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Effect of Temperature on Electrochemical and Magnetic Performance of CoPtMo Coating Electrodeposited on Monocrystalline Silicon

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CoPtMo coating with better magnetic performance was prepared on the surface of monocrystalline silicon as computer storage material. The electrodeposition of CoPtMo belongs to an irreversible diffusion-controlled process. Proper bath temperature is prone to accelerating the mass transfer rate of metal ions and increasing deposition rate resulting in the increase of coating thickness. When the bath temperature increases from 20 ℃ to 60 ℃, the content of cobalt in the CoPtMo coating increases gradually and the surface particles are refined increasingly. However, when the bath temperature is 80 ℃, the cobalt content in CoPtMo coating decreases obviously and the surface roughness of the coating increases extremely due to the agglomeration of particles, resulting in poor magnetic performance. The CoPtMo electrodeposited coating prepared at the temperature of 60 ℃ possesses the best magnetic performance with the largest coercivity and saturation magnetization.

Keywords: CoPtMo coating; Computer storage material; Monocrystalline silicon; Electrodeposition;

1. INTRODUCTION

Magnetic materials are widely used in modern industry and all electronic components are basically inseparable from magnetic materials. According to the magnetic performance of material in the external magnetic field, magnetic material can be divided into permanent magnetic materials and soft magnetic materials [1-4]. Permanent magnetic materials are widely used in computer field, especially in computer storage technology [5-8]. Computer storage technology requires permanent magnetic coatings with micron size which cannot be processed from traditional block permanent magnets. The existing permanent magnet is brittle. It is hard to cut it to magnetic coating only with micron thickness. Therefore, the magnetic coating required by computer system can only be deposited by physical and chemical methods to meet the size requirements.

At present, high performance cobalt based magnetic coatings are widely concerned. Common magnetic coatings with excellent performance include CoNi, CoNiMnP, CoWP and so on [9-13]. CoPt has attracted much attention due to its advantages of high coercivity, good oxidation resistance and optimal corrosion resistance. In recent years, many scholars have prepared CoPt thin coatings with acceptable performances by electrodeposition method [14-18]. However, CoPt coating belongs to noble metal alloy, and the high cost greatly restricts the application. It is found that the addition of metal or nonmetal particles in the electrodeposition of CoPt coatings can not only further improve the magnetic performance of the coatings, but also save the cost [19-20]. As the deposition of cobalt is controlled by diffusion during electrodeposition, temperature becomes an important parameter. In this paper, CoPtMo magnetic coatings used for computer storage were prepared on the surface of monocrystalline silicon by electrodeposition method. The effects of temperature on deposition rate, morphology, composition, roughness, and magnetic performance of CoPtMo magnetic coating were studied.

2. EXPERIMENTAL

2.1 Materials and plating solution composition

The monocrystalline silicon (20 mm×30 mm×0.5 mm) was used as the substrate to be electrodeposited CoPtMo magnetic coating from an acidic plating solution. The anode electrode is pure platinum sheet (30 mm×30 mm×1 mm). The detailed information about plating solution composition is: $CoSO_4$ 30 g/L, $(NH_4)_2PtCl_6$ 10 g/L, $Na_3C_6H_5O_7$ 100 g/L, H_3BO_3 35 g/L, Na_2SO_4 30 g/L, Na_2MoO_4 10 g/L. The CoPtMo electrodeposited magnetic coating is prepared in 100 ml plating solution with pH=6 at the current density of 25 mA/cm^2 for one hour. The plating temperature ranges from 20 ℃ to 80 ℃ to study the effect of temperature on performance of CoPtMo magnetic coatings.

2.2 Experimental procedure and testing

The monocrystalline silicon substrate was firstly cleaned by toluene, acetone and ethanol respectively. Secondly, the cleaned substrate was immersed into HF solution (20%) to do corrosion for 10 minutes. Finally, the substrate was washed and dried to do the CoPtMo electrodeposition. After the electrodeposition was finished, the CoPtMo magnetic coating was cleaned and dried to do the testing. The thickness and roughness was tested by surface profilometer (MMD-100A). The scanning length for thickness testing is 1000 μm with 5 μm/s scanning rate and the scanning length for roughness testing is 2000 μm with 5 μm/s scanning rate. Cyclic voltammetry curves of CoPtMo coatings were tested by electrochemical station (CHI700E) with scanning rate ranged from 10 mV/s to 50 mV/s. The scanning electron microscope with energy spectrum function (Hitachi S4800) was used to characterize the surface morphology and composition of CoPtMo coatings. The magnetic performance of coatings was tested by vibrating sample magnetometer (Lakeshore 7410) with 1.5 T applied magnetic field.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry curves of CoPtMo electrodeposited coating on silicon

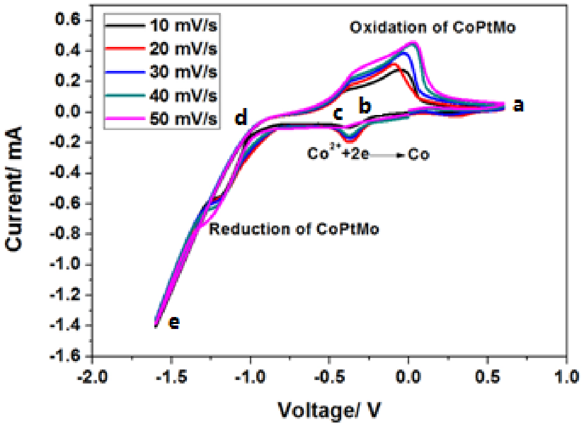

Figure 1. Cyclic voltammetry of CoPtMo electrodeposited coating on silicon from plating solution with 0.01 mol/L $CoSO_4$, 0.01 mol/L $(NH_4)_2PtCl_6$ and 0.01 mol/L Na_2MoO_4. The high voltage is 0.6 V while the low voltage is -1.6 V. The scanning rate is from 10 mV/s to 50 mV/s at 20 ℃. The monocrystalline silicon (1 cm×1 cm) is the cathode while the pure platinum (2 cm×2 cm) is the anode. Saturated calomel electrode is the reference electrode.

From the cyclic voltammetry curve of 10 mV/s scanning rate, it can be found that when the deposition potential is scanned from 0 V to -0.2 V, the reaction current on the cathode basically does not change, indicating that the reduction reaction of metal ions has not taken place dramatically. An obvious reduction peak can be observed near -0.35 V, mainly corresponding to the reduction reaction of cobalt. As the scanning potential continues to shift negatively, another significant reduction peak could be observed near -1.30 V, indicating for CoPtMo reduction. From the cyclic voltammetry, the electrochemical window of CoPtMo metal deposition is clear. The electrodeposition of cobalt starts from b to c while the CoPtMo begins to be electrodeposited in large quantities in the interval from d to e.

Moreover, the reduction peak of CoPtMo electrodeposition appears at -1.30 V. With the increase of scanning rate, the deposition potential of reduction peak gradually shifts negatively and the cathode current increases gradually. The reduction peak and oxidation peak are not symmetrical. Therefore, it can be judged from these phenomena that the electrodeposition of CoPtMo is an irreversible process. According to the cyclic voltammetry curves of different scanning rates, the relationship between the square root of scanning rate and peak current is made shown in Figure 2. It can be found that there is an approximate linear relationship indicating that the electrodeposition of CoPtMo on silicon is a typical diffusion-controlled with irreversible process. The diffusion-controlled transport in electrochemical reaction has been reported in detail [21-22]. For diffusion-controlled electrochemical reaction, due to the slow mass transfer rate of metal ions in the bath, it is easy to form concentration gradient [23-24]. Increasing the bath temperature can accelerate the mass transfer rate of metal ions and reduce the concentration gradient. Therefore, the effects of temperature on deposition rate, morphology, composition, roughness, and magnetic performance of CoPtMo electrodeposited magnetic coating are studied.

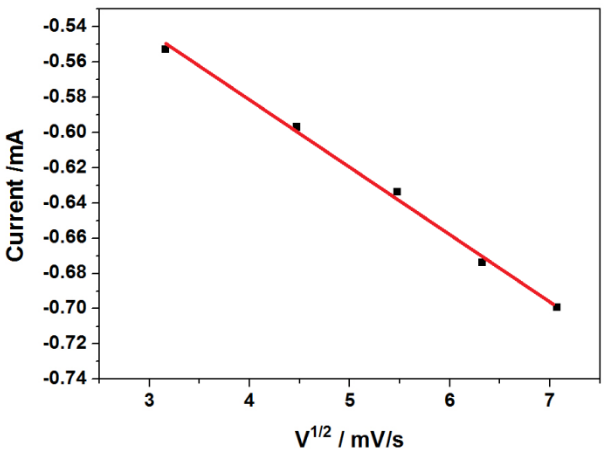

Figure 2. The relationship between square root of scanning rate and reduction peak current based on cyclic voltammetry curves with different scanning rates. The high voltage is 0.6 V while the low voltage is -1.6 V. The scanning rate is from 10 mV/s to 50 mV/s at 20 ℃. The monocrystalline silicon (1 cm×1 cm) is the cathode while the pure platinum (2 cm×2 cm) is the anode. Saturated calomel electrode is the reference electrode.

3.2 Thickness and roughness of CoPtMo electrodeposited coating on silicon

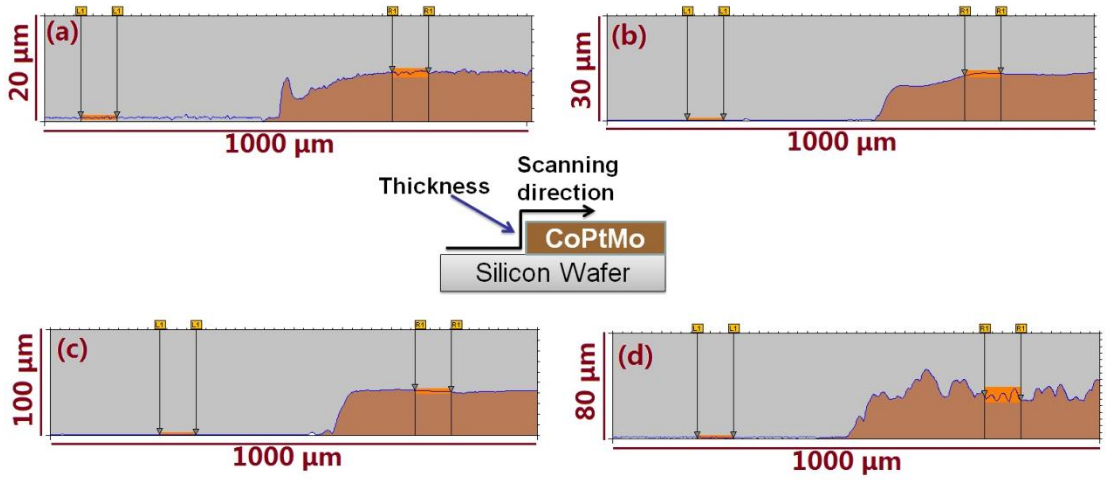

Figure 3. Effect of temperature on thickness of CoPtMo electrodeposited coating on silicon; (a) 20 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C; The scanning length for thickness testing is 1000 μm with 5 μm/s scanning rate. Applied force is 2 mg.

The effect of temperature on the thickness and deposition rate of CoPtMo electrodeposited coating is shown in Figure 3 and Figure 4. It can be seen that, temperature definitely affect the thickness of CoPtMo coating. With the temperature of plating solution increases from 20 °C to 80 °C, the thickness of CoPtMo coating increases gradually and then decreases. When the plating solution keeps at 60 °C, the CoPtMo magnetic coating obtained possesses the maximum thickness and deposition rate which are equal to about 38.5 μm and 6.4 μm/hcm^2 respectively.

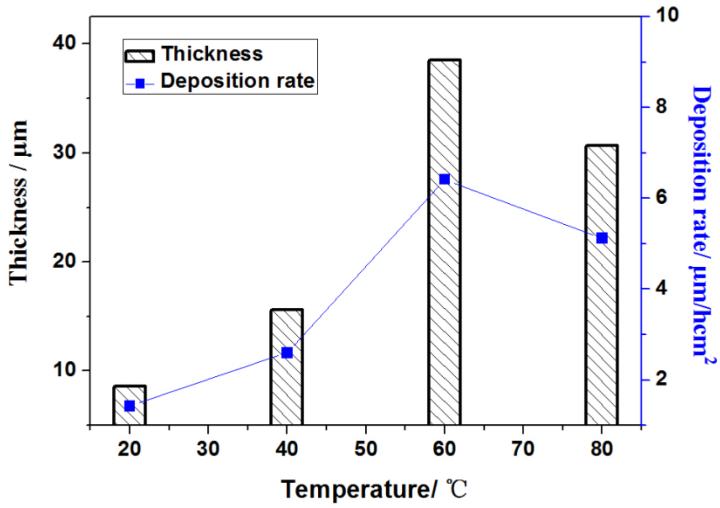

Figure 4. Effect of temperature on deposition rate of CoPtMo electrodeposited coating on silicon; (a) 20 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C; The scanning length for thickness testing is 1000 μm with 5 μm/s scanning rate. Applied force is 2 mg.

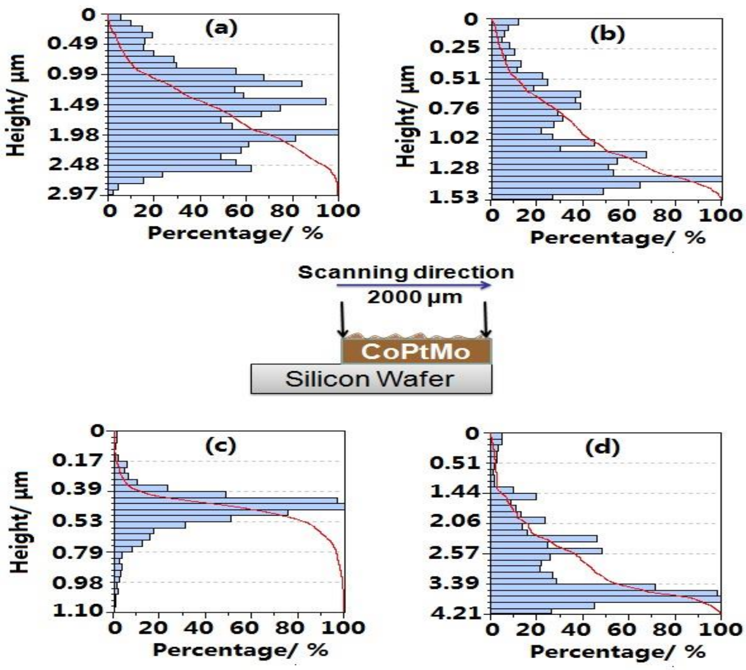

Figure 5. Effect of temperature on roughness of CoPtMo electrodeposited coating on silicon; (a) 20 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C; The scanning length for roughness testing is 2000 μm with 5 μm/s scanning rate. Applied force is 2 mg.

Temperature is an important parameter affecting the kinetics of electrochemical reaction, especially for diffusion-controlled electrochemical reaction.

Temperature can improve the mass transfer rate of ions and reduce the viscosity of bath to accelerate deposition rate resulting in the improvement of coating thickness. The relationship between conductivity, viscosity and temperature of bath has been described in Equation 1 and some works [25-27].

$$\mu\lambda = KT \qquad (1)$$

Meanwhile, μ represents the conductivity of the bath, λ represents the viscosity of the bath, K is a constant and T represents the temperature. Therefore, it can be found that the conductivity of the bath is inversely proportional to the viscosity. Increasing the temperature of the bath is beneficial to decrease the viscosity of the bath, thus improving the conductivity of the bath and promoting the chemical reaction. However, when the temperature is 80℃, the high temperature also leads to the increase of hydrogen ion migration rate. A large number of hydrogen evolutions will reduce the deposition efficiency and decrease the coating thickness.

Table 1. Roughness of CoPtMo electrodeposited coating on silicon; The scanning length for roughness testing is 2000 μm with 5 μm/s scanning rate. Applied force is 2 mg.

Temperature/ ℃	Maximum Height/ μm	Roughness/ μm
20	2.97	1.23
40	1.53	0.97
60	1.10	0.39
80	4.21	2.13

Figure 5 and Table 1 list the roughness of CoPtMo magnetic coatings electrodeposited from plating bath of different temperatures. It is clear that with the increase of temperature, the roughness of CoPtMo ranges from 1.23 μm to 2.13 μm. The increase of temperature accelerates the deposition rate of cobalt and molybdenum, and a large amount of cobalt and molybdenum easily occupy the lattice of CoPtMo coating, refine the grain and inhibit the agglomeration of CoPtMo particles, thus reducing the roughness. However, a large amount of hydrogen is precipitated at higher temperature, which increases the porosity and roughness of the coating surface.

3.3 Composition and surface morphology of CoPtMo electrodeposited coating on silicon

The relationship between temperature and composition of CoPtMo coating is shown in Figure 6. It can be seen from Figure 6 that temperature has a significant impact on the composition of CoPtMo coating. When the temperature rises from 20 ℃ to 60 ℃, the content of cobalt and molybdenum in the CoPtMo coating increases gradually, while the content of platinum decreases. The synergistic effect of cobalt and molybdenum is mainly attributed to the induced codeposition. When the solution temperature reaches 80 °C, a large amount of hydrogen is precipitated, resulting in an increase of pH near the cathode. The decrease of deposition efficiency and the precipitation of cobalt hydroxide inhibit the deposition of cobalt and molybdenum, which result in the decrease of cobalt and molybdenum contents in CoPtMo coating. The electrochemical reaction of CoPtMo electrodepostion is listed in Equations [28-29].

$$MoO_4^{2-} + 4H_2O + 2e^- \rightarrow MoO_2(2H_2O) + 4OH^- \quad (2)$$

$$MoO_2(2H_2O) + 4H(Co) \rightarrow Co(Mo) + 2H_2O \quad (3)$$

$$PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^- \quad (4)$$

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^- \quad (5)$$

The codeposition of molybdenum and cobalt is induced by the catalytic action of primary hydrogen on the surface of cobalt, and the CoMo alloy is obtained. Therefore, the deposition of cobalt and molybdenum is an induced codeposition process, and molybdenum alone cannot be deposited from aqueous solution [30-31]. Cobalt and platinum are completely mutually soluble and belong to the disordered face centered structure, thus forming CoPtMo alloy.

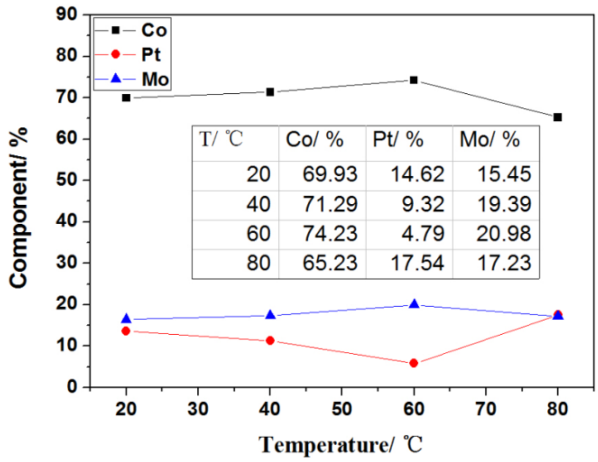

Figure 6. Effect of temperature on composition of CoPtMo electrodeposited coating on silicon; (a) 20 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C; Energy resolution is 160 eV, tube flow is 1000 μA and test time is 60s.

The surface morphology of CoPtMo coating is shown in Figure 7. It is clear that the surface of CoPtMo coating is composed of many nodular particles. The coating prepared at 20 °C has rough surface and larger particles. With the increase of bath temperature, the particle size and roughness of the coating decrease gradually. CoPtMo coating prepared at 60 °C has uniform and compact surface with minimum roughness. The increase of temperature accelerates the diffusion rate of cobalt ions, a large number of cobalt ions enter the lattice of CoPtMo and play the role of grain refinement. However, CoPtMo coating obtained at 80°C possesses the roughest and darkest surface composed of obvious agglomeration particles.

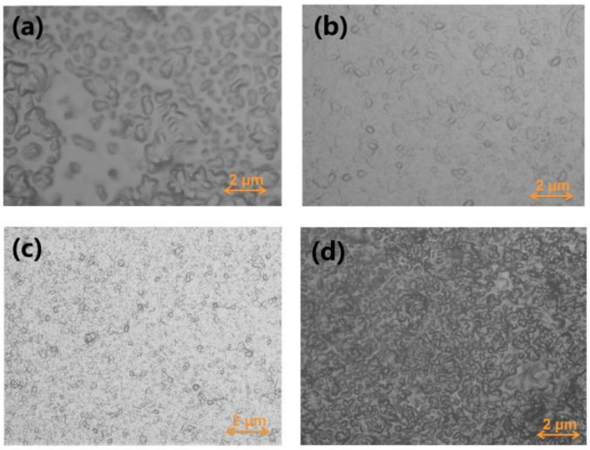

Figure 7. Effect of temperature on surface morphology of CoPtMo electrodeposited coating on silicon; (a) 20 ℃; (b) 40 ℃; (c) 60 ℃; (d) 80 ℃; Acceleration voltage is 10 kV and working distance is 8 mm.

3.4 Magnetic performance of CoPtMo electrodeposited coating on silicon

The magnetic performance of CoPtMo is shown in Figure 8 and Table 2. It can be found that the coercivity and saturation magnetization of coatings can be improved by proper temperature. With the increase of bath temperature from 20 ℃ to 60 ℃, the coercivity and saturation magnetization of CoPtMo coating increase obviously. CoPtMo coating prepared at 60 ℃ has excellent magnetic performance with maximum coercivity and saturation magnetization.

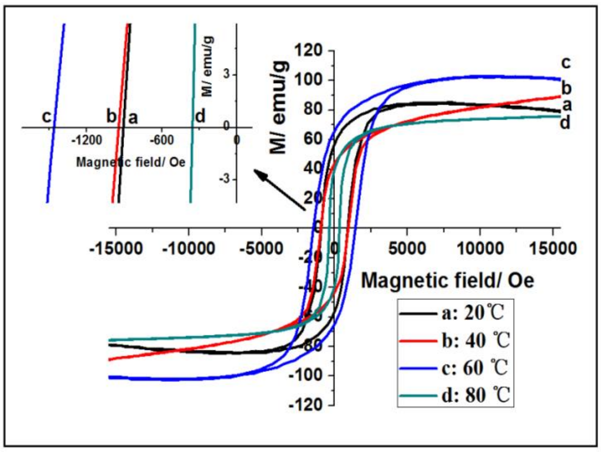

Figure 8. Effect of temperature on magnetic performance of CoPtMo electrodeposited coating on silicon; (a) 20 ℃; (b) 40 ℃; (c) 60 ℃; (d) 80 ℃; The applied magnetic field is 1.5 T; The magnetic field resolution is 1 mT.

As can be seen from the results above, increasing the bath temperature is beneficial to increase the deposition rate and the cobalt content in CoPtMo coating, and thus improve the saturation magnetization of the coating. In addition, increasing the temperature can also help to refine the surface particles of the coating, reduce the roughness, and improve the coercivity of the coating. The relationship between grain size and coercivity has also been reported by some scholars in some works [32-33]. Good coercivity is an important parameter for computer storage material. However, when the bath temperature is 80 ℃, the cobalt content in CoPtMo coating decreases obviously and the surface roughness of the coating increases extremely due to the agglomeration of particles, resulting in poor magnetic performance.

Table 2. Coercivity and saturation magnetization of CoPtMo electrodeposited coating on silicon. The applied magnetic field is 1.5 T; The magnetic field resolution is 1 mT.

Temperature /℃	Coercivity/ Oe	Ms / emu/g
20	899.23	185.03
40	935.32	193.96
60	1437.39	102.95
80	359.29	76.61

4. CONCLUSIONS

The CoPtMo coating was electrodeposited on the surface of monocrystalline silicon as computer magnetic storage material. The effect of temperature on thickness, deposition rate, composition, surface morphology and magnetic performance of CoPtMo coating was studied. The electrodeposition of CoPtMo on silicon is a typical diffusion-controlled with irreversible process. Bath temperature effectively affects the composition and thickness of CoPtMo coating. Increasing the bath temperature is beneficial to refine the surface particles of the coating, reduce the roughness, and improve the magnetic performance of the coating. However, when the bath temperature is 80 ℃, the cobalt content in CoPtMo coating decreases obviously and the surface roughness of the coating increases extremely due to the agglomeration of particles, resulting in poor magnetic performance. The CoPtMo coating obtained at the temperature of 60 ℃ has the best magnetic performance with the largest coercivity and saturation magnetization.

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