

Effect of mechanical attrition on microstructure and property of electroplated Ni coating

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Abstract: Ni coating was deposited on carbon steel by a mechanical attrition enhanced electroplating (MAEE) process. During the electroplating, the mechanical attrition (MA) was introduced by impact of glass balls on the sample surface with a special vibrating frequency. The surface and cross-sectional images of Ni coating were observed with SEM. The microstructure and crystallinity of coating were examined with TEM and XRD. The electrochemical performance of coating was measured with polarization curves and electrochemical impedance spectroscopy (EIS) and its mechanical behaviours, such as tensile strength and hardness, were studied. The results show that the MA has significant effects on the microstructure and property of the electroplated Ni coating. By MA, the coating becomes smooth, compact, thin and has refined grains and is free of cracks and pores. Consequently, the adhesion, tensile strength, hardness and corrosion resistance of coating are improved significantly.

Key words: electroplating; mechanical attrition; Ni coating; corrosion resistance

1 Introduction

Ni coating has been widely used in industries to improve the surface properties of various substrate materials due to its good corrosion resistance, high hardness and excellent wear resistance. There are some weak features in Ni coating formed by the traditional electroplating (CE). First, the traditional Ni coating is rich in micropores so that it must be formed enough thickly for use in air or other corrosive conditions. Second, the surface of traditional Ni coating becomes coarse with prolongation of electroplating time. Finally, with the increase in electroplating current density, dendritic crystals begin to develop on the coating, leading to its pulverization and reduction in the fatigue resistance [1–3]. Recently, much attention has been paid to surface modification techniques associated with mechanical action. For example, the microstructure in the surface layer of metals and alloys can be refined at the nanometer scale by means of surface mechanical attrition treatment (SMAT), ball milling (BM) and ultrasonic shot peening (USP). It is interesting to see that the subsequent surface chemical treatments, such as nitriding and

chromizing, can be enhanced by SMAT [4–6]. It has been reported that the nano-crystallized aluminized coatings can be prepared at a relatively low temperature with a high rate by a technique combined SMAT with aluminizing. Furthermore, a novel ultrasonic-based dry mechanical process has been proposed for coating metallic surface with other metal or ceramic materials [7–9]. NING et al [10–12] reported the effect of mechanical attrition on the crystal growth of electroplating Ni and Cu coatings and found that the mechanical attrition can flatten the coating surface and refine the grains on them. In this work, our work based on the above concepts was reported, using MA to enhance electroplating of Ni alloys. It is believed that Ni atoms are deposited one by one during electroplating. Therefore, the stacking of atoms and the resulting microstructure of coating can be affected by the mechanical attrition with even a low energy, resulting in coatings with different microstructure and properties.

2 Experimental

2.1 Electroplating process

The mechanically assisted electroplating set-up is

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schematically shown in Fig. 1. As shown in Fig. 1, the plating bath was placed on the top of a vibrator. The vibrator provided a sinusoidal vibration of 1 mm amplitude and 0–6.0 Hz frequency in the horizontal direction. Samples to be plated were made of carbon steel or stainless steel and each sample had dimensions of 20 mm×10 mm×2 mm. Two carbon steel samples were mounted in epoxy resin as a whole and worked as the cathode. The anode was a high-purity nickel ingot with an effective surface area of 30 mm×20 mm and parallel to the cathode surface. The sample surfaces were ground with SiC papers to 1200-grit finish. Glass balls with diameters of 1 mm and 5 mm were equally dispersed on the cathode surface. About 1/3 surface area of each sample was covered by the glass balls. When the plating bath was vibrated, these glass balls rolled horizontally forth and back and provided mechanical ball-rolling to coatings simultaneously during the plating process. The electrolyte was composed of 300 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 45 g/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 40 g/L H_3BO_3 . The electroplating process was carried out at 40 °C for 20 min with 25 mA/cm² of current density.

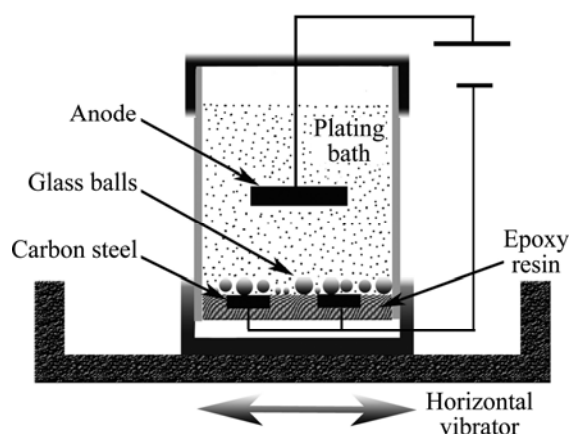


Fig. 1 Schematic illustration of mechanically assisted electroplating set-up

2.2 Morphology and microstructure examination

The coated specimens were washed with deionized water and dried. Field emission scanning electron microscope (FESEM) (JSM–6700F) was used to observe the surface and cross-sectional morphologies of coatings. The coatings were stripped from stainless steel specimen and thinned in 10% HClO_4 ethanol solution to a proper thickness with twin-jet electropolishing to examine the coatings' microstructure and crystallinity under a transmission electron microscope (TEM) (Hitachi H-800H) at 175 kV. A camera length of 80 cm was adopted as the nanobeam electron diffraction was performed. X-ray diffraction tests (XRD, PW3710, MAC Science Co. Ltd M21X) were conducted to characterize crystal structures of as-deposited coatings.

2.3 Electrochemical property measurement

To evaluate the corrosion resistance of the plated Ni coatings, the polarization curves (PC) and electrochemical impedance spectroscopy (EIS) tests were performed on a galvano-chemistry Workstation (CHI660C, Shanghai) in a 3.5% NaCl solution at room temperature by using a traditional three-electrode electrochemical cell with a platinum plate as the counter electrode and a saturated calomel electrode as the reference electrode. During the electrochemical test, the samples were covered by an anticorrosion tape so as to expose only the testing area of 1 cm². The PC measurements were carried out with a sweep rate of 0.1 mV/s. The EIS spectra were obtained over the frequency range of 10 mHz–100 kHz with an applied AC perturbation potential of 10 mV amplitude. The experimental results were interpreted on the basis of an equivalent circuit determined using a suitable fitting procedure described in Zsimpwin software.

2.4 Mechanical property measurement

Hardness of the coatings was measured by using a digital microhardness tester (HVS–1000) with a load of 2.94 N and a duration time of 20 s. At least ten indents were performed to gain the average hardness value for each sample. The coatings were stripped from stainless steel specimen and fixed on a holder for tension strength measurement by a universal material testing machine.

3 Results and discussion

3.1 Effect of MA on morphology and microstructure

Figure 2 shows the surface morphology of Ni coatings deposited at a current density of 25 mA/cm² with or without supplying MA. From Fig. 2(a), it can be seen that many large pyramid-like crystals form uniformly on the surface of Ni coating after traditional electroplating (TEP). The surface is rough and uneven. While, from Figs. 2(b–d), it can be found that, with MAEE process and increasing vibrating frequency, the pyramid-like crystals gradually disappear from the surface of Ni coating and the surface becomes smoother and smoother. Therefore, MA action can affect the electroplating process and lead to a finer coating surface.

Figures 3(a) and (b) show SEM images of the cross-sections of Ni coatings electroplated without and with mechanical assistance, respectively. It can be found that the thicknesses of the traditionally electroplated and mechanically assisted electroplated Ni coatings are about 13 μm and 10 μm, respectively. The mechanically ball-rolling makes the Ni coating thinner by about 3 μm.

Meanwhile, the traditional Ni coating is porous and the MA-assisted Ni coating is pore-free, which probably accounts for the improvement of the hardness, tensile

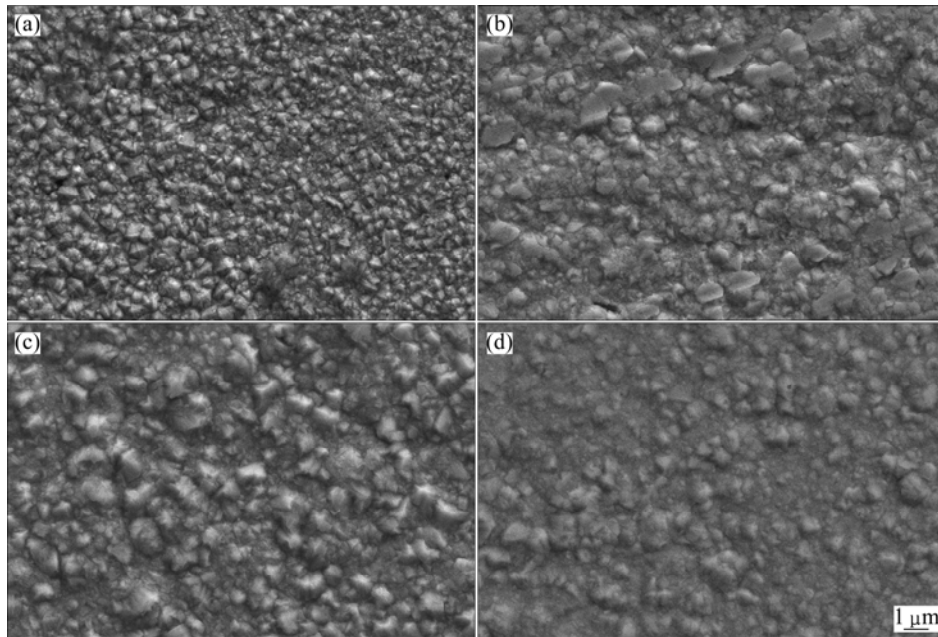


Fig. 2 Surface morphologies of Ni-coatings formed under different vibrating frequencies: (a) 0 Hz; (b) 4.0 Hz; (c) 5.0 Hz; (d) 6.0 Hz

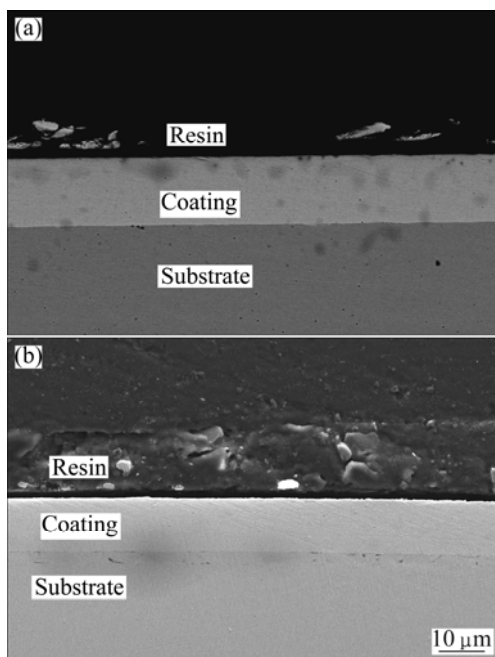


Fig. 3 Cross-sectional SEM images of Ni coatings on carbon steel substrate by TEP (a) and by MAEE ($f=6.0$ Hz) (b)

strength and corrosion resistance of coating. In addition, the roughness of both substrate-coating interface and resin-coating interface is reduced by the mechanically ball-rolling. These results imply that mechanically ball-rolling might in-situ mechanically polish the surface during the electroplating process. Any protruding summits were worn out by the mechanically ball-rolling, thereby yielding the smoother interface and surface and reducing the coating thickness.

Figures 4(a) and (b) show TEM cross-section

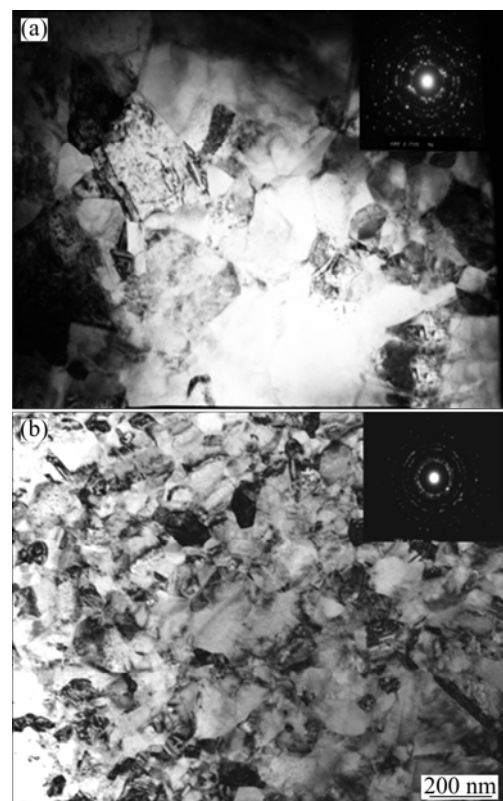


Fig. 4 TEM images and electron diffraction patterns of Ni-coatings by TEP (a) and by MAEE ($f=6.0$ Hz) (b)

images and electron diffraction patterns of the Ni coatings formed by TEP and MAEE at 6.0 Hz, respectively. From Fig. 4(a), the traditional Ni coating is mainly composed of large crystals, characteristic of twins, high density dislocation lines and noticeable grain

boundaries. The electron diffraction pattern of the traditional Ni coating is characteristic of polycrystal rings and bright monocrystal spots, indicating its composing crystals are large in size. From Fig. 3(b), the MA-assisted Ni coating is mainly composed of small crystals and the grain boundaries become obscure. The electron diffraction pattern of MA-assisted Ni coating is characteristic of vague polycrystal rings and faint monocrystal spots, further demonstrating that its composing crystals are small in size. Therefore, MA action can refine the grain size of Ni coating.

Figure 5 shows the XRD patterns of traditionally electroplated (0 Hz) Ni coating and mechanically assisted electroplated Ni coatings under different vibrating frequencies. All reflection peaks can be indexed with face-centered cubic Ni, with main diffraction peaks of (111), (200), (220) and (331). The traditional Ni coating possess (111) texture and Ni atoms preferentially electrodeposited on the (111) crystal face to make its (111) peak highest and narrowest among all specimens. However, with MAEE process and increasing vibrating frequency, the (111) peak gradually becomes weak and the (200) peak turns strong and narrow in shape, which suggests the Ni atoms begin to preferentially electrodeposit on the (200) crystal face instead of (111). In addition, with the increase of vibrating frequency, the (220) and (331) peaks get more and more weak in intensity and more and more broad in FWHM. According to Scherrer equation: $D = k\lambda / (B \cdot \cos \theta)$ where k is the X-ray wavelength, B is the FWHM of the diffraction peak, θ is the diffraction angle and the constant k is about 0.89, it can be estimated that the mechanically ball-rolling generally has promoted refinement of grain in the Ni coating, consistent with Fig. 2 and Fig. 4.

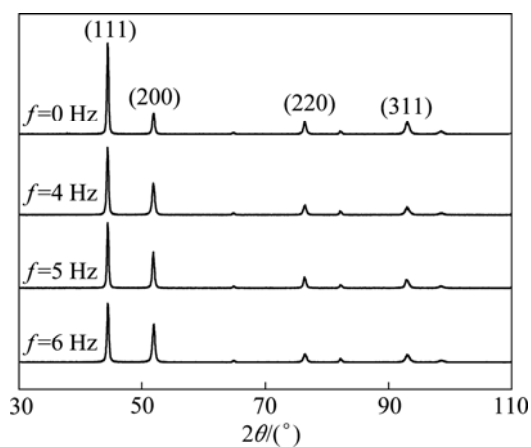


Fig. 5 XRD patterns for Ni-coatings formed with different vibrating frequencies

LIU et al [13] presented that the texture of electroplated Ni coating depended on cathodic

overpotential. They found that under high cathodic overpotential, the (111) texture easily appears and under low cathodic overpotential, the (200) texture develops [13,14]. The mechanical attrition can help to reduce cathodic concentration polarization and facilitate reduction of Ni^{2+} , leading to (200) texture.

The MA-induced crystal refinement can be explained by the following reasons. First, it is difficult for Ni atoms to arrange in a long range under strong mechanical attrition. Second, MA can produce many macro-plastic and micro-plastic deformations in the coating, which promotes crystal nucleation and restrain crystal growth.

3.2 Electrochemical performance of Ni coatings

Figure 6 shows the PC and EIS of carbon steel, traditional Ni coating and MA-assisted Ni coating in the 3.5% NaCl solution at room temperature. Figure 6(a) illustrates the difference in the corrosion potential (φ) and corrosion current density (J) among the three samples. The results of PC are listed in Table 1. The substrate has the most negative corrosion potential of -0.387 V and the most positive corrosion current of 24.05 mA/cm^2 . Once the substrate was coated by the traditional Ni coating, the corrosion potential and corrosion density were shifted to about -0.299 V, 13.01

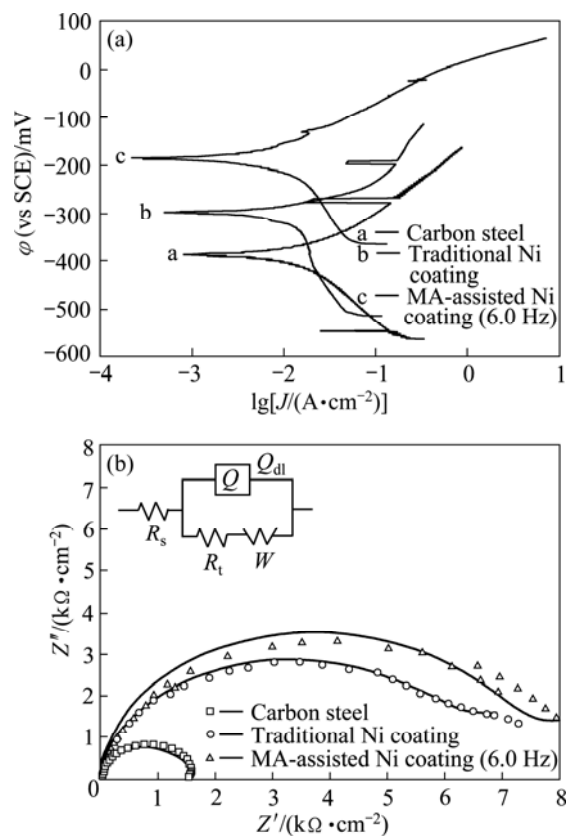


Fig. 6 Effect of mechanical attrition on electrochemical properties of Ni coating: (a) Polarization curves; (b) Electrochemical impedance spectra

Table 1 Equivalent circuit parameters of EIS and results of PC

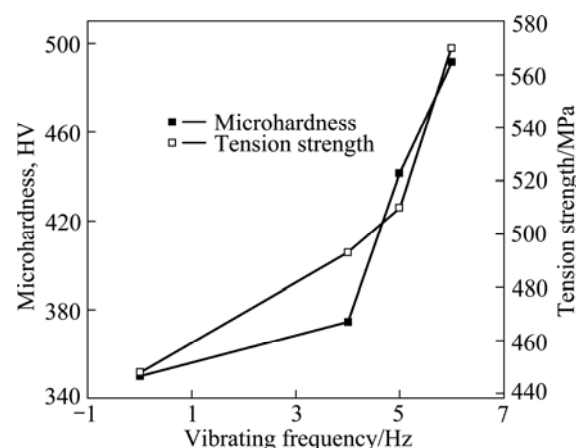
Sample	$R_s/(\Omega \cdot \text{cm}^{-2})$	$R_t/(\Omega \cdot \text{cm}^{-2})$	$Q_{dl}/(\text{F} \cdot \text{cm}^{-2})$	$W/(\Omega \cdot \text{cm}^{-2})$	$J_{\text{corr}}/(\text{mA} \cdot \text{cm}^{-2})$	$\phi_{\text{corr}}/\text{mV}$
Substrate	3.47	1582	1.086×10^{-4}	1.256×10^{-8}	24.05	−387
Traditional Ni coating	0.1982	6064	1.224×10^{-4}	2.328×10^{-3}	13.01	−299
MA-assisted Ni coating	0.8358	7105	5.492×10^{-5}	2.03×10^{-3}	6.45	−186

mA/cm^2 , respectively. The MA-assisted Ni coating exhibits the most positive corrosion potential and the most negative corrosion density, about -0.186 V and $6.45 \text{ mA}/\text{cm}^2$, respectively. These results indicate that the corrosion resistance of the Ni coating is greatly improved by the mechanical attrition. Under MA action, plastic deformation takes place continuously on the surface of Ni coating, which can eliminate the pores and cracks in Ni coating and insulate the possible galvanic cell between Ni coating and steel substrate, accounting for improvement in the corrosion resistance of Ni coating [15].

The experimentally measured EIS data are presented in Fig. 6(b) in the Nyquist format. The high-frequency impedance arc is attributed to the processes occurring at the electrode-electrolyte interface. The inserted figure shows an equivalent circuit[16], consisting of a solution resistance (R_s), an electrical double layer capacitance at the interface of electrode and electrolyte (Q_{dl}), a charge-transfer resistance (R_t), and a Warburg component (W). The circuit parameters were approximately determined by fitting the experimental data with the equivalent circuit and tabulated in Table 1. Table 1 shows that R_t of the MA-assisted Ni coating is higher than that of the traditional Ni coating, indicating again that MA indeed improves the corrosion resistance of coating, consistent with Fig. 6(a). R_t includes intrinsic electron transfer resistance, concentration polarization resistance in the diffusion layer and ohmic polarization resistance on the electrode surface. MA not only densifies the Ni coating so as to add ohmic polarization resistance but also flattens the Ni coating surface, weakens the electrolyte convection and thickens the diffusion layer so as to enhance concentration polarization resistance. As a result, the R_t and corrosion resistance of coating are improved under MA action.

3.3 Mechanical performance of Ni coatings

Figure 7 shows the effects of MA on the mechanical properties of the Ni coating. It can be seen that the hardness and tensile strength of the Ni coating increase with increasing the frequency, indicating that the wear resistance of the Ni coating will be greatly improved by mechanical attrition. This behaviour can be attributed to the effect of grain refinement under the MA action. According to Hall-Petch relation [17], the hardness and tensile strength of crystalline material are related to its

**Fig. 7** Microhardness and yield strength of electroplated Ni coatings vs vibrating frequency

grain size by $H=H_0+Kd^{-1/2}$, where H is hardness or tensile strength, d is grain size, H_0 and K are constants. The refined Ni-coating will show excellent mechanical properties. High compression stress and low density of micropores in the mechanically assisted electroplated Ni coating might be mainly responsible for its increase in hardness and tensile strength.

4 Conclusions

1) The microstructure of traditional Ni coatings is changed by the combined mechanical attrition during plating. With MA, the coating becomes smooth and pore-free and the composing grains are refined, leading to improvement in the mechanical properties and corrosion resistance.

2) The hardness and tensile strength of MA-assisted Ni coating increase with increasing the vibrating frequency, due to grain refinement, compressive stress and densification of the coating under the MA action.

3) Under MA action, plastic deformation takes place continuously on the surface of Ni coating, which can eliminate active areas such as pores and cracks in the Ni coating, so as to insulate the possible galvanic cell between Ni and steel and improve the corrosion resistance of Ni coating.

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机械研磨对电沉积 Ni 镀层微观结构与性能的影响

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摘要: 在电沉积 Ni 过程中, 向镀液中加入介质小球, 介质小球以不同频率冲击镀件表面对镀层形成机械研磨。用 SEM 观察镀层表面、截面形貌, 用 TEM、XRD 研究镀层的微观结构与结晶状态, 测试镀层的极化曲线(PC)与交流阻抗频谱(EIS)等电化学性能。测试镀层的显微硬度与抗拉强度等力学性能。结果表明: 在电沉积 Ni 过程中, 对镀层实施机械研磨使镀层表面变得光滑, 镀层孔隙率降低, 致密度增加, 镀层厚度减小, 机械研磨促进镀层表面与内部晶粒尺寸的明显细化及镀层内部的压应力形成, 从而导致镀层的耐蚀能力显著增强, 抗拉强度与硬度显著提高。

关键词: 电镀; 机械研磨; 镍镀层; 耐蚀性

(Edited by LI Xiang-qun)