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Effect of power supply on the deposition of Zn on a steel substrate using cathodic plasma electrolysis

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ABSTRACT

Cathodic plasma electrolysis (CPE) has been used as an environmentally-friendly process to deposit metal coating on metal substrate. In this work, a coating of zinc was deposited via CPE on a low carbon steel wire using direct current (DC) and square wave pulsed current (SWPC) power. The experimental results showed that application of continuous DC power did not produce zinc deposition, but a dense coating of zinc was easily applied to the substrate with the application of SWPC power at 120 V, 4000 Hz and an 80% duty cycle. The resulting coating was porous with some imperfections on the surface, but the morphology and quality of the coating could be controlled by adjusting the parameters of the SWPC power. Increasing both the duty cycle and frequency of the power resulted in a lower deposition rate, but the coating was denser. The steel wire surface was cleaned using plasma generated in the CPE process and the Zn coating was found to accumulate during the rise in the power pulse. A linear regression model was established to describe the relationship between coating thickness and power parameters.

1. Introduction

Zinc coating has been widely used in a range of industrial applications as the main protective coating of iron and steel materials for many years [1–3]. Traditional coating processes, including hot-dip galvanizing, thermal spraying and electrodeposition, etc. have their own limitations. Electrodeposition is relatively slow and usually accompanied by environmentally hazardous chemicals, while hot-dip galvanizing and thermal spraying may bring adhesion problems in some cases [4]. So there is strong demand for new technics of coating deposition to replace traditional process in some fields.

Cathodic plasma electrolysis (CPE) is a novel surface treatment that was studied widely for application in the cleaning of metal surfaces and deposition of metal or ceramic coatings [5–9]. Compared to traditional plating techniques, the CPE process offers many advantages including high deposition efficiency, low energy consumption, good coating adhesion and environmentally friendliness [10–13]. This method is usually used to produce adherent, dense and uniform metal and ceramic coatings that can retard corrosion, wear and oxidation of substrates.

Several different metal (e.g. Zn, Ni, Cu, Zn–Ni, etc.) coatings have been deposited using the CPE process and it has been found that the quality of the coating is influenced by many a wide variety of parameters (e.g. substrate and coating materials, solution concentration, processing time, temperature, type of power, etc.) [5,14]. Recently, there were some studies focused on the relationship between the quality of the coating and the process conditions. For instance, Smith reported that full coverage of a Ni coating on aluminum substrates can be obtained after a short deposition time of 20 s [15]. Meletis' results showed that the rate of metal deposition can be improved when a Zn anode was used to produce a smoother surface during deposition of a Zn coating [4]. Substrate materials and pretreatment of the substrate can influence the coating morphology during deposition of Mo due to the reaction between the substrate and the electrolyte [14]. The deposition process can also be significantly affected by the concentration of the plating solution. A high H_2SO_4 concentration in solution was found to easily produce a plasma arc at the surface of the cathode, which resulted in a smooth, dense metal coating [16]. Although much work has been done to understand how these conditions affect the quality of the coating, the influence of the power parameters on the quality of the coating has not been systemically studied. The relationship between the pulsed power parameters (voltage, frequency and duty cycle) and the quality of the deposition in the CPE process remains unclear, which has produced an incomplete understanding of the mechanism of CPE deposition.

In this work, the relationship between coating quality and the power parameters of the process power supply will be determined during CPE

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deposition of Zn coating. A linear regression model will be established to explain how these variables affect the deposition process and to evaluate deposition rate under different duty cycles and frequencies.

2. Experimental details

The experimental apparatus used for the CPE deposition is shown in Fig. 1. A glass beaker containing circulating cooling water was used to control the temperature of the reaction electrolyte during the CPE process. The direct-current (DC) or square wave pulsed current (SWPC) source was connected to the graphite plate anode and the substrate material constituted the cathode. The system voltage was 0–400 V and the range of pulse frequency was 0–4000 Hz. Both the anode and cathode were immersed in the electrolyte and the distance between the anode and cathode was 50 mm.

A cold-drawn low carbon steel Q195 wire with a diameter of 2.5 mm after annealing treatment was selected as the substrate material. An 80 mm length of the Q195 wire was in contact with the electrolyte and the rest of the wire was wrapped with insulating tape to avoid point discharge. Before CPE deposition, the substrate was cleaned using the CPE process in an electrolyte of 10% $NaHCO_3$ at 70 °C with 40 s of 130 V DC power. After cleaning, Zn was coated on the cleaned wire substrate using the CPE process. The test electrolyte was composed of an aqueous solution of 18% $ZnSO_4$ held at 70 °C. The voltage used for the deposition process was 120 V and both the duty cycle and frequency were adjusted. In all cases, the processing time was fixed at 40 s. During the plasma processing, a silicon p-n photodiode BPW21R, with wavelength 420–675 nm and on/off switch time of 3 μs, was used to determine changes in the light emitted by the plasma that was generated by the SWPC power. The photodiode open circuit voltage increased with the increase of the plasma light intensity when the photodiode was exposed to the cathode. Both the electrode voltage and the open circuit voltage values were then instantaneously recorded using a Tektronix TDS2022C oscilloscope. After processing, X-ray diffraction (XRD, Dmax-RB, Rigaku) was used to analyze the phase constituent of the deposited coatings. The coating surface morphology was examined using a scanning electron microscopy (SEM, Zeiss Supra55) and the compositions of the coatings were analyzed using Energy-dispersive X-ray Spectroscopy (EDS, Thermo Scientific UltraDry). The coating thickness was determined as the mean values of five measurements obtained using SEM on different locations from five cross-sectional measurements. The surface roughness of the coatings was evaluated by using an Olympus LEXT OLS4000 3D laser measuring microscope. Corrosion experiments were conducted in 3.5% NaCl solution in samples produced at the same processing conditions by utilizing a multichannel potentiostat (VersaSTATMC). The electrochemical cell consisted of working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the counter electrode. Measurements started at 200 mV below and ended at 800 mV above the open circuit potential (OCP) at a scanning rate of 1 mV/s. Corrosion current densities were determined using Tafel extrapolation.

3. Results

3.1. Characterization of the prepared coatings

Fig. 2(a) shows the original surface morphology of the coating surfaces and the cross section of the steel wire after CPE cleaning process. A large number of craters with diameters ranging from 1 to 3 μm can be seen on the surface of the wire. These craters reshaped the surface, but the drawing scratches along axis of the wire were quite apparent. There were some circles on the peaks of scratches, but no mill scale or other contaminants were observed on the wire surface. The results of EDS analysis of the surface are presented in Table 1. As can be seen, a small amount of oxygen at <5 at.% was presented, which possibly resulted from the lack of a protective coating after the cleaning process.

Fig. 2(b) and (c) illustrate typical deposition morphologies of the zinc coatings after CPE processing of the wire using constant DC power and SWPC power. As shown in Fig. 2(b), the drawing scratches on the wire were still visible after deposition and the steel wire was covered by very little Zn after it was subjected to CPE processing using constant DC power. As shown from the wire cross sections micrographs in upper-right corner of Fig. 2(b), no apparent Zn coating was found to adhere to the steel surface after the processing at 120 V DC, although the Zn was found on the wire through the EDS analysis. Iron and some O were detected as well, because of the thinness of the deposited coating, which allowed penetration of the EDS electron beam.

Typical deposition morphology after CPE processing using SWPC power is shown in Fig. 2(c). A distinct coating with thickness of about 18 μm can be seen, but there were some holes in the coating as revealed by the cross section analysis. The EDS composition analysis listed in Table 1 confirmed that the coating primarily consisted of the Zn element. There were some impact craters and Zn particles at the rim of the craters, which was evidenced of the bursting of gas bubbles in the electrolyte that were generated by the plasma [4,15]. The craters in the coating were similar to those shown in Fig. 2(a), but their size

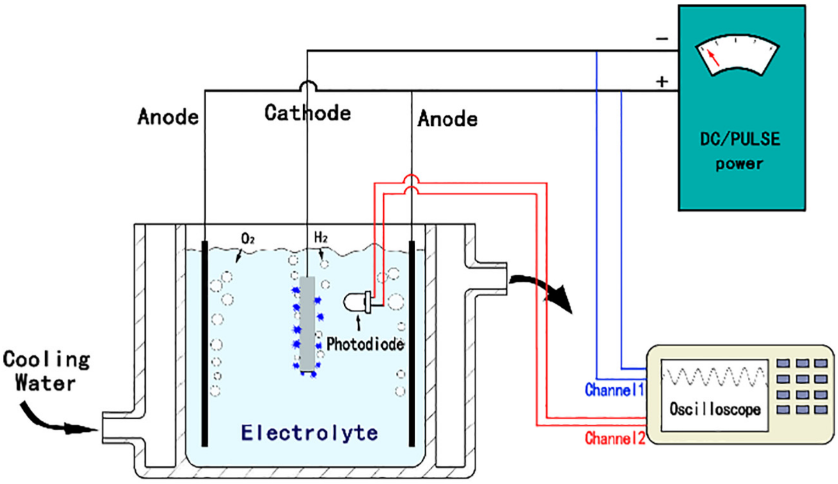

Fig. 1. Experimental apparatus used for the CPE deposition [17].