Development of Dense Corrosion Resistant Coatings
By an Improved HVOF Spraying Process

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Abstract
For 6 years, we have developed corrosion resistant coatings for the marine structural steels by using a thermal spray technique. Such a coating requires primarily impermeability and secondarily cleanliness. In order to make denser and highly corrosion resistant coatings, we selected spray materials and improved fabrication processes. In addition, some new methods were designed to evaluate the sprayed particle’s state and coating properties with high accuracy and sensitivity. An inert gas shroud system was attached with the commercial HVOF apparatus and this attachment enabled in-flight spray particles to be accelerated over 750 m·s⁻¹ and simultaneously to avoid to be oxidized. The coating of HastelloyC nickel base alloy by this process had zero through-porosity and 0.2 mass% of oxygen content, leading to be comparable to the bulk material of HastelloyC in terms of corrosion resistance. This coating, formed on steel, demonstrated an excellent protective performance over 10 months in the marine exposure test.

Introduction
Nowadays in Japan, long lifetime over 100 years is required of infrastructures because the environmental regulation and labor costs on repairing are expected to become increasingly severe hereafter. In order to obtain such a long lifetime, corrosion of structural steels is one of the problems to be solved. Especially in the marine environment, the structural steels are subject to severe corrosion damage because there are sea salt and water abundant enough to cause corrosion. Up to now, cathodic protection and thick anticorrosion paint have been used for corrosion protection for marine corrosion. However, it is questionable whether these methods can provide 100 years’ service life without any maintenance. Since 1995, we have researched and developed coatings of anticorrosion materials such as stainless steel and nickel base alloy. These types of coatings demand impermeable nature above all. This is because if a sprayed coating has a penetrable path to the substrate, the corrosive media such as seawater can 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 a galvanic cell and 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. As a coating method, we selected High Velocity Oxy-Fuel (HVOF) thermal spraying technique because we expected to be able to deposit a dense metal coating with comparatively little change in sprayed particle properties during spraying. This high performance is caused by the characteristics that this technique enables us to obtain sprayed particles with a supersonic speed over 500 m·s⁻¹ and with a comparatively lower temperature up to 2000°C, compared to other conventional method such as plasma spraying. The particles are heated and accelerated by a jet flame made from high-pressured mixture of oxygen and fuel. A large part of particles are impinged to a target substrate in the semi-molten and the molten states. The impinged particles are deposited and piled up, leading to form the coating. The HVOF process is often used for hard coating of cermets such as WC-Co in order to increase wear resistance to the material surface.

In order to apply this process to anticorrosion metal coatings, we carried out screening of materials and improved coating fabrication processes; parameter optimization, post treatment, and in particular a gas shroud attachment, which was an innovative method designed by us. In addition, we investigated highly accurate and sensitive methods to evaluate coating properties; through-porosity and adhesive state, and to
monitor one of particle states, molten fraction, upon spraying. Such monitoring is extremely significant technique because the particle state is related closely to the coating properties. Actual marine tests as well as the laboratory corrosion tests were carried out to demonstrate high anticorrosion performance of our coatings. In this paper, we explained results of research and development for the anticorrosion coatings, by separating sections into spray material, coating fabrication process, and evaluation.

**Spray Material**

AISI 316L stainless steel (SUS316L) and nickel base alloy, HastelloyC (HstC) were selected as spray materials because of their well-known corrosion resistance of bulk materials, especially the high resistance of HstC against crevice and pitting corrosion in the presence of chloride. These coatings prepared by HVOF spraying were examined with respect to chemical composition, open porosity, polarization resistance and corrosion potential, which were determined by the inert gas fusion method, mercury intrusion porosimetry, electrochemical impedance measurement, respectively [1,2]. The results showed that SUS316L was an unfavorable material to make impermeable anticorrosion coatings by the HVOF process whereas HstC was a comparatively suitable one. This is because SUS316L is subject to thermal oxidation and crevice corrosion in seawater but HstC is high resistant against such reactions. Lower resistance against thermal oxidation indicated difficulty in adopting higher flame energy essential for making dense deposits by the HVOF process because the sprayed particles tend to be highly oxidized, i.e. deteriorated, upon spraying with the higher flame energy. At the lower flame energy, deposit oxidation was suppressed meanwhile there remain considerable amount of pores between deposited particles. As is the case for SUS316L, pores near the coating surface provided a reaction site feasible for crevice corrosion. Moreover, the pores in the coatings may be connected with each other to form a penetrating path through the coating to the substrate. The penetrating pores can cause the galvanic corrosion of the substrate when it is electrochemically less noble material than the coating. On the other hand, the high resistance of HstC against thermal oxidation allowed us to raise the flame energy to a comparatively large extent. Therefore, lower open porosity below 0.1vol% was attained for coatings prepared under higher flame energy conditions. Furthermore, such a low porosity was compatible with smaller oxygen content of 0.2mass% by attaching gas-shroud system to the HVOF spraying apparatus. The on-shroud coatings were impermeable and highly corrosion resistant comparable to the bulk material of HastelloyC, as shown in Fig. 1. Moreover, no local corrosion was observed on the surface of HstC coating because of its high resistance against local corrosion. In addition, our trial to coat Titanium (Ti) by HVOF spraying was not satisfactory with respect to oxidation and porosity because of significantly high affinity between Ti and oxygen. From these results, we summarized that the impermeable anticorrosion coatings by HVOF spraying required high resistance against thermal oxidation and local corrosion.

**Coating Fabrication Process**

Parameter optimization: We used the apparatus of HVOF spraying (JP5000, TAFACo., Concord, NH, US). In order to optimize spray condition, we varied some spray parameters such as combustion pressure, fuel / oxygen ratio, spray distance, barrel length, substrate temperature, coating thickness and so on [1,2]. The typical deposition conditions are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel flow rate</td>
<td>dm³·min⁻¹</td>
<td>0.25 ~ 0.49</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>mm³·min⁻¹</td>
<td>760 ~ 1080</td>
</tr>
<tr>
<td>Combustion pressure</td>
<td>MPa</td>
<td>0.43 ~ 0.86</td>
</tr>
<tr>
<td>Fuel/oxygen ratio*₁</td>
<td>—</td>
<td>0.7 ~ 1.3</td>
</tr>
<tr>
<td>Barrel length</td>
<td>mm</td>
<td>102, 204</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>g·min⁻¹</td>
<td>60 ~ 70</td>
</tr>
<tr>
<td>Torch velocity</td>
<td>mm·s⁻¹</td>
<td>700</td>
</tr>
<tr>
<td>Spray distance*₂</td>
<td>mm</td>
<td>200 ~ 450</td>
</tr>
<tr>
<td>Powder feed gas</td>
<td>—</td>
<td>Nitrogen (N₂)</td>
</tr>
<tr>
<td>Substrate temp.</td>
<td>K</td>
<td>373 ~ 873</td>
</tr>
<tr>
<td>Coating thickness</td>
<td>µm</td>
<td>50 ~ 400</td>
</tr>
</tbody>
</table>

*₁ 1.0 corresponds to stoichiometric mixture ratio.

*₂ From exit of combustion chamber.

![Figure 1: Relation between polarization resistance and pitting potential, \( \Delta V'_{c100} \), of HVOF sprayed coatings on low carbon steel SS400 under various conditions, ■: SUS316L, ▲: HastelloyC, and ○: on-shroud HastelloyC. ×: HastelloyC276 and +: SS400 bulk plates.](image-url)
The temperature and flight velocity of sprayed particles were measured by the in-flight diagnostic equipment (TECNAR Co., DPV-2000, St-Hubert, Qc, Canada).

High deformation and low temperature upon impingement of sprayed particles are required for making a denser and less oxidized coating. Deformability depends on the flight velocity of the particle. It is known that the combustion pressure is related mainly to the average flight velocity of sprayed particles and that the fuel/oxygen ratio is related to their temperature. The stoichiometric ratio (= 1.0) is expected to bring about the highest temperature at each mixture amount of fuel and oxygen. Therefore, the deviation from the stoichiometric ratio can make the particle temperature lower. In particular, the reducing ratio over 1.0 could form the less oxidized coating than the oxidizing ratio below 1.0. This is explained by the deduction that the reaction of excess fuel and atmospheric oxygen suppressed oxidation of particles more effectively than the cooling of flame by excess flowing oxygen.

Although shorter spray distance below 380 mm can acquire the higher flight velocity upon impingement, it increased the oxygen content because the deposited coating was heated directly by the flame.

Longer barrel length increased the flight velocity of sprayed particles because the sprayed particle can be accelerated in the long distance. However, simultaneous increase in temperature of sprayed particles caused further oxidation of coatings. The increase of substrate temperature improved the adhesiveness between the substrate and the coating while the oxygen content of coatings increased. On the other hand, the decrease of substrate temperature lead to increase coating porosity while it could not decrease the oxygen content. These phenomena are due to the deduction that wettability of the sprayed particle and target depends on substrate temperature and that the oxygen content of the coating is determined by the degree of the in-flight oxidation of sprayed particles and of thermal oxidation of deposited particles on the surface.

Coating thickness was related to the coating porosity because chances for connecting open pores decreased stochastically as sprayed layers accumulated. In our case, an impermeable coating demanded 200 µm in thickness at least. The coating thickness was also related to the corrosion resistance because the target temperature increased when the spray gun traversed repeatedly. The latter deposited particles were oxidized further and the coating corrosion resistance became lower.

From these results, we obtained the guideline for optimization of the deposition condition to form a dense and less-oxidized coating of anticorrosion alloys by the HVOF spray process. As a general tendency, however, the porosity of the coatings was inversely related to oxygen content open porosity, as shown in Fig. 2.

Post-treatment: We examined the effect of heat treatment and polishing treatment of coatings [1, 3]. As for the heat treatment, the adhesiveness was improved because the diffusion of some elements at the interface between the coating and the substrate made the interface junction ambiguous. In addition, the corrosion resistance of coated steels was improved because disappearance of some pores increased the coating impermeability and because surface oxides of the sprayed particles were gathered and surrounded by the metal particles, in particular at the coating surface, the oxides could be removed by the heat treatment under evacuated atmosphere. The polishing treatment increased the corrosion resistance of coatings mainly because of the removal of the surface layer with a lot of pores appropriate for the starting point of crevice corrosion. In addition, we found out the phenomenon that the impermeability was improved presumably because the pores were filled with the polishing agent and the fine metal powder formed by abrasion. In the actual application, the polishing treatment was considered as effective and inexpensive method.

Gas shroud attachment: In order to realize both the high impermeable and the less oxidized coatings by HVOF spraying, the mechanism that flying particles were surrounded by an inert gas was devised [4,5]. A pipe was attached to one end of the barrel of a commercial HVOF gun, as illustrated schematically in Fig. 3. The inert gas was injected from both the ends of this pipe. This mechanism was termed as the “gas shroud mechanism” or the “shroud mechanism”. It can accelerate the flying particles and simultaneously cool them during spraying. When AISI 316L stainless steel (SUS316L) was used as the feed stock powder, the average flight velocity of flying particles was over 750 m·s⁻¹ and their molten fraction was below 40 mass% [5]. As a result, significantly
denser and less-oxidized coatings were obtained so that this shroud mechanism allows the flying particles to avoid encountering atmosphere in the longer distance than as usual. Adoption of the nitrogen gas shroud mechanism to HVOF spraying also decreased both the through-porosity and the oxide content of the HastelloyC coating. Its through-porosity attained to be zero simultaneously with the oxygen content of 0.2 mass% [2]. Such decreases allowed the corrosion resistance of coated carbon steel to increase relatively up to that of the bulk material of HastelloyC276 in seawater (see Fig. 1). A reaction similar to local corrosion, however, might take place on the surface of this coating. The cause of this phenomenon and its effect on the protective performance of the coating is studied in progress.

Figure 3: Schematic illustration of gas shroud attachment with HVOF spray gun.

Evaluation

Essential corrosion resistance: In general, the corrosion resistance of the coated steel indicated that of entire coating/substrate system. In combination of electrochemically noble coating and less noble substrate, the substrate has a stronger corrosion tendency than the coating, and the substrate corrosion takes place in preference to the coating corrosion because of the galvanic effect, as mentioned above. Accordingly, shieldability or impermeability determines the protective performance of the coating rather than its corrosion resistance. However, if the coating has no penetrating path, i.e. no through-pores, the corrosion resistance of coated steels depends on the corrosion resistance of the coating itself, in other words, the essential corrosion resistance of the coating. Furthermore, it is expected to differ from that of the corresponding bulk material. Therefore, the essential corrosion resistance of the coating was examined in order to determine and extend the lifetime of the coating [3,6]. In our study, the spray materials were deposited onto the bulk plate of the same material as them in order to ignore the contribution of the substrate. The electrochemical impedance technique and polarization measurement were carried out.

A degradation reaction similar to crevice corrosion took place on the pores, especially near the coating surface, where the seawater can permeate, depending on the amount of pores and sensitivity of the spray material to such corrosion reaction, as shown in Fig. 4. In thermal spray process, the existence of boundary or pores between the deposited particles is generally inevitable because the coating is composed of the stacking of small particles. In addition, the pore is liable to remain near the surface so that there was no peening effect by the subsequent sprayed particles. At the depth of such pores, the concentration of dissolved oxygen became small as dissolved oxygen was consumed by the cathodic reaction, leading to change of the surrounding metal particles from the passive state to the active state, indicating initiation and propagation of the corrosion reaction. The chemical composition of the coating is almost identical to that of the feedstock powder except for the oxygen content. The contamination of oxygen to the coating caused the oxidation of coating surface and simultaneous formation of metals different from the feedstock powder in terms of the chemical composition. The surface oxides are not dense and such a metal is considered to be less corrosion resistant than the metal with the original chemical composition. Accordingly, the coating composed of such degraded particles has not as high corrosion resistance as the original metal, e.g. the bulk plate. From these results, we suggested that the higher corrosion resistance of the HVOF sprayed coating demanded the suppression of crevice corrosion near the surface and of particle degradation.

Coating porosity: 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 0.1 vol% under 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.

The through-porosity of such dense coating was determined by using inductively coupled plasma (ICP) emission spectroscopy to analyze substances dissolved from the substrate through the penetrating path composed of connecting pores during immersion in hydrochloric acid (HCl) [7]. Through-porosity depended on coating thickness and on the
sprayed-particle’s stacking structure, as shown in Fig. 5. One coating prepared under a spray condition with the gas-shroud attachment showed zero through-porosity even at about 200 µm thick.

Adhesive property: The adhesiveness between the coating and substrate is important because it is closely related to the problem of peeling off. Although the HVOF sprayed coatings are generally more adhesive than the coatings formed by other spray process, when a coating / substrate couple is exposed to a corrosive media, the interface can be preferentially corroded, leading to the rapid decrease in adhesiveness. The reaction rate of such an interfacial corrosion depended on the micro-gap in the order of 1 nm at the coating / substrate interface, which was estimated by the classical Washburn-Ridiel theory [8]. As shown in Fig. 6, such a micro-gap was detected by fluorescent dye penetration in combination with pin-type tensile test technique according to the following procedure. (1) The coating was formed onto the tensile test holder containing a pin at its center. (2) The fluorescent dye was poured into the hole formed by pulling out of pin from the holder. (3) The coating was detached from the holder. (4) The extent of dye penetration on the holder surface was measured under an UV light illumination.

Molten fraction of flying particles: The surface temperature of in-flight particles during spraying could be determined by using DPV-2000. It was calculated from the amplitude ratio at two wavelengths on the basis of the relation between the temperature and blackbody radiation of substance. This was originally developed for measuring the temperature of ceramic particles by plasma spraying and we should pay attention to apply this technique to metals and alloys. It was reasonable that metal particles were oxidized during spraying and that the calculated temperature may be different from the actual temperature of metal parts. Therefore, we found out simple and highly accurate measuring technique of in-flight particles’ thermal state by their molten fraction [9]. It could be evaluated by capturing the sprayed particles softly by an agar gel as the target material, followed by separating their melted and unmelted parts. A cross sectional view of the sprayed gel shows clearly that spray particles were captured by the gel target separately at a shallow and a deep parts, as seen in Fig. 7. The gels containing the particles captured at each part were separated by shaving with a cutter. The amount of the particles in each part was determined by the chemical analysis and the molten fraction of the sprayed particles was calculated from the ratio of the particle amounts in each part. This technique revealed that the molten fraction of sprayed particles was below 40 % at most in the on-shroud HVOF process, and this comparatively small fraction contributed to form the less-oxidized coating with the impermeable nature [5].

Figure 5: Dependence of dissolution rate of Fe ion from SS400 substrate on thickness of coating, (▲: standard HastelloyC and ●: on-shroud HastelloyC).

Figure 6: Illumination of fluorescent dye after penetration for 3days at the interface between a SUS 316L coating and the substrate. The hole at the center was used to introduce penetrant.

Figure 7: Cross-section of gel target with captured particles.

Marine Durability

In order to demonstrate the protective performance of the coating in the actual marine environment, we have carried out the exposure test of coated steel at Chikura coast, which is situated in the middle latitude of Japan and faced to Pacific Ocean [10]. The test pieces with A4 sheet size were prepared and fixed to 3 height levels of frames at the test site, which are
situated in the splash, tidal and submerged zones. Most test pieces seemed to be corroded faster at the actual marine environment, especially in the submerged zone, than expected from the result of the laboratory tests. This is due to the effect of temperature variation on corrosion rate and the prevention of seawater flow from closing of the pores by the corrosion products. The corrosion amount of the test pieces in the 3 months exposure seemed larger at submerged, tidal and splash zones by turns, as shown in Fig. 8. This result showed that the corrosion rate of the spray-coated steel with through-pores depends on the contact time of test piece and seawater because permeation of seawater is a critical factor for substrate corrosion. On the other hand, impermeable HastelloyC coatings formed by on-shroud spraying kept intact against corrosion attack in all zones for 3 months, as seen in Fig. 8. These coatings had continued to be intact over 10 months in September 2002.

In order to acquire the dense and anticorrosion coatings available in the marine environment, we used HVOF thermal spray method and investigated

1) HastelloyC was a suitable material for HVOF spraying because of its high resistance against thermal oxidation as well as seawater corrosion.

2) Denser and less-oxidized coatings required higher velocity and lower temperature of sprayed particles. Although these are not compatible in general, we overcame this problem by using the inert gas shroud attachment. The characteristic was that the flame was surrounded by the high flow rate inert gas. This gave us the particles with in-flight speed over 750 m·s⁻¹ and molten fraction below 40%. Post-treatment of coating by polishing and heating was effective to increase corrosion resistance.

3) When a coating is impermeable, its essential corrosion resistance determines the lifetime. It was determined by using the specimen prepared by coating on the corresponding bulk material to avoid substrate corrosion by the galvanic effect. The through-porosity of the coating with open porosity below 0.1% was determined by using the highly sensitive chemical analysis of dissolved substance from substrate through the penetrating path composed of connecting pores. The micro-gap at the substrate/coating interface controlled the relation between adhesiveness and interfacial corrosion rate by using the fluorescence dye penetration technique in combination of a pin-type tensile test. Thermal property of in-flight spray particles was revealed by molten fraction of spray particles, determined by quantitative analysis of melted and unmelted particles captured in an agar gel.

4) In the actual marine environment, corrosion of coated steels proceeded faster than expected from the result of laboratory electrochemical tests. The corrosion rate depended on the contact time of the coated steel and seawater. The HastelloyC coating prepared by HVOF spraying attaching gas shroud system demonstrated the excellent protective performance, i.e. no signs of corrosion damage over 10 months.

Acknowledgement

This research has been funded by the Ultra Steel Research Project (STX-21) in National Institute for Materials Science.

We greatly appreciate to Mr. M. Komatsu and Mr. T. Ono for their experimental assistance.

References


