Importance of the Adhesion of HVOF Sprayed Coatings for Aqueous Corrosion Resistance*

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Importance of coating adhesion in an aqueous corrosion environment was studied experimentally. Tensile adhesion strength of HVOF sprayed 316L stainless steel and Hastelloy C coatings were tested in as-sprayed condition as well as after immersion in seawater. It was found that the adhesion strength of the stainless steel coatings degraded rapidly whereas that of the Hastelloy coatings remained almost intact. Specimens with an artificial defect were also immersed in seawater. The cross sectional observation after the test revealed that the corrosion at the coating-substrate interface proceeded much faster with the stainless steel coating as compared to the Ni-base alloy coating. A model experiment to simulate the galvanic corrosion of a coating-substrate couple was carried out and no significant difference in the galvanic current density was found between the two coatings when coupled with the steel substrate. The tightness of the coating-substrate interface was then tested with a fluorescent dye penetration test. The dye could penetrate the boundary between the stainless steel coating and the substrate whereas the boundary between the Ni-base alloy coating and the substrate was so tight that no penetration occurred. The penetration behavior of the dye into the micro-gaps at the coating-substrate boundary was discussed from the viewpoint of classical Washburn-Rideal theory applied to a model of capillary flow between a pair of parallel circular disks. It was concluded that such micro-gaps between the coating and substrate must be eliminated for these barrier-type coatings to be used in corrosive environments. Heat treatment was highly effective for suppressing the preferential corrosion at the coating-substrate boundary.

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1. Introduction

Adhesion of surface coatings is a critical but not fully understood property. High Velocity Oxy-Fuel (HVOF) thermal spray is a relatively new thermal spray technique, which propels powder material by a supersonic flame jet to velocity well over 500 m/s. HVOF sprayed coatings are attractive for corrosion resistance, as they are dense with reduced oxidation of raw materials as compared to coatings formed by other atmospheric thermal spray processes such as plasma spray or wire arc spray. In a previous report, we evaluated the corrosion resistance¹ of HVOF sprayed 316L stainless steel and Hastelloy C coatings in artificial seawater. It was found that with a commercial HVOF spray apparatus powered by kerosen, Hastelloy C coatings can be fabricated to such a high density that the porosity within the coating is below the detection limit of a mercury porosimeter used, which was about 0.3 vol%. On the contrary, the minimum porosity obtained with 316L stainless steel coatings was just below 1 vol%. Consequently, the corrosion performance of the stainless steel coatings was rather poor: the corrosion rate as evaluated by an AC impedance technique degraded to the level of bare steel substrate after 3 days of immersion in seawater. In contrast, Hastelloy C coatings retained high resistance and exhibited little rusting even after 1 month of immersion test in laboratory.

Another concerns for this type of coatings is galvanic corrosion. Even with a perfectly dense coating, if it should be damaged during service and thus allow seawater to penetrate through the coating to the substrate, severe corrosion of steel substrate is expected due to the potential difference between the noble coating and steel. The large ratio of cathode to anode area will further accelerate the corrosion process. Such situation will lead to a rapid propagation of corrosion at the coating-substrate interface and result in a large-scale failure of the coating, which must be prevented. Therefore, it is essential to evaluate the stability of the coating-substrate interface in a corrosive media before it can be put into real use. In order to examine the stability of the coating-substrate interface in a corrosive media, an artificial defect was made into a coating by drilling a hole through the coating to the substrate and the specimen was immersed in seawater. It was found that the interface of 316L stainless steel coating corrodes at a much faster rate as compared to that of Hastelloy C coating. In this paper we examine the mechanism of such interfacial corrosion in more detail and demonstrate the importance of coating adhesion in a corrosive environment.

2. Experimental Procedures

316L stainless steel and Hastelloy C powders were sprayed by a high-pressure HVOF spraying equipment (JP5000, TAFA, Concord, NH, US) onto standard tensile adhesion test specimens of 25 mm diameter made of SS400 (JIS) mild steel as shown in Fig. 1. These powders are gas-atomized spherical powders manufactured by TAFA (product name: 1236F for SUS316L, 1268F for Hastelloy C respectively) with the size range of 22 to 53 μm. The chemical composition of the powders and substrate are listed in Table 1 and the spraying conditions are given in Table 2. Substrates were blast cleaned with alumina grit and degreased in acetone through the coating to the substrate, severe corrosion of steel substrate is expected due to the potential difference between the noble coating and steel. The large ratio of cathode to anode area will further accelerate the corrosion process. Such situation will lead to a rapid propagation of corrosion at the coating-substrate interface and result in a large-scale failure of the coating, which must be prevented. Therefore, it is essential to evaluate the stability of the coating-substrate interface in a corrosive media before it can be put into real use. In order to examine the stability of the coating-substrate interface in a corrosive media, an artificial defect was made into a coating by drilling a hole through the coating to the substrate and the specimen was immersed in seawater. It was found that the interface of 316L stainless steel coating corrodes at a much faster rate as compared to that of Hastelloy C coating. In this paper we examine the mechanism of such interfacial corrosion in more detail and demonstrate the importance of coating adhesion in a corrosive environment.

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ultrasonically before spraying. Coating thickness was aimed at 400 μm. Adhesion strength was measured in the as-sprayed condition and after immersion in aerated artificial seawater kept at 300 K. Before immersion, plastic molding and silicone resin were used to seal the specimen to allow only the coating surface to be exposed to seawater.

In order to investigate the corrosion along the coating/substrate interface, a hole with 1 mm diameter was drilled from the coating surface to the substrate as shown in the inset of Fig. 1 and the specimen was immersed in seawater thereafter. After 72 h it was taken out to examine the cross section.

Galvanic current between a coating of each material and a mild steel substrate in artificial seawater at 300 K was measured by a setup as shown in Fig. 2. Ideally a detached coating should be used for this experiment but seawater could penetrate into a porous coating and reach the spot-welded joint between the contact rod made of 304 stainless steel and the coating. Since such complication must be avoided for reliable measurement, a coating sprayed onto a Hastelloy C276 substrate was used as the coating specimen instead, assuming that the substrate is so inert that it will not interact with seawater. It was designed to simulate the corrosion at the interface between a coating with narrow through-pores by providing oxygen gas to the coating while suppressing the oxygen concentration on the steel substrate by bubbling nitrogen gas into the anode cell. The unit consists of a pair of cells connected by a glass filter (40 mm dia. × t5 mm) with pore size ranging from 150 to 250 μm, which was used to suppress the diffusion of oxygen across the cell boundary while allowing current to flow with negligible resistance. A stainless steel rod was spot-welded to each specimen and silicone resin was used to define the area of exposure of both specimens as 2 cm². A zero-resistance ammeter was inserted between the coating (cathode) and the substrate (anode) to monitor the galvanic current while a high-input impedance voltmeter was used to monitor the potential of the coating specimen with respect to the Ag/AgCl reference electrode.

In order to examine the tightness of the coating-substrate interface, a modified pin-test specimen was designed for fluorescent dye penetration test. The procedure is depicted in Fig. 3. (1) A metal pin (SUS304, 2 mm diameter) was

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Table 1 Chemical composition of the spray powders and the substrate. (Mass%)

<table>
<thead>
<tr>
<th></th>
<th>SUS316L</th>
<th>Hastelloy C</th>
<th>Low carbon steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe bal, Cr 16.8, Ni 10.8, Mo 2.05, N 0.131, O 0.026</td>
<td></td>
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<tr>
<td>Ni bal, Mo 16.95, Cr 16.57, Fe 6.21, W 4.52, Mn 0.72, Co 0.31, Si 0.73</td>
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</tr>
<tr>
<td>Fe bal, C 0.11, Si 0.22, Mn 0.5, P 0.017, S 0.016</td>
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Table 2 List of HVOF spray conditions for the powders used in the experiments.

<table>
<thead>
<tr>
<th></th>
<th>SUS 316L</th>
<th>Hastelloy C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel flow rate (l/min)</td>
<td>0.322</td>
<td>0.379</td>
</tr>
<tr>
<td>Oxygen flow rate (sl/min)</td>
<td>850</td>
<td>861</td>
</tr>
<tr>
<td>Fuel/oxygen ratio*</td>
<td>0.7</td>
<td>0.82</td>
</tr>
<tr>
<td>Barrel length (mm)</td>
<td>102</td>
<td>102</td>
</tr>
<tr>
<td>Powder feed rate (g/min)</td>
<td>70</td>
<td>59</td>
</tr>
<tr>
<td>Torch velocity (mm/s)</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>380</td>
<td>380</td>
</tr>
<tr>
<td>Powder feed gas</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
</tr>
</tbody>
</table>

*1.0 corresponds to the stoichiometric mixture.
inserted at the center of a tensile test specimen (SS400, 25 mm diameter) and the surface was alumina sand blasted. Then, (2) HVOF coating was formed to a thickness of about 400 \( \mu \)m and (3) a counter block was joined to the coating surface by using an epoxy adhesive. (4) The pin was pulled out by a tensile test machine and (5) a fluorescent dye (Super Glo OD-7000, MARKTEC, Tokyo, Japan) was poured into the hole and left for a predetermined period (30 min, 2 h, and 24 h). (6) Post emulsifier (OD-1700B, MARKTEC) was poured into the hole to make the remained penetrant on the surface soluble by water and the hole was washed with water and dried with air blow. Then, (7) the coating was detached by the tensile test machine and brought into a dark room, where (8) the substrate surface was observed and photographed under an UV light illumination to measure the extent of dye penetration.

Coated specimens were heat treated in vacuum at temperatures of 1023, 1173 and 1323 K for 1 h respectively to investigate the effect of diffusion across the coating-substrate boundary on the corrosion resistance of the interface. Then, artificial defect was made by drilling a 1 mm diameter hole and the specimens were immersed in aerated seawater for cross sectional observation as described above and the extent of corrosion at the interface was measured. Diffusion profile of alloying elements was measured by EPMA line analysis.

3. Results and Discussion

3.1 Adhesive strength after immersion

Figure 4 shows the change in adhesion strength with the immersion period. The solid plots represent the average values of 5 specimens and cross plots represent each test value. Error bars are the standard deviations. Even though the two coatings possessed similar adhesion strength around 60 MPa in the as-sprayed condition, the strength degraded to less than 20 MPa in 72 h for the SUS 316L coatings whereas it remained relatively high for the Hastelloy C coatings even after 30 days. A typical cross section of 316L stainless steel coatings immersed in artificial seawater for 72 h is shown in Fig. 5, which exhibited severe corrosion at the coating/substrate interface. This corrosion was caused by penetration of seawater through porosity in the coating but the rate of corrosion is remarkably high. The cross sections of the coatings with a drilled hole after immersion are shown in Fig. 6. The interface corrosion for the SUS coatings

![Fig. 3 Procedure to apply fluorescent dye penetration test to the interface between a thermal sprayed coating and the underlying substrate.](image)

![Fig. 4 Change in the adhesion strength of HVOF sprayed coatings of SUS316L and Hastelloy C immersed in aerated artificial seawater.](image)

![Fig. 5 Cross section of a SUS 316L coating after 72 hours of immersion in aerated artificial seawater.](image)
proceeded as long as 5 mm whereas it was only about 1 mm for the Hastelloy C coating.

3.2 Galvanic corrosion test

Galvanic corrosion test between each of the coatings and a mild steel substrate was carried out in order to examine if such difference in the rate of interfacial corrosion between the two coating-substrate systems discussed in the previous section is due to the difference in the rate of galvanic corrosion. Figure 7 shows the result of the galvanic corrosion experiment as depicted in Fig. 2. It shows that the galvanic current density between each of the coatings and the steel substrate is similar at around 30 $\mu$A cm$^{-2}$ and the potential is around $-650$ mV vs. Ag/AgCl. Therefore, the results indicate that there is not a significant difference between the two coatings in terms of cathodic activity with respect to the steel for galvanic corrosion (This may be as expected because the free corrosion potentials of both materials in seawater lie in a same range.$^{2}$).

3.3 Fluorescent dye penetration test

Tightness of the coating-substrate interface was examined by the fluorescent dye penetration test shown in Fig. 3.

Figure 8 shows the surface of steel substrates under UV light illumination after fluorescent dye penetration test for each period. These photos were taken for the 316L stainless steel...
coatings but such penetration of the dye into the coating-substrate interface was not observed for the Hastelloy C coatings. Therefore, the results suggest that the existence of such thin gaps under the 316L stainless steel allowed rapid penetration of seawater under the coating and hence was the reason behind the marked difference in the rate of corrosion along the coating-substrate boundary between the two systems. According to the classical Washburn-Rideal equation for the penetration of liquid into a capillary, the period \( t \) required for the liquid to penetrate for a distance \( l \) within a capillary of radius \( R \) is expressed as

\[
l^2 = \frac{R \cos \theta \gamma}{2\mu} t, \tag{1}
\]

where \( \gamma \) is the surface tension, \( \mu \) the coefficient of viscosity of the liquid and \( \theta \) the wetting angle of the liquid on the capillary surface.\(^3,4\) Penetration distance was read from the photos in Fig. 8 at each period and related with eq. (1) but it was found\(^5\) that experimental values of \( l \) are better related to \( t \) by the relationship \( l^3 \propto t \).

As a more realistic model for the gaps in between the coating and the substrate, a radial capillary flow between a pair of circular disks as shown in Fig. 9 was analyzed. The upper plate has a hole of radius \( R_o \) from which the liquid is supplied and penetrates radially into the gap of height \( h \) between the two plates. The following expression for the penetration distance \( l \) was derived (see Appendix for derivation).

\[
l^2 \left\{ 2 \ln \left( \frac{l}{R_o} \right) - 1 \right\} + R_o^2 = \frac{2yh \cos \theta}{3\mu} t. \tag{2}
\]

Comparison between the model calculation using eq. (2) and the experimental data is shown in Fig. 10. Three curves in the figure correspond to the calculated distance of penetration \( l-R_o \) from the edge of the hole in the upper plate (substrate) for three different values of \( h \). It is evident that the experimental data do not fit to a curve with any value of \( h \). The data indicate that the flow decelerated as a function of time at a much greater rate than the model prediction. Also, the values of \( h \) used in the calculation are probably too small for such flow calculation to be valid. Possible explanation of the discrepancy between the model calculation and much slower rate of penetration observed in the experiment are the followings.

1. Measurement by a mercury porosimeter revealed that the SUS316L coating has a porosity level of about 1 to 2 vol\%, majority of which exist in the radius range between 10 nm and 100 nm.\(^1\) Therefore, it is possible that significant amount of dye which penetrated laterally to a certain radius through the coating-substrate boundary was absorbed vertically into the coating. If the size of the micro-gaps between the coating and the substrate is comparable or smaller than the pore size in the coating, this diversion of the liquid into the coating could reduce the supply of liquid for further spreading along the coating-substrate boundary and hence decelerate the penetration rate.

2. The micro-gap between the coating and the substrate cannot be a simple planar gap as assumed in the model of Fig. 9. There must be some areas of contact between the coating and the substrate. How this will affect the capillary flow is not clear at the moment. Therefore, estimation of the size of micro-gaps between the SUS316L coatings from the time-penetration data was not successful. It should be noted that the porosity of Hastelloy C coatings was below the detection limit of the mercury porosimeter (less than 0.3 vol\%).\(^1\) These data seem to indicate that Hastelloy C powder has a higher deformability as compared to SUS316L powder at the impact onto the substrate and coating surface but further study is necessary.

3.4 Heat treatment

Figure 11 shows the effects of heat-treating temperature on the cross sections of corrosion test specimens of SUS316L coatings with an artificial defect. The photos show that heat treatment even at a modest temperature of 1023 K is remarkably effective for reducing the rate of corrosion along the interface. At higher temperatures, the interface becomes more corrosion resistant due to the diffusion of corrosion resistant elements such as Cr and Ni from the coating to the substrate. Figure 12 shows the penetration distance as

Fig. 9 Capillary flow of liquid between a pair of parallel circular disks. The liquid is fed from the hole with radius \( R_o \), situated at the center of the upper plate. The gap between the plates is \( h \) and the distance of penetration from the center is \( l \).
functions of the treating temperature for the two kinds of coatings as a summary of these experiments. Figures 13(a) and (b) show the atomic concentration profiles of chromium across the coating-substrate boundary for the 316L stainless and Hastelloy C coatings before and after heat treatment at these temperatures.

Considering the fact that the diffusion layer for the two types of specimens at 1023 K is so narrow as 1 μm, its effect on the suppression of interfacial corrosion is rather remarkable. This suppression of interfacial corrosion may be attributed to narrowing or closure of micro-gaps between the coatings and the substrate but further study is necessary to clarify this point. At higher temperatures, the diffusion layer becomes thicker than 20 μm and the chromium concentration profile extends deeper into the steel; nickel was also found to behave similarly, providing higher corrosion resistance to the top layer of the substrate. Such graded composition profile is ideal for prevention of coating failure caused by interfacial corrosion because the interface is not attacked preferentially any more as shown in Fig. 11 at 1323 K.

4. Conclusions

Even though the adhesive strength of HVOF coatings is generally better than that of coatings sprayed by other atmospheric thermal spray processes, when a coating-substrate couple is exposed to a corrosive media, the interface can be preferentially attacked. In this study, 316L
stainless steel and Hastelloy C coatings were HVOF sprayed onto mild steel substrates and tested in artificial seawater by several testing methods including mechanical, electrochemical and fluorescent dye penetration techniques. The following results were obtained.

1) The adhesion strength of the stainless steel coatings degrades rapidly in seawater whereas that of the Hastelloy coatings remains almost intact. When seawater is allowed to reach the interface between the coating and the substrate, corrosion proceeds preferentially along the interface. The rate of such interfacial corrosion is much faster with the stainless steel coating as compared to the Ni-base alloy coating.

2) Such difference is not due to the electrochemical properties of these coatings because the galvanic current between each of these coatings and steel substrate is almost the same with each other.

3) The interface between the Hastelloy C coating and the steel substrate is so tight that fluorescent dye cannot penetrate into, whereas it can penetrate into the interface of the 316L stainless coating. In order to analyze the penetration mechanism, the classical Washburn-Rideal theory has been extended to a radial viscous flow between parallel circular disks. The expression for the distance of penetration in terms of time has been obtained and compared with the experimental data. Agreement is not good and the porosity of coatings is considered as a major reason behind the discrepancy.

4) Heat treatment above 1023K for 1h significantly improves the durability of the coating-substrate interface in seawater, which is due to the enhancement of coating adhesion and the diffusion of alloying elements into the steel substrate.

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REFERENCES


Appendix

The radial flow of an incompressible viscous fluid in a configuration shown in Fig. 9 is analyzed. The upper plate has a hole of radius $R_o$ from which the liquid is supplied and penetrates radially into the gap of height $h$ between the two plates. For slow motion of liquid with viscosity $\mu$ in steady-state in such system with circular symmetry, the equation of motion reduces to

$$\frac{\partial p}{\partial r} = \mu \frac{\partial^2 v_r}{\partial z^2}, \quad (A-1)$$

where $p$ is pressure in the liquid, $v_r$ is the radial velocity. Because of circular symmetry, $v_z = 0$. As long as we restrict our analysis to the region where $h$ is small as compared to $r$, $v_r = 0$ is a good approximation. By assuming that $v_r = 0$ at $z = 0$ and $z = h$, and integrating eq. (A-1) twice with respect to $z$, a parabolic flow field is obtained:

$$v_r = \frac{1}{2\mu} \left( \frac{\partial p}{\partial r} \right) z(z - h). \quad (A-2)$$

The total outward flow rate $U_o$ is obtained by integrating $v_r$,
over the entire circular surface,

$$U_o = \int_0^h v \cdot 2\pi r h \, dr.$$  \hspace{1cm} (A.3)

$$= - \frac{h^2 \pi r}{6 \mu} \left( \frac{\partial p}{\partial r} \right).$$

Since the liquid is incompressible, $U_o$ is constant regardless of $r$. Hence eq. (A.3) is integrated with respect to $r$,

$$p = - \frac{6\mu U_o}{\pi h^2} \ln r + C_1,$$  \hspace{1cm} (A.4)

where $C_1$ is a constant of integration. It is assumed that the gap is connected to the ambient air of pressure $P_o$ and hence the pressure within the gap ahead of the liquid is also $P_o$. Also it is assumed that the head due to the height of the liquid in the hole at the center is negligibly small as compared to the capillary pressure, i.e., $p(r) = P_o$ at $r = R_o$, then,

$$\Delta p(r) = p(r) - p(r = R_o)$$

$$= \frac{6\mu U_o}{\pi h^2} \ln \left( \frac{R_o}{r} \right).$$  \hspace{1cm} (A.5)

The pressure difference $\Delta p(r = l)$ is given by the capillary pressure, assuming that $1/h \gg 1/r$,

$$\Delta p = \frac{2\gamma \cos \theta}{h} = \frac{6\mu U_o}{\pi h^2} \ln \left( \frac{R_o}{l} \right),$$  \hspace{1cm} (A.6)

where $\gamma$ is the surface tension of the liquid and $\theta$ the wetting angle of the liquid on the disk surface. Consider now that the wetting front is at $r = l$. Then, the total volume $V$ of the liquid between the plates is expressed by

$$V = \pi (l^2 - R_o^2)h.$$  \hspace{1cm} (A.7)

Then, the flow rate $U_o$ is given as

$$U_o = \frac{dV}{dt} = 2\pi hl \frac{dl}{dt},$$  \hspace{1cm} (A.8)

By inserting eq. (A.8) into eq. (A.6) and simplifying,

$$- \frac{\gamma h \cos \theta}{6\mu} \frac{dl}{dt} = \int \frac{1}{l} \ln \left( \frac{R_o}{l} \right) dl.$$  \hspace{1cm} (A.9)

By executing the integration of eq. (A.9) and noting that $l = R_o$ at $t = 0$, the relationship between the penetration distance $l$ and time $t$ is obtained as the following.

$$l^2 \left[ 1 + 2 \ln \left( \frac{R_o}{l} \right) \right] - R_o^2 = - \frac{2\gamma h \cos \theta}{3\mu} t.$$  \hspace{1cm} (A.10)

Equation (2) is obtained by changing the sign on the both sides of (A.10).