Anti-corrosive Effects of Multi-Walled Carbon Nano Tube and Zinc Particle Shapes on Zinc Ethyl Silicate Coated Carbon Steel

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Zinc ethyl silicate coatings containing multi walled carbon nanotubes (MWCNTs) were prepared, to which we added spherical and flake shaped zinc particles. The anti-corrosive effects of MWCNTs and zinc shapes on the zinc ethyl silicate coated carbon steel was examined, using electrochemical impedance spectroscopy and corrosion potential measurement. The results of EIS and corrosion potential measurement showed that the zinc ethyl silicate coated with flake shaped zinc particles and MWCNT showed lesser protection to corrosion. These outcomes were in agreement with previous results of corrosion potential and corrosion occurrence.

Keywords : EIS, zinc ethyl silicate, corrosion potential, slat spray, MWCNT

1. Introduction

Corrosion protection of carbon steel has been the important subject for many corrosion scientists and lots of researches were conducted to find the best methods for corrosion protection. However, an ideal corrosion protection method is still examined. The most common and convenient corrosion protection methods are coatings, especially organic coating. The main corrosion protection mechanism of organic coating is barrier protection providing physical barrier against penetration of corrosion species into the coating such as water and various ions, however, there are no permanently impermeable organic coating materials available.

Zinc particles or zinc dust is effectively used additives as an anti-corrosion pigment in organic or inorganic coating systems using the sacrificial action of zinc providing both cathodic protection and barrier protection[1]. Hence, zinc is widely used in anticorrosion coating industries, where corrosion protection of the metal system is required for long service life[2-3]. Organic and inorganic zinc-rich primers (ZRPs) are used in severe corrosion environments including shipbuilding, offshore platforms and industrial areas because of their unique corrosion protection property[4-5]. During the service life of coated structure, the ZRP is providing good cathodic protection in early stages as well as barrier protection with stable zinc corrosion products in later stages[6]. The corrosion protection mechanism of zinc-containing paints was studied since the early of 1940s. Mayne reported that the importance of volume concentration of zinc pigment determining the corrosion protection performance of zinc-containing paints[7]. Accordingly, high concentration of zinc particle in coating is requested to achieve the highest electrical conductivity resulting in better corrosion protection by cathodic protection. However, the application of high zinc concentration ZRP coatings has problems such as high viscosity, difficulties in spraying, poor surface levelling and segmentation of zinc dust during storage. The other researchers also investigated the corrosion protection performance of zinc-containing paints[8-14].

Several efforts of carbon nanotubes application to the coating have been studied. Chen et al. studied the effect of a nickel coating with carbon nanotubes on the corrosion protection of carbon steel[15]. The corrosion protection of nickel coating with carbon nanotubes was improved compare to the pure nickel coating in a 3.5 wt% NaCl solution, suggesting that the nanotubes acted as an efficient physical barrier by filling the micro pores and flaws on the surface of the nickel coating.

In our previous research, it was reported that the corrosion protection performance of epoxy zinc-coated carbon steel was increased with an increase in MWCNT contents[16,17]. However, the effects of MWCNT addition on the corrosion protection of partially electrical conductive

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Table 1. MWCNTs' properties

Properties	Value
Net density (g/㏄)	1.3 ~ 1.8
Aspect ratio	103 ~ 104
Electric conductivity (S/㎝)	6000
Thermal conductivity (W/(m·K))	2000

Table 2. The contents of zinc and MWCNT in various zinc ethyl silicate coatings

Specimen name	Spherical zinc (wt %)	Flake zinc (wt %)	MWCNTs (wt %)
S60	60	0	0
SF60	40	20	0
SFC60	40	20	0.1
S70	70	0	0
SF70	40	30	0
SFC70	40	30	0.1

coating system like zinc ethyl silicate coating was rarely reported.

The objective of the present work is to investigate the effect of MWCNTs and zinc particle shapes on the corrosion protectiveness of zinc ethyl silicate coated carbon steel

2. Experimental

2.1 Material and specimen preparation

The ethyl silicate binder and spherical zinc particle (average particle size: 5 μm) used in this study were supplied by Sigma coatings. Flake zinc particle (average particle size: 10–20 μm) was supplied by TNC, Korea and MWCNTs (Diameter: 0–15 nm, length < 200 μm) was purchased by Hanhwa Nanotech, Korea, having a Young's modulus of approximately 1 to 2 TPa, tensile strength in the range 30 to 180 GPa, and a specific surface area of up to 150 m²/g. The detailed physical properties of the MWCNTs are listed in Table 1.

Zinc ethyl silicate coatings were prepared by mixing of ethyl silicate binder, zinc particles, and MWCNTs in the desired ratio as described in Table 2. MWCNTs were first dispersed in thinner by mechanical homogenizer, then vigorously stirred in the presence of ethyl silicate binder and zinc particles for 1 h, and then degassed for 10 min in sonicator. Before coating, the surface of the carbon steel

was treated by steel grit blasting and degreased using acetone. The average surface roughness after steel grit blasting was approximately 20 μm, and surface cleanness grade was Sa 3 by ISO 8501-1. The zinc ethyl silicate with MWCNTs were coated on carbon steel plates (150 × 70 × 3 mm) by bar coater, resulting in a coating thickness of 30 μm, then cured at 25 °C for 7 days at 60 % of relative humidity. The zinc ethyl silicate coatings were coated on a polypropylene film by same coating method and examined the cross section of coating by SEM.

2.2 Coating surface observation in 3.5 wt% NaCl solution immersion.

The coating surface of zinc ethyl silicate coated specimens were scribed by a knife with 100 mm in length and 2 mm in width of X-cut, and the surface of the coated specimens was observed visually after 8 weeks of immersion in 3.5 wt% of NaCl solution.

2.3 Corrosion potential measurement and EIS analysis

After immersion in 3.5 wt% NaCl solution, the corrosion potential of zinc ethyl silicate coated carbon steel was measured in terms of immersion time to 8 weeks. EIS analysis was also performed at open circuit potential, using electrochemical impedance analyzer (SP-240, Biologics). The three-electrode electrochemical cell in EIS analysis consisted of the zinc ethyl silicate coated carbon steel as a working electrode (exposed area: 13.9 cm²), a saturated calomel electrode as a reference, and a carbon counter electrode in 3.5 wt% NaCl solution. Impedance values were obtained by applying a sine wave of 20 mV amplitude in a frequency range of 100 kHz to 100 mHz.

3. Results and Discussion

3.1 Observation of zinc ethyl silicate coating cross section

The cross section of zinc ethyl silicate coatings were observed using SEM as shown in Fig. 1. All samples showed a uniform particle distribution across the coating. Zinc ethyl silicate coatings with 70 vol% of zinc particles were denser than those of 60 vol% of zinc particles independent of zinc particle shapes. It was also shown that the flake zinc particle was well contacted with spherical zinc particle and it may give a good cathodic protection property to zinc ethyl silicate coatings due to the good electrical connection between zinc particles and carbon steel substrate.

3.2 Corrosion potential and EIS analysis

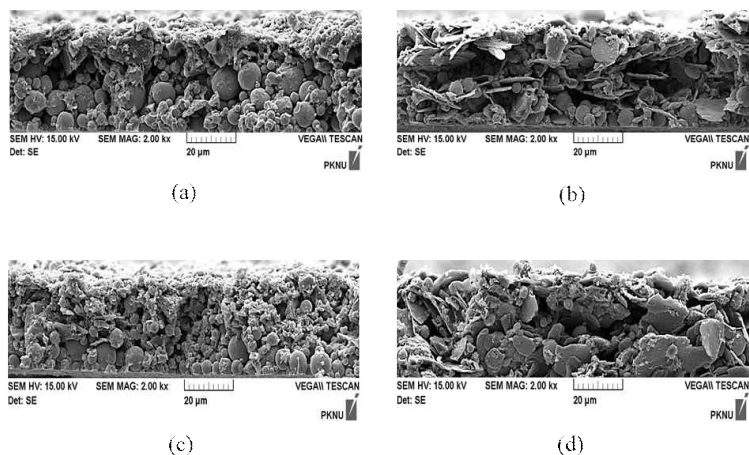Fig. 2 shows the scribed surface of zinc ethyl silicate coated carbon steel after 8 weeks of immersion in 3.5

Fig. 1. SEM images of the cross sections of the prepared zinc ethyl silicate coatings: (a) S60, (b) SF60, (c) S70, (d) SF70.
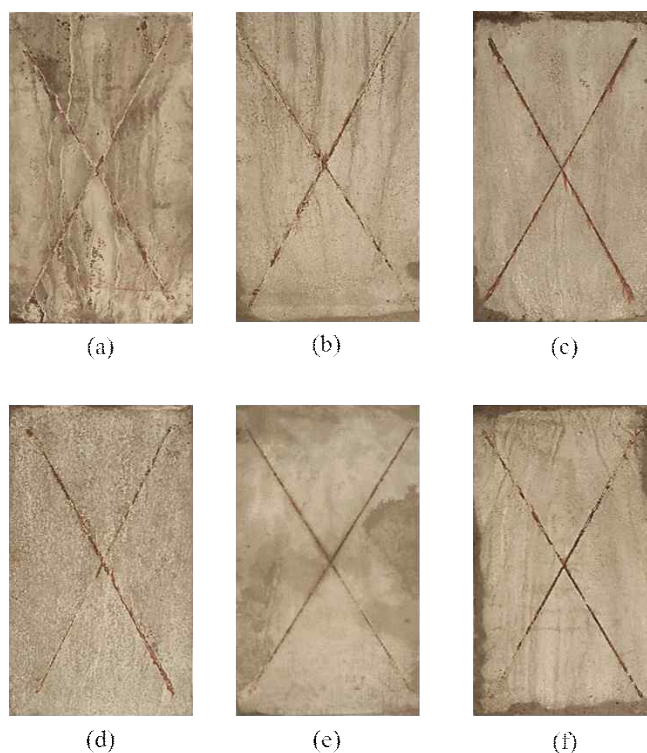

Fig. 2. Corrosion occurrence of zinc ethyl silicate coated carbon steel after immersion of 8 weeks in 3.5 wt% NaCl solution: (a) S60, (b) SF60, (c) SFC 60, (d) S70, (e) SF70 and (f) SFC 70.

wt% NaCl solution. The corrosion product (red rust) was observed at the scribed areas, and the increase of corrosion products was observed when flake zinc was added into the coating. The highest amounts of corrosion products at the scribed areas of the zinc ethyl silicate coating was observed in spherical zinc, flake zinc and MWCNT mixing system (SFC60 & SFC70). Comparing the zinc concentration (60 wt% and 70 wt%) in coating independent of zinc shape and addition of MWCNTs, higher zinc con-

centration of zinc ethyl silicate coated carbon steel showed less corrosion product than the lower zinc concentration. The corrosion potential of zinc ethyl silicate coated carbon steels in 3.5 wt% NaCl solution were measured in terms of immersion time as shown in Fig 3. The initial corrosion potential of all specimens was less than −1.10 V (referring to SCE) indication good cathodic protection of carbon steel by zinc particles. The corrosion potential was increased to positive value with increase of immersion time.
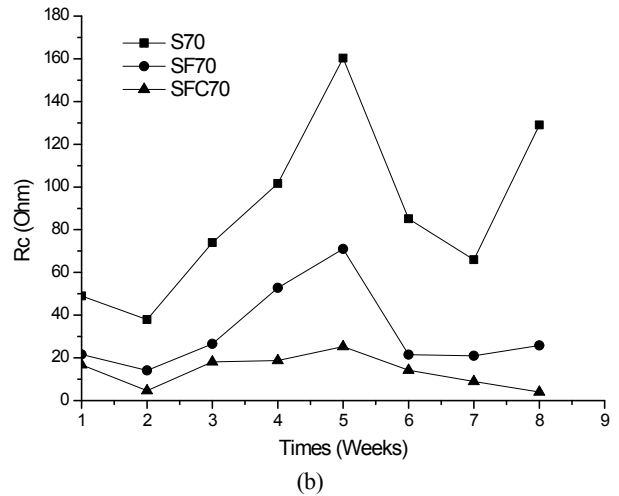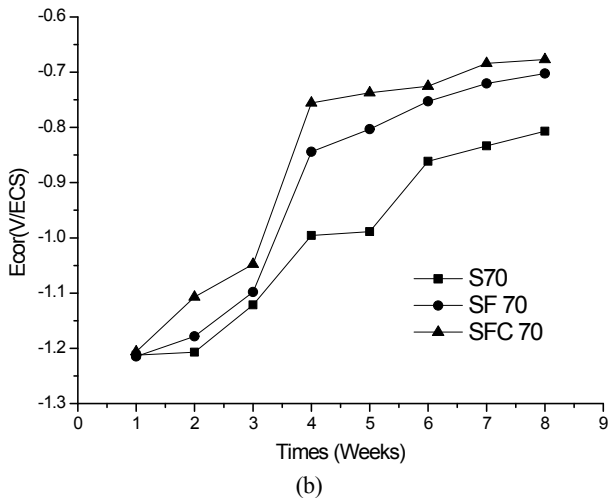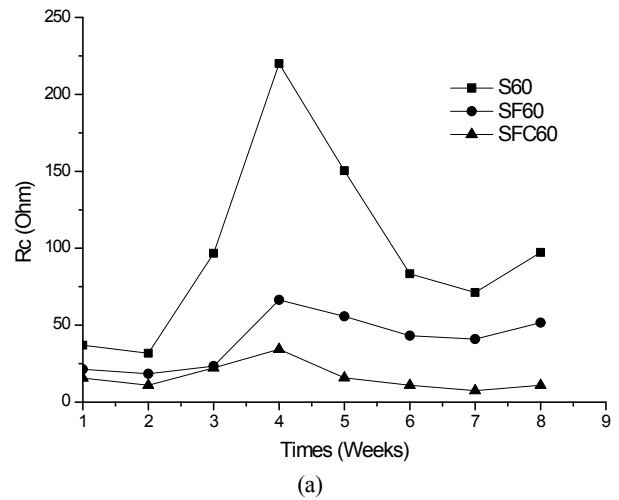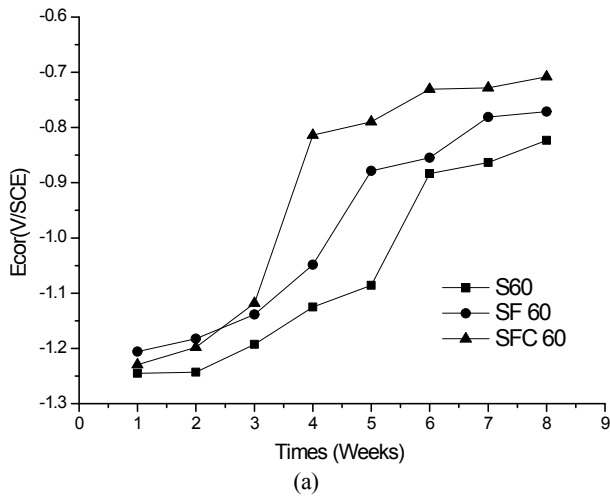
Fig. 3. Corrosion potential of zinc ethyl silicate coated carbon steel in terms of immersion time in 3.5 wt% NaCl solution: (a) 60 wt% of zinc contents and (b) 70 wt% of zinc contents.

Fig. 4. Electrical coating resistance of zinc ethyl silicate coated carbon steel in terms of immersion time in 3.5 wt% NaCl solution: (a) 60 wt% of zinc contents and (b) 70 wt% of zinc contents.

It is indicating that the cathodic protection was weakened. Fig. 3(a) shows the results of zinc ethyl silicate coated carbon steel with 60 wt% of zinc particle concentration. The different increasing rate of corrosion potential was observed according to the mixing of flake zinc and MWCNTs. The increasing rate of corrosion potential for S60 after 8 weeks of immersion in 3.5 wt% NaCl solution was less than that of SF60 and SFC60. Fig. 3 (b) shows the results of zinc ethyl silicate coated carbon steel with 70 wt% of zinc particle concentration. The corrosion potential changes of 70 wt% of zinc silicate coated carbon steel after 8 weeks of immersion in 3.5 wt% NaCl solution was similar to the results of 60 wt% of zinc particle concentration. Comparing to the increasing rate of corrosion potential between zinc ethyl silicate coated carbon steel with 60 wt% and 70 wt%, better cathodic protection

performance was observed in 70 wt% of zinc concentration. Accordingly, there is a clear correlation between corrosion protection of coating and the concentration of zinc particles, the shapes of zinc particle and MWCNT addition. Consequently, the addition of flake zinc particle and MWCNT showed negative influence to the cathodic protection of carbon steel in long term immersion and it might be caused by higher consumption of zinc particle due to the galvanic corrosion. The galvanic corrosion of zinc particles was accelerated by improvement of electrical contact between zinc particles due to the favorable shapes of flake and MWCNT rather than single spherical shape of zinc particle application and it resulted in reducing the sacrificial cathodic protection of zinc ethyl silicate coating to carbon steel.

Fig. 4 shows the results of EIS analysis of zinc ethyl

silicate coated carbon steel in 3.5 wt% NaCl solution in terms of immersion time. The electrical coating resistance (R_c) was extracted by EIS data and plotted with the immersion time. The R_c of S60 specimen showed relatively higher values than those of SF60 and SFC60 in terms of immersion time, as shown in Fig. 4(a). During the immersion, R_c value was decreased in 2 weeks and increased to 4 weeks, and then decreased slightly further. Initial decreasing of R_c value might be the dissolution of Zn to the electrolyte and later increasing of R_c value might be the enhancement of zinc corrosion products which can block the pore in coating resulting in improvement of barrier performance. And final decreasing of R_c value might be the aging of coating and additional penetration of electrolyte in to the aged coating. The similar tendency of R_c value change was observed in zinc ethyl silicate coated carbon steel with 70 wt% of zinc concentration as shown in Fig 4(b). From the results, the corrosion protection performance of zinc ethyl silicate coated carbon steel was more appreciable when spherical zinc was used in ethyl silicate binder rather than blending of spherical zinc with flake zinc and MWCNT.

4. Conclusions

The conclusions drawn from this work are as follows:
1. Higher zinc concentration of zinc ethyl silicate coated carbon steel showed less corrosion rust than the lower zinc concentration
2. Improved electrical connections of zincs with addition of flake zinc and MWCNTs was considered as accelerating of zinc consumption and it resulted in reducing the sacrificial cathodic protection performance of zinc ethyl silicate coating to carbon steel.
3. The corrosion protection performance of zinc ethyl silicate coated carbon steel was more appreciable when spherical zinc was used in ethyl silicate binder rather than blending of spherical zinc with flake zinc and MWCNTs.

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