Effects of Silica Nanoparticle Co-Deposition on Macrothrowing Power of Zinc-Nickel Alloy Plating from an Acid Sulfate Bath*

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Zinc–nickel–SiO2 electrodeposits have been produced from an acid sulfate bath. The co-deposition behavior of SiO2 and the macrothrowing power of plating baths were examined. The presence of SiO2 nanoparticles in the plating bath appears to change the alloy deposition behavior. The rate of nickel deposition was considerably decreased by the presence of SiO2 nanoparticles in the bath. The macrothrowing power of plating was improved by adding SiO2 nanoparticles to the bath. An early stage of electrodeposition, it seems that the SiO2 nanoparticles act as a nucleus for the precipitation. The SiO2 nanoparticles did not disperse uniformly in a plating bath; they distributed only in a SiO2 rich layer (~50 nm thick) that formed beneath the surface. In addition, this SiO2 rich layer can improve anticorrosive performance. Therefore, zincic use can be suppressed because film thickness can be reduced compared to zinc and zinc–nickel alloy electroplating.


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1. Introduction

Currently, iron and steel, which are low cost materials with excellent workability, are the most widely used as basic materials world-wide. However, since these materials are vulnerable to red rust under corrosive environments, performance deterioration occurs, particular in relation to mechanical properties. To satisfy long-term reliability, zinc electroplating is widely used for iron and steel materials due to its protective ability against corrosion.1) Zinc plating, which is a well-known, low cost process, has been applied as a rust prevention surface treatment for iron and steel materials.2)

However, zinc resources are scarce; the Clarke number of zinc is 0.004%. The global demand for zincic resources has increased concurrent with the rising demand for iron and steel materials. This increase in demand is associated with rapidly expanding economies in Southeast Asia and the BRIC nations (i.e., Brazil, Russia, India, and China). Given the known anti-corrosive properties of zinc plating and the rising demand for iron and steel materials, it has been projected that zincic resources could be completely depleted within 20 years.3) Therefore, finding ways to reduce the use of zinc is an important undertaking.

The anticorrosive performance of zinc plating is directly related to the thickness of the film. However, a thin film is insufficient to ensure long-term reliability of iron and steel materials. To improve anticorrosive performance, zinc-based alloy plating, such as Zn–Ni and Zn–Mn plating, as well as Zn-composite plating and zinc-based alloy composite plating have been developed.4,5) Zinc–nickel–SiO2 composite plating was remarkably improved due to the SiO2 nanoparticles.5) Compared with zinc plating, the excellent anticorrosive performance of zinc–nickel–SiO2 plating makes it possible to reduce film thickness. Consequently, it may be possible to reduce zincic use by the application of zinc–nickel–SiO2 composite plating. In addition, reduced power consumption and reduced manufacturing time can be expected. Although the co-deposition behavior of zinc–nickel–SiO2 composite plating has been reported,6–10) the effects of SiO2 co-deposition on the macrothrowing power as well as the relations between corrosion resistance and film thickness are not clear.

In this study, we investigate the effects of SiO2 co-deposition on macrothrowing power and the relations between corrosion resistance and film thickness for zinc–nickel–SiO2 composite plating from an acid sulfate bath, which has excellent anticorrosive properties. The overall goal of this investigation is to find ways to reduce zincic use and power consumption.

2. Experimental

Experiments were conducted using cold roll steel sheets (SPCC, JIS G 3141, Standard refining, Bright finish, 50 mm × 50 mm × 0.6 mm). Zinc–nickel alloy plating was obtained from sulfate baths, and zinc–nickel–SiO2 composite plating was obtained from sulfate baths with SiO2 sol. Zinc and zinc–SiO2 composite plating were also undertaken as comparison specimens. Table 1 shows the bath composition and plating conditions. Colloidal silica (Nissan Chemical Industries, Ltd., SNOWTEX-O, specific gravity: 1.12, average particle size: 20 nm, SiO2 content rate: 20 mass%) was used in this study. A cylindrical glass cell containing 2.0 × 10−3 m3 of electrolyte, which was stirred constantly, was used. Prior to plating, the steel cathode was degreased by solvent, electrocleaned cathodically for 1 min in an alkaline solution, pickled by 10% hydrochloric acid for 10 s, and washed. An insoluble electrode, which was plated platinum on a titanium substrate, was used as the anode electrode. The film thickness ranged from 1–10 µm.

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The electroplated specimens were subjected to salt spray tests in accordance with Japanese Industrial Standard Z 2371, and the corrosion resistance of each specimen was evaluated by red rust occurrence time. The composition of the electroplated film was determined using an X-ray fluorescence spectrometer. To examine the effects of SiO$_2$ co-deposition on the macro throwing power of deposits, electroplated specimens were studied using field-emission electron probe microanalysis (FE-EPMA, JEOL, JXA-8500FS), and the crystal structure of the deposit was studied with an X-ray diffractometer (Cu-K$_\alpha$, 40 kV, 200 mA, Rigaku, RINT-1300), transition electron microscopy (TEM, JEOL, JEM-2100F) observation and energy dispersive X-ray spectroscopy analysis (JEOL, JED-2300T).

### 3. Results and Discussion

#### 3.1 Effects of SiO$_2$ nanoparticles on deposits

Figure 1 shows the appearance of each deposit (thickness ranging from 1–10 µm). For zinc plating, the 1 µm deposit was white, approximately uniform, and perfectly covered the substrate. As the film thickness increased, the white color peculiar to the zinc electroplating resulting from an acid sulfate bath increased, as did the coverage factor of the film.

For zinc–nickel alloy plating, the film (thickness less than 3 µm) was deposited non-uniformly, and the iron substrate was partially exposed. However, at a thickness of 5 µm, the deposits were approximately uniform and covered the substrate perfectly. The expected silver-white film was obtained. The uniformity was improved with film thickness of 10 µm.

As noted, zinc–nickel alloy plating could not completely cover the substrate at a thickness of 3 µm. However, 1 µm thick zinc–nickel–SiO$_2$ composite plating film was uniformly deposited, and uniform films were obtained at greater thicknesses. It was found that the macro throwing power of the zinc–nickel alloy plated film at an early stage of electrodeposition can be improved by adding silica to the bath.

Figure 2 shows the scanning electron images of the plated film (thickness 1–10 µm) obtained by different plating types. For zinc plating, despite varying film thickness, deposits of the hexagon board state depending on the hexagonal close-packed structure were observed. These zinc deposits then grew as film thickness increased.

For the zinc–nickel alloy plating, it was observed that the surface morphology of the deposit (1 µm thick) was finely granular, i.e., approximately 1 µm in diameter, and the surface seemed to be a substrate. As the film thickness increased to 3 µm, a smooth film with fine granularity was formed; however, a partially un-deposited area (broken line,
Fig. 2) was observed. For film thickness over 5 µm, fine and uniform deposits perfectly covered the substrate.

The SiO$_2$ nanoparticles were added to the zinc–nickel alloy plating bath, and, even at a thickness of 1 µm, the obtained film perfectly covered the substrate, and the fine granular deposits seen in the zinc–nickel alloy plating were not observed. In addition, fine and uniform films were formed in films of thickness greater than 3 µm. Thus, it was found that addition of silica sol to the plating bath influenced the morphology of the obtained film.

Figure 3 shows the scanning electron images and X-ray maps for zinc, nickel, and iron obtained by FE-EPMA analysis for the surfaces of the zinc–nickel alloy and zinc–nickel–SiO$_2$ composite plated films. For the zinc–nickel alloy plating, zinc, nickel, and iron in a film (1 µm thick) were distributed non-uniformly. Since the granular deposits shown in Fig. 2 corresponded with the zinc and nickel of the element map, the deposits occurred partially at an early stage of electroplating, and the iron substrate was partially exposed. The non-uniform deposits of zinc and nickel were observed with 3 µm film thicknesses; however, zinc, nickel, and iron were almost distributed uniformly in the films of thickness greater than 5 µm. These results indicate that the deposits of thickness greater than 5 µm covered the substrate perfectly.

As SiO$_2$ nanoparticles were added to the zinc–nickel alloy plating bath, zinc and nickel were distributed uniformly, even with 1 µm film thickness. Note that a non-uniform distribution was not observed on iron. Thus, the SiO$_2$ nanoparticle composite film was deposited uniformly and covered the substrate perfectly at an early stage of electroplating.

The SiO$_2$ nanoparticle used in this study has negative surface charge; therefore, the repulsive force works for the cathode during electrolysis. However, Nishimura et al.\textsuperscript{11)} have reported that, in zinc–nickel alloy plating, the nickel ions adsorb preferentially to the SiO$_2$ nanoparticle in the acid sulfate bath, and the SiO$_2$ nanoparticles, which are adsorbed by the nickel ions, act as a cation.\textsuperscript{11)} Thus, these SiO$_2$ nanoparticles migrate to the cathode side, and then act as a nucleus of precipitation on the cathode surface. In addition, large numbers of precipitation nuclei exist because the SiO$_2$ particles are nanometer scale particles. Therefore, it seems likely that the SiO$_2$ particles in the zinc–nickel alloy plating bath enable formation of uniform deposition. The SiO$_2$ nanoparticles in the bath demonstrate activity that is equal to the additives in the plating.

To add new functions, such as wear resistance, self-lubrication, corrosion resistance, and polymer adhesion to the plating film, various composite platings co-deposited with fine particles, such as oxides and carbides, and organic substance particles (e.g., PTFE), have been developed.\textsuperscript{11–13)} On the other hand, it was found that the SiO$_2$ nanoparticle demonstrated a function that is unlike conventional composite plating, i.e., the macro throwing power of the plated film is improved.

Figure 4 shows the X-ray diffraction patterns of the zinc–nickel alloy plating and zinc–nickel–SiO$_2$ composite plating. Each film structure was composed of the $\gamma$-phase (Ni$_5$Zn$_{21}$) orientated in the (411) plane; thus, the crystal structures could not be differentiated. The results of Figs. 2 and 3, show that the SiO$_2$ nanoparticles in the plating bath facilitated a change in the form of precipitation; specifically, uniform precipitation was promoted at an early electrodeposition stage. However, it was found that the SiO$_2$ nanoparticles in the plating bath did not affect the crystal structure of the obtained
films. Note that zinc–nickel alloy plating deposited in only the γ-phase shows excellent corrosion resistance.\(^{14}\)

Table 2 shows the zinc, nickel, and SiO\(_2\) content of the plating films obtained via different platings using an X-ray fluorescence spectrometer. For zinc–nickel alloy plating, it is evident that there is significant nickel content in 1 µm thick films and that nickel content decreased and zinc content increased as the film thickness increased. This result indicates that more much nickel is depositing at an early stage of electrodeposition. Zinc–nickel alloy plating in which zinc less noble than nickel, preferentially deposits is well known as an abnormal co-deposition type.\(^{15}\) However, from the above results, in the acid sulfate bath used for this study, the abnormal co-deposition is suppressed at an early stage of electrodeposition, while the abnormal co-deposition is promoted as electrodeposition proceeds.

On the other hand, when the silica sol was added to the zinc–nickel alloy plating bath, the SiO\(_2\) nanoparticles were co-deposited in a film. The SiO\(_2\) content, which differed depending on film thickness, was in the range of 1.00–2.03 mass%. There appears to be little correlation between SiO\(_2\) content and film thickness. In the case of films of the same thickness, since the nickel content in the films decreased, depending on the SiO\(_2\) co-deposition, the abnormal co-deposition was accelerated. In addition, this tendency became more noticeable as film thickness decreased. With regard to the acceleration mechanism of the abnormal co-deposition, which is dependent on SiO\(_2\) co-deposition, as previously described, the SiO\(_2\) nanoparticles that are absorbed by nickel ions migrate to the cathode surface and consequently suppress the reduction of nickel ions on the cathode surface. On behalf of the reduction of nickel ions, hydrogen ions are reduced, pH near the cathode surface rises, and zinc hydroxide is formed. Therefore, it is reasonable to assume that zinc precipitation increases.\(^{16}\)

These results revealed that the SiO\(_2\) nanoparticles in the bath contributed to the deposition of a uniform film at an early stage of electrodeposition and reduced the nickel content in the film due to acceleration of the abnormal co-deposition. In addition, the SiO\(_2\) nanoparticles suppressed the

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**Fig. 3** Secondary electron images and X-ray maps for zinc, nickel and iron by FE-EPMA analysis for the various specimens.
change of nickel content associated with different film thickness and contributed to homogeneous deposition of the composition in the film thickness direction.

3.2 Co-deposition of SiO₂ nanoparticles and corrosion resistance

Table 3 shows the results of red rust occurrence time for various electroplated specimens after a salt spray test. On the zinc plating, at a 1 µm thickness, red rust occurred within 8 h, and an increase in film thickness proportionately increased the red rust occurrence time. Thus, for zinc plating, corrosion resistance is improved proportional to film thickness. Therefore, for use in a severely corrosive environment and when long-term corrosion resistance is required, it is difficult to reduce the thickness of the film.

On the other hand, the corrosion resistance of zinc–nickel alloy plating was remarkably improved compared to that of zinc plating. The corrosion resistance of zinc–nickel alloy plating with a 3 µm thick film was much better than that of zinc plating with a 10 µm thick film. The corrosion resistance of zinc–nickel alloy plating improved significantly when film thickness was greater than 5 µm. Thus, the corrosion resistance of zinc–nickel alloy plating was not proportional to film thickness and differed from that of zinc plating. This result can be explained by the non-uniform deposition for film thickness up to 3 µm film thickness, as shown in Figs. 2 and 3, and the reduction of the sacrificial protection associated with the increase in the nickel content.

Compared to zinc plating, the corrosion resistance of the zinc–nickel–SiO₂ composite plating improved more than that of zinc–nickel alloy plating. In particular, the corrosion resistance of zinc–nickel–SiO₂ composite plating with a 3 µm thick film improved by approximately three times compared to the corrosion resistance of the zinc–nickel alloy plating of equal film thickness. It is supposed that the uniform film deposition and the suppression of nickel content due to the SiO₂ nanoparticles result in improved corrosion resistance.

Cross-sectional TEM observation and element map results for zinc–nickel–SiO₂ composite plating for a 10 µm thick film are shown in Fig. 5. TEM observation revealed that a SiO₂ nanoparticle-rich layer of 50 nm in thickness was formed on the surface of this film. In the acid solution, the dispersiveness of the silica sol used in this study is extremely good. However, silica sol aggregates and gels as pH rises to near neutral. The result of accelerating the abnormal co-deposition by adding the silica sol to the zinc–nickel alloy plating bath indicates the formation of zinc hydroxide at the electrode surface simultaneously accelerated the aggregation and gelation of the SiO₂ nanoparticles, which are adsorbed by nickel ions, and the formation of the silica-rich layer. This silica-rich layer may contribute to the improvement in anticorrosive performance.

From these results, because the corrosion resistance of the zinc–nickel–SiO₂ composite plating where silica sol was added to the zinc-nickel alloy plating bath, was significantly better than that of zinc plating and zinc–nickel alloy plating, it is possible that film thickness can be reduced. Consequently, zincic use can be reduced. In addition, plating time and power consumption may also be reduced.

4. Conclusion

For the purpose of reducing zincic use, effects of SiO₂ co-deposition on the macro throwing power of deposits and the relations between corrosion resistance and film thickness on
zinc–nickel alloy plating from an acid sulfate bath were investigated. The following results were obtained.

(1) The SiO$_2$ nanoparticles, which are adsorbed by nickel ions, in the zinc–nickel alloy plating bath act as a cation and then migrate to the cathode surface during electrolysis. Consequently, these SiO$_2$ nanoparticles act as a nucleus of precipitation and allow the formation of a uniform deposit. In addition, the SiO$_2$ nanoparticles that migrate to the cathode surface cause the reduction of the hydrogen ion, and promote the abnormal co-deposition in which zinc is deposited preferentially based on the rise in pH near the cathode surface.

(2) The film structure of both the zinc–nickel alloy plating and the zinc–nickel–SiO$_2$ composite plating was composed of the $\gamma$–phase (Ni$_5$Zn$_{21}$), which showed excellent corrosion resistance. The SiO$_2$ nanoparticles did not affect the film structure significantly.

(3) The corrosion resistance of the zinc–nickel–SiO$_2$ composite plating was significantly better than that of the zinc plating and zinc–nickel alloy plating due to uniform deposition and the silica-rich layer formed beneath the surface. Therefore, zincic use can be reduced, because with zinc–nickel–SiO$_2$ composite plating it becomes possible to reduce film thickness. In addition, we might expect reduction of both plating time and power consumption.

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