Evaluation of through-porosity of HVOF sprayed coating

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Abstract

Anticorrosion coatings must be impermeable to protect steel structures in marine environments. We evaluated the through-porosity of HastelloyC high-velocity oxyfuel (HVOF) sprayed coatings by quantitatively analyzing dissolved substances derived from coated steel during immersion in HCl solution. This enabled us to detect slight amounts of through-pores, which depended on the coating thickness and on the coating’s stacking structure. It also enabled us to separately calculate both coating through-porosity and corrosion resistance when electrochemical measurements could not selectively detect either of these properties.

Keywords: High-velocity oxyfuel (HVOF); Nickel alloy; Through-porosity; Inductively coupled plasma (ICP) atomic emission spectrometry; Electrochemical

1. Introduction

One of the objectives of the ‘Ultra Steel’ research project started in 1995 at Japan’s National Institute for Materials Science was to improve the corrosion resistance of structural steels in marine environments by depositing anticorrosion materials through thermal spraying. The sprayed coating is expected to be used in on-site repair of damaged clad steel and as an alternative to clad steel. Such a coating must be both impermeable and highly corrosion-resistant. We used high-velocity oxyfuel (HVOF) spray because it enabled us to deposit a dense coating with comparatively little change in sprayed particle properties during spraying.

Coatings of HVOF sprayed AISI316L stainless steel and HastelloyC nickel-base alloy have been studied to determine the relationship between spray conditions and properties such as porosity, oxygen content, and corrosion resistance [1–4].

If a sprayed coating has through-porosity, seawater may permeate the coating beneath the splash zone of a marine structure and reach the interface between the coating and substrate. When a conductive solution contacts different conductive material, it forms what is called a galvanic cell, where a combination of the noble coating and the less-noble substrate accelerates substrate corrosion more than, for example, a bare substrate with the same surface area.

The porosity of most HVOF sprayed coatings has been measured by image analysis of their cross-sectional views [5–8]. The accuracy of this method is not sufficiently high because the cross-section aspect depends significantly on sample preparation. Other methods to measure porosity include computed simulation [9] and mercury intrusion porosimetry [1,10]. Although mercury intrusion porosimetry measures open pores comparatively precisely, it could not determine the open porosity of HVOF sprayed HastelloyC coatings because these coatings had extremely low open porosity below the detection limit for mercury intrusion porosimetry. Mercury porosimetry also requires that a coating be at least 1 mm thick and that the coating be stripped from the substrate. We thus required detection with higher sensitivity to estimate through-pores.

We evaluated the through-porosity of HastelloyC HVOF sprayed coatings on low-carbon steel substrates to determine their dependence on coating thickness and on combustion pressure in spraying. To evaluate the through-porosity, we used inductively coupled plasma (ICP) emission spectroscopy to analyze dissolved substances derived from through-pores after dissolution.
Table 1
Spray conditions and properties of the HastelloyC coatings

<table>
<thead>
<tr>
<th>Unit</th>
<th>HP</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel (kerosene) flow rate</td>
<td>dm³ min⁻¹</td>
<td>0.47</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>dm³ min⁻¹</td>
<td>1080</td>
</tr>
<tr>
<td>Combustion pressure</td>
<td>MPa</td>
<td>0.86</td>
</tr>
<tr>
<td>Fuel/oxygen ratio</td>
<td>–</td>
<td>0.82</td>
</tr>
<tr>
<td>Barrel length</td>
<td>mm</td>
<td>102</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>g min⁻¹</td>
<td>60</td>
</tr>
<tr>
<td>Torch velocity</td>
<td>mm s⁻¹</td>
<td>700</td>
</tr>
<tr>
<td>Spray distance</td>
<td>mm</td>
<td>380</td>
</tr>
<tr>
<td>Powder feed gas</td>
<td>–</td>
<td>Nitrogen (N₂)</td>
</tr>
<tr>
<td>Film thickness</td>
<td>µm</td>
<td>50–400</td>
</tr>
<tr>
<td>Open porosity vol.%</td>
<td>–</td>
<td>0 &lt; 0.1</td>
</tr>
<tr>
<td>Oxygen content wt.%</td>
<td>–</td>
<td>1.10</td>
</tr>
</tbody>
</table>

*1.0 corresponds to the stoichiometric mixture ratio.

from the steel substrate in corrosion during immersion in hydrochloric acid (HCl). We then compared the amount of through-porosity determined by chemical analysis to results of electrochemical measurement.

2. Experimental

HastelloyC was coated by HVOF spraying with a TFAA apparatus (JP-5000). The chemical composition of the HastelloyC (TAFA 1268F) feedstock was as follows: Mo 16.95, Cr 16.57, Fe 6.21, W 4.52, Mn 0.72, Co 0.31, Si 0.73, and Ni balance. We varied combustion pressure and the traverse number of the spray gun. Combustion pressure was 0.68 MPa, termed standard pressure (SP), and 0.86 MPa, termed higher pressure (HP) below. Table 1 lists combustion pressure and primary spray conditions recommended by the manufacturer. The substrate materials we used were JIS SS400 low-carbon steel and HastelloyC276 nickel base alloy. The substrate was 2t = 50 × 100 mm. Before spraying, substrates were blasted with alumina grit and degreased ultrasonically in acetone. Coatings with four coating thicknesses from 50 to 400 µm were obtained by changing the traverse number. Other properties of resultant coatings are listed in Table 1. We measured open porosity using mercury intrusion porosimetry and determined the oxygen content of the coating using inert-gas fusion.

Coated plates were cut into 2.5 cm² sections and repeatedly cleaned ultrasonically in acetone and ion-exchanged water.

We chemically analyzed and electrochemically measured the through-porosity of the HVOF sprayed coating as follows: a coated specimen was connected with a stainless rod and used as an electrode whose surface, except for 2 cm² of the sprayed surface, was covered with silicone resin. For comparison, an electrode of SS400 and HastelloyC276 bulk plates was prepared the same way. The electrode was immersed at 300 K in 0.5 mol dm⁻³ of HCl, used to avoid filling through-porosity with solid corrosion products and to include chloride ions with almost the same concentration as in seawater. At predetermined times, 5 ml of test solution was sampled and iron (Fe) and nickel (Ni) elements dissolved in sampled solutions determined by ICP atomic emission spectrometry using an analyzer (SPS 3000, Seiko Instruments Inc.). Both elements were the base of the substrate and coating metals. We measured dissolved ions once for the same experimental conditions, but twice for coatings approximately 400 µm thick. The results for the coatings which were approximately 400 µm thick, were consistent and measurement was satisfactorily replicable. We obtained the corrosion potential of the electrode and its polarization resistance, which indicates the degree of corrosion resistance and was measured by alternating current (a.c.) impedance [11] using a corrosion monitor (Model CT-5, Riken Denshi). The electrode potential was referenced to the standard potential of the Ag/AgCl electrode in a saturated KCl solution.

3. Results and discussion

3.1. Chemical analysis

Fig. 1 shows typical variations over time in elemental Fe dissolution from different specimens immersed in HCl solution. Dissolution is represented per geometric surface area of the exposed sprayed face (2 cm²). Differences were observed in Fe dissolution among specimens even for 30 min immersion, i.e. in initial
sampling, implying the degree of corrosion for each specimen. Iron dissolution increased with immersion time, indicating that the reaction on the specimen was continuous. Iron was dissolved from both the substrate and coating because HastelloyC contained the Fe element. When the coating had a connecting pore reaching the substrate, Fe ions formed in the substrate corrosion reaction passed outside of the coating through such pores. Fe ions were also dissolved by the corrosion reaction of the coating in preference to the substrate when through-pores in the coating did not exist or were extremely few in number. We define the dissolution rate by calculating the average dissolution by dividing the difference between maximum and minimum dissolution during immersion by the immersion time of 72 h (curves, Fig. 1). Average dissolution of Fe from coated specimens depended on coating thickness (Fig. 2). Dissolution of both HP and SP coatings which were 50 μm thick, is comparable to that of bulk SS400 plate, indicating that these coatings had numerous through-pores and did not shield against penetration by the solution. Dissolution decreased significantly with increasing coating thickness because chances for open pores to connect decreased stochastically as sprayed layers accumulated under the same spraying conditions. Fe dissolution continued to decrease with coating up to 385 μm thick in SP spraying, but did not reach that for coating sprayed on the HastelloyC276 substrate, i.e. the value of the coating itself, shown by the black dot in Fig. 2. This indicates that SP coating retained through-

![Fig. 2. Dependence of dissolution rate of Fe from specimen on coating thickness in 0.5 M HCl: ○, HastelloyC coating (SP) on SS400; △, HastelloyC coating (HP) on SS400; ●, HastelloyC coating (SP) on HastelloyC276; and ▲, HastelloyC coating (HP) on HastelloyC276. Two dotted lines are bulk plates: --, HastelloyC276; and -, SS400.](image-url)

Example of figure caption: Fig. 2. Dependence of dissolution rate of Fe from specimen on coating thickness in 0.5 M HCl: ○, HastelloyC coating (SP) on SS400; △, HastelloyC coating (HP) on SS400; ●, HastelloyC coating (SP) on HastelloyC276; and ▲, HastelloyC coating (HP) on HastelloyC276. Two dotted lines are bulk plates: --, HastelloyC276; and -, SS400.

Fe dissolution in HP coating decreased up to approximately 200 μm, more rapidly than the SP coating, indicating that HP coatings had a denser structure than SP coating because the spray particle in HP spraying impinged on the target at a higher speed and deformed more highly than particles sprayed under SP. Above a thickness of 200 μm, Fe dissolution for the HP coating increased gradually with coating thickness. As is shown later, this is due to decreased coating corrosion resistance, not due to increased substrate corrosion rate through pores.

Fig. 3 shows typical variations in Ni element dissolution for the same specimens as in Fig. 1. Ni detected from the SS400 plate dissolved less than 1/1000 of Fe (Fig. 1), and Ni dissolution from the substrate was thus negligible. Accordingly, we attributed all Ni dissolution to being from the coating. Fig. 4 shows Ni dissolution dependence on coating thickness. Ni dissolution was calculated according to the same method as Fe. Dissolution for the SP coating increased continuously as a function of coating thickness up to approximately 400 μm. HP coating over 200 μm thick maintained almost the same dissolution rate. If SS400 is coupled with HastelloyC in the presence of a conductive solution, SS400 corrosion accelerates while HastelloyC corrosion is suppressed, because SS400 is electrochemically less noble than HastelloyC. Paradoxically, the increase in Ni dissolution should be related closely to the decrease in substrate dissolution, caused by the decrease in coating through-porosity. We thus surmised that some through-pores remained even at a 400 μm thickness in SP
coating, while through-pores were absent in HP coating over 200 μm thick. A slight increase in dissolution with a coating over 200 μm thick in HP coating may be due to coating corrosion resistance decreasing as coating oxygen content increased. The oxide content of the HP coating was higher than that of the SP coating due to higher substrate temperature during spraying.

To separate Fe dissolution from the substrate from that from the coating, we tested HastelloyC276 bulk plate in the same HCl solution. Results showed that the ratio of Ni and Fe in dissolution was almost equal to that in the composition of the bulk alloy. Such a ratio thus persists for the coating, depending on spray conditions. From the result for the coatings sprayed on HastelloyC276 plate, we calculated the Ni and Fe ratio (Table 2). Fe dissolution from the substrate is expressed as follows:

\[
\text{Fe(S)} = \text{Fe(T)} - \text{Fe(C)} = \text{Fe(T)} - \text{Ni(C)} \times \text{dissolution ratio} = \text{Fe/Ni}
\]  

In this equation, uppercase S, T and C in brackets indicate the substrate, coating, and total.

Fig. 5 shows Fe dissolution from the substrate, calculated by the above equation, and clarifying the difference between HP and SP coating. The Fe ion detection limit in this analysis is \(2.89 \times 10^{-10}\) mol cm\(^{-2}\) h\(^{-1}\). HP coating 350 μm thick resulted in a calculation below this limitation, so we plotted the limitation in the figure for this HP coating. We found that HP coating at approximately 400 μm had no detectable through-pores even though SP coating had through-pores even at the same thickness. This was confirmed by the cross-sectional views of tested specimens (Fig. 6). SP coating sustained corrosion partially at the interface between the coating and substrate, while the HP coating appeared to be completely intact.

Fig. 7 shows the dependence of the Fe and Ni element dissolution on specimen coating thickness. Total dissolution is thus the comprehensive coating performance consisting of impermeability and corrosion resistance. With increasing coating thickness, total dissolution decreased rapidly, then tapered off to a moderate state. The rapid decrease in total dissolution was mainly due to decreased substrate corrosion caused by decreased through-porosity. The moderate state was caused by preferential coating corrosion, clearly observed in total HP coating dissolution above 200 μm, and its slight increase in this region indicates decreased corrosion resistance of coatings due to the above reason.

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### Table 2

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Dissolution rate (mol cm(^{-2}) h(^{-1}))</th>
<th>Dissolution ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Ni</td>
</tr>
<tr>
<td>SP coating</td>
<td>(5.53 \times 10^{-9})</td>
<td>(7.46 \times 10^{-8})</td>
</tr>
<tr>
<td>HP coating</td>
<td>(1.02 \times 10^{-8})</td>
<td>(1.46 \times 10^{-7})</td>
</tr>
<tr>
<td>Bulk plate</td>
<td>(2.18 \times 10^{-9})</td>
<td>(2.44 \times 10^{-8})</td>
</tr>
</tbody>
</table>

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Fig. 4. Dependence of dissolution rate of Ni from specimen on coating thickness in 0.5 M HCl: ○, HastelloyC coating (SP) on SS400; △, HastelloyC coating (HP) on SS400; ●, HastelloyC coating (SP) on HastelloyC276; and ▲, HastelloyC coating (HP) on HastelloyC276. Two dotted lines are bulk plates: --, HastelloyC276; and : SS400.

Fig. 5. Dependence of dissolution rate of Fe from substrate on coating thickness in 0.5 M HCl: ○, HastelloyC coating (SP) on SS400; and △, HastelloyC coating (HP) on SS400. Dotted line is SS400 bulk plate.

Fig. 7 shows the dependence of the Fe and Ni element dissolution on specimen coating thickness. Total dissolution is thus the comprehensive coating performance consisting of impermeability and corrosion resistance. With increasing coating thickness, total dissolution decreased rapidly, then tapered off to a moderate state. The rapid decrease in total dissolution was mainly due to decreased substrate corrosion caused by decreased through-porosity. The moderate state was caused by preferential coating corrosion, clearly observed in total HP coating dissolution above 200 μm, and its slight increase in this region indicates decreased corrosion resistance of coatings due to the above reason.
3.2. Electrochemical measurement

Creus et al. evaluated the porosity of protective coatings on steel electrochemically [12], reporting thin films a maximum of 10 μm thick, for which they assumed that the less noble metal of the couple was fully anodic and the more noble metal fully cathodic. In our HOVF coatings, corrosion may take place competitively on both the coating and substrate because most of them are so thick and dense that a potential difference exists between the substrate and the electrolyte outside the coating. Such a potential difference corresponds to the IR drop based on the resistance to ions moving through connecting pores in coatings. Open porosity could thus not be calculated simply based on the equation in Creus’ paper.

The rest electrode potential of the specimen immersed in a corrosive medium is often regarded as the corrosion potential and is used to evaluate its corrosion resistance. Fig. 8 shows typical variations in corrosion potential of the specimens in Fig. 1. The corrosion potential indicates the corrosion state of a specimen, not the corrosion rate of the specimen, such as the reaction type. Electrochemically noble HastelloyC had a higher electrode potential than less noble SS400. The relatively stable potential...
we observed indicates that the same corrosion reaction continued occurring on the specimen. Fig. 9 shows the dependence of the corrosion potential of specimens on coating thickness for SP and HP coatings. Note that the corrosion potential plotted here represents the average from 24 to 72 h because it reached almost the steady state. Coatings 50 μm thick had a more noble corrosion potential than SS400 plate although dissolution of the coatings 50 μm thick was comparable to that of bulk SS400 plate (see Figs. 5 and 7). This is because of the progress of galvanic corrosion at the interface between the substrate and coating with numerous through-pores. As through-porosity decreased, the contribution of SS400 on the corrosion potential decreased, increasing corrosion potential. The SP coating has an ascending curve with thickness up to 385 μm, implying the SP coating had some through-pores even when 400 μm thick. The HP coating kept almost the same potential over 200 μm, confirming its absence of through-pores. Above 200 μm, however, a gap was observed between the coating and bulk plate in addition to a gradual decrease in corrosion potential, suggesting some slight difference in the corrosion state between specimens.

Polarization resistance \( R_p \) indicates the degree of corrosion reaction and is inversely proportional to corrosion rate \( R_c \) [11,13]:

\[
R_c = B \times R_p^{-1}, \quad B = \frac{b_a \times b_c}{2.3(b_a + b_c)}
\]  

(2)

\( B \) is a conversion coefficient consisting of \( b_a \) and \( b_c \), which are polarization resistance constants for anodic and cathodic reactions. Note that \( R_c \) is only proportional to \( R_p^{-1} \) if \( b_a \) and \( b_c \) are constant and this may not be the case for different coatings and different degree of porosity. Fig. 10 shows how \( R_p^{-1} \) changes after immersion for the same set of specimens as in Fig. 1. It is reasonable that low-carbon steel SS400 had a higher \( R_p^{-1} \) than HastelloyC276 bulk material because \( R_c \) corresponds to the dissolution rate. The initial decrease and subsequent fluctuation for SS400 in \( R_p^{-1} \) are explained by the change in surface area caused by \( \text{H}_2 \) evolution upon the corrosion reaction. Since our coated specimens consist of two materials with significantly different corrosion resistance, we must determine carefully how \( R_p^{-1} \) relates to \( R_c \), i.e. the dissolution rate. Fig. 11 shows the dependence of \( R_p^{-1} \) of the specimen series made under SP and HP on coating thickness. Compared to dissolution rate results (Fig. 7), \( R_p^{-1} \) in Fig. 11 represents general trends in the dissolution rate comparatively well. They are, however, different aspects between the results of the dissolution rate and \( R_p^{-1} \) when examined more closely: (1) the dissolution rate changes over a wider range than for \( R_p^{-1} \); and (2) more porous coatings 50 μm thick showed higher \( R_p^{-1} \) than bulk SS400, whereas the dissolution rate from the coated specimen was always smaller than that from bulk SS400. Using data on \( R_c \) and \( R_p^{-1} \) for the bulk plate of HastelloyC276 and SS400, we found that \( B \) for HastelloyC276 is significantly smaller than that for SS400. We therefore expect that a combination of porous HastelloyC coating on a SS400
Fig. 11. Dependence of reciprocal of polarization resistance, \( R_p^{-1} \), of specimen on coating thickness in 0.5 M HCl: \( \bigcirc \), HastelloyC coating (SP) on SS400; \( \triangle \), HastelloyC coating (HP) on SS400; \( \bullet \), HastelloyC coating (SP) on HastelloyC276; and \( \blacktriangle \), HastelloyC coating (HP) on HastelloyC276. Two dotted lines are bulk plates: --, HastelloyC276; and , SS400. substrate have lower B than bulk SS400 plate. This shifts \( R_p^{-1} \) upward for the same value of \( R_c \) as indicated by Eq. (2) and explains why \( R_p^{-1} \) for 50 \( \mu \)m specimens were somewhat above that for bulk steel plate. These results indicate that although \( R_p^{-1} \) may be used to relatively compare the barrier capability of HVOF coatings, it remains difficult to calculate the dissolution rate from \( R_p^{-1} \).

4. Conclusions

The through-porosity of the HVOF sprayed HastelloyC coating (below 0.1 vol.% in open porosity) was chemically detected using ICP atomic emission spectrometry of dissolved substances permeating via connecting pores in such coatings.

Through-porosity depended on coating thickness and on the sprayed-particle stacking structure. One coating showing zero through-porosity was prepared under a higher combustion pressure than the standard and was approximately 400 \( \mu \)m thick.

This chemical detection method was also allowed to determine the corrosion resistance of the coating itself, excluding the contribution of the substrate. This corrosion resistance predominates the coated material as coating density increases. Particularly for coatings without through-pores, it determines service life. Not all sprayed coatings had the same corrosion resistance as their corresponding bulk material.

Electrochemical parameters such as corrosion potential and polarization resistance could not be used to evaluate through-porosity selectively. They showed total coating performance, consisting of through-porosity and coating corrosion resistance.

References