

Short Communication

Pulse Electroplating of Ultra-Fine Grained Zinc Coating on 316L Stainless Steel and its Corrosion Behaviour

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Pulse electrodeposition (PED) was used to produce nanocrystalline zinc film from zinc sulphate electrolyte. Differences reductive/oxide voltage were employed to study the grain size and surface morphology of these ultra-fine zinc coating with SEM. Also pulse times were discussed for the same electricity. The corrosion behaviour of these as formed zinc coating are investigated by potentiodynamic polarization. The different corrosion resistances of SS316L under different applied voltages and pulse time conditions are summarized, providing a foundation for further consideration of electroplating zinc.

Keywords: pulse voltage; electroplating zinc; zinc coating; corrosion behaviour

1. INTRODUCTION

Electroplating is the process of plating a thin layer of another metal or alloy on the surface of certain metals by electrolysis. It is a process of using electrolysis to attach a metal film to the surface of a metal or other material to prevent metal oxidation (such as rust); improve the ability of wear resistance[1-2], conductivity[3-4], reflective[5-6], and anti-corrosion[7-8] (copper sulphate, etc.); and enhance the appearance, among other effects. In recent years, pulse electrodeposition (PED) technology has developed rapidly, and the application range has become more extensive, promoting the improvement of coating quality and performance.

Compared with DC electroplating, pulse electroplating has many advantages. The pulse electroplating current density is high, which can increase the nucleation rate of the electrode surface and increase the limiting current density to achieve the grain refinement effect. The pulse parameters can improve the composition and morphology of the coating and even the preferred orientation of the crystal. With minimal additive consumption, pulsed electroplating using bidirectional currents can

increase the stability and efficiency of the bath, eliminating the need for high-current density regions. The presence of the resulting coating pores has the effect of significantly improving the coating performance.

Various coating such as Chromium [9], Cobalt [10], Copper [11], Gold [12], Nickel [13], Platinum [14], Silver [15], Zinc [16-18] and their composites/alloys can be electrodeposited by pulse current method. Zinc and zinc alloy coatings have many excellent properties, in addition to good resistance to hydrogen embrittlement and corrosion resistance, as well as multi-layer and nanodirection development. The nanocomposite coating and nanocrystalline coating prepared by pulse electroplating can improve the creep resistance, wear resistance, corrosion resistance, high-temperature oxidation resistance and high-temperature strength of the substrate. Thus, it has been widely used. The most common types of zinc alloy coatings are zinc-iron, zinc-nickel and zinc-cobalt alloys. In recent years, it has been shown that normalized Zn coating can effectively change the surface properties of the substrate; thus, it has received extensive attention.

Hyde et al. [19] studied the effect of ultrasonic on metal electrodeposition. The results indicated that at low concentrations, the electrodeposition process is controlled by diffusion, and the ultrasonic waves have a greater influence on metal electrodeposition. At high concentrations, the electrodeposition process is subject to the control of charge transfer steps. The impact of ultrasound is smaller. Saber et al. [20] studied the effect of the pulsed current on the grain size, surface morphology, microhardness, and preferred orientation of zinc in zinc plating baths containing polyacrylamide and thiourea. Cachet et al. [21] used ac impedance to study the anodic dissolution and corrosion kinetics of steel plate electrodeposition and hot-dip zinc coating in aerated sulphate media. The results showed that the corrosion processes of different coatings have their own three different parallel steps. Ahsassi-Sorkhabai H. et al. [22] electroplated zinc-nickel alloys on steel using a chloride bath, DC and pulsed currents and studied the effects of some electrodeposition parameters on the coating composition, current efficiency, and so on. Belotwksa et al. [23] reported on the addition of acetate as a stabilizing agent for zinc-nickel alloy sulphate plating baths with pH values ranging from 2 to 2.5. Studies have shown that zinc-nickel co-deposition is characterized by abnormal co-deposition. Mulef C. et al. [24] studied some properties of zinc-nickel alloy co-deposition and found that two structures were formed in the zinc-nickel alloy coating. Syna et al. [25] studied zinc-manganese alloy electroplating and investigated the influence of the plating solution composition on the potential composition of the zinc-manganese alloy on the steel surface by constant potential deposition.

At low current densities, irregular and regular co-deposition can be observed both in DC current and pulse current plating. Mass transport plays an important role in limiting the deposition rate, influences the morphology, deposit properties and the macro- and micro-throwing power [26]. The pulse current can improve the finish of the coating and reduce the deposition of $Zn(OH)_2$ on the cathode surface. The polarization curve of the pulsed current deposition layer shifts to a positive potential. The use of pulse electroplating is superior to direct current electroplating in stabilizing coating composition, inhibiting the precipitation of hydrogen to reduce the hydrogen permeation to the substrate, reducing the porosity of the coating, and improving current efficiency. For some electroplating solutions, even if no brightener is used, bright coatings can also be obtained.

In this experiment, various ultra-fine grained zinc coatings on stainless steel are prepared by PED. And different cathodic and anodic applied voltage are employed to investigate their application on the zinc film. Additionally, their corrosion behaviour is investigated by potentiodynamic polarization.

2. EXPERIMENT

2.1 Preparation of a 316L Stainless Steel Sample

The 316L stainless steel (the main component of 316L stainless steel is $C \leq 0.03$, $Si \leq 1.00$, $Mn \leq 2.00$, $P \leq 0.045$, $S \leq 0.030$, $Ni: 10.0-14.0$, $Cr: 16.0-18.0$, $Mo: 2.0-3.0$) plate with a thickness of 0.5 mm was cut to the size of 18 mm×18 mm and ultrasonically cleaned with an ultrasonic cleaner for 10 min with anhydrous ethanol and deionized water; it was then dried for use.

2.2 Preparation of electroplated zinc sample by the pulse electrodeposition

A $ZnSO_4$ solution with a concentration of 0.1 M was prepared. The 316L stainless steel sample prepared above was immersed in this solution (0.1 M $ZnSO_4$), and the electrochemical method was applied. A platinum electrode was used as the counter electrode, and an Ag-AgCl electrode was used as the reference electrode. The three-electrode system with 316L stainless steel as a working electrode was used with an electrochemical analyser (Shanghai Chenhua Instrument Co., Ltd.), which electroplated Zn on the 316L stainless steel sample. The applied voltage method was pulse boosting, in which the voltage is first added from the 0 V pulse to an anodic voltage as E_A with a duration time T_A , and then, the reverse pulse is applied to a cathodic voltage as E_C for the duration of T_C ; the final voltage is restored to 0 V. This process is set as one cycle. The specific application process of the applied voltage is shown in Figure 1.

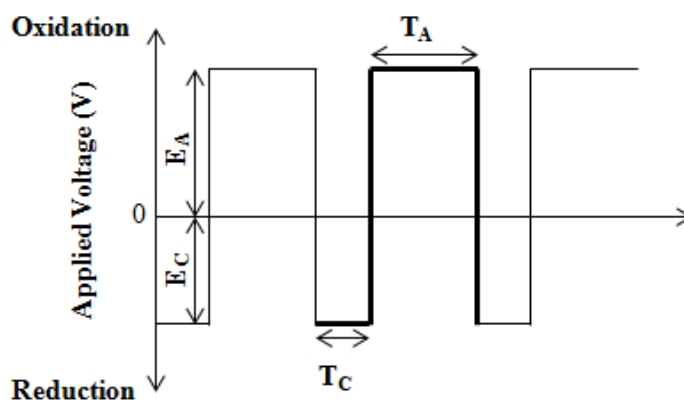


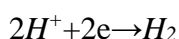
Figure 1. Applied voltage application process. The black and bold part indicates one pulse.

where, T_A is the anodic time, T_C is the cathodic time, E_A is the anodic voltage and E_C is the cathodic voltage.

Table 1. Electrochemical parameters of nano zinc on SS316L

Sample	E _A	mV vs.SCE	E _C	mV vs.SCE	T _A	S	T _C	S	cycle
A	1000		-200		0.1		0.1		5000
B	800		-400		0.1		0.1		5000
C	600		-600		0.1		0.1		5000
D	800		-400		0.5		0.5		1000

The investigation focused that the effect of the different pulse time and different applied voltage on the corrosion resistance of the sample when the total plating time was the same. The preparation of the sample should include pulse time, cycle times, and applied voltage (E_A and E_C). These are several of the factors. Among them, for the different selection of pulse time values, the number of cycles should be appropriately adjusted so that the total time for the total electrochemical galvanizing is consistent. Therefore, the samples prepared under various conditions are named as A, B, C and D as different E_A and E_C, listed as Table.1. Samples A, B, and C were used to investigate the effects of anodic and cathodic potential on corrosion behaviour; samples B and D were used to investigate the effects of anodic and cathodic time on corrosion behaviour. The anodic and cathodic potentials were discussed by the followed reaction, were M is the metal plated and may be accompanied by hydrogen evolution:



2.3 Electrochemical test analysis

As discussed, the three-electrode system was used to study the above experiments. In this experiment, a three-electrode system was adopted in which the working electrode was the electrode prepared by the above experiment, and a potentiodynamic scan was performed by electrochemical analyser with a scan rate of 1 mV/s. Cyclic voltammetry (CV) is a commonly used electrochemical analysis method. The principle of this method is to alternately generate different voltages on the electrode by controlling the potential of the electrode with time and repeatedly scanning the potential range one or more times with a triangular wave. The oxidation-reduction reaction was performed, and the current-potential curve was recorded. According to the shape of the recorded curve, the degree of electrode reaction was judged. The three-electrode system was used to test the cyclic voltammogram curve. The prepared sample was used as the working electrode, the Ag-AgCl electrode was the reference electrode, Pt was the counter electrode, the test solution was 0.1 M Na₂SO₄ solution, and the scan rate was 1 mV/s.

2.4 Morphologies analysis

The morphology of the sample was characterized using a cold field emission scanning electron microscope JSM-4800F (Japan Electronics Co., Ltd.).

3. RESULTS AND DISCUSSION

3.1 Morphology investigation

The surface morphology of each sample is as follows:

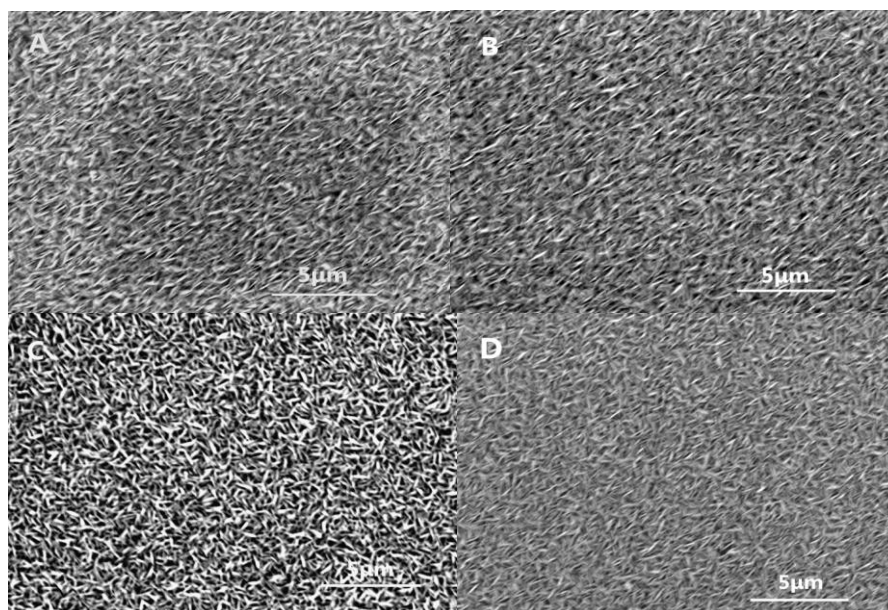


Figure 2. SEM micrographs surface morphology

As seen from Figure 2, samples A, B, C, and D are all needle-shaped and have a length of approximately 1 μm . However, the tightness of the array of needles in each sample is different, which is in contrast to the oxidation of the sample. The reduction potential, the pulse time and the cycle number are inseparably related to each other. By analysing the number of needles in the image under the unit pixel (250*200) [27], the degree of pinning in the sample is discussed. Among them, the arrangement of needles in sample A and D is more compact than that of the rest of the samples. The number of needles under the unit pixel is 45 and 47, respectively; the samples B and C are sparse, and the needles under the unit pixel are 26 and 28, respectively. According to comparative analysis, the higher the value of the applied voltage E_A is, the more favourable the formation of the needles is, and the longer the pulse time is, the better the formation of the needles is.

3.2 Effect of different applied voltages on corrosion behaviour

In this experiment, the electrochemical properties of samples prepared from different applied voltages E_A and E_C were tested to analyse the effects of different applied voltages on the corrosion behaviour. The tested samples were all prepared at the same pulse time and cycle times, in which the pulse time was $T_A=T_C=0.1\text{S}$ and the number of cycles was 5000. The results obtained by the electrochemical analysis of the above sample are as follows:

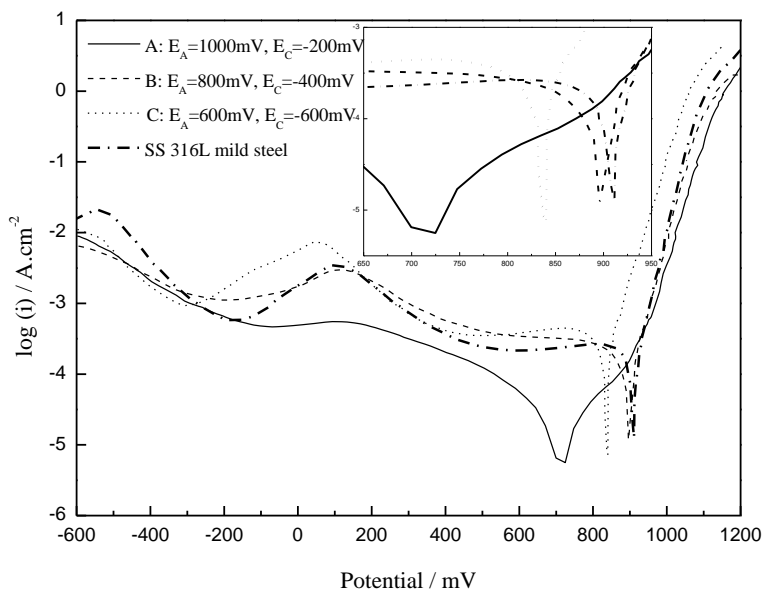


Figure 3. Semi-logarithmic polarization curves of different applied voltage E_A and E_C values in Na_2SO_4 0.1M solution

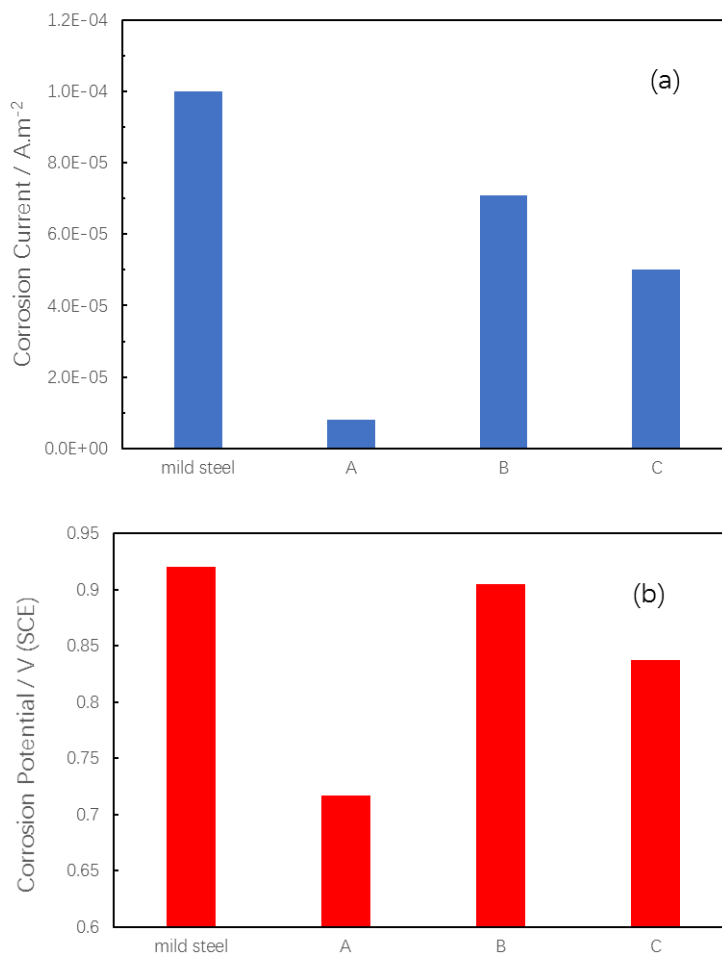


Figure. 4 Variation of corrosion current (a) and corrosion potential (b) as a function of anodic and cathodic potential of coating deposition..

Thus, a more insight into corrosion behaviour can be gained from Fig.4 (a & b) wherein corrosion current (measured from Tafel plots) and the corrosion potential are presented in the form of bar charts for the zinc coatings obtained by various PED. Amongst the electrodeposited coatings, Sample A exhibits the lowest corrosion rate and therefore effectively protects the underlying mild steel substrate for long duration. Combined with the morphology analysis, it is concluded that the sparse distribution of needles in the sample is beneficial to improve the corrosion resistance of the sample.

3.3 Effect of different pulse time values on corrosion behaviour

In this experiment, the electrochemical properties of samples prepared from different anodic and cathodic times T_A and T_C were employed to analyse the effects of different applied voltage values on corrosion behaviour. The samples tested in this sample were all made at the same applied voltage, with $E_A=800$ mV and $E_C=-400$ mV. A sample not electro-galvanized is referred to as a blank sample. The results obtained by the electrochemical analysis of the above sample are as follows.

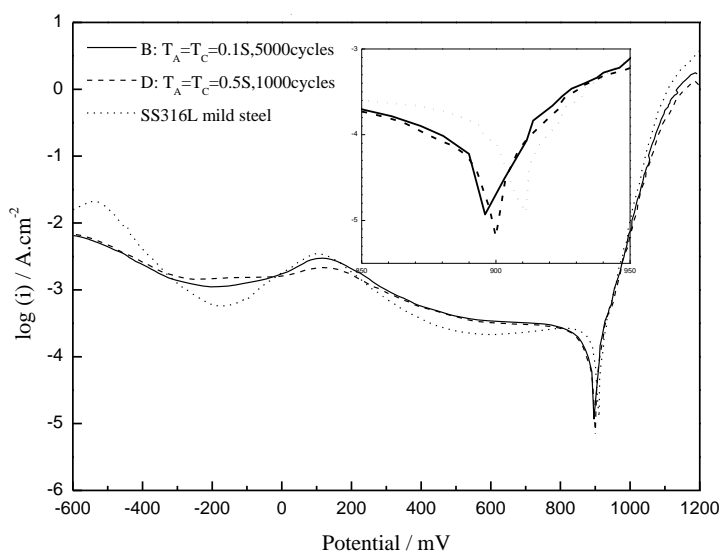


Figure 5. Semi-logarithmic polarization curves of different applied values of T_A and T_C on in NaCl 0.1M solution

Also, histograms of corrosion current and corrosion potential are employed to show the results of application of anodic and cathodic potential times as in Fig.6. The comparative analysis shows that the sample after electroplating of zinc by pulse method reduces the corrosion current and corrosion potential of the sample, and its corrosion resistance is significantly improved. The comparative analysis showed that the corrosion resistance of sample B as $T_A=T_C=0.1$ S, and 5000 cycles was the best. Combined with the morphology analysis, the sparse distribution of the needles in the sample was beneficial to improve the corrosion resistance of the sample.

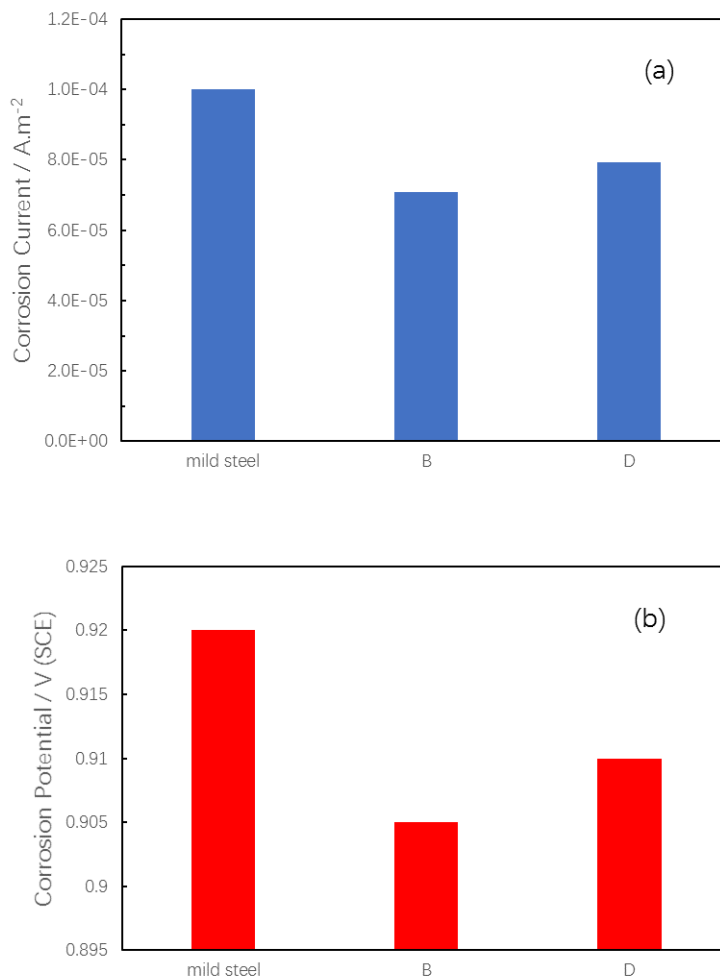


Figure 6. Variation of corrosion current (a) and corrosion potential (b) as a function of anodic and cathodic times of coating deposition.

3.4 Measurement of cyclic-voltammetry

The effect of pulse time on the corrosion behaviour of 316L stainless steel was discussed by a cyclic-voltammetry (CV) plot as shown in Fig.7. The potential of the control sample was measured from -600 mV to 1200 mV in the forward and rewards direction at a scan rate of 1 mV/s. The sample was not electrogalvanized, and sample B was prepared under the following conditions: $E_A=800$ mV, $E_C=-400$ mV, $T_A=T_C=0.1$ cycle 5000. All the plots were characterised by an active peak, typical of metals that exhibit active passive behaviour. It indicated a shrinking peak at more than 1000mV and a less average passive current from -200 to +800mV by PED zinc coating. This decrease was consistent with expectation, and is compatible with results obtained on stainless steel with various deposition [28-30].

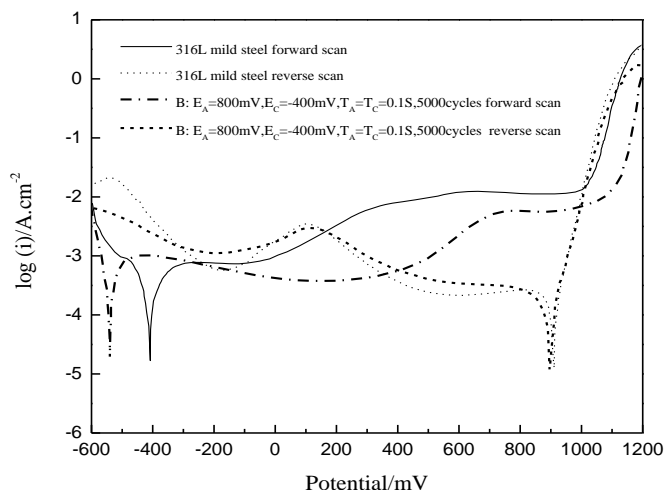


Figure 7. Cyclic voltammetry plot of the sample

4. CONCLUSION

This paper studied the effect of different applied voltages and different pulse times on the corrosion resistance of the sample. When the pulse time is the same, different applied voltages have an effect on the sample. Electrochemical zinc plating is beneficial to reduce the electrode potential when the sample is prepared. When the applied voltage is the same, different pulse times have little effect on the sample; when performing the cyclic voltammetry test, the two samples have similar properties in the forward scan but have different electricity in the reverse scan. The chemical properties and the appearance of each sample are approximately the same. They are all needle-like structures with a length of approximately 1 μm , and each needle-like substance is closely arranged. This article innovatively proposed the use of a simple single-salt pulsed method to prepare ultra-fine grained zinc coating, and the prepared coating can effectively change the corrosion resistance of stainless steel.

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