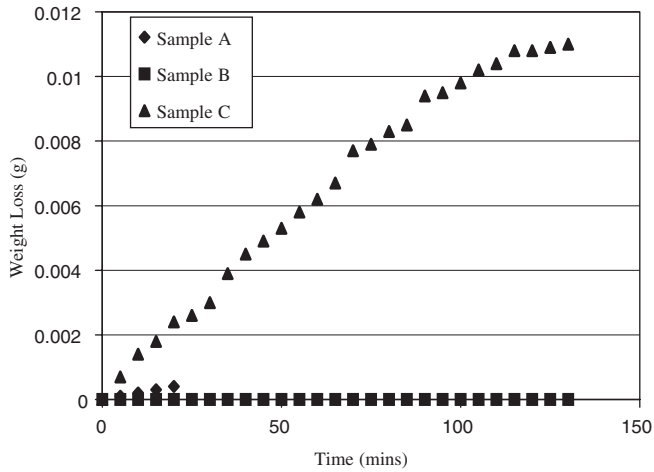


Fig. 5. Accelerated corrosion test by weight loss in 50 vol% HCl solution.

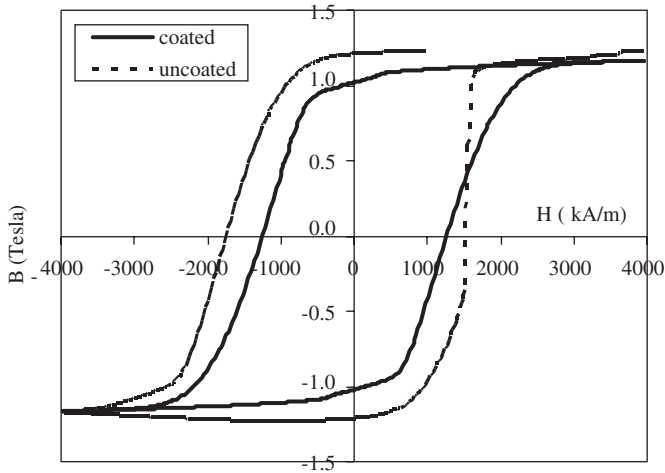


Fig. 6. Hysteresis curves of coated and uncoated magnets.

good ductility during scratch test. Corrosion experiment shows excellent corrosion resistance when the P content is above 11 wt%. There is a loss in magnetic properties after coating, but remaining values are still very attractive for practical applications.

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