Journal of Ceramic Processing Research. Vol. 8, No. 4, pp. 296~299 (2007)

J O U R N A L O F
Ceramic Processing Research

Investigation of optimum materials selection in thermal spray coating for the corrosion protection of STS 304

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Various thermal spray methods were electrochemically investigated to optimize the anticorrosion protection for 304 stainless steel (STS 304) shafts used in small ships. In the presence of seawater, thermal spray coatings applied to STS 304 act as a sacrificial anode, allowing the coating to preferentially corrode over the stainless steel. For STS 304 alone and with the various coating materials tested, Tafel analysis indicated the following corrosion current densities: STS 304, 7×10^{-7} A/cm^2; Zn, 2.4×10^{-5} A/cm^2; Al, 7×10^{-6} A/cm^2; and Zn+15%Al, 1×10^{-5} A/cm^2. The corresponding corrosion potentials were STS 304, –0.1877 V; Zn, –1.1482 V; Al, –0.8119 V; and Zn+15%Al, –1.0108 V. Tafel current densities were the lowest for Al-coated specimens and highest for Zn-coated specimens. The corrosion protection characteristics and the lifetime of the thermal spray coating layers were also estimated. In general, the anticorrosion properties were excellent, exhibiting a noble potential and low corrosion current density.

Key words: Corrosion resistance, Thermal spray coating, STS 304, Sacrificial anode.

Introduction

Seafaring ships and offshore structures are exposed to harsh marine environments that include waves, storms, and tides, with maintenance and repair becoming increasingly important economic and industrial factors. Corrosion resistance of these structures is essential to ensure a long and useful life. Since many marine structures are fixed under seawater, such as static platforms, inspection and maintenance costs further emphasize the necessity of corrosion resistance.

The fracture of these marine structures is mainly associated with corrosion and welding [1-7]. Corrosion protection methods are largely divided into anodic and cathodic protection. Anodic protection is limited to the passivity characteristics of the materials in their environment. Cathodic protection methods include sacrificial anodes and impressed current cathodic protection. The sacrificial anode method is widely used for marine structures and vessels in seawater environments.

In this study, thermal spray coating technology was adapted to prevent corrosion in small-ship shaft systems. While shaft systems commonly employ STS 304, 316, and 630, STS 304 was selected for this study based on electrochemical and economic factors. A thermal spray coating provides a sacrificial anode based on differences in the galvanic potential [8-12] between the stainless steel and the coating material, thereby extending the life span of the shaft. In this investigation, Zn, Al, and Zn+15%Al thermal sprays were adapted to provide corrosion resistance.

Materials and Experiment Methods

Wires for thermal spray coatings of Zn, Al, and Zn+15%Al were 1.6 mm in diameter and possessed purities greater than 99.7%. Table 1 lists the thermal spray coating conditions employed. For the electrochemical experiments, specimens employed an exposed area of 100 mm^2. Each specimen was carefully degreased with acetone and rinsed with distilled water. The corrosion potential was measured for 24 h at room temperature using an electrochemical apparatus consisting of a Pt coil as the counter electrode and a Ag/AgCl (saturated KCl) reference electrode. Anodic and cathodic polarization experiments were conducted using a scan rate of 2 mV/s from the open circuit potential (OCP) over a range of +5 V and –2 V. For potentiostatic measurements, a variety of polarization potentials were applied in seawater over 1,200 s and evaluated over time for current density. The current density remaining after 1,200 s at the applied potential was also determined. In addition, Tafel analyses were performed under both anodic and cathodic conditions from OCP to ± 250 mV under an aerated condition. The corrosion potential and corrosion current density were compared with the Tafel analytical results obtained from various reference specimens.

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Table 1. Thermal spray coating conditions

Wire	Voltage (V)	Ampere (A)	Wire Feed (m/minute)	Spray Distance (mm)
Zn	23	80	2.0	120
Al	26	90	1.5	150
Zn-15%Al	25	100	1.9	140

Results and Discussion

Figure 1 presents the various potentials over time for thermal spray-coated specimens and STS 304 in natural seawater. Al-coated specimens had a potential of –0.709 V at the earliest stages of immersion. Following 600 s of immersion, the potential remained steady, thereafter decreasing gradually until the experiment was completed. The early stage potential for Zn and Zn+15%Al coated specimens were –0.975 and –0.934 V, respectively. After a brief duration of immersion, stable potentials developed and remained throughout the experiment. Upon completion of the experiment, Al and Zn demonstrated the highest and lowest potentials, respectively.

The potential of STS 304 during the initial stages of immersion was significantly greater (–0.214 V) than those of the thermal spray-coated specimens. This high potential of STS 304 is believed to result from a passive film formed in seawater. Following 2,100 s of immersion, the potential peaked at –0.1422 V, with a stable potential of –0.2627 V developing by 7,200 s and remaining until completion of the experiment.

Given the substantially reduced potentials obtained with the coatings, it is evident that the thermal spray coatings prevent corrosion by providing an environmental interception barrier. Damage to the coatings results in the formation of a galvanic cell between STS 304 and the coating, allowing the coatings to preferentially corrode. If the base metal (STS 304) is exposed by damage to the coating, the life span can be estimated based on the difference in potentials between the coating and STS 304, as well as the Tafel analysis and slope of the anodic polarization of the galvanic cell formed. The Al coating provides the longest corrosion protection since its potential is closest to the base metal [13].

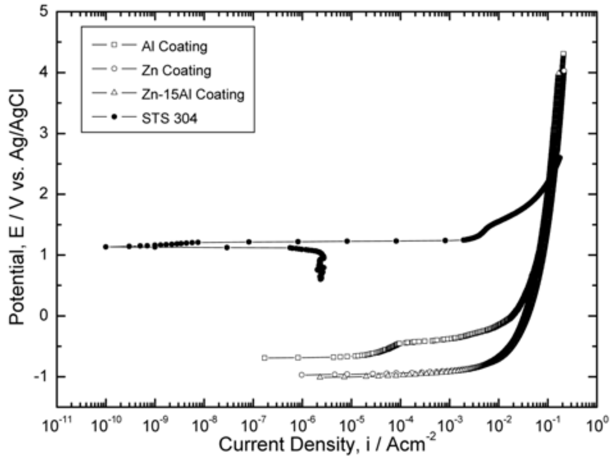

Fig. 2. Anodic polarization curves for the various thermal spray coatings and STS 304 in seawater.

Figure 2 depicts anodic polarization curves for the various thermal spray coatings and STS 304 in seawater. Al had the highest potential among the coated specimens, with a current density of 1×10^{-4} A/cm^2, which increased to 1.5×10^{-3} A/cm^2 as the experiment progressed. Thereafter, at above 1 V, the current density of the Al-coated specimens had similar values as the Zn+15%Al samples. The current density was the greatest for Zn specimens throughout the experiment. These anodic polarization results indicate that the Al thermal spray coating provides the greatest protection against corrosion, while Zn provides the least protection. In comparison, STS 304 had the highest potential and lowest current density. However, the current density increased abruptly above 1×10^{-8} A/cm^2 as the

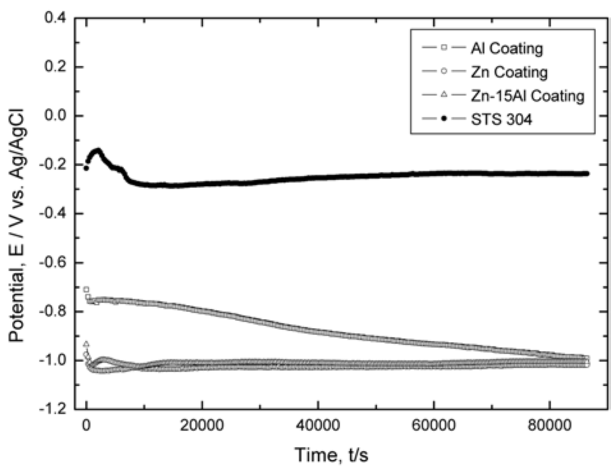

Fig. 1. Variation of potentials over time for thermal spray-coated specimens and STS 304 in natural seawater.

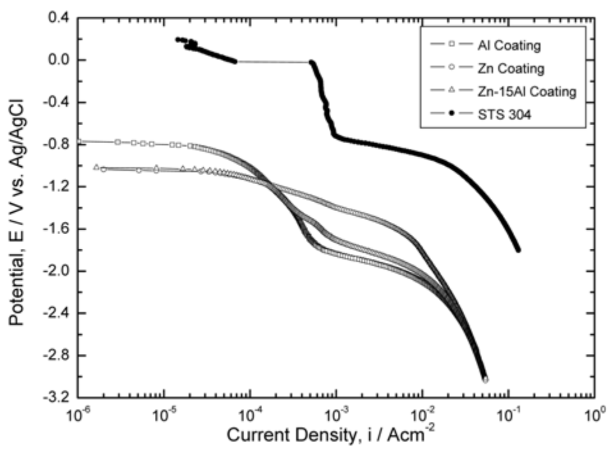

Fig. 3. Cathodic polarization curves for the thermal spray coatings and STS 304.

fracture of the passive film by Cl^- led to pitting.

Cathodic polarization curves for the thermal spray coatings and STS 304 are shown in Fig. 3. The open circuit potential for the Al coating showed the highest value, followed by Zn+15%Al and Zn coatings, coinciding with the anodic polarization trends. The polarization trend in Al coatings showed the effects of concentration polarization due to dissolved oxygen ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) and activation polarization due to hydrogen generation ($2H_2O + 2e \rightarrow H_2 + 2OH^-$). Since the range of concentration polarization due to dissolved oxygen occurs over a wider range of potential with Al-coated specimens, the anticorrosion properties of Al were superior to the other coatings. Concentration polarization due to dissolved oxygen was minimal for Zn-coated specimens, allowing the current density to increase with the increasing potential. The cathodic polarization behavior of Zn+15%Al coated specimen showed slight concentration polarization due to dissolved oxygen.

The turning points, the point at which concentration polarization due to dissolved oxygen and activation polarization due to hydrogen generation occurs, were –1.8, –1.7, and –1.6 V for Al-, Zn+15%Al-, and Zn-coated specimens, respectively. Comparing current density at a corresponding potential of –1.8 V, the values for Al-, Zn+15%Al-, and Zn-coated specimens were 6×10^{-4}, 2.0×10^{-3}, and 1×10^{-2} A/cm^2, respectively. Thus, Al provided the most favorable anticorrosion properties.

Cathodic polarization trends for STS 304 presented slowly increasing current density from OCP to –0.01398 V, with an abrupt increase thereafter. Concentration polarization due to dissolved oxygen occurred between –0.01398 and –0.725 V, with hydrogen generation beginning at –0.725 V. Therefore, the limit point of hydrogen embrittlement in STS 304 is –0.725 V, indicating that optimum corrosion protection through cathodic protection occurs at –0.725 V. However, hydrogen embrittlement by overprotection is not observed with

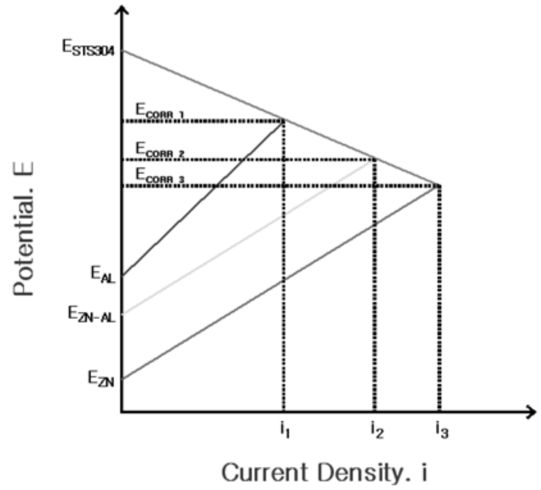

Fig. 5. The polarization diagram comparing the results of corrosion potential, Tafel analyses, and anodic and cathodic polarization.

spray coatings since they act as a sacrificial anode with self-control function.

Figure 4 depicts the results of the Tafel analyses. Overall, trends were similar regardless of the specimen. However, passivity trends were observed in STS 304 with positive potentials. In addition, corrosion current density decreased with shifting noble corrosion potential, regardless of specimens. The corrosion current densities for STS 304, Al-, Zn-, and Zn+15%Al-coated specimens were 7×10^{-7}, 7×10^{-6}, 2.4×10^{-5}, and 1×10^{-5} A/cm^2, respectively. The Al-coated specimen showed the lowest corrosion current density, while Zn presented the highest. The corrosion potentials for the STS 304, Al, Zn, and Zn+15%Al coatings were –0.18768, –0.81191, –1.14821, and –1.01081 V, respectively. Given that Al showed the highest potential and Zn showed the lowest, these results further corroborate that Al provides the greatest corrosion protection.

The polarization diagram comparing the results of corrosion potential, Tafel analyses, and anodic and

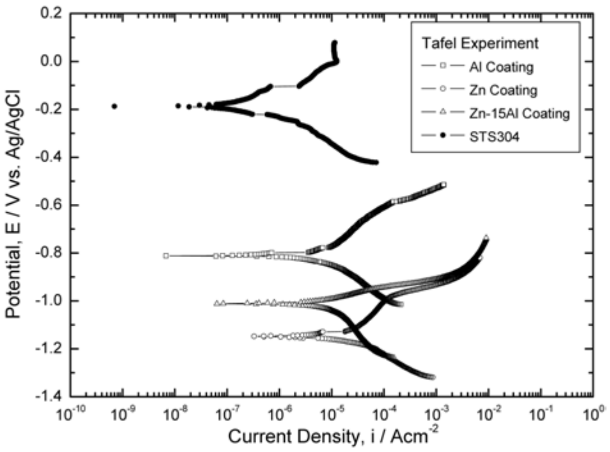

Fig. 4. Tafel experiment for various thermal spray coatings and STS 304 in natural seawater

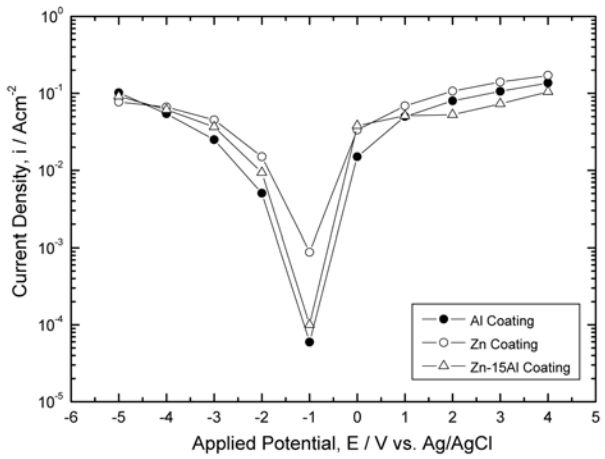

Fig. 6. The current densities after the potentiostatic experiment, which employed a 1,200 s immersion in seawater.

cathodic polarization is shown in Fig. 5. The Al coating had the highest corrosion potential ($E_{CORR\ 1}$) and the lowest corrosion current density ($i_1 = 7\times10^{-8}$ A/cm^2). The corrosion potential with the Zn coating ($E_{CORR\ 3}$) had a low value (–1.1482 V), indicating a rapid progression of cathodic and anodic polarization. The corrosion current density for Zn+15%Al (i_2) was similar to Zn, as would be expected given their similar compositions. The corrosion potential in Zn+15%Al ($E_{CORR\ 2}$ = –1.0108 V) and current density ($i_2 = 1\times10^{-5}$ A/cm^2) had intermediate values.

Figure 6 compares the current densities after the potentiostatic experiment, which employed a 1,200 s immersion in seawater. Under the applied reference potential of –1 V, anodic and cathodic polarization behaviors showed nearly symmetrical trends; anodic polarization currents were higher. As shown in the polarization curves, the anodic polarization trend indicated an active dissolution reaction with no passivity phenomenon. Cathodic polarization trends showed concentration polarization due to dissolved oxygen and activation polarization due to hydrogen gas generation. Therefore, the potentiostatic experiments had trends similar to the polarization trends.

Conclusions

Stainless steel 304 exposed to seawater can be protected against corrosion through the thermal spray-coated application of a sacrificial anode. This study investigated the protective benefits of Al, Zn, and Zn+15%Al thermal spray coatings as applied to STS 304 for marine applications. Corrosion current densities obtained by Tafel analyses were the lowest for Al-coated specimens and the highest for Zn-coated specimens. Based on the galvanic cell formed between the thermal spray coating and STS 304, the Al coating was determined to provide the most advantageous corrosion protection characteristics and coating life span. These results indicate that Al provides the greatest benefit as a sacrificial anode to STS 304 in a seawater environment.

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