

EFFECT OF ULTRASOUND ON Ni-Co/ZrO₂ COMPOSITE ELECTRODEPOSITION AND CORROSION RESISTANCE STUDY OF COATINGS

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In order to study the effect of ultrasonic waves on Ni-Co/ZrO₂ composite coatings in the codeposition process, Linear sweep voltammetry and Tafel test techniques were used to offer favorable reference. Using Scanning electron microscope and X-ray diffraction to analysis the effect of ultrasonic power on surface morphology and microstructure of Ni-Co/ZrO₂ composite coating. The results indicated that the ultrasonic waves caused the reduction potential of Ni-Co/ZrO₂ composite coatings to shift to more positive potentials and decreased cathodic polarization, and ultrasonic power directly affected the grain size of composite coating, thus influenced the microstructure and properties of the coatings. The composite coating prepared under ultrasonic power of 240 W had compact and uniform surface morphology with good corrosion resistance.

Keywords: composite coatings; ultrasonic; cathodic polarization; corrosion resistance

INTRODUCTION

Composite electrodeposition is the process of matrix metal and solid particles codeposition by electroplating to obtain a special coating [1]. It can give the unique properties of solid particles to the metal coatings. The mechanical, physical and chemical properties of the material can be changed and regulated according to the design requirements [2]. Composite coatings have been widely applied in aerospace, power, machinery and metallurgy.

The coating performance can be adjusted by changing the compound quantity of nanoparticles in the composite coatings. Ultrasonic vibration is an effective way to control the nanoparticles content. However, there is no unified understanding about the influence of ultrasound on the electrodeposition process. The study of electrodeposited Ni by Prasad [3] et al. showed that the ultrasonic oscillation in the electrodeposition process could increase the current efficiency, expanded the applicable range of the current density and reduced the concentration polarization, so that the deposition layer of Ni had high hardness, wear resistance and fatigue strength. The studies of Yang [4] et al. about Ni-Co/TiCN composite coating showed that ultrasonic wave refined the grains and increased nucleation rate of Ni-Co/TiCN composite coating, the surface of composite coatings was smooth. Zhang [5] et al. reported that ultrasonic power in the electroplating process was helpful to improve the performance of the coating, but the ex-

cessive ultrasonic power was bad the properties of the coatings.

It is advanced and feasible to study the composite electrodeposition process by electrochemical means [6]. However, few studies on the electrochemical behavior of ultrasonic power during codeposition by electrochemical techniques. The aim of chief work was to manufacture Ni-Co/ZrO₂ composite coatings by electroplating under ultrasonic vibration, studying influence of ultrasonic waves on the mechanism for Ni-Co/ZrO₂ composite deposition in a acidic amino sulfonate plating bath. For this reason, using linear sweep voltammetry and Tafel electrochemical techniques to offer favorable reference for composite coatings, Scanning electron microscope and X-ray diffraction techniques were applied for characteristic of coating.

EXPERIMENT MATERIALS AND METHODS

Ni-Co/ZrO₂ composite coatings were electrodeposited from a sulfamate electrolyte. Analytical reagents and distilled water were used to prepare the plating solution. The composition and electroplating parameters are given: Ni(NH₂SO₃)₂·4H₂O ~ 80 g/L, Co(NH₂SO₃)₂·4H₂O ~ 10 g/L, ZrO₂ 10 g/L, Current density ~ 4 A/dm², Temperature 40 °C, Ultrasonic power ~ 160, 240, 320, 400 W. For Ni-Co-ZrO₂ composite coatings, the solution was stirred magnetically with 1200 rpm speed for 6 h in order to get good dispersion of particles. The pH was adjusted to 4 by using H₃BO₃.

Pure copper was used as the cathode substrate. A pure nickel plate was served for anode in the deposition process. Prior to plating experiments the copper plates

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were polished to smooth surface using different grits of emery paper and nickel surface was activated by dipping in 10 % HCl for a few seconds. A direct currents galvanostat model PS-618 was used for the deposition of the coatings. The experiments were performed under a constant current density of 4 A/dm² and the deposition time was 40 min. Ultrasound with a frequency of 35 kHz and a peak output of 400 W was applied.

An Autolab electrochemical workstation was used for linear sweep voltammetry and Tafel tests. The corrosion resistance of composite coatings was carried out in 3,5 % NaCl solution. The X-ray diffraction technique was used to determine phase composition and an average grain size of deposits (Cu K α filtered radiation). The surface morphology of the coatings was complemented by SEM (Zeiss-SIGMA HD).

RESULTS AND DISCUSSION

Ultrasound is the mechanical wave with a frequency range of 10 kHz~10⁶ kHz. The wave speed is about 1 500 m/s and the wavelength is 0,01 cm~10 cm. The ultrasonic wave in the long term is larger than the molecular size, which means that ultrasound itself can not play a role directly in the molecule, but through the physical action of the surrounding environment to influence the molecules, so the effect of ultrasonic is closely related to the environment of its action[7]. The cathodic polarization curves of different composite coatings prepared under different ultrasonic power are shown in Figure 1.

It can be seen that when the ultrasonic was not applied to the electrodeposition process, the curve obviously changed at the potential of $\sim -0,66$ V, this is the starting potential of the matrix metal codeposition. With the increase of ultrasonic power, the deposition potential was more negative, and the current corresponding potential decreased gradually. When the ultrasonic power increased to 320 W, the deposition current increased. The change of the deposition current could be associated with the codeposition of the nanoparticles.

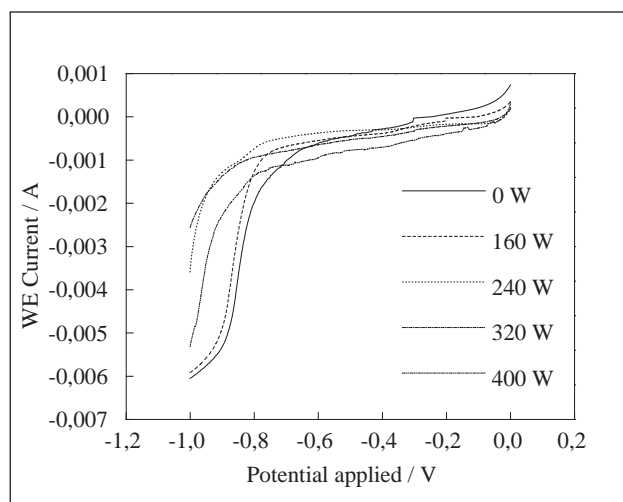


Figure 1 Cathodic polarization curves of electrodeposition under different ultrasonic power

When the ultrasonic power was lower, nanoparticles were not easy to codeposition with the matrix metal in the electrolyte solution. The spherical wave was not enough to cause the microscopic vorticity of the reaction liquid on the surface. The composition of nanoparticles and metal matrix and the cathode polarization were low. When the ultrasonic power was too high, the main effect of ultrasonic vibration on the nanoparticles and metal ions deposited on the cathode surface was scour, and the composition of nanoparticles and matrix metal decreased, but the deposition current increased.

The surface morphology and XRD of composite coatings

Figure 2 is the surface morphology of composite coatings obtained electrodeposition under different ultrasonic power.

The surface topography of composite coatings prepared at different ultrasonic power was shown in Figure 2. Atomic percentage of each element in the coatings are shown in Table 1. From the Figure 2a, it can be observed that there is a compact cell like tissue on the surface of the composite coatings, and it is more uniform. When the ultrasonic power increased to 240 W, the cell structure of the coating surface is more uniform and the grain size is smaller. For Figure 2c and d, the uniformity of the cellular tissue on the surface of the coating decreases and the grain size increases obviously. The changes in the surface morphology of the coating can be linked to the changes in the ultrasonic power. When the ultrasonic power is low, the mechanical wave produced by the ultrasonic oscillation plays a small role in the

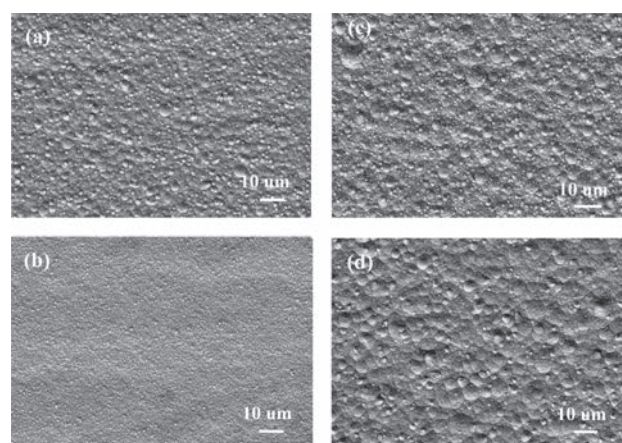


Figure 2 Surface morphology of the composite coatings under different ultrasonic power for (a) 160 W; (b) 240 W; (c) 320 W; (d) 400 W

Table 1. Atomic percentage of each element in the coatings / wt. %

Coatings	Ni	Co	O	Zr	Total
a	63,55	26,90	6,75	2,80	100
b	59,66	21,39	12,57	6,38	100
c	60,13	28,54	7,88	3,45	100
d	58,67	30,81	7,42	3,10	100

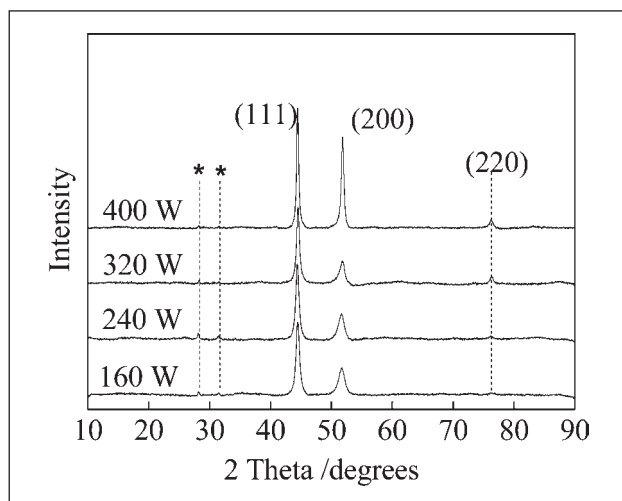


Figure 3 X-ray diffraction of different composite coatings

suspension of the nanoparticles in the electrolyte solution, the composite count of the nanoparticles and the matrix metal is low, and the fine grain strengthening of the nanoparticles is small. When the ultrasonic power is too high, the scour effect of the ultrasonic oscillation on the cathode surface is so great that the effective composite of the nanoparticles and the matrix metal reduced, the surface grain of the coating is coarser and the uneven surface morphology could be because of this.

In order to study the effect of ultrasonic power on the phase structure of Ni-Co/ZrO₂ composite coatings deposited on the pure copper plate by assisted different ultrasonic power, the X ray diffraction method was used. Figure 3 is the X ray diffraction curves of four Ni-Co/ZrO₂ composite coatings. The results showed that the structure and diffraction angle of the diffraction peak did not obviously changed, the auxiliary effect of ultrasound did not change this phenomenon. However, it can be observed that the diffraction peak intensity of the composite coatings was discrepant under different ultrasonic power. Comparing with the other coatings, the diffraction peak of the coatings prepared in the ultrasonic power 240 W was wider and blunt, and it had smaller grain size. The results calculated by the Scherrer formula proved that the average grain size of the composite coating is 35,4 nm.

Corrosion resistance of different coatings

It is practical and accurate to study the corrosion resistance of the composite coatings by electrochemical methods. As shown in Figure 4, the Tafel curves of the composite coating were measured in 3,5 % NaCl solution by an electrochemical workstation.

From the Figure 4, it can be found that the corrosion potential of the deposited coatings was the highest when the ultrasonic power is 240 W, which indicated that the corrosion resistance of this coating was stronger than other composite coatings. However, the corrosion resistance of the coatings was poor when the ultrasonic power was too high or too low. The corrosion current

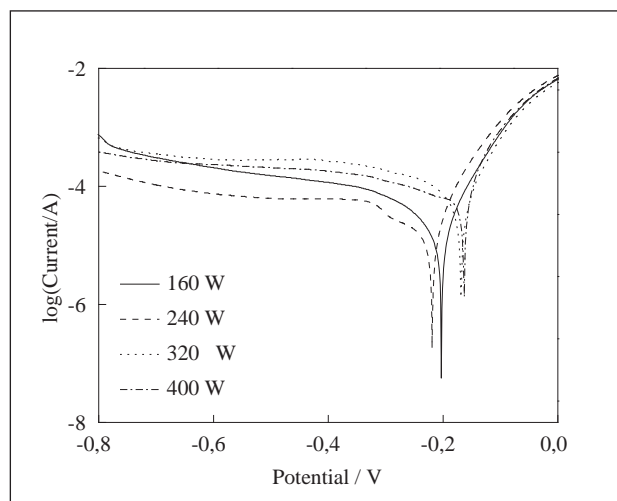


Figure 4 Tafel curves of different coatings

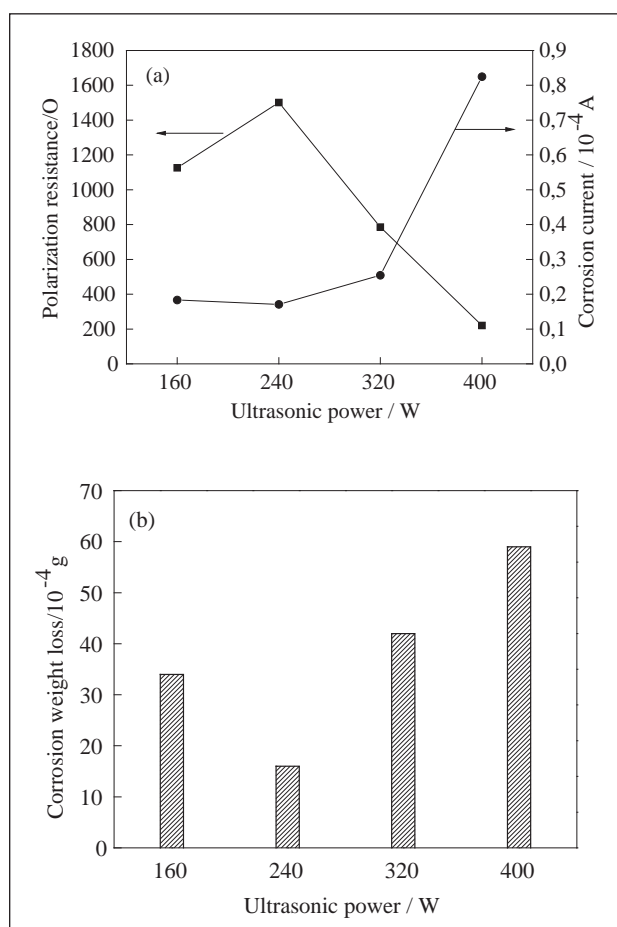


Figure 5 (a):corrosion current and polarization resistance curves of different coatings (b):corrosion loss results of different coatings

and curve slope of different coatings were obtained by extrapolation of curves, and the polarization resistance of different coatings was calculated by Stern-Geary formula [$1/R_p = 2,303i_{corr}(1/\beta_a + 1/\beta_c)$]. Where R_p is the polarization resistance, i_{corr} is the corrosion current, the β_a is the anode slope, and the β_c is the cathode slope. The polarization resistance is approximately equal to the charge transfer resistance in the solution. Corrosion current and calculated polarization resistance are shown in Figure 5.

From Figure 5a, it could be found that the corrosion current of the deposited coating assisted 240 W ultrasonic power was the lowest but the polarization resistance was the largest, which indicated that the corrosion resistance of the composite coating was the best in the electrochemical corrosion experiment. The corrosion resistance of the composite coating is related to the density of the coating surface and the composite of nanoparticles. In the corrosion process of the coating, the presence of nanoparticles hinders the corrosion path and improves the corrosion resistance of the coating; on the other hand, the compact surface makes it difficult to form corrosion points and affect the corrosion process at the initial stage of corrosion. The corrosion resistance of the composite coating was studied by the static immersion of the coating in 3.5 % sodium chloride solution for 168 h. The corrosion resistance of the composite coating was studied by the corrosion weightlessness of the coating. The results of the corrosion loss of different coatings were shown in Figure 5b. This experimental result was consistent with the Tafel curves.

CONCLUSION

(1) The surface of the composite coating electrodeposited under 240 W of ultrasonic power was more compact, the grain size was the smallest and the corrosion resistance was stronger.

(2) When the ultrasonic power was too high or too low, the cathode polarization of the composite electrodeposition reduced, and the composite amount of the nanoparticles in the composite coating decreased.

(3) The assist of ultrasonic in the composite electrodeposition process did not effect the phase structure of the coatings, but changed the grain size of the composite coatings, and improved the composite amount of the nanoparticles, the properties of the coatings enhanced.

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Note: Y.Y.WANG is responsible for English language, Liaoning, China