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Effect of mechanical attrition on microstructure and properties of electro-deposition coatings on NdFeB

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Abstract: Surface mechanical attrition treatment (SMAT) was developed to synthesize nanostructure coatings on alloy surface. The SMAT action was applied in the process of Ni and Cu electroplating coatings on NdFeB substrates in this paper. The role of mechanical attrition during barrel plating on the microstructure, mechanical and corrosion resistant properties of the coatings was examined. The scanning electron microscopy (SEM) observation showed that the mechanical attrition could refine grain size, markedly smooth the coating surface and obviously decrease the number of pore in the coatings. The continuous collisions of glass balls onto the NdFeB samples could induce more beneficial nucleation defects on the coating, which was helpful for increasing nucleation sites and the nucleation rate. The mechanical attrition could also restrain the heterogeneous growth of the coating grain tips due to the abrasive action of stainless steel balls. The Tafel polarization curve experimental results indicated that SMAT process could enhance the corrosion resistance of coatings on NdFeB. The scratching test revealed that the binding force between coating and NdFeB substrate could be improved dramatically with SMAT process.

Keywords: surface mechanical attrition treatment; NdFeB; electro-deposition; Ni/Cu/Ni coatings; rare earths

The third generation rare earth permanent magnet NdFeB is well known for its high magnetic energy product, coercive force and energy density. Therefore, it is known as “the king of magnetic materials” and has been widely used in modern industry and electronics industry, especially the electrical instrument, electrical magnetic separation, motor market, hard disk storage materials, NMR (nuclear magnetic resonance) et al. However, multiple phases exist in sintered NdFeB[1], of which the neodymium-rich phase with distribution on grain boundaries will possess priority corrosion due to its lower corrosion potential[2]. Rare earth Nd element is very active to be oxidized to form Nd_2O_3, which affects the magnetic performance and stability of the product[3]. Now there are two main methods to protect the NdFeB substrate: adjusting grain boundary chemistry composition[4–6] to optimize the boundary microstructure and adopting surface protective coatings[7]. Jurczyk et al.[8] reported an increase in the anisotropy field with Zr substitution for rare earth atoms in $Re_2Fe_{14}B$. At the same time, Betancourt et al. and Capehart et al.[9,10] studied the location of Zr in $Nd_2Fe_{14}B$. However, the addition of alloy elements will reduce magnetic property or stability of NdFeB at high temperature.

The electrical efficiency of copper plating directly on NdFeB matrix is very low. The common NdFeB surface protective coatings mainly consist of chemical plating of Ni-P[11], electroplating Ni coating and Ni/Cu/Ni (the outmost Ni coating/the middle Cu layer/the inner most Ni coating) multilayer coatings[12]. The middle Cu coating was used to reduce the influence of nickel layer on the magnetic property of NdFeB. In the study of surface mechanical attrition treating (SMAT), Zhang et al.[13] has suggested that mechanical attrition by grinding balls can induce the surface of matrix to produce numerous twins and planar dislocation arrays in deformed grains. Some Scholars[14–17] put forward a series of coating grain growth mechanisms at the condition of stirring grinding plating.

In order to clarify the influence of SMAT coatings on the properties of NdFeB, coating morphology, corrosion resistance, porosity, binding force and other properties of the NdFeB coatings with SMAT have been studied in this research.

1 Experimental

The schematic diagram of mechanical attrition electro-deposition device is shown in Fig. 1. The size of the grinding glass ball is from 1 to 3 mm in diameter in the stirred grinding device (Fig. 1(a)), and this device was used to prepare the middle Cu coating. Rectangular specimens of 12 mm×10 mm×1.5 mm were prepared. A

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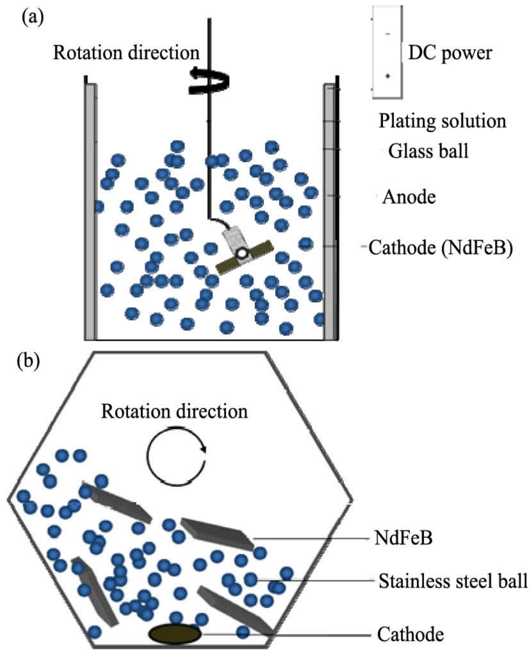

Fig. 1 Schematic diagrams of mechanical attrition electroplating devices

(a) Stirred grinding for Cu coating; (b) Barrel grinding for outmost Ni coating

hole of 1 mm in diameter was drilled on the one edge for convenient suspension in solution. And the specimens were mechanically polished by SiC paper from grit 240# to 1000#. Barrel grinding device (Fig. 1(b)) illustrates the specimens rolling with the rotation of stainless steel balls, the most outside Ni coating was prepared by this device. The cathode was pinned down on the bottom of the device and the NdFeB would be conducted indirectly by the steel balls. The diameters of the 304 stainless steel balls include three kinds: Φ1 mm, Φ1.5 mm and Φ2.0 mm.

The surface and cross-sectional morphologies of the traditional electronic plating (TEP) coating and the SMAT coating on NdFeB were checked by scanning electronic microscopy (SEM), equipped with the energy dispersive X-ray analysis facility. The X-ray photoelectron spectroscopy was used to analyze the distribution of elements in the coatings. Adhesion strength measurement was carried out using scratch method with WS-2005. The macro-porosity of the coating was examined by sticking filter papers according to GB5935-86. The tafel polarization curve was measured by Versa STAT. MC electrochemical workstation. Coating sample is mounted as anode, Pt foil is auxiliary electrode, reference electrode is

Table 1 Bath composition and operating conditions of Cu plating process

Bath composition	Amount	Operating condition	
$Cu_2P_2O_7$	50 g/L	pH	10
$K_4P_2O_7$	350 g/L	Temperature	80 ℃
$NH_3{\cdot}H_2O$	0.3 mL/L	Time	30 min
SeO_2	0.02 g/L		

Table 2 Bath composition and operating conditions of Ni plating process

Bath composition	Amount/(g/L)	Operating condition	
$NiSO_4{\cdot}6H_2O$	200	pH	4.4–4.8
$NiCl_2{\cdot}6H_2O$	60	Temperature	45–60 ℃
H_3BO_3	40	Time	30 min
$C_6H_5NaO_2S$	0.1	Current density	0.5–0.8 A/cm^2
$C_{12}H_{25}SO_4Na$	0.1		

saturated calomel and scanning speed is 10 mV/s. The corrosion resistance performance of the coatings was evaluated by neutral salt spray (NSS) test with FQY-O25 test chamber.

2 Results and discussion

2.1 Morphologies of Cu and Ni coatings with and without SMAT

The surface microstructure of the SMAT coatings was characterized using scanning electron microscopy (SEM) and cross-sectional SEM observation was also performed to reveal the binding status between coating and substrate. Surface morphologies of Cu coatings and Ni coating with different treatment process are shown in Fig. 2. The micro morphology of Fig. 2(a) demonstrates that a lot of large bump particles dispersed on the coating surface. Particles observed under SEM at high magnification seem like “tumor structure”, which is related to the roughness of substrate and uneven edge effect. Fig. 2(b) shows that the surface of Cu coating with stirring grinding is smooth and uniform, compared to the TEP Cu coating, the microstructure of coating changes from “island shape” into “nice clouds” structure. Moreover, the Cu coating with SMAT has compact microstructure and lower porosity since mechanical attrition can reduce surface reaction activation energy and increase the interface reaction rate. Consequently, the nucleation rate is greater than the grain growth rate, and then grain refinement is achieved.

Compared with Fig. 2(c), smaller average grain size can be easily found in Fig. 2(d). The TEP Ni coating seems like “pyramid structure” and big grain is surrounded by large smaller grains, which reveals that the appearance of micro-convex body is related to the content of nickel chloride[18] from the orthogonal experiment results and the observation at high magnification. The ridge of structure will become more acute as the content of nickel chloride increases. The TEP Ni coating exhibits a continuous and compact nodules microstructure while the SMAT coatings do not possess this phenomenon. The grain size of outmost SMAT Ni layer is between 500 to 700 nm, without any micro cracks. Low coating porosity can be attributed to the multi-rhombus structure arranged each other closely.