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Effects of Arc Spray Process Parameters on Corrosion Resistance of Ti Coatings

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In order to improve the corrosion resistance of carbon steel structures in marine environment, Ti wires were sprayed to a steel substrate using arc spray technique, and orthogonal experimental design was used to investigate the effects of the fluctuation in the main parameters of spray process on the microstructure and the corrosion resistance of sprayed coatings. The results show that the corrosion resistance of sprayed coatings is very sensitive to spray process parameters, corrosion current density can decrease from 997.7 to 5.08 μA cm^{-2} by optimizing process parameters. The coatings are composed of TiN and Ti_2O, and the corrosion resistance of coatings can be improved with the decrease in the contents of oxides. The spray distance should be exactly monitored and controlled in arc spray process because of its great effects on the quality of sprayed coatings.

Keywords arc spray, coating, electrochemical corrosion, titanium

1. Introduction

The offshore industry is moving forward at a quickened pace due to the growing demand for hydrocarbon energy sources. New platforms, oil carriers or pipelines are being required because the new energy sources are being found in deeper water depths and in more hostile environments. Considering the project fabrication cost and the overall properties, various carbon steels and HSLA steels are widely used in constructing marine structures (Ref 1). Steel constructions are susceptible to corrosion, and the preferred technique for mitigating marine corrosion is in use of coatings combined with cathodic protection (Ref 2). Coatings can provide a barrier against moisture reaching the steel surface therefore defense against external corrosion. Organic coating is a proven technique today, but the coatings' service life is limited because of corrosion progression from coating defects. Zinc, aluminum, and their alloys are commonly used as thermally sprayed metal coatings (TSMCs) on steel in water immersion. The sacrificial corrosion protection in combination with their relatively low corrosion rates, make them suit for harsh environments (Ref 3). However, in the splash and tidal zone, anticorrosive coatings with high strength and hardness should be prepared so as to resist the impact of floating things or cavitation erosion. Therefore, it is necessary to carry out studies on some new coating materials.

Titanium's unique properties such as high strength to weight ratio, excellent corrosion resistance have made this material a favorable option for many applications. However, the high-oxygen affinity of titanium limits the application of this material in preparing functional coatings. Some researchers used spraying techniques to prepare Ti coating, such as cold spray (Ref 4, 5), warm spray (Ref 6), or thermal spray (Ref 7-9). Cold spray is a deposition process in which small particles in the solid state accelerate to high velocities (normally above 500 m s^{-1}) in a supersonic gas jet and deposit on the substrate material. Deposition parameters in cold spray process for elimination of porosity were identified (Ref 4, 5), and the fabricated Ti exhibits a higher hardness compared with wrought Ti (Ref 4). Warm spray is an atmospheric coating process through continuous impact and deposition of solid particles heated and accelerated by a supersonic jet controlled between 800-1900 K and 900-1600 m s^{-1}. So far, even the highly active metals such as titanium have been successful used in fabricating the coatings with high purity and high density by this technique (Ref 6). Thermal spraying techniques are coating processes in which melted or half-melted materials are sprayed onto a surface. The "feedstock" (coating precursor) is heated by electrical (plasma or arc) or chemical means (combustion flame). Wang deposited Ti layer by a pulse cathodic arc plasma source before preparing the MoS_2 layer by a radio frequency (RF) magnetron sputtering system on 2Cr13 substrate, and the resistance to wear and corrosion can be improved significantly (Ref 7). However, all the abovementioned studies have been carried out with Ti in the form of powder while Ti wires are safer and easer for packing and carrying than Ti powders. Wire arc spraying is a thermal spray process in which an arc is struck between two consumable electrodes of a coating material, and compressed gas is used to atomize and propel the material to the substrate (Ref 10). It has demonstrated arc spray has the ability to process metals at high spray rates, and is, in many cases, less expensive to

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operate than other spray methods. Zha et al. investigated Ti coatings deposited by supersonic arc spray, and found that the coatings were mainly composed of Ti and TiO, meanwhile the average microhardness of the coatings researched up to 770 $HV_{2.0N}$ (Ref 11). The arc-sprayed Ti coatings may suit for applying in the splash and tidal zone because of the high corrosion resistance of Ti phase and high hardness of the coatings. However, the density of the Ti coatings are still relatively low (Ref 11).

In order to improve the corrosion resistance of carbon steel structures in marine environment, Ti wires were sprayed to a steel substrate using arc spray technique in this paper. The factorial design approach was used to investigate the effects of the fluctuation in the main parameters of spray process on the corrosion resistance of the sprayed coatings.

2. Experimental Procedure

The substrate material used was a commercial low carbon steel that was cut to yield 50 mm × 25 mm × 3 mm specimens. TA2 Ti wires with 2 mm diameter were used as coating material.

Prior to spraying, one face of the steel substrate was cleaned in acetone and then sandblasted using corundum powder. A CMD-AS-1620 arc spray system was used to deposit the coatings. Capacity FAD of compressor is 11 mm^3/min, and working pressure is 0.7 MPa. Previously, it has been shown that the spray current (I), spray voltage (U), and spray distance (L), largely control the quality of sprayed coatings. Therefore, these three process parameters were chosen as the investigation factors. Three different levels were used for each investigation factor in the factorial design, and the detailed levels and codes for the three factors are listed in Table 1. The span of levels for each factor was determined according to practice, and equidifferent arrangement (Ref 12) was applied following the design requirement of orthogonal experimental design. The combination design of the three factors is listed in Table 2.

Table 1 Levels and code for factors

	Factors		
Levels	Spray current *I*, A	Spray voltage *U*, V	Spray distance *L*, mm
1	100	34	120
2	130	36	150
3	160	38	180

All the coatings were sprayed to a thickness of about 0.5 mm. The surface and cross section of coatings were surface ground with 220 grit through 1200 grit SiC papers in water suspension and were polished using 5 μm diamond paste. The coating samples were examined by optical and scanning electron microscopy (SEM) as well as x-ray diffraction (XRD).

The corrosion resistance of sprayed coatings was evaluated with corrosion current density obtained by electrochemical methods. Corrosion tests were carried out in a three-electrode system, i.e., working electrode, a platinum counter electrode, and a SCE/saturated potassium chloride reference electrode. The working electrode exposed area was 1 cm^2. The corrosive medium was a quiescent 3.5% NaCl electrolyte, and held a temperature of 30 ± 1 °C. By means of a PerkinElmer Galvanostat/Potentiostat model 283, Tafel Polarization curves of specimens were obtained and compared. For the series of Tafel tests, the specimens were scanned from −250 mV versus open circuit potential (OCP) up to 250 mV versus OCP at 0.166 mV/s.

3. Results and Discussion

3.1 Corrosion Test Results and Optimizing the Process Parameters

The Tafel polarization curves of various coatings were tested in 3.5% NaCl electrolyte, and the corrosion current

Table 2 Results of $L_9(3^3)$ orthogonal experiment of arc-sprayed Ti coating

No.	Spray current *I*, A	Spray voltage *U*, V	Spray distance *L*, mm	Corrosion current density i_{corr}, μA cm^{-2}
1	1	1	3	440.3
2	1	2	2	368.1
3	1	3	1	39.36
4	2	1	1	462.6
5	2	2	3	997.7
6	2	3	2	89.33
7	3	1	2	100.1
8	3	2	1	504.6
9	3	3	3	688.1
Corrosion current density				
k_{1j}	847.76	1003.0	1006.56	
k_{2j}	1549.63	1870.4	557.53	Order of factor significance: *LUI*
k_{3j}	1292.8	816.79	2126.1	
$k_{1j}/3$	282.59	334.33	335.52	Optimized design: $I_1U_3L_2$
$k_{2j}/3$	516.54	623.47	185.84	i_{corr} of coating under $I_1U_3L_2$: 5.08 μA cm^{-2}
$k_{3j}/3$	430.93	272.26	708.7	
R_j	233.95	351.21	522.86	

density (i_{corr}) was calculated using PARCalc Tafel analysis routine that uses all of the data to perform a nonlinear least-squares fit of the data to the Stern-Geary equation and ceases its iteration when the new result differs from the old one by <0.1%. The experimental standard error (ε) was also calculated according to Eq 1

$$\varepsilon = \sqrt{\frac{\sum_{l=1}^{N}(x_l - \bar{x})^2}{N}} \qquad \text{(Eq 1)}$$

where N is the number of test times with the same condition, $\bar{x}$ is the mean value of the total corrosion current densities obtained from the N times testing. The reproducibility of the test results can be reflected by ε/i_{corr}. The No. 3 experiment has been done three times, and the corrosion current density is 49.11, 32.73, and 36.24 μA cm^{-2}. The standard error is 7.04 while the ε/i_{corr} is 17.89%.

The corrosion current densities obtained from the polarization curves are listed in Table 2, where "i_{corr}" is the corrosion current density in microampere per square centimeter. Since corrosion rate V is in direct proportional to corrosion current density "i_{corr}," therefore, the lower the "i_{corr}" is, the better the corrosion resistance of coating is. It can be seen from Table 2 that the corrosion current density is very sensitive to spray process parameters.

The significance of the effect of every factor on corrosion rate is different, and this significance can be evaluated by the maximum difference R. R can be determined as followings: (1) Calculating K_{ij}, where K_{ij} is used to designate the sum of corrosion current density of coatings for level i (1/2/3) of factor j ($I/U/L$); (2) Calculating the mean value of corrosion current density for level i of factor j ($K_{ij}/3$); (3) Calculating the maximum difference between $K_{1j}/3$, $K_{2j}/3$, $K_{3j}/3$, which be designated as R_j. R_j reflects the maximum change of corrosion current density induced by the change of levels for factor j. The bigger the R_j value is, the more significant the effect of the corresponding factor (j) on corrosion current density is. All the R_j values are listed in Table 2. It seems from Table 2 that the effect of spray distance (L) is the greatest among the three factors, then spray voltage (U), and finally spray current (I).

The optimized combination of process parameters can be obtained basing on the $K_{ij}/3$ value. With Table 2, it is easer to see that replacing spray current at level 2 (130 A) by spray current at level 3 (160 A) induces a decrease of corrosion current density from 516.54 to 430.93 μA cm^{-2}. On the other hand using spray current at level 1 (100 A), rather than at level 3, leads to a further decrease of corrosion current density to 282.59 μA cm^{-2}. The mean value of corrosion current density for level 1 of spray current is the smallest among $K_{iI}/3$, then level 1 of spray current should be choose in order to decrease the corrosion current density of coatings. The level for spray voltage or spray distance may be deduced by analogy, thus level 3 of spray voltage and level 2 of spray distance are determined.

The new combination of process parameters (I_1 U_3 L_2) is not listed in Table 2, so new coatings were prepared by electric arc spraying under this new process parameters combination. The electrochemical behavior of the new coatings was compared with that of the No. 3 coating, which has the smallest corrosion current density among the coatings from No. 1 to No. 9, and the polarization curves were illustrated in Fig. 1. Comparing with No. 3 coating, the curve of the optimized coating moves toward the top left which shows the OCP becomes more positive and the current density corresponding the same applied potential becomes smaller. The more positive OCP means a less thermodynamic tendency to corrosion, and corrosion current density of the new coating obtained from the polarization curve is 5.08 μA cm^{-2} which is smaller than that of No. 3 coating (39.36 μA cm^{-2}). The corrosion resistance can be greatly improved by optimizing the process parameters.

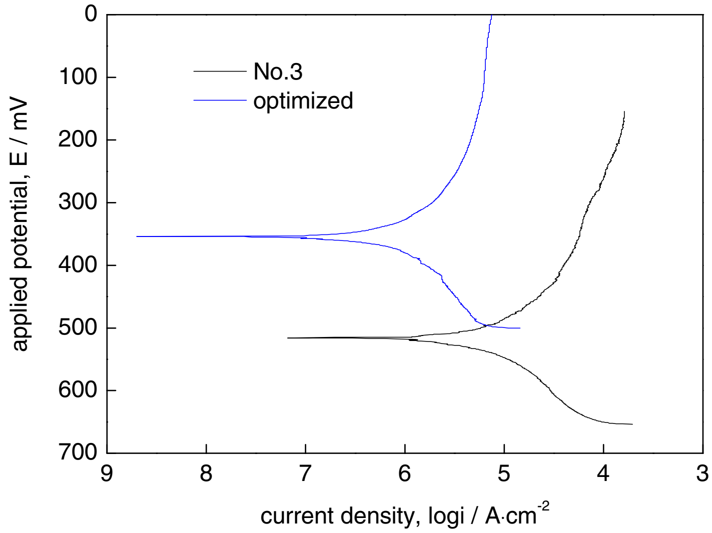

Fig. 1 Tafel polarization curves of arc-sprayed coatings in 3.5% NaCl solution

3.2 Effects of Process Parameters on the Quality of Coatings

The corrosion resistance of coatings is determined by its microstructure, while the microstructure is influenced by spray process parameters.

Figure 2 presents the microstructure for both No. 3 coating and the optimized coating. It can be seen that the uniformity of the microstructure for optimized coating is better than that of No. 3 coating, and the amount of inclusions is greatly reduced. The surface morphology of the optimized coating under as-polished state was observed using SEM (see Fig. 3). Inclusions can easily fall off from the surface of the coating, and this shows that the inclusions are loose and brittle which weaken the cohesive strength of the coating. From XRD analysis of the optimized coating, it could be deduced that the coating comprised a TiN and Ti_2O (Fig. 4). It can be concluded that the white phase should be TiN, because the hardness of this phase is as high as HV_{300} 1074.9, while the inclusions are oxides. No Ti can be found in the coating, and this may be directly related to the high tendency of Ti to react with the atmosphere. In the arc spray process two Ti wires are melted by means of an electric arc, and the molten material is atomized by compressed air and propelled toward the substrate surface to form a coating. Therefore, Ti can react with O_2 or N_2 in the compressed air thus form Ti oxide or nitride. Comparing the microstructure and corrosion current density of the optimized coating with that of No. 3 coating, it can be seen that the amount of inclusions determines the corrosion resistance of coatings. The resistance of coatings will be improved with the decrease in the amount of oxide; therefore, the effect of spray process parameters on the corrosion resistance of coatings is a direct consequence of the effect of process parameters on the amount of inclusions.

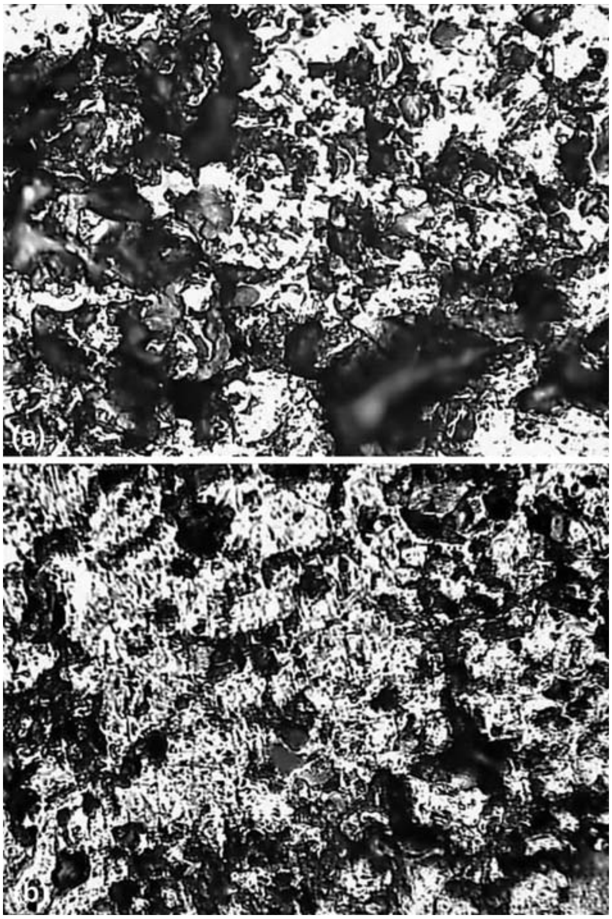

Fig. 2 Microstructure of No. 3 and optimized coatings: (a) No. 3 and (b) optimized coating

Figure 5 presents the relationship of corrosion current density with levels of spray current, spray voltage, and spray distance. It seems that the corrosion rate of coatings will increase with the increasing of both spray current and spray voltage, and then decrease after both reach a suitable level (2). However, the effect of spray distance on corrosion rate is different from that of spray current and spray voltage. The corrosion rate of coatings will decrease with the increase in spray distance, and then increase after reach level 2. These can be explained as follows:

- Arc voltage mainly influences the atomizing of molten droplets, the diameter of particles decreases with the decrease in arc voltage. In the particles with small diameter, a large percentage of the atoms are located in surface regions thus chemical reactions between metallic particles and the atmosphere happen more easily. High arc voltage would retard the oxidizing of big particles because of poor atomizing, thereby oxides in the coatings prepared under high arc voltage can be reduced. However, the diameter of particles determines the density and roughness of the coatings, there will be much more porosities in the coatings with coarse particles. Therefore, the corrosion current density increases with the increase in arc voltage at the first stage because of the retardation of oxidizing,

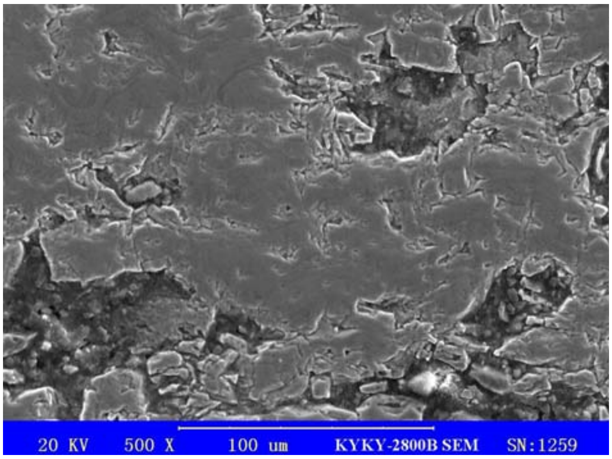

Fig. 3 Morphology of as-polished coating

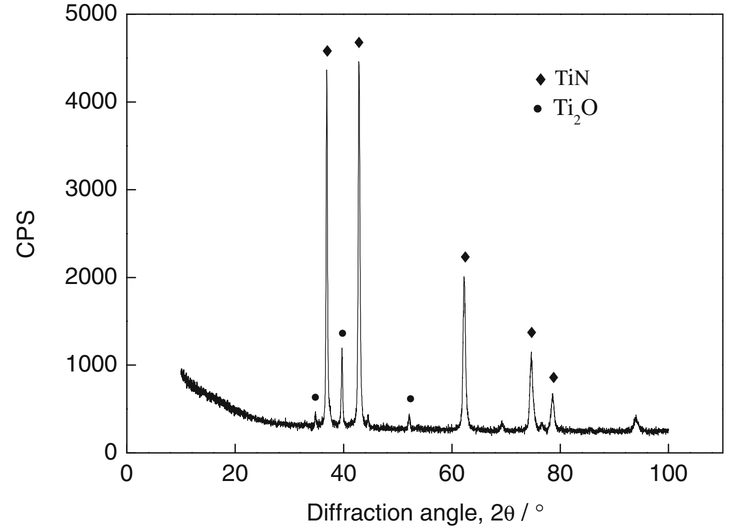

Fig. 4 XRD spectra of arc-sprayed coating

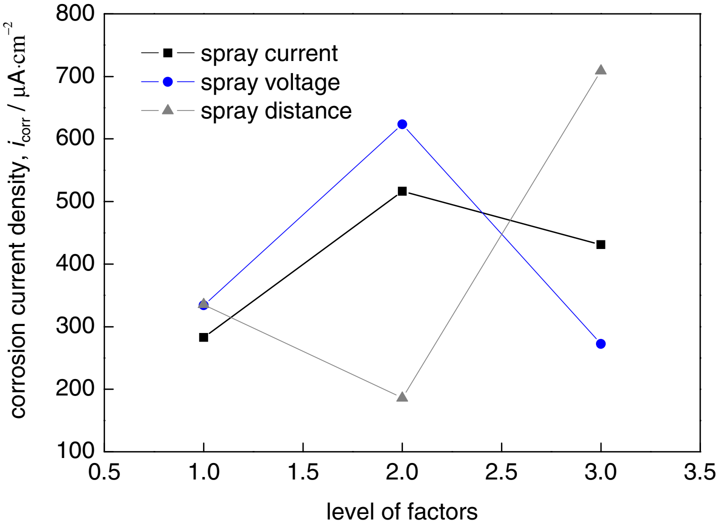

Fig. 5 Relationship of corrosion current density with levels of various factors

then decrease after reach a suitable level because of the low density of coatings.

- Spray current influences the temperature and diameter of particles. The increase in current can result in the increase in heat input. With high heat input, high arc energy induces overheating of molten droplets and thus more severe oxidation. However, surface tension of droplets will substantial decrease after the current reach a critical value, then very fine droplets or particles are produced thus the density of coatings will be greatly improved. Therefore, the overall quality of the coatings will be reduced with the increase in spray current, and then improved after reach a suitable level.
- The increase in spray distance can result in two opposing effects: (1) the amount of oxides in coatings will be improved because the reaction time between the molten droplets and atmosphere will be prolonged; (2) the flying rate of droplets will be slowed down after reaching a maximum value, thus influence the flatten extent of the droplet upon impacting base metal. Higher flying rate does better to obtain coatings with high density. Therefore, high quality and corrosion resistance can be achieved when the spray distance reaches a suitable level. The spray distance should be exactly monitored and controlled in arc spray process because of its great effects on the quality of sprayed coatings.

In the end, it should be noticed that the corrosion resistance of coatings can be greatly improved not only by optimizing spray process parameters, but also by applying new arc spray process. As abovementioned, the oxides weaken the cohesive strength and corrosion resistance of the coatings, so the properties of the coatings can be improved by reducing the content of oxides. Xu proposed an active protection arc spray technology (Ref 13) in which both propane and compressed air were used as atomizing gases, and propane would consume the oxygen in the compressed air by combusting thus reduce the oxides in the coatings. Further studies should be carried out on the microstructure and corrosion behavior of coatings prepared by this active protection arc spray technology.

4. Conclusions

(1) The corrosion resistance of sprayed coatings is very sensitive to spray process parameters, corrosion current density can decrease from 997.7 to 5.08 μA cm^{-2} by optimizing the process parameters.

(2) The effect of spray distance is the greatest among the three factors, then spray voltage, finally spray current.

(3) Almost all the Ti reacts with oxygen or nitrogen during spraying, and the oxides weaken the cohesive strength and corrosion resistance of the coatings. The corrosion resistance of coatings can be improved with decreasing the contents of oxides.

Acknowledgments

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