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LETTER

NdFeB magnetic powders surface modification by a fluid-bed electrodeposition

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Permanent magnets based on $Nd_2Fe_{14}B$ compound are widely used in many applications, e.g. motors, electric and computer peripherals[1–3]. The main problems related with these and others applications are low temperature coefficients of remanence and coercivity as well as low corrosion resistance. The unacceptable corrosion behavior of NdFeB magnets derives from high Nd content and Nd-riched phase [1]. Two methods are commonly applied to improve the magnets corrosion resistance: (1) coating of the bulk magnet and (2) alloy modifications. NdFeB magnets surface coated with Zn, Sn, Al, Ni, Cr, or Cu have good corrosion resistance [1, 4, 5]. In general, chemical or electronic deposition was widely applied for magnetic powders metallic surface coating. The chemical deposition layer was relatively loose and the thickness cannot be controlled effectively; most of all, it cannot deposit those metals whose electrode potential was negative than NdFeB substrate [6]. The normally applied electrodeposition method was difficult for complete coating due to the un-uniform of matter transfer, conductivity and current distribution on the scattered and overlapped powders. To get a complete metallic coating in a nanometer size is of promising interest. On the other hand, it is still unclear how a nanosize metallic layer influences the NdFeB magnetic powders properties. We have recently developed a fluid-bed electrodeposition method to modify the magnetic powders surface [7, 8]. The purpose of the present letter is to study the effect of nanosize metallic layer coating treatment on the properties of magnetic powders. The feasibility of the fluid-bed electrodeposition was investigated.

Commercial rapidly quenched NdFeB magnetic powders (MQP-O, Magnequench International, Inc.) was used for this study. The powder is a multimodal mixture of ribbon-like particles [7]. The particle average length is about 30 times larger than that of the thickness, as shown in Fig. 1. Owing to the presence of a preferred direction of magnetization in the ribbon-like particles, the magnetic induction of particle is the biggest among all directions when the magnetic field is applied parallel to the surface of ribbons. The magnetic moment tends to align parallel to the applied magnetic field direction, and magnetic poles are fighting off for each other. Accordingly, we developed the fluid-bed electrodeposition method with magnetic force agitation for metallic layer coating, as given in Fig. 2 [7]. As can be seen in Fig. 2, a stuttle bar magnet was placed under the electrobath, and the magnet moves continuously along the length direction of the electrobath during the process of electrodepositing. The movement frequency of bar magnet was controlled. Such design made NdFeB powders in a well fluid state and separated each other, which gave relatively uniform distribution to the matter transfer and current distribution in the process of electrodepositing.

The coated layer thickness was observed using Hitachis-4700 scanning electron microscope. The magnetic properties of magnetic powders with and without coating were measured with a vibrating sample magnetometer (Lake Shore 4500). The electrode potential was investigated by a double electrode system; the error was controlled within ±3%. The bonded permanent magnets were fabricated by mixing the metal-coated powder and epoxy resin in the ratio of 97:3. Compression moldings were performed in a lab-scale compression molding press. Small

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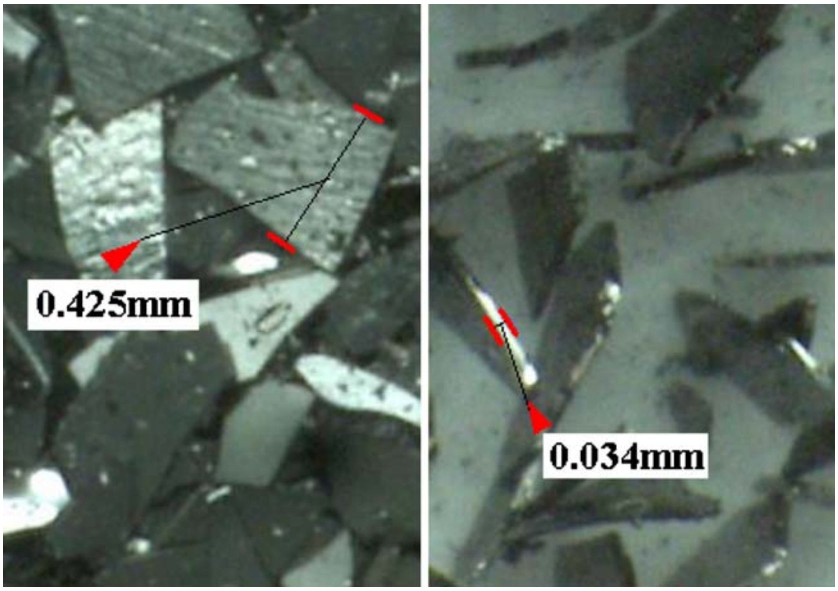

Fig. 1 Morphology of MQP-O rapidly quenched NdFeB magnetic powders

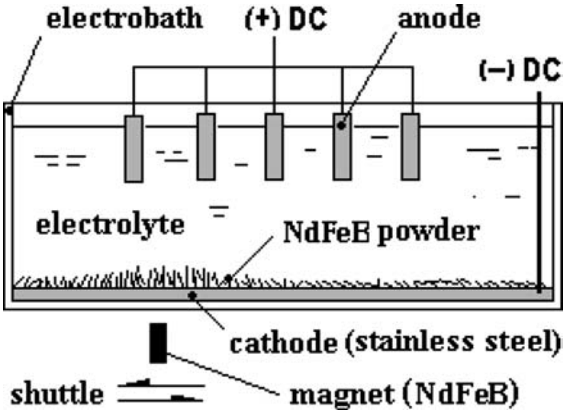

Fig. 2 The structure of the fluid-bed electrobath with magnetic force agitation

disks (10 mm diameter × 10 mm thick) were compression molded under a pressure of 700 MPa. The compressive strength of magnets was tested by a WE-100 hydraulic pressure omnipotent testing machine.

In order to get a well fluid and dispersive state of magnetic powders, the amount of treated magnetic powders was limited. When the amount of added magnetic powders was controlled in about 3 g/100 cm^2 (cathode area), the current distributing is uniform and thus the flake powders was completely coated. As given in Table 1, single coated Fe, Cu, Ni, Zn, and double coated Fe + Ni, Zn + Ni metallic layers were studied.

According to the Farady Second Law, the deposited metallic layer thickness was controlled by electrical quantum as

$$Q_i = \frac{2 \times m \times F \times K_i \times \rho_i \times \delta_i}{Eq_i} \tag{1}$$

where Q_i is electrical quantum, which is measured by a voltameter; m is the mass of magnetic powders; F is the Farady constant; K_i is the cathode current efficiency; ρ_i is the density of coated metal; δ_i is coated metallic layer thickness; and Eq_i is the electrochemical equivalent of the coated metal. Therefore, the metal deposition duration was changed with types of metals and surface area of magnetic powders. Fig. 3 gives the cross sectional image of NdFeB powders coated with Cu. As shown in Fig. 3, completely coating was observed, and the layer thickness was around 100 nm. Other metals showed the same results. Therefore, the nanosize metallic layer on magnetic powders could be obtained using the fluid-bed electrodeposition process with magnetic force agitation.

It has been shown that the nanosize metallic layer coated on NdFeB powders altered the physical and chemical properties of the powders [9–12]. When coated with anodic metal, the electrochemical activity of NdFeB powders decreased, and then the corrosion resistance improved [1]. As can be seen in Table 1 and Fig. 4, the measured electrode potential of NdFeB powders coated with nanosize metallic layer in this study moved to the value of the coated pure metal, which shows a mixture potential of the alloy and metal. The mixture electrode potential value of Cu coated sample was −0.15 V, which was close to the pure Cu^{2+}/Cu potential, indicating a complete coating situation. The mixture electrode potential values of Zn or Ni coated samples were more negative than that of NdFeB, thus Zn and Ni were acted as anode in the NdFeB/Zn or NdFeB/Ni corrosion battery. The Zn or Ni coating provided the anode protection to NdFeB powders, and the corrosion resistance of NdFeB improved significantly. The electrode potential of Fe coated samples was almost no change.

Table 1 Sample metal clad structure and properties

No.	Sample metal clad structure			Mixture electrode potential (V_{SCE})	$(BH)_{max}$ (kJ/m^3)	B_r (T)	$_jH_c$ (kA/m)	$_bH_c$ (kA/m)
	Basic phase	First layer	Second layer					
0	NdFeB	/	/	-0.636	105.57	0.832	775.20	493.10
1		Fe(40 nm)	/	-0.635	100.88	0.818	761.77	497.25
2		Cu(40 nm)	/	-0.150	101.62	0.813	778.43	500.49
3		Zn(40 nm)	/	-0.716	103.32	0.828	743.66	471.54
4		Ni(40 nm)	/	-0.721	96.30	0.825	617.27	434.59
5		α-Fe(30 nm)	Ni(30 nm)	-0.447	89.10	0.820	569.55	394.20
6		Zn(30 nm)	Ni(30 nm)	-0.540	79.44	0.813	434.64	334.16

Samples for the measurements of magnetic properties were made by mixing the powders with epoxy resin in suitable moulds. All data have been normalized with respect to 100% density. Table 1 summarizes the maximum energy product, $(BH)_{max}$, the remanence, B_r, intrinsic coercive force, $_jH_c$, and coercive force, $_bH_c$, of NdFeB powders with and without coatings, indicating that the magnetic properties depended on the coating metals. As expected, both $(BH)_{max}$ and B_r decreased after metallic coatings. For the Cu coated sample, both $_jH_c$ and $_bH_c$ slightly increased. The Cu-riched phase interdicted the magnetic exchange of major phase grains and hindered the diffusion of reversal magnetic domain. The magnetic properties of Fe coated sample had almost no change, but its $_jH_c$ and $_bH_c$ showed a different change tend. The results of Fe coated sample present the possibility of modifying the NdFeB powders by means of the exchange coupling effect between the soft and hard magnetic phase [13, 14]. Magnetic properties of Ni coated sample were decreased. It was noted that when the powders were coated with double metallic layers (Fe + Ni and Zn + Ni), the magnetic properties obviously decreased. It might because of the formation of a magnetic shielding system [15].

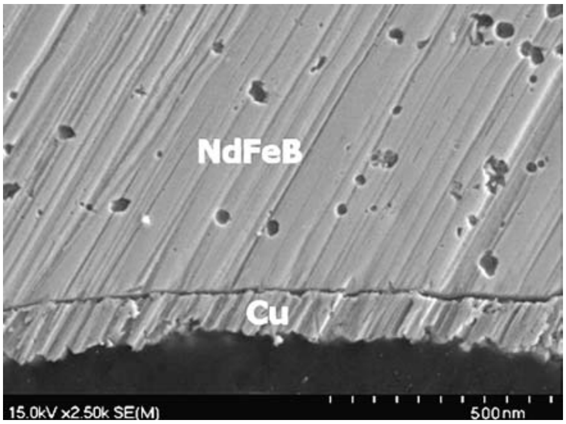

Fig. 3 SEM cross sectional image of NdFeB powders coated with Cu

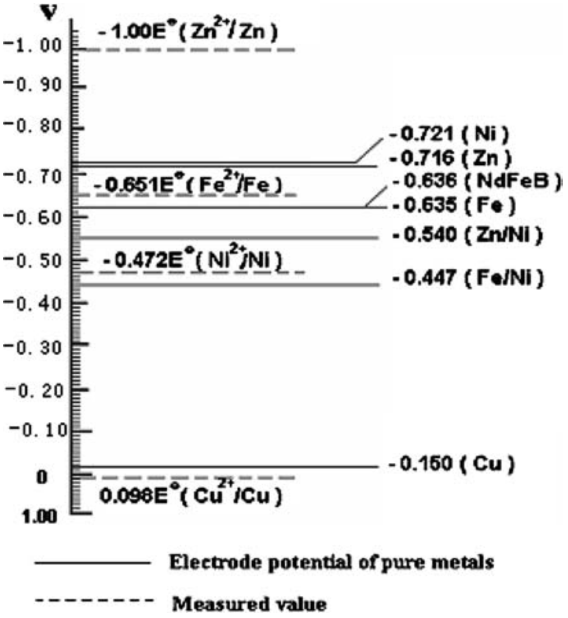

Fig. 4 Electrode potential values of NdFeB powders (with and without coatings) and pure metals

The compressive strength of bonded magnet made from varied thickness Cu-coated NdFeB powders were showed in Fig. 5. The compressive strength increased with the layer thickness. This might because of the bond Cu–S and Cu–O formation between Cu and binder [16]. The compressive strength rapidly increased with the layer thickness increasing when the layer thickness was less than around 100 nm, and then increased slowly after the layer thickness was larger than 200 nm.

In summary, a fluid-bed electrobath with magnetic force agitation was designed to completely coat metallic layer in NdFeB magnetic powders, according to the magnetization properties of flake magnetic powders in magnetic field. Four kinds of metals and two double metallic layers were deposited on NdFeB. The coating layer thickness was well controlled in the nanometer size. The electrode potential of NdFeB powders coated with nanosize metallic layer moved to the value of the coated pure metal. The electrode potential of Zn coated sample was more negative than that of NdFeB, indicating the anode protection of Zn coating to improve the corrosion resistance of NdFeB. The maximum energy product and remanence values decreased after

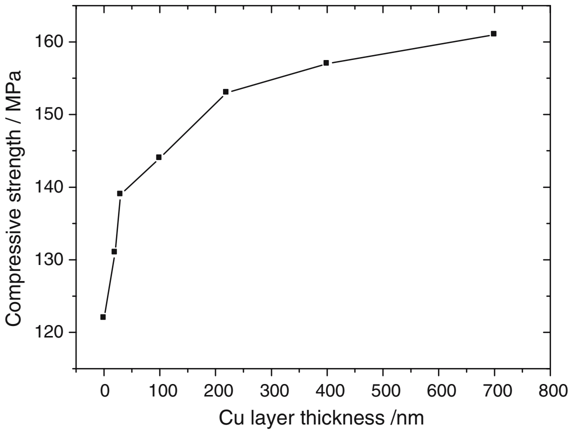

Fig. 5 The compressive strength of Cu-coated bonded magnet as a function of Cu layer thickness

coating. The coercive force of Cu coated sample increased. The magnetic properties of Fe coated sample had almost no change while its intrinsic coercive force and coercive force showed a different change tend. The compressive strength of Cu-coated powder bonded magnet increased with the coated layer thickness.

Modification of the magnetic and electrochemical properties of NdFeB powders coated with nanosize metallic layer was observed in this study. Since the remanence and coercive force values of some modified powders are decreased, it is not very clear that such surface modification method significantly improve the magnetic properties of the MQP powders or not. Due to the limit data, we could not conclude that such powder modification improved the corrosion stability of the NdFeB powder or polymer bonded magnets. Maybe other properties could be improved, which is one of our next research topics. Anyway, this study found a new method to coat the metallic layer on magnetic powders.

References

1. Jakubowicz J, (2001) J Alloys Comp 314:305
2. Campbell P (1994) Permanent magnet materials and their application, Cambridge University Press
3. Furlani EP (2001) Permanent magnet and electromechanical devices: materials, analysis, and applications, Academic Press
4. Cheng CW, Man HC, Cheng FT (1997) IEEE Trans Magn 33:3910
5. Tenaud P, Vial F, Sagawa M (1990) IEEE Trans Magn 26:1930
6. Henry J (1995) Electroless (autocatalytic, chemical) plating, Metal finishing, 93:401
7. Lin M (2004) M.S. Thesis, Zhejiang University of Technology, Hangzhuo, China
8. Li H (2004) M.S. Thesis, Zhejiang University of Technology, Hangzhuo, China
9. Higuchi M, Tsuchida M, Osawa Z (1992) J Mater Sci 27:5795
10. Osawa Z, Higuchi M (1992) J Mater Sci 27:5445
11. Zhang YL (1997) J Magn Magn Mater 171:305
12. Milazzo G, Caroli S (1978) Tables of standard electrode potentials, John Wiley and Sons, New York
13. Kneller EF, Hawig R (1991) IEEE Trans Magn 27:3588
14. Coehoorn R, de Mooij DB, de Warrd C (1989) J Magn Magn Mater 80:101
15. Huang CY, Mo WW, Roan ML (2004) Surf Coat Technol 184:163
16. Su YY, Shemenski RM (2000) Appl Surf Sci 161(7):355