

Short Communication

The Effect of Magnetic Field on CoNiFe/Al₂O₃ Composite Coating Properties Prepared by Electrodeposition

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The CoNiFe/Al₂O₃ composite coating was electrodeposited on copper by magnetic field-assisted electrodeposition. The effect of magnetic fields on the structure, composition, morphology and magnetic property of the CoNiFe/Al₂O₃ composite coating was investigated. The disturbance effect produced by the Lorentz force as the result of the interaction between magnetic field and electric field can affect electrochemical reaction to increase deposition rate, refine coating particles, reduce roughness and enhance magnetic performance. The CoNiFe/Al₂O₃ composite coating is composed of granular particles. The composite coating prepared at 1.5 T magnetic field intensity possesses the best magnetic performance and optimal corrosion resistance.

Keywords: Electrodeposition; Magnetic field; Magnetic Performance;

1. INTRODUCTION

With the rapid development of micro-electro-mechanical systems (MEMS) and the trend of miniaturization of components, magnets used in the MEMS must be small in size. Magnetic thin coating plays an important role in MEMS, and is widely used in micro-actuators, micro-sensors, micro-switches, micro-pumps, etc [1-4]. Cobalt metal has the advantages of high melting point, high hardness, high temperature oxidation resistance and excellent tensile strength. It is found that cobalt alloy coatings have compact structure, high hardness and excellent magnetic properties, which can be used as magnetic components for MEMS. In recent years, the magnetic thin coatings mainly include CoNiP, CoNiMn, CoFeP and other noble metal coatings which have been investigated in some literatures [5-10]. The compatibility between electrodeposition technology and micro-motor manufacturing process is very good. Therefore, the preparation of magnetic coatings for micro-motor system by electrodeposition technology has attracted the attention of many researchers. So far, some

magnetic thin coatings can be successfully electrodeposited from aqueous solution, including CoNi, NiFe, CoNiFe, FePt and so on. However, NiPt, FePt and other noble metal alloy coatings are mainly used in military industry due to their high cost. Therefore, electrodeposition of Co alloy magnetic coating has become one of the research hotspots. Moreover, it is found that the magnetic performance of electrodeposited magnetic coating can be improved effectively by adding some nano-particles, such as SiC, ZrO₂, SiO₂ and so on [11-15]. However, electrodeposition technology has some defects, such as hydrogen evolution, concentration polarization and so on. In recent years, with the development of magnetoelectric technology, magnetic field electrodeposition technology has attracted more and more attentions [16-18]. The introduction of magnetic field in the process of electrodeposition can improve the mass transfer rate of ions and affect the nucleation process, so as to improve the magnetic performance and enhance the corrosion resistance of the electrodeposited coating. It is innovative to prepare magnetic composite coatings by introducing magnetic field electrodeposition. Therefore, magnetic field was introduced in the electrodeposition process of CoNiFe/Al₂O₃ composite coating to study the influence of magnetic field on the structure, composition, morphology and magnetic property of the coating during the electrochemical process.

2. EXPERIMENTAL

2.1 Materials

The copper with size of 2 cm×2 cm×0.1 cm was chosen as the substrate in the experiment. The CoNiFe/Al₂O₃ composite coating was prepared on the substrate by magnetic field assisted electrodeposition. The effect of magnetic intensity on the structure, composition, morphology and magnetic property of the coating was investigated. The technological condition is as follows: 15 g/L CoSO₄·7H₂O, 10 g/L NiSO₄·6H₂O, 15 g/L FeSO₂·7H₂O; 180 g/L Na₃C₆H₅O₇·2H₂O, 30 g/L H₃BO₃, 0.1 g/L sodium dodecyl sulfate, 5 g/L Al₂O₃ nano-particle, current density 25 mA/cm², magnetic field intensity 0~2 T, solution temperature 60 °C, pH=5 and deposition time 1 h;

2.2 Experimental process

The copper substrate was polished using a polishing machine. After the polishing, the substrate was cleaned by acetone and pure water sequentially. And then, the substrate was immersed in an alkaline solution (25 g/L Na₂CO₃, 30 g/L Na₃PO₄) to remove oil at 60 °C for 3 minutes. The pure platinum net was as the anode while the copper was as the substrate. A magnetic field (produced by electromagnet) parallel to the electric field was applied externally with the strength of 0~2 T. After magnetic field-assisted electrodeposition for 1 hour, the coating was taken out and dried for testing.

2.3 Testing

Surface roughometer (RC50H) was used to measure the roughness of the sample. The scanning length was 1000 μm with 2 μm/s scan rate, 2 mg applied force and 100 Hz sampling rate. The hardness

of composite coating was tested by digital Vickers hardness tester HVS-1000P with load of 9.8 N and holding time of 5 s. The magnetic property of composite coating was tested by vibrating sample magnetometer (VSM-380) with 1.5 T magnetic field intensity. The corrosion resistance of samples is evaluated by potentiodynamic polarization curves and electrochemical impedance spectroscopy in 3.5% sodium chloride solution. The CoNiFe/Al₂O₃ coating of 1 cm×1 cm is used as the working electrode, platinum sheet of 2 cm×2 cm is used as the auxiliary electrode and saturated calomel electrode is the reference electrode. For the potentiodynamic polarization curve testing, the scanning rate is 1 mV/s. The amplitude is 10 mV from 100 kHz to 100 mHz for the electrochemical impedance spectroscopy testing.

3. RESULTS AND DISCUSSION

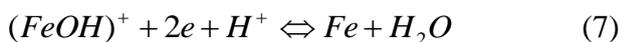
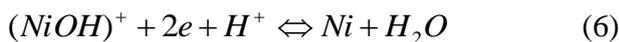
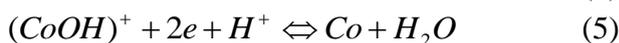
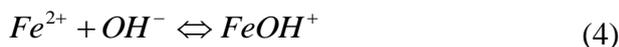
3.1 Effect of magnetic field on deposition rate and hardness of CoNiFe/Al₂O₃ coating

Figure 1 shows the effect of different magnetic field intensities on the deposition rate of electrodeposited CoNiFe/Al₂O₃ composite coating. According to Figure 1, with the increase of magnetic field intensity, the deposition rate of CoNiFe/Al₂O₃ shows a trend of first increasing and then decreasing. When the magnetic field intensity is 1.5 T, the maximum deposition rate of CoNiFe/Al₂O₃ composite coating is 159.7 mg/h. Because CoNiFe/Al₂O₃ is a particle coating, the current distribution on the cathode surface is not completely parallel to the magnetic field in the actual electrodeposition process. The interaction between magnetic field and electric field produces Lorentz force, which disturbs the cathode surface and reduces the thickness of double electric layer, thus promoting the deposition rate.

$$F_L = J \times B \quad (1)$$

Where, J represents current density, B represents magnetic field intensity, and Lorentz force is the main cause of magnetic convective disturbance (MHD) in the process of magnetic field electrodeposition. MHD effect can disturb the diffusion layer of cathode and increase the mass transfer rate of ion to increase deposition rate which are reported and proved by many scholars [19-21]. Moreover, the disturbance caused by Lorentz force is beneficial to disperse Al₂O₃ nano-particles near cathode and further promote the deposition rate of CoNiFe/Al₂O₃. When the magnetic field intensity is greater than 1.5T, the disturbance effect is strong, and the hydrogen adsorbed on the cathode surface is precipitated in large quantities. A large amount of hydrogen precipitation leads to an increase in the pH value of the cathode surface, which is prone to metal hydroxide precipitation and hinders the reaction, so the deposition rate decreases. The co-deposition mechanism of CoNiFe/Al₂O₃ composite coating is listed in Equations below [22-24].





In the process of electrodeposition, hydrogen is precipitated on the surface of the cathode, resulting in the increase of pH value to generate $CoOH^{+}$, $NiOH^{+}$ and $FeOH^{+}$ which gains electrons to be reduced to the corresponding metal. During the co-deposition of CoNiFe, nano-alumina is distributed and adsorbed at the lattice and grain boundary to form CoNiFe/ Al_2O_3 composite coating.

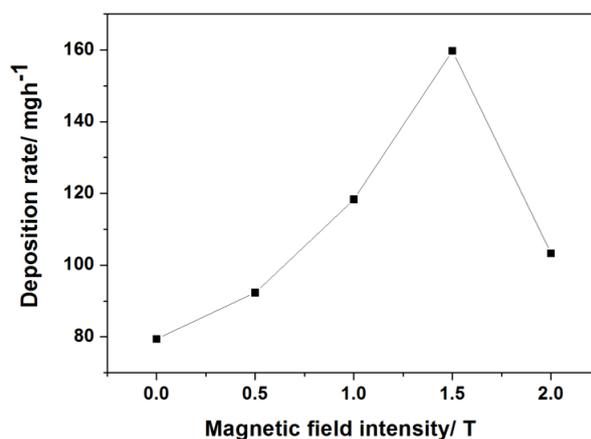


Figure 1. Effect of magnetic intensity on deposition rate of CoNiFe/ Al_2O_3 composite coating; The magnetic intensity is from 0 T to 2 T and the weighing precision is 0.1 mg.

Vickers hardness of CoNiFe/ Al_2O_3 composite coating prepared with different magnetic field intensities are shown in Figure 2. The Vickers hardness of electrodeposited CoNiFe/ Al_2O_3 composite coating is about 372.3HV in the absence of magnetic field. With the increase of magnetic field intensity, the Vickers hardness of CoNiFe/ Al_2O_3 composite coating increased significantly. When the magnetic field intensity is 1.5T, the composite coating has the maximum hardness, which is about 579.9 HV. The interaction of magnetic field and electric field can disturb and level the cathode surface, which can refine the surface particles of the coating and improve the hardness of the coating. Moreover, the disturbance effect produced by Lorentz force near the cathode can better disperse alumina nano- particles, increase the content of alumina in the composite coating, and further improve the hardness of the composite coating. The effect of magnetic field on the hardness and mechanical properties of metal alloys is reported and investigated by some people [25-26]. However, when the magnetic field intensity is greater than 1.5T, hydrogen evolution is also accelerated resulting in loose and rough surface which contributes directly to the decrease of hardness.

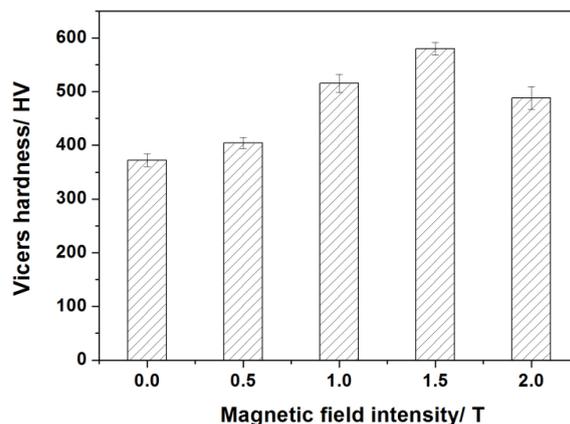


Figure 2. Effect of magnetic intensity on Vickers hardness of CoNiFe/Al₂O₃ composite coating; The hardness is tested at 9.8 N loading force with holding time 15 s.

3.2 Effect of magnetic field on roughness and morphology of CoNiFe/Al₂O₃ coating

Roughness is an important parameter for electrodeposited coating, reducing roughness is beneficial to reduce surface friction coefficient and improve mechanical performance. Roughness of CoNiFe/Al₂O₃ composite coatings obtained with different magnetic field intensities is shown in Figure 3. Increasing magnetic field intensity is beneficial to reduce the surface roughness of composite coating. Because CoNiFe/Al₂O₃ is a typical particle coating, agglomeration phenomenon is easy to occur during electrodeposition. The roughness of CoNiFe/Al₂O₃ composite coating prepared without magnetic field is about 0.832 μm . With the increase of magnetic field intensity, the roughness of the composite coating decreases significantly, which is mainly attributed to the disturbance effect caused by the interaction of magnetic field and electric field, which refines the surface particles and effectively reduces the roughness. Secondly, Al₂O₃ particles adsorbed on the surface of CoNiFe alloy particles can inhibit the growth of particles, refine particles and reduce roughness.

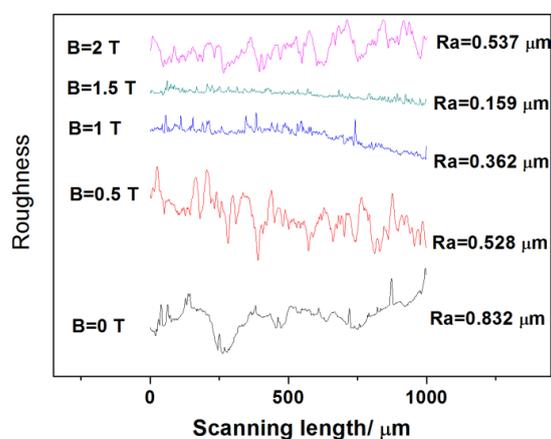


Figure 3. Effect of magnetic intensity on surface roughness of CoNiFe/Al₂O₃ composite coating; The scanning length is 1000 μm at 2 $\mu\text{m/s}$ scan rate; The applied force is 2 mg and 100 Hz sampling rate;

The effect of nano- particles on surface roughness of material has been investigated and researched in detail [27-29]. However, when the magnetic field intensity increases to 2T, the roughness of the composite coating increases significantly. The disturbance effect caused by Lorentz force due to the interaction of magnetic field and electric field accelerates the mass transfer rate of metal ions as well as hydrogen ions. At 2 T magnetic field intensity, a large amount of hydrogen is precipitated from the cathode surface, which increases the porosity and roughness of the coating.

It can be seen from the surface morphology in Figure 4 that CoNiFe/Al₂O₃ is composed of many granular particles. It is reported that the surface morphology of Co-based electrodeposited coating usually shows granular particles which is similar to the results in the paper [30-32]. When the magnetic field is 0 T, the particles of electrodeposited CoNiFe/Al₂O₃ coating surface are larger and agglomeration is obvious. With the increase of magnetic field intensity, the surface particles of the coating gradually decreased and the compactness increased. In addition, with the increase of magnetic field intensity, it can be found that some small protuberances are distributed on the surface of particles, which are the result of co-deposition of Al₂O₃ and CoNiFe. The magnetic field is beneficial to improve the deposition rate and promote the co-deposition of Al₂O₃ and CoNiFe. When the magnetic field intensity is 2 T, the coating roughness increases and the agglomeration phenomenon are obvious due to the severe hydrogen evolution.

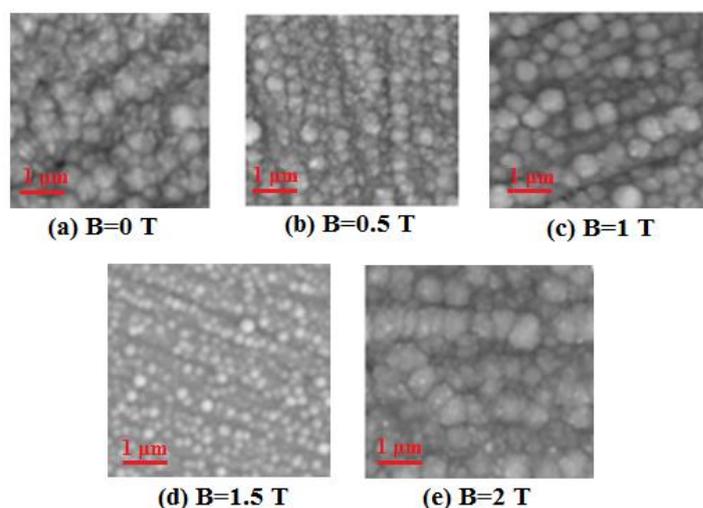


Figure 4. Effect of magnetic intensity on surface morphology of CoNiFe/Al₂O₃ composite coating; The accelerating voltage is 20 kV and the working distance is 8 mm.

3.3 Effect of magnetic field on magnetic performance and corrosion resistance of CoNiFe/Al₂O₃ coating

The magnetic performance of CoNiFe/Al₂O₃ composite coating prepared by magnetic field-assisted electrodeposition is shown in Figure 5 and Table 1. According to the results, it is clear that magnetic intensity plays a role in the magnetic performance of composite coating. The magnetic properties of metal alloys can be improved by magnetic field-assisted electrodeposition which is

verified by some researchers [33-35]. When the applied magnetic field increase from 0 to 2 T, the coercivity ranges from 52.34 kA/m to 89.65 kA/m while the saturation magnetization ranges from 67.05 Am²/kg to 88.29 Am²/kg. According to the previous analysis, the disturbance effect of Lorentz force generated by interaction of magnetic field and electric field can reduce the thickness of the double electric layer, improve the deposition rate, refine the surface particles, and thus improve the coercivity and saturation magnetization of the composite coating. When the magnetic field is 2 T, the pH value of the cathode surface increases due to serious hydrogen evolution and a large amount of metal hydroxide inhibits the electrochemical reaction. The porosity of the coating increases, and the magnetic properties decrease obviously. The composite coating prepared at 1.5T has the best magnetic properties with 113.14 kA/m coercivity and 118.59 Am²/kg saturation magnetization.

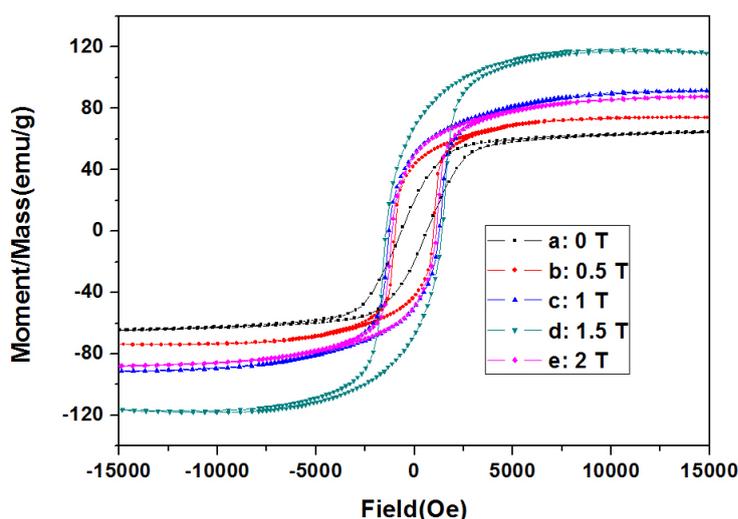


Figure 5. Effect of magnetic intensity on magnetic performance of CoNiFe/Al₂O₃ composite coating; The lower magnetic field is -1.5 T while the higher magnetic field is 1.5 T;

Table 1. Magnetic performance of CoNiFe/Al₂O₃ different CoNiFe/Al₂O₃ composite coating prepared by magnetic field-assisted electrodeposition

B/ T	M _s /Am ² /kg	H _c / kA/m
0	67.05	52.34
0.5	74.12	77.67
1	91.81	101.82
1.5	118.59	113.14
2	88.29	89.65

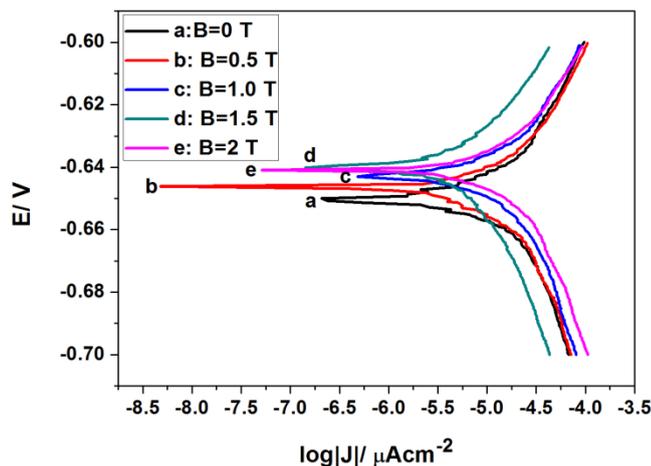


Figure 6. Potentiodynamic polarization curve of different CoNiFe/Al₂O₃ composite coatings in 3.5% sodium chloride solution; The CoNiFe/Al₂O₃ coating of 1 cm×1 cm is used as the working electrode, platinum sheet of 2 cm×2 cm is used as the auxiliary electrode and saturated calomel electrode is the reference electrode; The scanning rate is 1 mV/s;

Table 2. Corrosion current density and corrosion potential of different CoNiFe/Al₂O₃ composite coating prepared by magnetic field-assisted electrodeposition

B/ T	$J_{\text{corr}}/\mu\text{Acm}^{-2}$	E_{corr}/V
0	50.122	-0.650
0.5	31.633	-0.646
1	15.802	-0.641
1.5	6.313	-0.639
2	19.955	-0.640

According to Figure 6 and Table 2, with the increase of magnetic field intensity, the corrosion potential of CoNiFe/Al₂O₃ composite coating gradually moved positively, and the corrosion current density shows a trend of decreasing first and then increasing. Proper magnetic field intensity is beneficial to promote the co-deposition of Al₂O₃ and CoNiFe, decrease the corrosion current density and improve the corrosion resistance. The coating prepared with 1.5T magnetic field intensity has the best corrosion resistance with the lowest corrosion current density (6.313 μA/cm²).

The electrochemical impedance spectroscopy of different CoNiFe/Al₂O₃ composite coatings electrodeposited at different magnetic fields is shown in Figure 7 and Table 3. The charge transfer resistance can be used to evaluate the corrosion resistance of CoNiFe/Al₂O₃ composite coatings. Generally speaking, the greater the mass transfer resistance, the better the corrosion resistance of the metal coating. It can be seen from the Figure 7 that, with the increase of magnetic intensity, the transfer resistance of CoNiFe/Al₂O₃ composite coating increases gradually to a max value and then decreases. The CoNiFe/Al₂O₃ composite coating electrodeposited at 1.5 T magnetic intensity has the largest charge transfer resistance equal to 6561.27 Ωcm², indicating the best corrosion resistance.

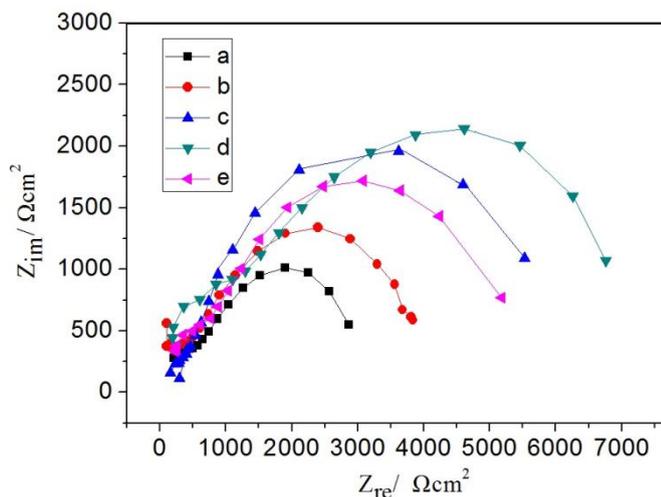


Figure 7. Electrochemical impedance spectroscopy of different CoNiFe/Al₂O₃ composite coatings in 3.5% sodium chloride solution; a:0T; b:0.5 T; c: 1 T; d: 1.5 T; e: 2 T; The CoNiFe/Al₂O₃ coating of 1 cm×1 cm is used as the working electrode, platinum sheet of 2 cm×2 cm is used as the auxiliary electrode and saturated calomel electrode is the reference electrode; The condition is 10 mV amplitude from 100 kHz to 100 mHz.

Table 3. Charge transfer resistance and solution resistance of different CoNiFe/Al₂O₃ composite coatings in 3.5% sodium chloride solution; a: 0T; b: 0.5 T; c: 1 T; d: 1.5 T; e: 2 T;

Samples	Charge transfer resistance	Solution resistance
a	2671.93	218.23 Ω
b	3634.08	213.13 Ω
c	5563.62	232.39 Ω
d	6561.27	253.93 Ω
e	4980.73	249.23 Ω

4. CONCLUSION

In this paper, CoNiFe/Al₂O₃ composite coatings were prepared on copper surface by magnetic field induced electrodeposition. The effect of magnetic intensity on deposition rate, hardness, surface morphology, magnetic performance and corrosion resistance property of composite coating was studied. The disturbance effect of Lorentz force generated by the interaction of magnetic field and electric field plays a role in electrochemical reaction. With the increase of magnetic field intensity from 0 T to 2 T, the deposition rate, hardness and roughness of composite coatings firstly increase and then decrease. CoNiFe/Al₂O₃ composite coating is composed of granular particles. The composite coating obtained at 1.5T magnetic field intensity has excellent magnetic performance and the best corrosion resistance with the smallest corrosion current density (6.313 μA/cm²) and the largest charge transfer resistance (6561.27 Ωcm²).

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