Corrosive Failure Analysis of Thermal Spray Coatings for Advanced Waste-to-Power Generation Plant at Elevated Temperatures

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Abstract

In order to assess an applicability of the thermal spray coating systems as the corrosion-resistant components such as boiler superheater tubes in highly aggressive environment for the high-temperature and high-efficiency waste-to-power generation plant, the corrosive failure analysis was conducted for different kinds of the thermal spray coating systems by HVOF, APS and LPPS, with corrosion-resistant coating alloys such as the 625 and 50Ni-50Cr alloys. On the basis of corrosive failure analysis by means of the metallography and x-ray microanalysis, the failure behaviour of coating systems was found to be classified into three modes according to the morphology of corrosive damage in the coating layer; a consumptive mode A with a general corrosion dominating, an incidental mode B in which the localized attack predominates, and another one is the mixed mode M that is composed of both A and B. Most improved protection against the oxy-chlorination dominating corrosion was found to be attainable for the 625 alloy coating onto the 304 stainless steel substrate by

HVOF followed by the post spraying heat-treatment. Furthermore, it was revealed that highly corrosion-resistant coating system should be obtainable provided for a combination of both the coating processing which can minimize the defect structures such as large numbers of pores together with the pronounced oxide phases incorporated in the coating layer and the post spraying heat-treatment suitable for the compositional and microstructural homogenization of the coating layer which is essential for preventing the localized attack. Coating requirements for the much increased performance against the corrosive attack were discussed from several aspects.

Introduction

Waste-to power generation is one of the most feasible energy recovery means both in the existing waste incineration plants and recently in the combined type systems of thermal decomposition (pyrolysis) and gasification followed by ash melting. In order to improve the thermal efficiency of these waste-to-power generation systems, it is required that the superheated boiler steam temperature to be sent to a steam turbine should be much increased up to around 500℃. This means for the hot section components such as superheater tubes to be subject to much severe and complicated corrosion attack which can be caused by both the aggressive molten salt containing the multi-components of chloride eutectics and the corrosive flue gases also rich in chlorides.

There are several approaches to prevent such a serious high-temperature corrosion problem; (1) modification of boiler design to minimize an ash deposition onto the alloy tube surface, (2) environmental control to mitigate the corrosivity and (3) materials innovation to overcome the corrosive damage. In particular, R&D of the superheater tube materials is a key issue for the advanced waste-to-power generation plant. Consequently, large numbers of research works about the development and evaluation of highly corrosion-resistant superheater materials have been conducted during the last decade in Japan, mainly as the national projects, to introduce

successfully in a practical service [#ref *1-3*]. However, only a limited number of information has been obtainable about an applicability of the protective coatings in spite of its practical importance [#ref *3,4*].

In the present study, in order to estimate an applicability and the requirements of the thermal spray coatings in such an aggressive environment, the corrosive failure analysis was conducted for three kinds of thermal spray coating systems; high velocity oxygen fuel flame (HVOF) spraying, atmospheric plasma spraying (APS) and low-pressure plasma spraying (LPPS), with highly corrosion-resistant coating alloys onto the stainless steel substrate, by means of different evaluation methodologies such as the corrosion mass change, the metallography and x-ray microanalysis.

Experimental

Thermal Spray Coating Systems

Three kinds of the thermal spray coatings; HVOF, APS and LPPS, were adopted onto the annealed 304 stainless steel substrate with the form of the basically disk-shaped specimen.   Specimen was machined to the form of not only a basic geometry with 16mm diameter and 3mm thickness, but also the specially designed geometry of both with a parallel portion of the width 15mm, and with the chamfer of 0.5mm in all the corner (edge), so as to make easily a preparation of cross-sectioning for the metallographic examination without a coating damage, and to avoid inducing preferentially the coating failure such as cracking and spalling from the edge of specimen, respectively. Two kinds of the corrosion-resistant coating alloys; 625 and 50Ni-50Cr alloys, were used as the spraying materials, and the coating thickness was approximately 200μm. Alloy compositions of these coating alloys are listed along with 304 steel for the substrate in Table 1.

A series of the coating processing with different spraying methodologies and materials are denoted with the coating system codes in Table 2. Influence of adopting the post-spraying heat-treatment (annealing) was considered, as also shown in Table 2. Furthermore, three kinds of the thermal spraying conditions basically according to their practical conditions are summarized in Table 3.

Table 1 Chemical composition of 304 stainless steel substrate and coating alloys (mass%).

Alloy		C	Si	Mn	P	S	Ni	Cr	Mo	Fe	Co	Nb+Ta	Others
Substrate	SUS 304	0.05	0.39	1.35	0.03	0.003	8.1	18.2		Bal.			
Coating Materials	50Ni-50Cr	0.01	0.66	0.19	0.001	0.002	Bal.	47.8				1.47	
Coating Materials	Alloy 625	0.04	0.11	0.33	0.005	<0.001	Bal.	21.7	8.82	3.36	0.27	3.75	Al 0.17 Ti 0.32

Table 2 Coating processings.

Code	Grit Blast →	Spray Processing & Materials →	Heat Treatment*
B	No	No-Coated	No
55H	Yes	HVOF/50Ni-50Cr	No
55HA	Yes	HVOF/50Ni-50Cr	Yes(Air)
62H	Yes	HVOF/Alloy 625	No
62HA	Yes	HVOF/Alloy 625	Yes(Air)
62HV	Yes	HVOF/Alloy 625	Yes(Ar)
62A	Yes	APS/Alloy 625	No
62AA	Yes	APS/Alloy 625	Yes(Air)
62L	Yes	LPPS/Alloy 625	No
62LA	Yes	LPPS/Alloy 625	Yes(Air)
62LV	Yes	LPPS/Alloy 625	Yes(Ar)

Table 3 Spraying conditions in HVOF, APS and LPPS.

Item	HVOF	APS	LPPS
Spray System	Diamond Jet	Metco 7MB	Metco 7MB (V)
Power	-	500A /75V	800A /50V
Gases	O_2/C_3H_6 /Air	-	-
Plasma Gases	-	Ar/H_2	Ar/H_2
Atmosphere	in Air	in Air	50hPa in Ar
Spray Distance (mm)	200	100	250

High-Temperature Corrosion Testing

High-temperature corrosion testing was conducted in the laboratory by means of the salt coating methodology [#ref 5], using the corrosion testing apparatus mainly composed of both the main testing zone within a quartz tube heated externally by an electric furnace and the gas supplying and cleansing systems, as schematically shown in Fig. 1. Then, a specimen was pre-coated with a given amount of the actual plant ash corrected from four principal cities of the municipal solid waste (MSW) incineration plants in Japan and blended evenly, of which chemical composition is listed in Table 4. This actual plant ash is characterized from the DTA-TG analysis by having the melting points at 286℃, 342℃, 378℃ and 513℃, suggesting the melting points of a variety of the mainly chlorides and/or partly chlorides-sulphates eutectics. The quantity of ash pre-coated is 40mg/cm² onto the entire specimen surface.
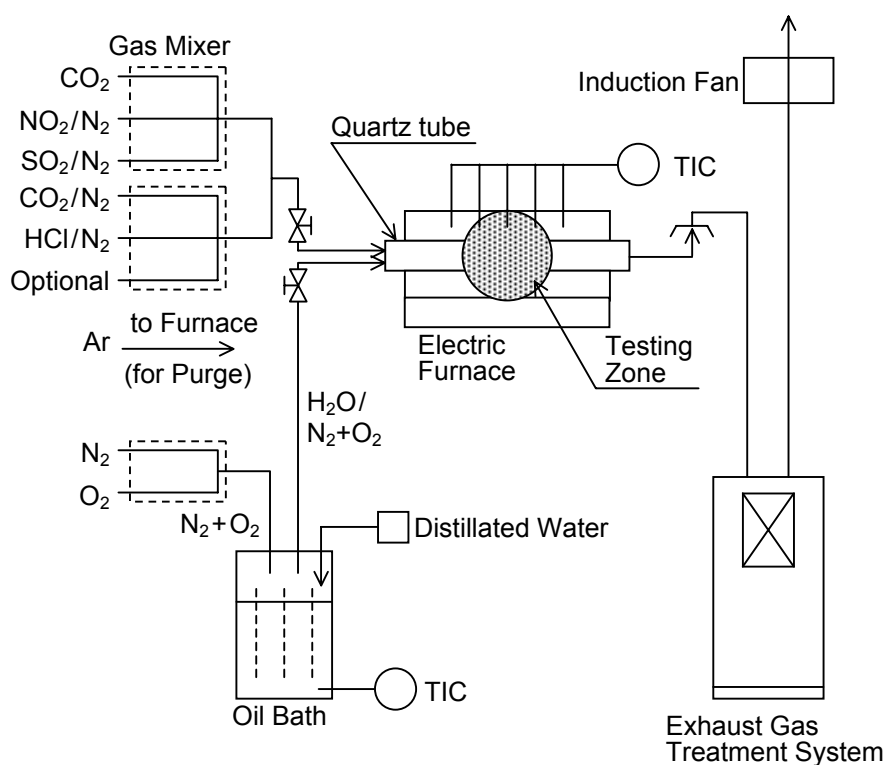
Fig.1 Schematic flow of apparatus for high-temperature corrosion testing.

Table 4 Chemical composition of ash collected from actual four plants (mass%).

Al	Si	Fe	Na	K	Ca	Mg	Pb	Zn	T-S	T-Cl	H_2O
3.80	5.07	1.72	6.43	7.77	14.20	1.56	0.78	1.95	13.45	2.06	0.43

The specimens pre-coated were settled by putting on the alumina boat into the quartz tube and then heated up. Prior to heating, vacuuming and introducing the argon gas was made for purging air from the quartz tube, and then heating was started up. When the temperature was attained to the testing range, the synthetic gas mixture was supplied into the quartz tube with the flow rate of 500cm^3/min. Chemical composition of the flow gas mixture is N_2–10% O_2–10% CO_2–20%H_2O–1000ppm HCl–100ppm CO–100ppm NO–50ppm SO_2 in volume fraction, which is the representative flue gas composition commonly experienced in the actual MSW incineration plants in Japan, and characterized by much higher HCl concentration.

High-temperature corrosion test was carried out at 450℃ and 550℃ which should correspond for enduring to the steam temperatures of 400℃ and 500℃, respectively. Both the isothermal corrosion tests for up to 200h and the thermal cycle corrosion tests of 50h-4cycles by the repeated coating with the same amount of ash were conducted. The corrosion testing was conducted by three times; using three specimens for each coating system, for the same testing condition. After the test, almost all the specimens were subjected to an electro-chemical descaling in the molten Na_2CO_3-NaOH salt followed by the mass measurement to determine the conventional corrosion mass change, except for the specimen sending to the x-ray microanalysis without descaling. Furthermore, the metallographic examination also was conducted at the cross-sections of all the specimens to determine quantitatively the different aspects of the corrosive damages, as described later in detail.

Results

Corrosion Mass Loss for Different Coating Systems

Figure 2 shows the corrosion mass losses for different kinds of the coating systems along with no-coated 304 steel obtained from both the isothermal corrosion test for 200h and the thermal cyclic corrosion test of 50h for 4 cycles, at 450℃ and 550℃. Here, the symbol * denotes that a part of the coating layer has experienced an exfoliation during mainly the descaling process. It is apparent that the corrosion mass loss is much significant under the conditions both at higher temperature of 550℃ and of the thermal cycling, suggesting the harmful effect of both an increased temperature and a thermal cycle on the coating failure. So long as the comparison of coating systems is concerned, HVOF and LPPS systems followed by the heat-treatment mainly in vacuum; such as 62HV and 62LV, exhibit generally a sound performance with the relatively reduced mass loss and without a coating exfoliation.

According to such an evaluation methodology based of the mass change, however, no information can be obtainable at all about the corrosion morphology and more importantly about the steel substrate.
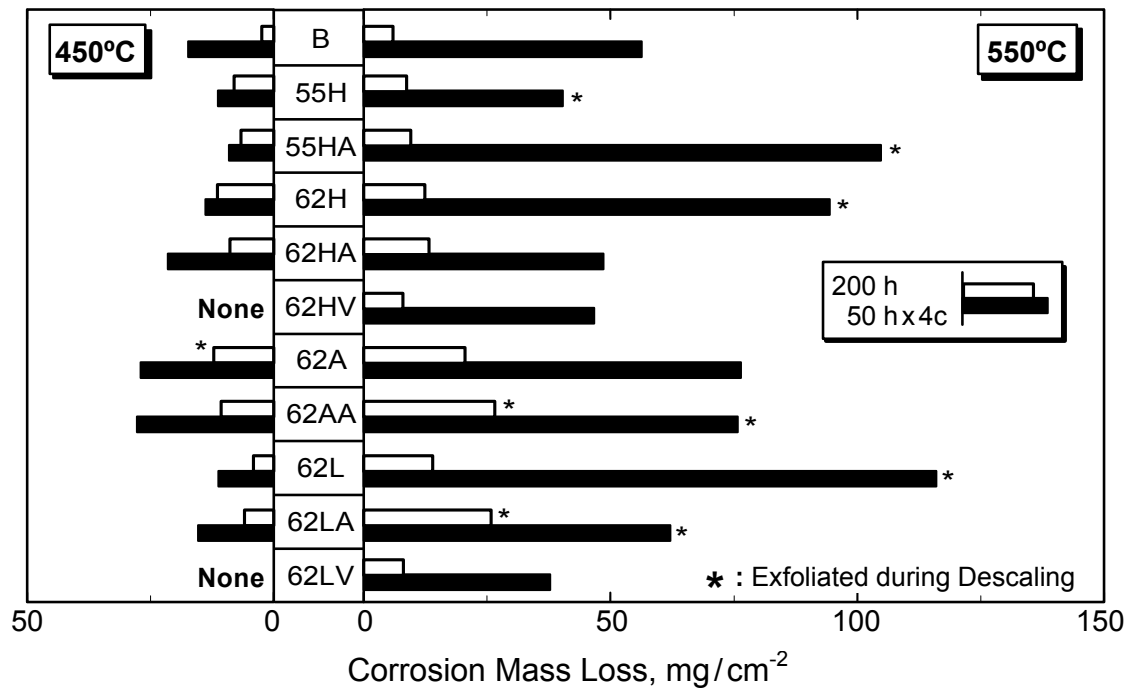
Fig.2 Corrosion mass loss of different coating systems and the un-
coated 304 steel (B).

Morphological Features of Corrosive Failure

From the metallographic examination at the cross-sections of all the
specimens in detail, the corrosive failure behaviour of different coating
systems was revealed to be classified generally into three modes by
virtue of the failure morphology in such an aggressive environment.
These three modes of failure behaviour are summarized schematically
in Fig. 3. Thus, the mode A is of the consumptive manner in which a
general corrosion is dominating in the coating layer. This mode was
representative for the HVOF systems with both 50Ni-50Cr (55H) and
625 (62H) alloys.

The mode B is of rather localized manner in which a localized
corrosion can occur preferentially along a number of defects such as
the pores and oxide micro-channels pre-existing in the coating layer
to be attainable rapidly to the steel substrate, prior to the general
attack progresses. In this case, a premature degradation in the
protective function of coating should be most significant, since the
localized attack toward the steel substrate and along the
coating/substrate interface tends to bring about a premature
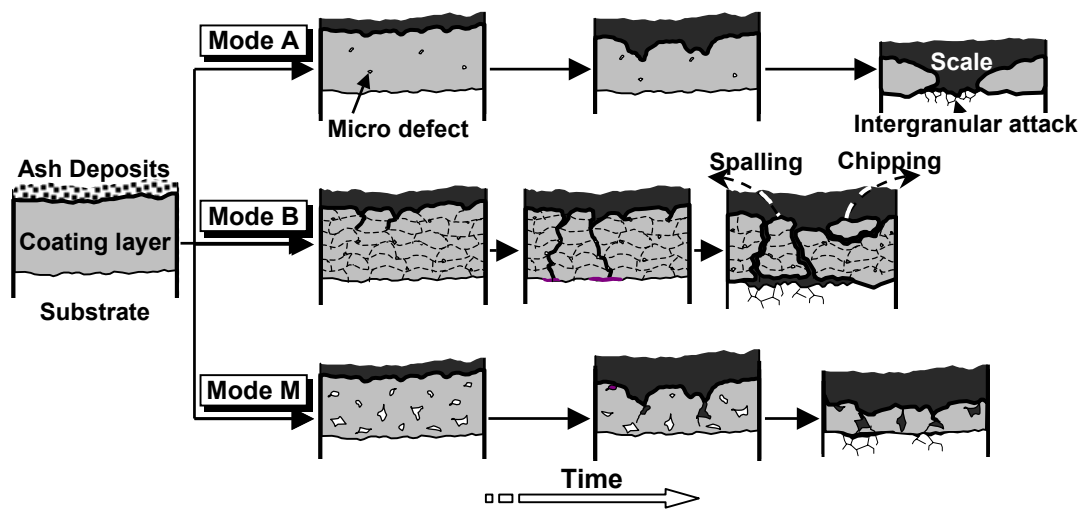exfoliation at the interfacial region, in spite of for the other coating

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Fig.3 Three modes of the corrosive failure behaviour observed in different coating systems at 450°C and 550°C.

portion remaining in sound. APS system with alloy 625 (62A) exhibited this mode of failure behaviour.   Third one is the mode M having commonly the mixed characteristics of both modes A and B. A part of the LPPS systems with alloy 625 (62L) is included in this mode.

Metallographic Evaluation of Corrosive Failure in Coating Systems

In order to evaluate appropriately both a variety of the coating failure modes and the information about the corrosive damage of steel substrate, a reasonable measurement methodology should be proposed with taking into account for the information both about the coating failure and about the depth of attack into the steel substrate. Figure 4 denotes the schematic illustration showing the measurement concept proposed in this study for different aspects of the corrosive failure observed in the coating systems. Then, the coating/substrate interface can be regarded as an apparent base line on the cross-section, and the outward and inward measurements from there should be indicative of the remaining coating thickness and the depth of attack into the steel substrate, respectively. A microscopic measurement was actually made for the representative ten fields of view on the whole specimen cross-section at a magnification x100.
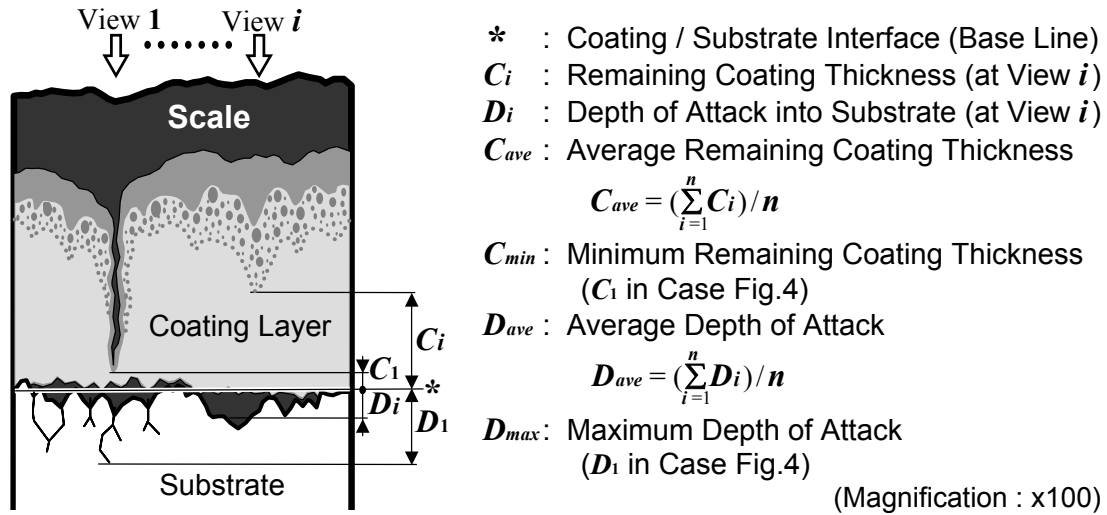
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* : Coating / Substrate Interface (Base Line)
C_i : Remaining Coating Thickness (at View i)
D_i : Depth of Attack into Substrate (at View i)
C_{ave} : Average Remaining Coating Thickness

$$C_{ave} = \left(\sum_{i=1}^{n} C_i\right)/n$$

C_{min} : Minimum Remaining Coating Thickness
(C_1 in Case Fig.4)
D_{ave} : Average Depth of Attack

$$D_{ave} = \left(\sum_{i=1}^{n} D_i\right)/n$$

D_{max} : Maximum Depth of Attack
(D_1 in Case Fig.4)

(Magnification : x100)

Fig.4 Concept of measuring methodology for different aspects of the corrosive failure in coating systems.

Figures 5 and 6 show the results obtained from the metallographic measurement for all the coating specimens at 450℃ and 550℃, respectively. Here, the information both about three modes of the corrosive failure denoted in Fig. 3, and about the corrosion morphology in the steel substrate are also noted. It was revealed that higher temperature testing of 550℃ results in the more significant corrosive damage both in the coating layer and namely in the steel substrate as compared to the case at 450℃. As regards an influence of the coating system, HVOF systems with alloy 625 which were follower by an appropriated heat-treatment in air or in vacuum; such as 62HA and 62HV, showed the minimized corrosive damage into the steel substrate, which is corresponding to the relatively mitigated coating failure. It is also apparent that the beneficial effect of HVOF is more pronounced in the combination with alloy 625 as compared with 50Ni-50Cr alloy. APS and LPPS systems with 625 alloys; such as 62A and 62L series, on the contrary, very rapid coating failure and consumption occurred according to the modes of either B or M to cause subsequently the significant corrosion attack into the steel substrate.

It is also indicative from Fig. 6 that an isothermal corrosion condition tends to bring about for the coating systems rather increased corrosive attack into the steel substrate as compared to the case of a
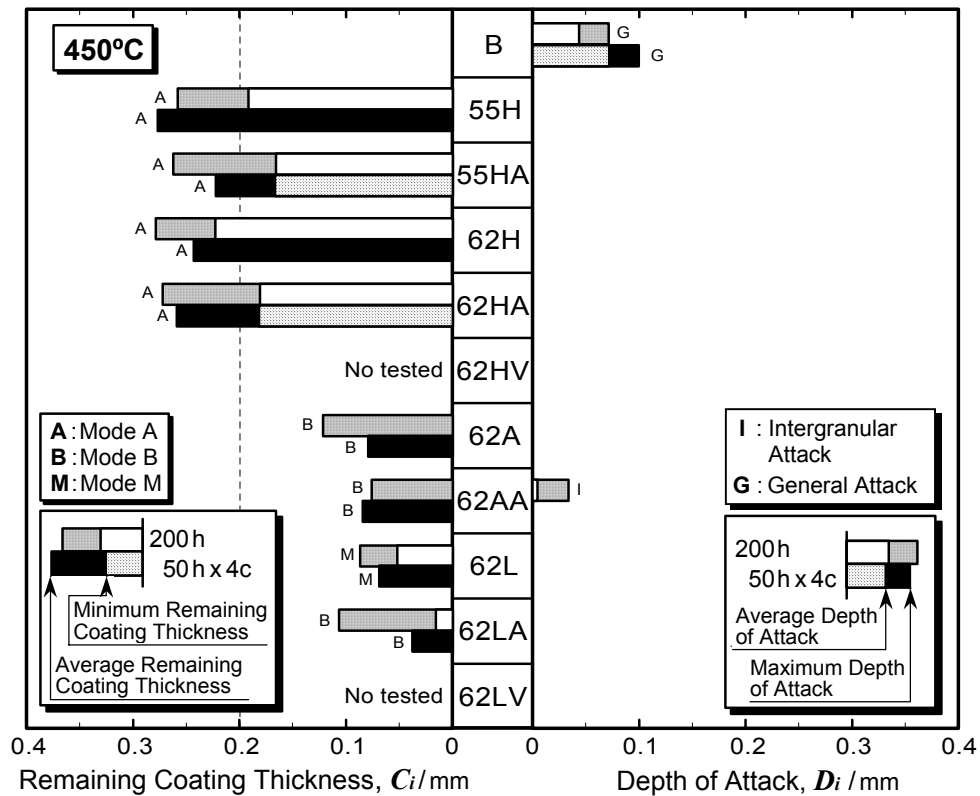
Fig.5　Result of the microstructural evaluation of corrosive failure both in coating layer and into steel substrate of various coating systems at 450°C.
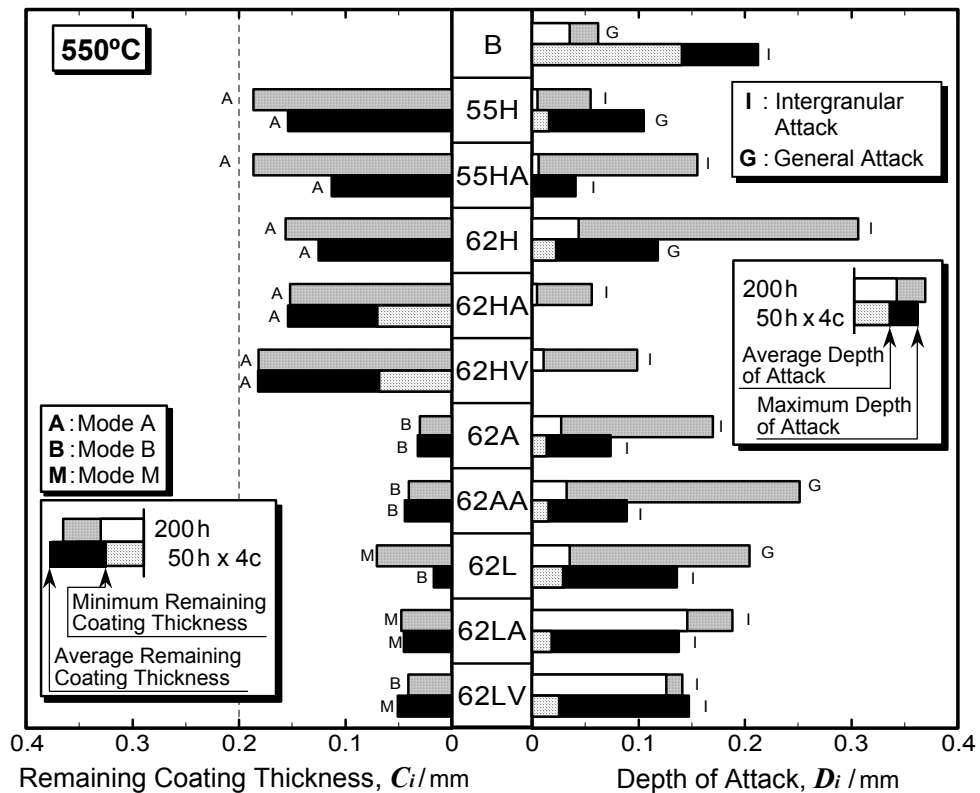

Fig.6　Result of the microstructural evaluation of corrosive failure both in coating layer and into steel substrate of various coating systems at 550°C.

cyclic corrosion, while for the no-coated 304 steel (B) the reversed result is obtainable. This might be attributed to the fact that a corrosive attack can be active for extending the corrosion front persistently for 200h under the isothermal condition, whilst under the thermal cycle condition the corrosive action must be interrupted at every thermal cycling of 50h by virtue of the solidification and modification of the molten phase in the ash constituents so as for the renewed ash to penetrate once again from the coating surface toward the corrosion front of the steel substrate. Anyway, it appears certain that the thermal cycling should be least harmful to the coating degradation such as an exfoliation for the thermal spray coating layer.

Figure 7 shows the representative micrographs by the backscattered electron (BSE) image at the cross-sectional surface zone of the two kinds of coating systems; 62HV and 62L, after the isothermal corrosion test at 550℃ for 200h. It is evident that both the integrity and protective effect of coating layer is superior for 62HV rather than for 62L. In 62HV which showed the failure behaviour of mode A, namely, distribution of the large scale defects was minimized, although even in this coating system the chloride-induced corrosion can be already attainable partly to the coating/substrate interface probably along the micro-channels such as the incorporated oxides lamella in the coating layer. In 62L which showed the mode M of failure behaviour, on the contrary, there are a number of the relatively
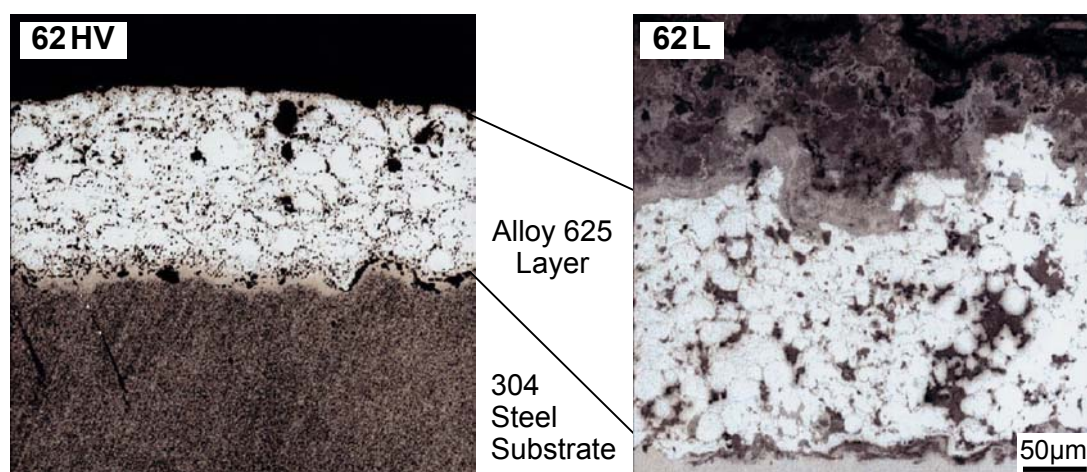

Fig.7 Backscattered electron (BSE) images at the cross-sectional surface zone of coating system 62HV and 62L specimens subjected to high-temperature corrosion at 550°C for 200h.

large pores in the coating layer capable of providing the preferential penetration path for the corrosive constituents such as chlorides. This situation observed in 62L is essentially similar to the case of APS system; such as 62A, which has shown the mode B of failure behaviour [#ref*3*].

Discussion

Influence of Coating Materials on the Corrosion Protection

From the result of quantitative corrosion failure analysis in Fig. 6, a protective effect of the coating materials by the same HVOF spraying was found to be different between alloy 625 and 50Ni–50Cr alloy; the former is much superior to the latter. In general, 50Ni–50Cr alloy is certainly regarded as one of the most corrosion–resistant alloys in the oxidation–dominant corrosive environments. In the aggressive environment which an oxy–chlorination may dominate as in this study, however, 50Ni–50Cr alloy becomes highly reactive to form easily the very volatile oxy–chlorides such as for example CrO_2Cl_2 [#ref*2,6*]. This suggests that increasing merely in the Cr content should be less effective for preventing the corrosive failure in the waste–to–power generation plants, because of the preferential reaction and consumption of the beneficial Cr [#ref*2*]. On the contrary, alloy 625 has been evaluated as the highly corrosion–resistant alloy in such an aggressive environment mainly by virtue of the good compositional balance composed mainly of Cr–Ni–Mo [#ref*6*]. Consequently, alloy 625 appears to be effective also as the spray coating material, provided for an appropriate control of the composition and microstructure in the coating layer.

Effect of Spraying Methodology on the Corrosion Protection

It was clarified that the protective effect in the coating system is strongly dependent on the defect structure such as pores and oxide phases incorporated and its population in the coating layer. Namely, HVOF spraying produces the highly densified coating layer with the minimized oxidation reaction mainly by virtue of the very high speed impingement of the half–melting splat onto the substrate surface. Figure 8 shows the comparison of the cross–sectional coating microstructures made by three kinds of the thermal sprayings. It was

revealed from the image analysis on the coating cross-sections that the average values of an apparent density of the defects such as pores and including the grey phase of oxides are approximately 13%, 37% and 16% for HVOF, APS and LPPS systems with alloy 625, respectively. It is surprising for the LPPS system has relatively higher density of defects as compared with the HVOF system. However, there are also a number of the experimental evidences that the coating layer made by HVOF spraying can be much densified so as for the distribution of through-porosity to be negligible [#ref7]. Anyhow, the HVOF spraying should be able to bring about the coating layer with a high performance barrier function against the penetration attack even in such an aggressive environment [#ref4].
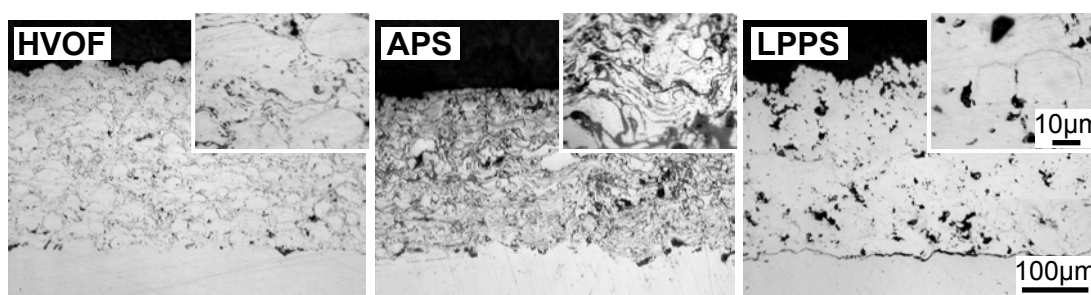

Fig.8 Comparison of the cross-sectional microstructures for different coating systems after spraying.

Effect of Heat-Treatment after the Spraying

From the corrosive failure analysis for different kinds of the coating systems, a beneficial effect of adopting the heat-treatment after the spraying was found to be pronounced only for the HVOF systems with alloy 625. For APS and LPPS systems with alloy 625; such as 62A and 62L series, on the contrary, an improvement of the corrosion protection by heat-treatment was hardly expected. These facts suggest that the beneficial effect of heat-treatment is strongly dependent on the inherent nature of coating layer; such as the density and population of different kinds of defects. Then, the inherently high-quality coating layer such as by HVOF spraying can be additively modified by adopting the heat-treatment both through the compositional equalization and microstructural control, which should

be much effective to remove the short circuit or easy penetration path for the corrosive constituents such as chlorides.

Conclusions

(1) The corrosive failure behaviour of the thermal spray coating systems by HVOF, APS and LPPS with 625 and 50Ni-50Cr alloys can be classified into three modes, according to the morphological features of corrosive damage in the coatings.

(2) The most improved corrosion performance was obtainable for the HVOF systems with alloy 625, with annealing heat-treatment after the spraying.

(3) Coating requirements for the much improved performance against the corrosive failure were discussed from the compositional and microstructural aspects of the coating through the spraying methodologies and materials along with heat-treatment.

Acknowledgments

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