

Effects of Current Density and Deposition Time on Corrosion Resistance of Electrodeposited Zn-Ni-SiO₂ Coating

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ABSTRACT

This work aims to evaluate the effects of current density and plating time on the corrosion resistance of ZnNiSiO₂ electroplated coating. For the plating time, the results showed that coating thickness increased with increasing the plating time. The average thickness was 6, 15 and 25 μm, when used plating time of 10, 30 and 50 minutes, respectively. Whereas, when the current density values varied from 1 A/dm² to 5 A/dm², the coating thickness was in range of 14.7 - 15.3 μm, with the same plating times. After 900 hours of exposure to salt spray, the surface appearance of coatings indicated that the plating time of 30 minutes provided the highest corrosion resistance. These data were coherent with the findings from polarization curve measurement.

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1. Introduction

To protect the ferrous metals against corrosion, zinc alloy coatings exhibited higher corrosion resistance than pure zinc coating, while maintaining their sacrificial protection effect [4-6]. It was reported in literature that zinc-nickel coatings provided higher corrosion protection for steel than the neat zinc and cadmium coatings [1-6]. Among the zinc alloy coatings, zinc-nickel alloy coating has attracted significant attention from both research and industry due to their high corrosion resistance [7-9] and good mechanical properties [10]. In fact, for industrial application, the improvement of both mechanical and anticorrosion properties for zinc-nickel alloy coatings necessary and required [2, 11, 12]. In case of zinc-nickel electroplated coatings, their properties mostly depended on both plating baths (composition/pH) and plating parameters (temperature, current density, plating potential) [13-15]. To evaluate the corrosion resistance of zinc-nickel alloy coating in aggressive environment, salt spray test has been considered as a typical method [17]. From the exposure to salt spray test, authors in [16] reported that there were various factors affecting the anticorrosion property of zinc-nickel alloy coating [16]. In this paper, the effects of current density and plating time on the corrosion resistance of ZnNiSiO₂ electroplated coating have been evaluated systematically.

2. Experiments

Mild steel (SPHC - JIS G3131) substrates were low carbon steel with the chemical composition: C(≤0.15%), Mn (≤0.6%), P (≤0.05%), S (≤0.05). The size of steel specimens was 100×50×1.2 mm. Before plating, the steel coupons was polished using silicon carbide (SiC) papers down to a grid size of #280 from #600, then degreased and pickled. The steel coupons were then activated with 5% HCl(aq) for 5 seconds.

The nanosilica powder (AEROSIL 200, Belgium) with average particle size of 15 nm and surface area of 200 m²/g was used as received without any further treatment or

modification. Before electrodeposition, the silica nanoparticles with concentration of 5 g/L were dispersed in the electrolytic bath by ultrasonic at 20 kHz for 30 min. These silica nanoparticles were maintained in an electrolytic bath in suspension by continuous magnetic stirring of 200 rpm for at least 24 hours before deposition. The composition of electrolytic bath (20 litres in volume) was 60 g/L ZnCl₂, 250 g/L NH₄Cl, 150 g/L NiCl₂; 20 g/L H₃BO₃, and 5g/L nanosilica at pH 5.6. The plating parameters were 1-5 A/dm² current density, 10-20 minutes plating time at plating temperature of 30°C.

After plating, the average thickness of the alloy coating was measured using MiniTest 600 (ElektroPhysik, Germany). The plated samples were kept in a desiccator at room temperature before surface analysis and corrosion tests. The surface morphology and chemical composition of plated samples were investigated by Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) – (SEM/EDX, JEOL -6510, Japan).

The corrosion behavior of the ZnNiSiO₂ coating in 3.5% NaCl solution was evaluated by polarization test (scan rate of 2 mV/s) using Bio-Logic VSP-300 potentiostat. For polarization test, a conventional three-electrode cell was used with the plated sample as working electrode, along with the Saturated Calomel Electrode (SCE) as reference electrode and the platinum mesh as auxiliary electrode.

The salt spray test for ZnNiSiO₂ coatings was performed in the Q-FOG CCT-600 chamber according to the standard JIS H8502 (using 5% NaCl solution at 35°C). The surface appearance (white/red rust corrosion products) of plated samples before and after exposure to salt spray was recorded and photographed.

3. Results and Discussion

3.1 Coating Characterization

Tables 1 and 2 present the values of average thickness of ZnNiSiO₂ coatings with various plating current densities and plating times, respectively. As can be seen in table 1, the thickness of ZnNiSiO₂ coatings slightly increased with increasing current density from 1 to 5 A/dm². Thus, the current density had only minor influence to the coating thickness. However, by increasing the plating time (Table 2), the thickness of ZnNiSiO₂ coatings steadily increased. After 50 minutes of plating, the coating thickness reached a value of 25 μm. For the comparative study on thickness measurement, Axiovert40MAT device was used for the ZnNiSiO₂ coating with plating time of 20 minutes and plating current density of 3A/dm² (Figure 1). As shown in figure 1, the values of coating thickness were quite similar at all positions with average value of 13.53± 0.66 μm. Thus, both methods of thickness measurement were good coherent.

Figure 2a presents the SEM image of ZnNiSiO₂ coating with plating time of 30 minutes and plating current density of 2A/dm². Figure 2b presents the SEM image of ZnNiSiO₂ coating with plating time of 20 minutes and plating current density of 3A/dm². As seen in Figure 2, the composite coating exhibited the pyramid-shaped crystal structure. EDX analysis (Figure 3 and Table 3) indicated the high content of SiO₂ in the coating (2.18 wt.%), with the Zn : Ni weight ratio of Zn (65.5 wt.%) : Ni (14.1 wt.%). High content of SiO₂ in the ZnNiSiO₂ coating confirmed the successful inclusion plating.

3.2. Electrochemical test

Figures 4 and 5 present the potentiodynamic polarization curves of ZnNiSiO₂ coatings plated with different current densities and plating times, respectively. From the measured curves, corrosion current density and corrosion potential of the coatings were deduced using Tafel extrapolation and summarized in Tables 4 and 5 respectively.

Regarding the corrosion potential E_{corr} , from these data the effects of Ni content in ZnNiSiO₂ coating on its corrosion potential could be evaluated roughly. In general, increasing the Ni content in ZnNiSiO₂ coating should lead to an increase in its corrosion potential. In other words, the shift of corrosion potential might indicate a change of composition ratio in the alloy coating.

In case of corrosion current density i_{corr} , as shown in Table 4, the plating parameters of 30 minutes plating time and 2 A/dm² current density provided the lowest corrosion current density (9.22×10^{-6} A/cm²). When increased the plating current density to 3 and 5 A/dm², the corrosion current density of coatings increased up to 35.12×10^{-6} and 25.95×10^{-6} A/cm², respectively. However, when increased the plating time to 40 and 50 minutes (Table 5), the corrosion current density of coatings decreased down to 6.75×10^{-6} and 5.75×10^{-6} A/cm², respectively.

Regarding the effect of coating thickness to the corrosion current (corrosion rate), the highest value of corrosion current density (39.40×10^{-6} A/cm²) was observed in ZnNiSiO₂ coating plated at current density of 2A/dm² during 10

minutes. This coating had the smallest thickness (6 μm) among these as-plated coatings (Tables 1 and 2). When increased the plating time, the coating thickness increased, leading to a decrease in corrosion rate. In case of plating times were 10; 20; 30; 40 and 50 minutes, the corrosion rates of as-plated coatings were 0.732; 0.264; 0.173; 0.125 and 0.106 mm/year, respectively.

3.3. Salt spray test

In addition to the electrochemical test, the corrosion resistance of ZnNiSiO₂ coatings was evaluated by salt spray test. Figure 6 shows the photos of surface appearance after 900 hours-salt spray test of ZnNiSiO₂ coatings plated at different plating current densities. Table 6 presents the time when first red rust spot was seen on the surface of these coatings. As seen in Table 6, the longest time (900 hours) for appearing the first red rust spot was observed on the surface of coatings plated at current density of 2A/dm². This is the reason why 2A/dm² current density was fixed/selected when studied the effects of plating time.

Figure 7 presents the photos of surface appearance after 900 hours-salt spray test of ZnNiSiO₂ coatings plated at different plating time. Table 7 shows the time when first red rust spot was seen on the surface of these coatings. As shown in Table 7, after 200 hours the coating plated in 10 minutes started appearing the first red rust spots on its surface, whereas it was 800 hours for the coating plated in 20 minutes. This result confirmed that the longer plating time (thicker coating) provided the better corrosion protection for steel substrates. The coatings with longer plating times, such as 40 and 50 minutes, began to appear the first red spots after 850 and 890 hours of salt spray test, respectively. Thus, the highest corrosion resistance was achieved by the optimal plating parameters of 30 minutes plating time and 2A/dm² current density. These findings are coherent with the results from polarization curve measurement.

4. Conclusions

The main findings of this study were:

1. Thickness of ZnNiSiO₂ coatings slightly increased with increasing current density from 1 to 5 A/dm². Thus, the current density had only minor influence to the coating thickness. By increasing the plating time, the thickness of ZnNiSiO₂ coatings steadily increased. After 50 minutes of plating, the coating thickness reached a value of 25 μm.
2. Potentiodynamic polarization indicated that the plating parameters of 30 minutes plating time and 2 A/dm² current density provided the lowest corrosion current density (9.22×10^{-6} A/cm²).
3. Salt spray test indicated that plating time of 20 minutes provided the highest corrosion resistance. The first red spot only began to appear on the surface of coating 900 hours of exposure to salt fog.

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Table 1. Average thickness of ZnNiSiO₂ coatings by different plating current densities, (measured by MINITEST600, plating time = 20 minutes)

Current density (A/dm ²)	1	2	3	4	5
Average thickness of coating (μm)	14.7	15	14.9	15.1	15.3

Table 2. Average thickness of the ZnNiSiO₂ coatings with different plating times (measured by MINITEST600, current density = 2A/dm²)

Plating time (min)	10	20	30	40	50
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Average thickness of coating (μm)	6	10	15	19	25
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Table 3. Chemical composition of ZnNiSiO₂ coating (plated during 20 minutes at current density of 3A/dm²).

Spectra	Si	Fe	Ni	Zn	Total
001	1,92	16,16	14,24	67,69	100
002	2,14	20,26	15,1	62,5	100
003	2,48	18,23	12,96	66,32	100
Average of 3 spectra	2,18	18,21	14,1	65,5	100

Table 4. Values of E_{corr} and i_{corr} for the ZnNiSiO₂ coatings with different plating current densities (plating time = 30 minutes)

Plating current density (A/dm ²)	E _{corr} (mV vs SCE)	i _{corr} (A/cm ²)
1	-733	14.77×10 ⁻⁶
2	-783	9.22×10 ⁻⁶
3	-697	35.12×10 ⁻⁶
4	-749	26.04×10 ⁻⁶
5	-713	25.95×10 ⁻⁶

Table 5. Values of E_{corr} and i_{corr} for the ZnNiSiO₂ coatings with different plating times (current density = 2A/dm²)

Plating time (min)	E _{corr} (mV vs SCE)	i _{corr} (A/cm ²)
10	-531	39.40×10 ⁻⁶
20	-570	14.24×10 ⁻⁶
30	-602	9.35×10 ⁻⁶
40	-662	6.75×10 ⁻⁶
50	-669	5.75×10 ⁻⁶

Table 6. Time for appearing the first red rust spot on the surface of ZnNiSiO₂ coatings, prepared at different plating current densities (plated during 30 minute)

Plating current density (A/dm ²)	Time for appearing the first red spot (hour)
1	670
2	900
3	850
4	700
5	650

Table 7. Time for appearing the first red rust spot on the surface of ZnNiSiO₂ coatings, prepared at different plating times (current density = 2A/dm²)

Plating time (min)	Time for appearing the first red spot (hour)
10	200
20	800
30	900
40	850
50	890

Figure 1. Thickness values of ZnNiSiO₂ coating, with plating time of 20 minutes and plating current density of 3A/dm² (measured by Axiovert40MAT)

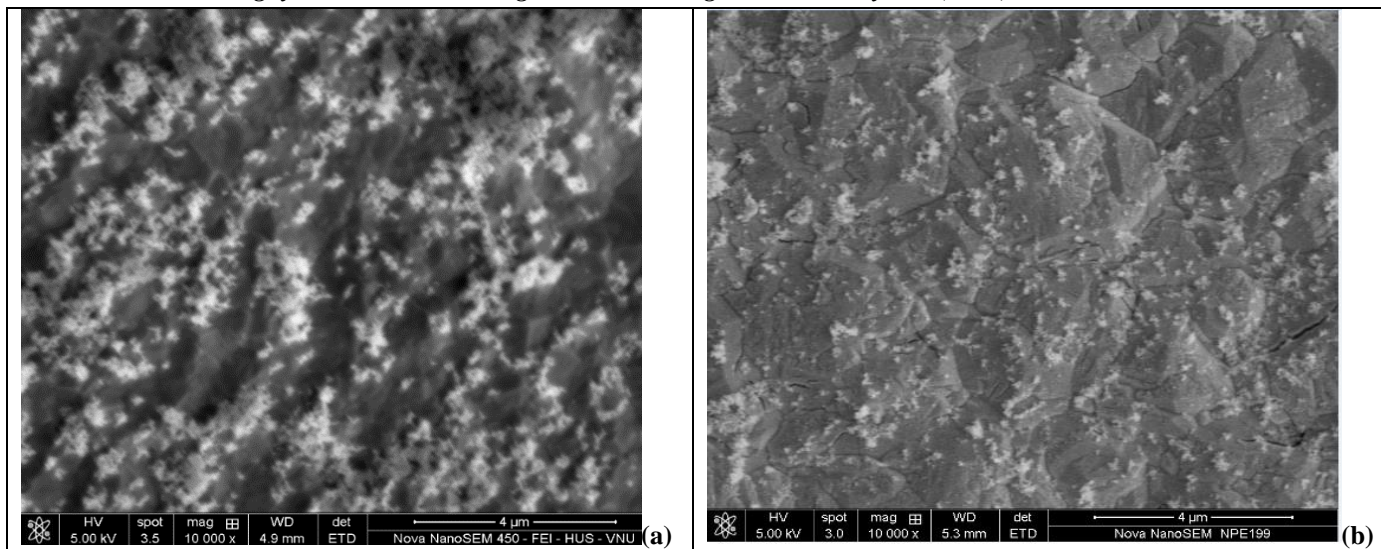


Figure 2. SEM image of ZnNiSiO₂ coating (at current density of 2A/dm² and 3A/dm²)

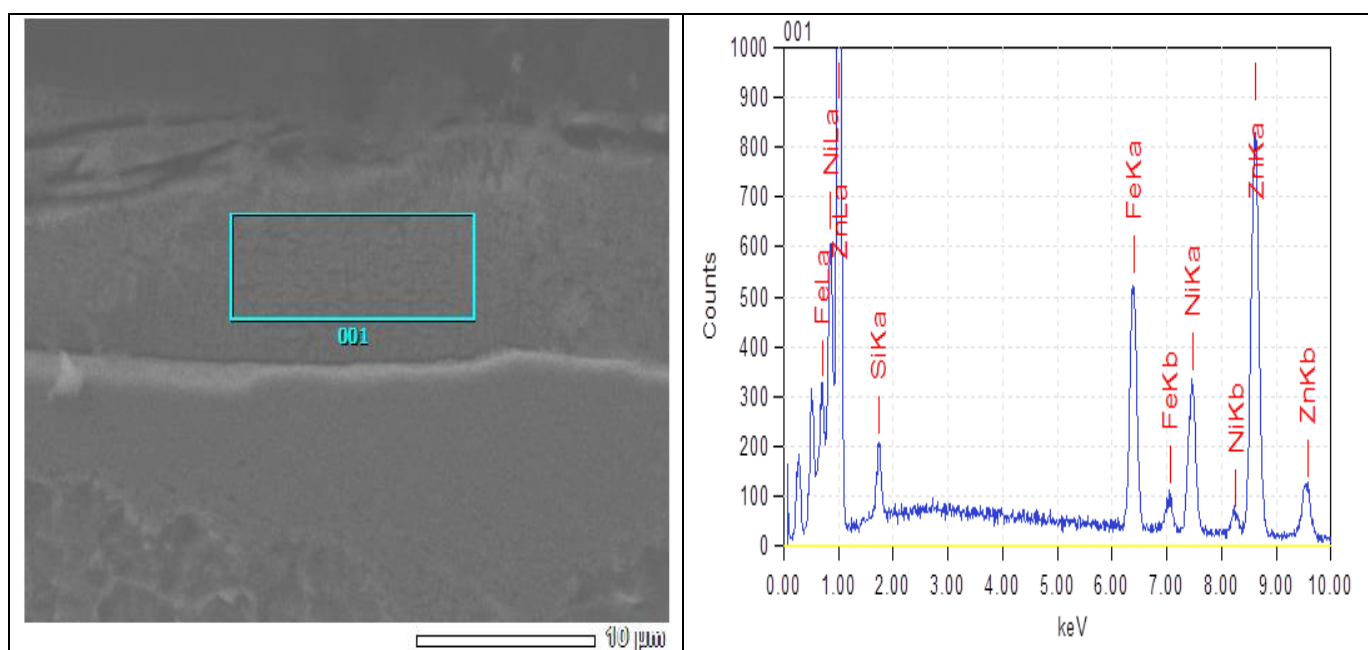


Figure 3. EDX spectrum of the ZnNiSiO₂ coating (plated during 20 minutes at current density of 3A/dm²).

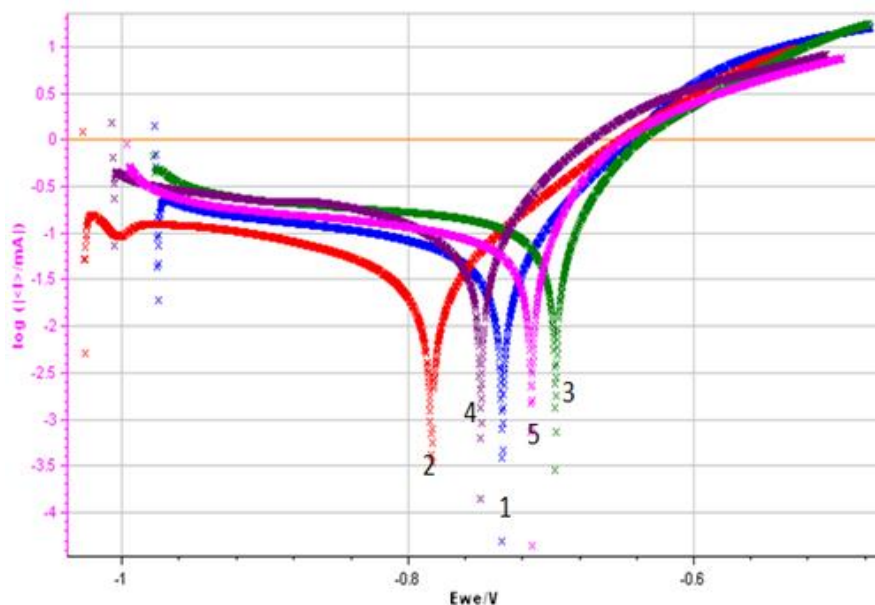


Figure 4. Polarization curves of ZnNiSiO₂ coatings with different plating current densities (plating time = 30 minutes): (1) 1 A/dm², (2) 2 A/dm², (3) 3 A/dm², (4) 4 A/dm² and (5) 5 A/dm².

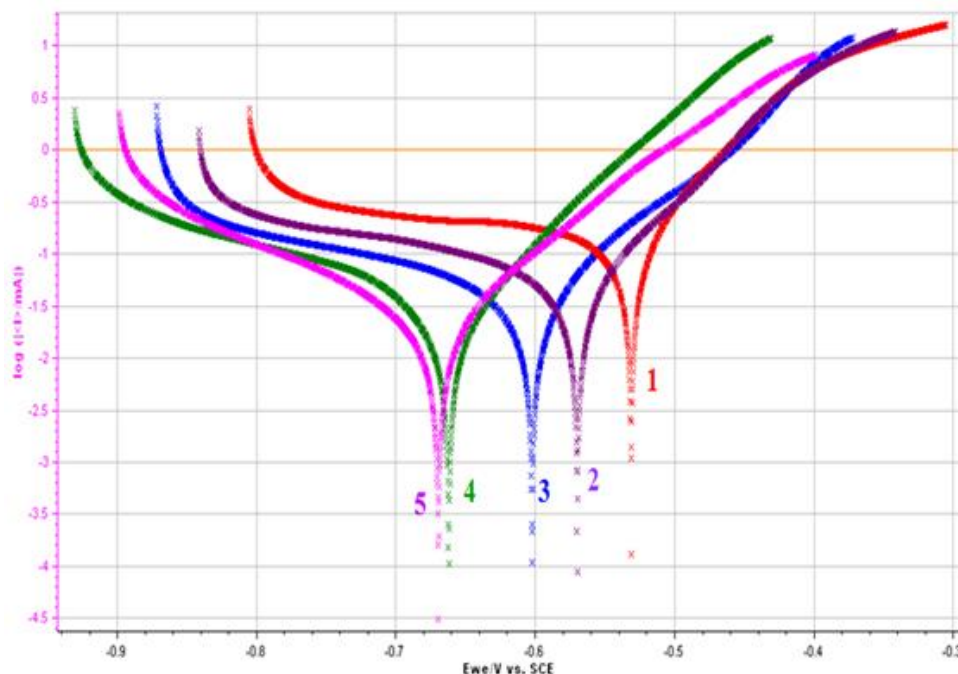


Figure 5. Polarization curves of ZnNiSiO₂ coatings with different plating times (current density = 2A/dm²):(1) 10 min, (2) 20 min, (3) 30 min, (4) 40 min and (5) 50 min.

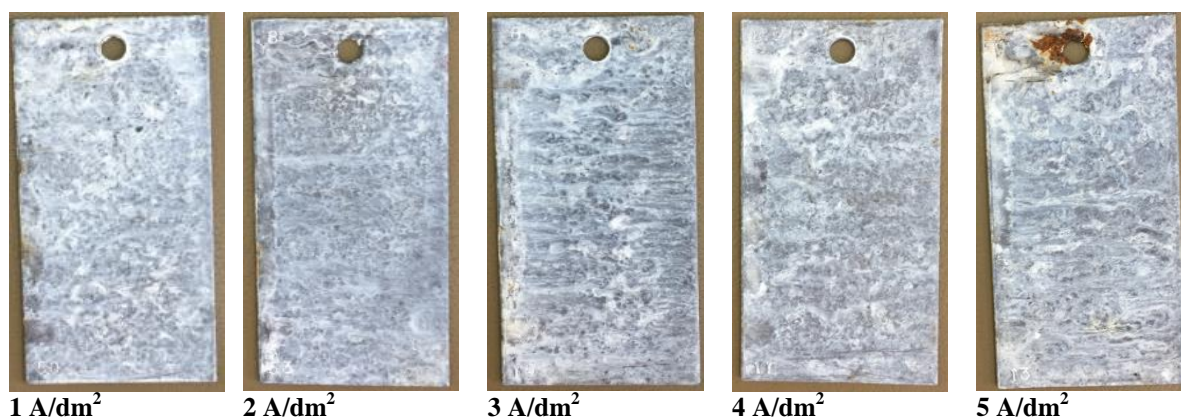


Figure 6. Photos of surface appearance for ZnNiSiO₂ coatings plated at different plating current densities (after 900 hours salt spray test)

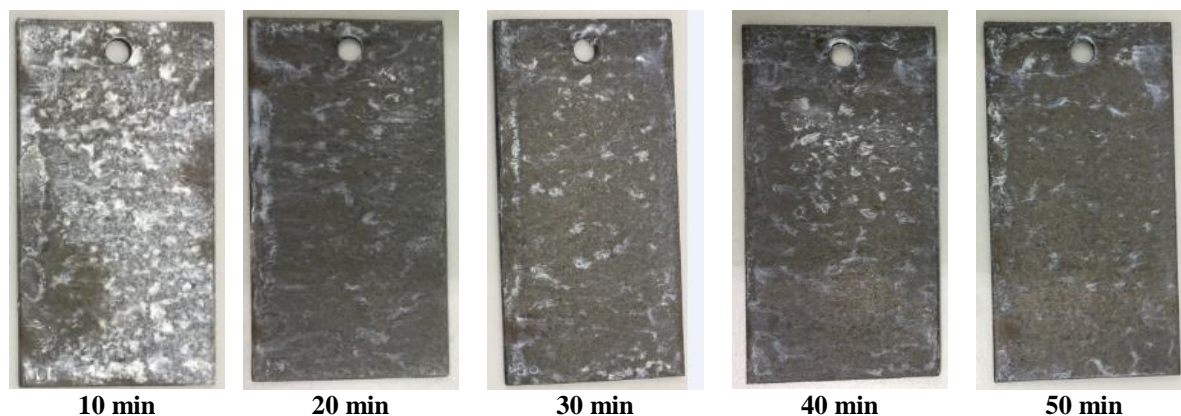


Figure 7. Photos of surface appearance for ZnNiSiO₂ coatings plated at different plating time (after 900 hours salt spray test)

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