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Application of High Temperature Corrosion-Resistant Materials and Coatings Under Severe Corrosive Environment in Waste-to-Energy Boilers

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Corrosion-resistant materials (CRMs) and coatings are key technologies to increase power generation efficiency and reduce maintenance in waste-to-energy (WTE) plants. Corrosion environment became severe as steam temperatures have increased. The steam condition of more than 400 °C/3.9 MPa became possible in WTE boilers by using highly durable corrosion-resistant coatings, such as thermal spray of Al/80Ni20Cr alloy, HVOF-sprayed NiCrSiB alloy, Alloy 625 weld overlay for waterwall tubes and also superheater tubes. Also, the use of 310S type stainless steels and high Cr-high Mo-Ni base and high Si-Cr-Ni-Fe alloys have progressed because of a better understanding of corrosion mechanisms. Furthermore, high durability coatings using cermet and ceramic materials were applied to high temperature superheaters. This paper describes the major developments and the application of CRMs and coating technologies in the last 30 years in WTE plants, the corrosion mechanisms of alloys, the deterioration mechanisms of spray coating layers, and future subjects for the development of corrosion-resistant materials and coatings.

Keywords corrosion monitoring, corrosion testing, corrosion-resistant materials, high-temperature corrosion mechanisms, Ni-base alloy, protective oxides layer, spray coating, waste-to-energy plants, weld overlay

1. Introduction

Promotion of waste recycling aims at a high level of material recirculation and reduction of environmental load such as CO_2, and dioxins are worldwide required. The concepts of higher efficiency waste-to-energy (WTE) plants and waste gasification and ash melting power generation plants are positioned in the center of recycling by means of thermal processing. The steam condition of 400 °C/3.9 MPa for WTE boilers has become the major development from the conventional condition of 300 °C/2.9 MPa and the first plant generating steam at 500 °C/9.8 MPa has achieved continuous operation for over 5 years in Japan (Ref 1). In the past, for the superheater tubes (SHTs) of the WTE boilers, where there is a severe high-temperature corrosion (HTC) environment containing a large amount of chlorides, the plants were operated by frequently replacing relatively inexpensive metal tubes. However, nowadays a high total cost performance is required in the storm surrounding the society such as the globalization of economy, and the strict pollution regulations. Therefore, the development of low-cost and highly durable materials and application processes have become issues that are essential for the a high thermal efficiency and economy of WTE plants.

In recent years, SHTs made of corrosion-resistant materials (CRMs) have been progressively used for reduction of maintenance. Also for the waterwall tubes (WWTs), the application of the corrosion-resistant coatings (CRCs) has been widespread, such as metal spray coating of highly corrosion-resistant Ni-base alloys, and weld overlay of Alloy 625, in order to reduce maintenance. Furthermore, new combustion systems to reduce dioxins and the development of the pyrolysis and gasification-melting furnaces have formed a field of new waste treatment systems. This report describes recent trends on the application of CRM and CRC technologies in severe HTC environment, the effect of alloying elements, the corrosion mechanisms in the WTE boilers, and the potential for further developments.

2. Corrosion Environment of WTE Boilers

In most WTE plants, the steam condition of 300-450 °C/2.9-5.8 MPa shown in Fig. 1 is adopted to avoid the corrosion damage of boiler tubes and assure stable operation. Due to a big change in life and production styles brought about by technological and economic development, the properties of the waste and the WTE plant operation have changed as follows (Ref 1):

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1. Strict pollution regulation: low O_2 operation, high temperature of combustion chamber, rise of plant operating rate, etc. to prevent generation of NOx and dioxins.
2. Energy saving and effective utilization of waste heat: severe corrosion environment due to improvement of heat efficiency such as high-temperature and high-pressure (400-500 °C/3.9-9.8 MPa) of boilers, etc.
3. Need to reduce volume of ash and produce non-polluting ash have led to the development of next generation plants, such as pyrolysis gasification-melting furnaces (Ref 2), oxygen-enriched combustion, etc.
4. Improved cost performance: Reducing cost of operation and advances in maintenance-free operation, such as advanced combustion control and monitoring technologies.

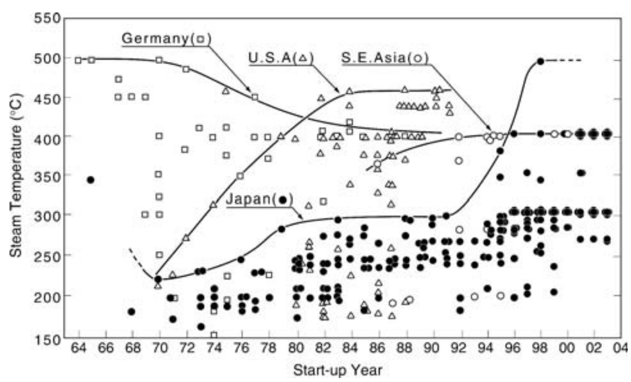

Fig. 1 Trends in steam temperature of WTE boilers

As various substances including incombustibles as well as combustibles such as woods, paper, plastics, etc. are mixed in the waste, the fluctuation of gas temperature and composition is larger than that in boilers combusting fossil fuels; also, a lot of low melting point deposits containing high concentration of chlorides is generated in the combustion gas. Figure 2 shows the explanatory drawing of factors of the HTC environment (Ref 3). Dusts containing high concentration of alkaline metals (Na, K, etc.), heavy metals (Pb, Zn, etc.), chlorides and sulfates adhere and deposit on the material surfaces exposed in the combustion gas, and severe corrosion is caused of the high-temperature components such as SHTs by ash deposits melting at 300-550 °C. Furthermore, on the WWT surfaces where the gas temperature is very high (850 °C or higher), the adherence of high concentration chlorides on the surface is promoted, and the corrosion damage is caused mainly by chlorination reactions. Also, a the metal temperature of SHT is as high as 300-550 °C salt deposits are easily molten, and corrosion rate as high as several mm/year or more is observed sometimes. Figure 3 shows the increase in corrosion rate of SHTs due to increase in the gas temperature (Ref 4). The metals are corroded by general corrosion and also intergranular corrosion and localized corrosion when the molten adhering ash causes the break-down of the protective oxide layer and attack even high corrosion-resistance alloys (Ref 5).

Both the adherence of dust constituents, such as strongly corrosive chlorides and sulfates, and the temperature

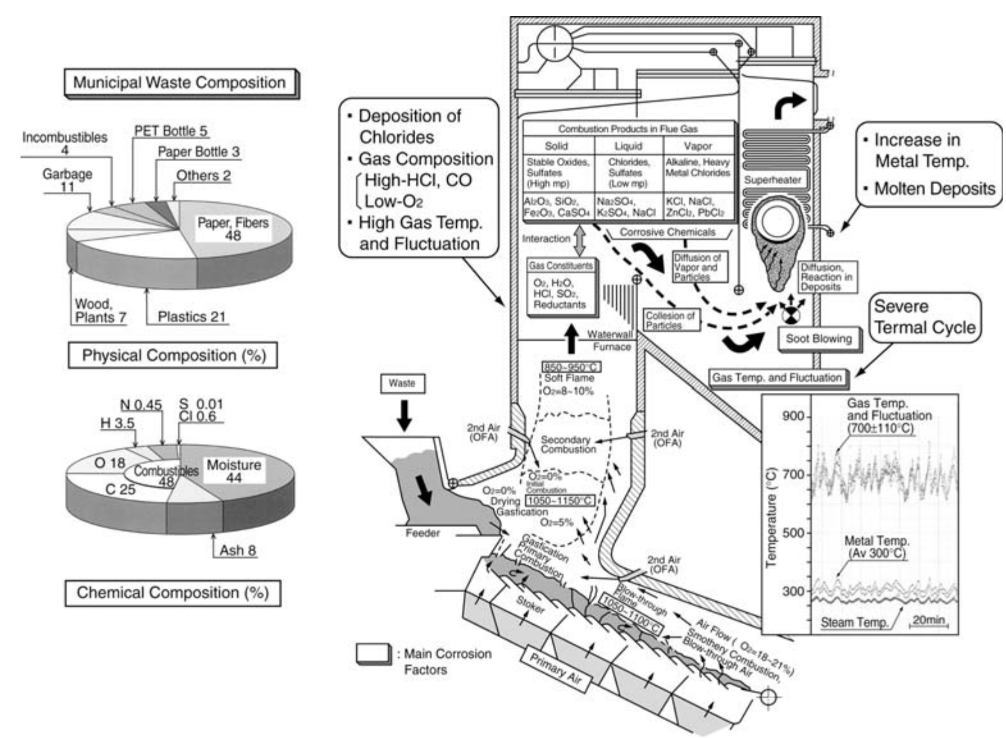

Fig. 2 Formation of corrosion environment in WTE boilers

fluctuation can be reduced by lowering the combustion gas temperature introduced into the SHTs, to less than 650 °C. The reduction in gas temperature is effective for stabilization of protective oxides layer on the metal surface. However, it is known that the soot blowers that are used for the purpose of dislodging deposits that decrease heat transfer may result in severe thermal cycling condition and even the protective oxides layer break down.

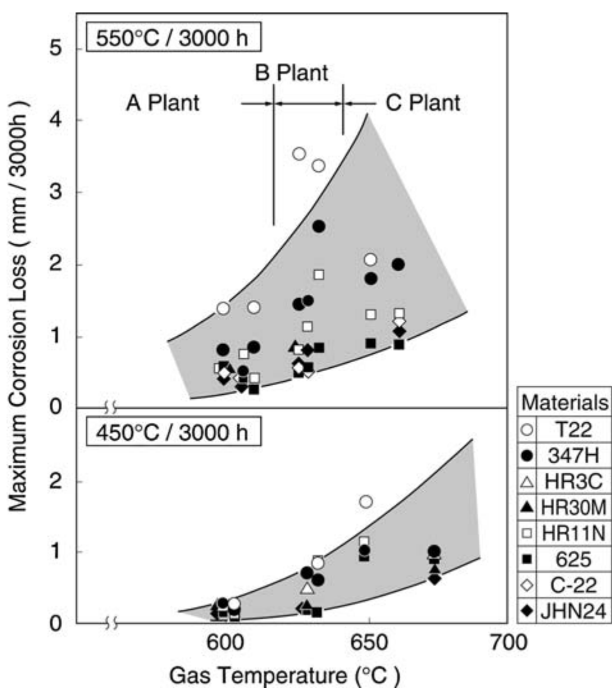

Fig. 3 Change in maximum corrosion thickness loss of superheater materials with gas temperature (metal temperature: 450, 550 °C)

3. Advances in HTC-Resistant Materials and Coatings

In response to the above-mentioned severe corrosive environments, the development and application of new CRMs and CRCs, corrosion resistance testing and evaluation methods, and methods for the analysis of corrosive environments have advanced, as shown in Fig. 4. and described below.

3.1 CRCs for WWTs

The metal temperatures of the WWTs are as relatively low as approximately 230-330 °C (2.9-9.8 MPa), depending upon the steam pressure. Here CRCs such as metal spray coatings, weld overlay, or the cladding with highly CRMs on the outer surface are applied on the base material of carbon steel as shown in Fig. 5. Table 1 shows the application examples of various CRCs to the WTE boilers.

3.1.1 Spray Coating. The metal spray coating of CRMs to thickness of 150-500 μm can be applied on site relatively quickly and at low cost. The actual application of mainly Al/80Ni20Cr alloy flame spray coating on WWTs started in 1985 (Ref 17). NiCrSiB alloy sprayed by the high velocity oxygen fuel (HVOF) process with high durability was also developed (Ref 18, 44, 6). HVOF coatings have been applied in over 50 WTE plants in Japan. In Europe and the United States, testing in actual plants was conducted for WWTs and SHTs (Ref 7-12). The spray coating systems (applied both off-site and

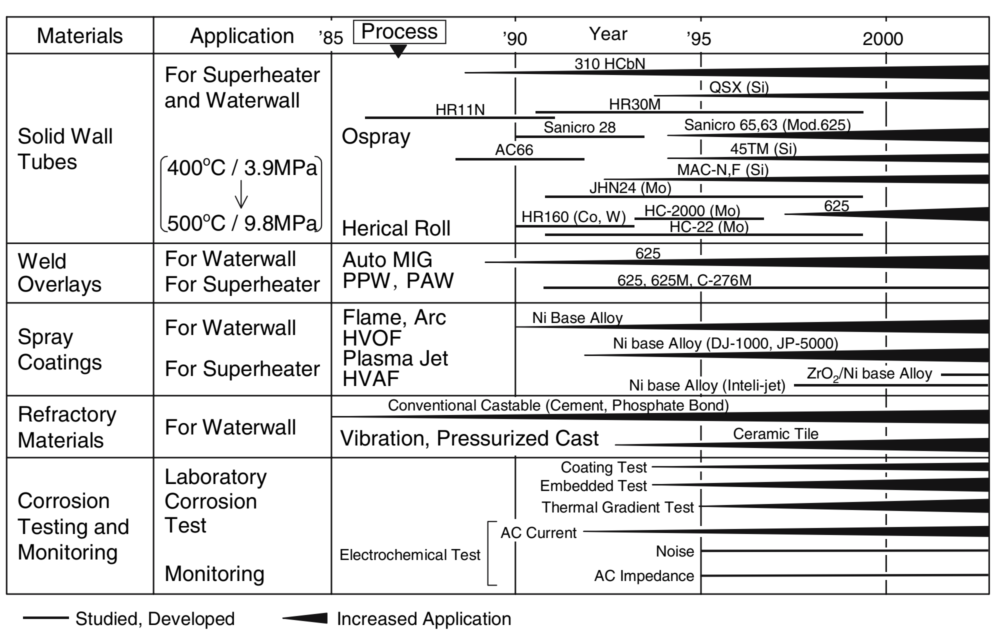

Fig. 4 Development and application of WTE material technologies

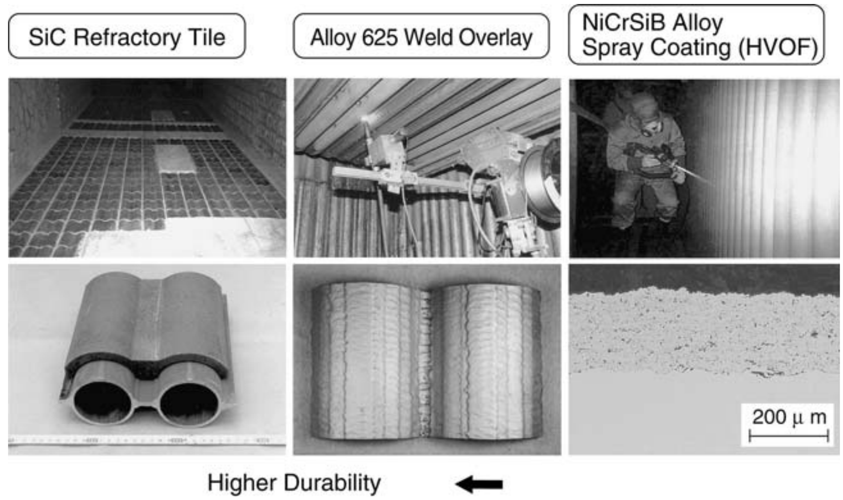

Fig. 5 Application of corrosion-resistant coatings to waterwall tube

Table 1 Durability of corrosion-resistant coatings in WTE boilers

		Applied condition, °C				
Coating process	**Chemical composition, materials**	**Parts**	**Metal**	**Gas**	**Durability, yr**	**Ref**
Widely overlay						
MIG	21Cr-9Mo-3.5Nb-Al,Ti-Ni base (Alloy 625)	WW, SH	270-330	700-1000	>10	Ref 20
PPW	18Cr-14Mo-4W-Ni base (C-276M, 625M)	SH	470-510	510-650	(≈625)	Ref 15
MIG	23Cr-16Mo-1.6Cu-Ni base (HC-2000)	WW, SH	260-480	870-1730	(0.52mm/y) (>625)	Ref 45
PAW	Alloy 625	SH	470-530	510-650	>1	Ref 19
Laser cladding	625, HC-22, NiCr 309L, 686 etc	WW	(Coal fired black liquor)		…	Ref 46
Spray coating, Flame						
Flame	Al/80Ni20Cr	WW	230-300	700-900	>3	Ref 17
Flame/fused	10Cr-Si, B-Ni base (12C)	SH	370-540	…	>1	Ref 17
Spray coating, Plasma						
Plasma/fused	15Cr-Si, B, Fe-75Ni base	WW	230	700-800	4	Ref 12
Spray coating, HVOF						
Hybride cap	18Cr-5Fe-5Nb-6Mo-Ni base (diamalloy)	SH	370-540	…	>0.4	Ref 18
DJ-1000	17Cr-4Fe-3.5B-4Si-Ni base (no-fused)	WW, SH	230-330	700-900	>3	Ref 44
DJ-Gun DJ-1000	$50TiO_2$-50 Alloy 625 (cermet)	SH	430-460	500	>3	Ref 6
JP-5000	17Cr-4Fe-3.5B-4Si-Ni base	WW	230	700-900	>3	…
Spray coating, Plasma jet						
Modified PJ	ZrO_2/Alloy 625, NiCrSiB alloy	SH	430-500	510-650	>3	Ref 13

WW (Waterwall), SH (Superheater).

on-site) are selected in accordance with the workability, the severity of corrosion environment, the required lifetime and the cost. The use of HVOF is prevalent. More recently, plasma jet coating system of ZrO_2/Ni base alloys were developed and applied on SHT operated at 500 °C/9.8 MPa WTE boilers (Ref 13).

3.1.2 Weld Overlay. As a dense coating layer that is chemically bonded with the base metal and as thick as several millimeters can be obtained by the weld overlay, the durability of weld overlays is higher than for thermal spray coatings. Alloy 625 weld overlays possess an excellent corrosion resistance and welding workability. Application started in around 1990 mainly on-site, and it is reported that the durability is 10 years or longer (Ref 14). Table 1 shows the list of weld overlay materials and processes that are now actually applied (Ref 15, 19, 20, 45, 46). In many cases of the WWTs, MIG automatic welding and shielded arc welding are adopted for both on-shop and on-site applications. For the SHTs, MIG welding and plasma powder welding (PPW) are applied, and the tube bending processing can be done even after weld overlay. For the 500 °C/9.8 Mpa, high efficiency boiler WWTs, the maximum corrosion loss rate of approximately 0.1-0.2 mm/year has been observed under metal temperatures of 330 °C by the 2-year field tests as shown in Fig. 6; the durability of these coatings for 15 years or longer has been verified (Ref 20).

3.1.3 Composite Tubing. Mainly in Europe, composite tubings with cladding of CRMs (outer tube) to carbon steel (inner tube) are used for WWTs and SHTs. There is

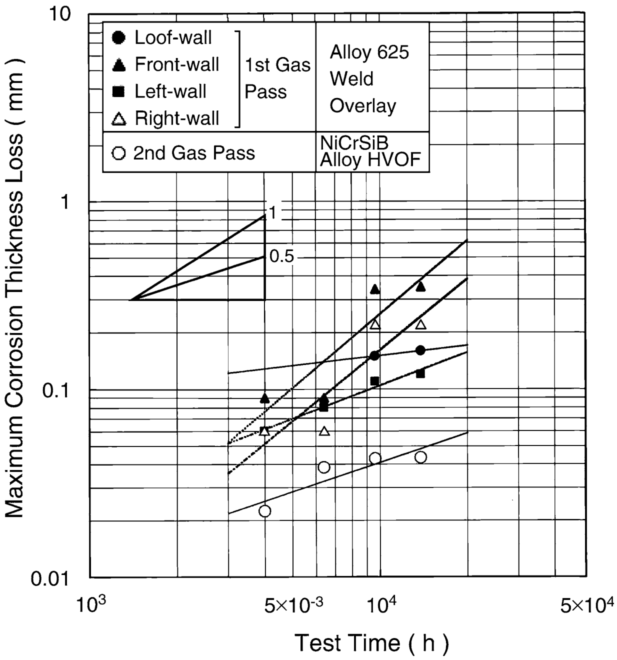

Fig. 6 Maximum corrosion thickness loss of weld overlay and HVOF coating on waterwall tubes of 500 °C/9.8 MPa boiler

a lot of application experience of high Cr-high Mo-Ni base alloy including Alloy 625 (Sanicro 63); a detailed experience survey has been reported for the durability of these systems (Ref 16, 21).

3.1.4 Refractory materials. Refractory tiles with longer lifetime than conventional castable refractory materials have been developed and used. As shown in Fig. 5, high-SiC tiles and sometimes high Al_2O_3 tiles are used in many cases. Basically, the tiles are installed by hanging or fixing to the outer surface of the WWTs and the surface of the tile reaches temperatures of approximately 900 °C or lower. The materials, production method, shape and installation method, are determined on the basis of evaluation of the oxidation resistance, thermal shock resistance, etc. in the high-temperature combustion gas.

3.2 Corrosion-Resistant Alloy Tubes and Coatings for Superheaters

The alloy design of seamless tubes for use as SHTs takes into consideration both corrosion resistance and heat-resistant characteristics. Furthermore, excellent weldability and plastic workability etc. are required for fabrication of the boilers. Generally, at temperatures of approximately 350 °C or lower, carbon steel is used. In the high-temperature region of 400 °C or higher where high corrosion resistance is required, Fe base and Ni-base austenitic materials (Table 2 and 3) are tested and used (Ref 27-39). Field corrosion tests have shown that the addition of alloying elements such as Mo, Nb, Si to Ni-Cr-Fe alloys is effective for corrosion resistance (Ref 22). The main corrosion-resistant alloys currently developed and applied are described below.

3.2.1 High Cr-High Ni-Fe Base Alloys. Austenitic stainless steels such as 309S and 310S of 25Cr-14-20Ni alloys (Ref 23) or 310HCbN (Ref 20) and NF709 (Ref 24) which are modified 310S alloys, are mainly used for 400 °C/3.9 MPa boilers. Since the difference of the corrosion resistance in Ni-Cr-Fe alloys is small among the various materials under the steam conditions below 450 °C, as shown in Fig. 7 (Ref 2, 25), 310S and modified 310S are selected because of their lower cost. Alloy 825, Sanicro 28 (composite tube) of 20-30 Cr-30-40Ni alloys are sometimes used by the high thermal efficiency plants in Europe, the United States and southeast Asia (Ref 26, 27).

3.2.2 High Cr-High Mo-Ni-Base Alloys. Alloy 625 and Sanicro 63 (composite tube) have an excellent corrosion resistance under high-temperature steam conditions of 450 °C or higher (Ref 16, 20, 21). Also, it is known that HC-22 and JHN24 (Ref 20, 25, 33) alloys, whose Mo content is higher than Alloy 625, show excellent corrosion resistance. For these high Mo containing alloys, it is required to take into consideration in the material selection that age deterioration of material may occur at high metal temperatures.

3.2.3 High Si-High Cr-High Ni Alloys. QSX3 (Ref 36) and QSX5 (Ref 37) are modified 310S alloys by adding Si of approximately 3%. It is known that Nicrofer 45TM (Ref 39) is used industrially and demonstrates good corrosion resistance. Furthermore, MAC-F and MAC-N alloys containing high Cr, high Ni, Fe and 4% Si, have lasted for 4 years in the 500 °C/9.8 MPa SHTs (Ref 28). High Si alloys have some difficulties from viewpoint of tube manufacturability, weldability and micro structural stability, but these MAC-F, N alloys have demonstrated good performance by optimization of the alloying elements for metals used in WTE boilers. Figure 8 shows an example of the corrosion rate of both Fe base and Ni-base alloys in field tests over 4 years (Ref 28). The corrosion resistance of materials (Ref 1) varies according to the locations in the superheaters, where corrosion environments are different. It is therefore necessary to make best use of the materials in accordance with the corrosion environment.

3.2.4 CRCs for Superheaters. In SHTs, corrosive condition is more severe than on WWTs due to higher metal temperatures and the presence of molten salts. Figure 9 shows the microstructures of TiO_2-Al_2O_3/625 cermet HVOF coating exposed for approximately 2 years in WTE superheaters (Ref 6). Remarkably low thickness loss and penetration of corrosive matter were observed and long-term durability of over three years was conformed. Furthermore, ZrO_2/625 dual layer system applied by the plasma jet process also showed large bonding strength (Fig. 10) after 2 years exposure in 500 °C high-temperature SHTs. Application of ceramics is considered to be effective to improve the durability in spray coatings (Ref 13).

Table 2 Ni-Cr-Fe-(Mo) alloy tubings tested and applied to WTE boilers

Trade Name	Shape of tubes (maker)	Chemical composition, mass %													Tensile properties, RT			Parts	References
		C	Si	Mn	Cr	Ni	Mo	Fe	Nb+Ta	N	Al	Ti	Cu	Others	TS, kgf/mm²	YS, kgf/mm²	E, %		
Alloy 825 (SB423)	Solid wall, composite (ASME)	≦0.05	≦0.5	≦1	19.5-23.5	38.0-46.0	2.5-3.5	bal.	…	…	≦0.2	0.6-1.0	1.5-3.0	…	≧67	≧30	≧30	SH (USA)	Ref 26
HR11N	Solid wall composite (Sumitomo Metal)	≦0.03	≦0.6	≦2.0	27.0-30.0	38.0-42.0	0.5-1.5	bal.	…	0.1-0.2	…	…	…	…	≧60	≧25	≧35	Tested (Japan)	Ref 30
MAC-F	Mitsubishi Heavy Industries	0.010-0.020	3.40-4.20	≦0.50	21.0-25.0	36.0-40.0	…	bal.	0.20-0.40	0.05-0.09	≦0.10	≦0.10	…	…	≧62.2	≧24.5	≧30	SH (Japan)	Ref 28
Sanicro 38	Composite/ SA210A (Sandvik)	≦0.025	≦0.5	0.8	20	38	2.5	bal.	…	…	…	≦1.0	1.7	…	≧33	≧18	≧35	Tested (Europe)	Ref 21
NF 707	Solid wall (Nippon Steel)	≦0.15	≦1.00	≦1.5	22.0-27.0	33.0-37.0	1.0-2.0	bal.	0.10-0.40	0.05-0.35	…	0.02-0.20	…	0.002-0.008B	≧58.2	≧20.4	≧30	Tested (Japan)	Ref 31
AC 66	Solid wall (Mannesman)	≦0.025	≦0.3	≦1.0	26.0-28.0	31.0-33.0	…	bal.	0.6-1.0	…	≦0.025	…	…	0.05-0.10Ce	≧51	≧18.9	≧35	SH (Europe)	Ref 32
Sanicro 28	Composite/T22 (Sandvik)	≦0.02	≦0.7	≦2.0	26.0-28.0	29.0-32.0	3.5	bal.	…	…	…	…	0.6-1.4	…	≧56	≧22	≧40	SH (Europe)	Ref 27
HR 30M	Solid wall (Sumitomo Metal)	≦0.02	≦0.50	≦1.00	27.0-30.0	28.0-32.0	0.80-1.20	bal.	…	0.10-0.30	…	…	…	…	≧65	≧28	≧35	Tested (Japan)	Ref 20
NF 709 (310J2)	Solid wall (Nippon Steel)	≦0.1	≦0.75	≦1.5	19.0-23.0	23.0-27.0	1.0-2.0	bal.	0.10-0.40	1.10-0.20	…	0.02-0.20	…	0.002-0.008B	≧65.3	≧27.6	≧30	SH (Japan)	Ref 24
QSX3	Solid wall (Sanyo Special Steel)	≦0.03	2.50-3.50	≦1.00	24.0-26.0	22.0-25.0	…	bal.	0.10-0.30	0.049	…	…	…	…	≧53	≧21	≧35	SH (Japan)	Ref 36
QSX5	Solid wall (Sanyo Special Steel)	≦0.03	2.50-3.50	≦1.00	24.0-26.0	22.0-25.0	1.00-2.00	bal.	0.10-0.30	0.042	…	…	…	…	≧53	≧21	≧35	SH (Japan)	Ref 37
310S	Solid wall (JIS)	≦0.08	≦1.50	≦2.00	24.0-26.0	19.0-22.0	…	bal.	…	…	…	…	…	…	≧53	≧21	≧35	SH (Japan)	Ref 23
HR3C (310HCbN)	Solid wall (Sumitomo Metal)	≦0.10	≦1.50	≦2.00	23.0-27.0	17.0-23.0	…	bal.	0.20-0.60	0.15-0.35	…	…	…	…	≧67	≧30	≧30	SH (Japan)	Ref 20
MN25R (309J3L)	Solid wall (Nippon Steel)	≦0.025	≦0.70	≦2.00	23.0-26.0	13.0-16.0	0.5-1.2	bal.	…	0.25-0.40	…	…	…	…	≧70.4	≧35.2	≧30	SH (Japan)	Ref 31
HR2M (309J2)	Solid wall (Sumitomo Metal)	≦0.04	≦1.00	2.50-3.50	21.0-23.0	12.50-15.50	1.00-2.00	bal.	…	0.10-0.25	…	…	…	…	≧60	≧25	≧35	SH (Japan)	Ref 35

WW, Waterwall; SH, Superheater.

Table 3 Ni-base alloy tubings tested and applied to WTE boilers

Name	Shape of tubes (maker)	Chemical composition, mass %												Tensile properties, RT			Parts	References
		C	Si	Mn	Cr	Ni	Mo	Fe	Co	Nb + Ta	W	Ti	Others	TS, kg/mm²	YS, kg/mm²	E, %		
Alloy 625 (SB 444)	Solid wall (ASME) Overlay (WSI, Daido)	≦0.1	≦0.5	≦0.5	20.0-23.0	bal.	8.0-10.0	≦5	≦1.0	3.15-4.15	…	≦0.4	Al ≦ 0.04	≧84.4	≧42.2	≧30	SH (Japan)	Ref 20
Sanicro 63	Composite/ T22 (Sandvik)	≦0.025	≦0.5	≦0.5	21	bal.	8.5	3	…	3.4	…	…	…	≧66.3	≧25.5	≧50	WW, SH (Europe)	Ref 21
Sanicro 65	Compostie/ T22 (Sandvik)	≦0.025	≦0.5	≦0.5	21	bal.	8.5	8	…	≦0.5	…	…	…	≧66.3	≧25.5	≧50	WW, SH (Europe)	Ref 16
Hastelloy C-22	Solid Wall (Haynes Alloy) Compostie/ 304H (Mitsubishi Materials)	≦0.015	≦0.08	≦0.5	20.0-22.5	bal.	12.5-14.5	2.0-6.0	≦2.5	…	2.5-3.5	…	V ≦ 0.35	≧70.4	≧31.6	≧45	Tested (Japan)	Ref 33
HC-276M	Composite (Daido)	≦0.12	≦1.5	≦1.0	15.5-21.0	bal.	12.0-16.0	≦5.25	≦2.5	…	≦5.25	…	…	≧53	≧21	≧35	Tested (Japan)	Ref 15
Inconell 686	Solid wall (Special Metals)	≦0.01	≦0.08	≦0.75	19.0-23.0	bal.	15.0-17.0	≦5	…	…	3.0-4.4	0.02-0.25	…	79.4	53.1	56	Tested (USA)	Ref 34
JHN 24	Solid wall (Mitsubishi Materials)	≦0.015	≦0.08	≦0.5	19.0-21.0	bal.	17.0-19.0	0.5-6.0	≦2.5	0.5-1.2	…	…	V ≦ 0.35 Hf ≦ 0.3	≧73.4	≧33.6	≧30	Tested (Japan)	Ref 20
HR 160™	Solid wall (Haynes Alloy)	≦0.15	2.4-3.0	0.5	26.0-30.0	bal.	≦1.0	≦3.5	27.0-33.0	≦1.0	≦1.0	0.20-0.80	…	≧66.8	≧24.7	≧40	SH (USA)	Ref 29
Nicrofer 45-TM	Solid wall (KTN)	0.05-0.12	2.5-3.0	≦1.0	26.0-29.0	≧45.0	…	21.0-25.0	…	…	…	…	Cu ≦ 0.3 0.05-0.15 REM	≧63.3	≧24.5	≧35	SH (Europe)	Ref 39
MAC-N	Mitsubishi Heavy Industries	0.010-0.025	3.20-3.80	0.20-0.60	24.0-28.0	bal.	…	9.0-13.0	…	0.20-0.40	…	≦0.30	Al ≦ 0.35 N ≦ 0.07	≧61.2	≧18.4	≧30	SH (Japan)	Ref 28

WW, Waterwall; SH, Superheater.

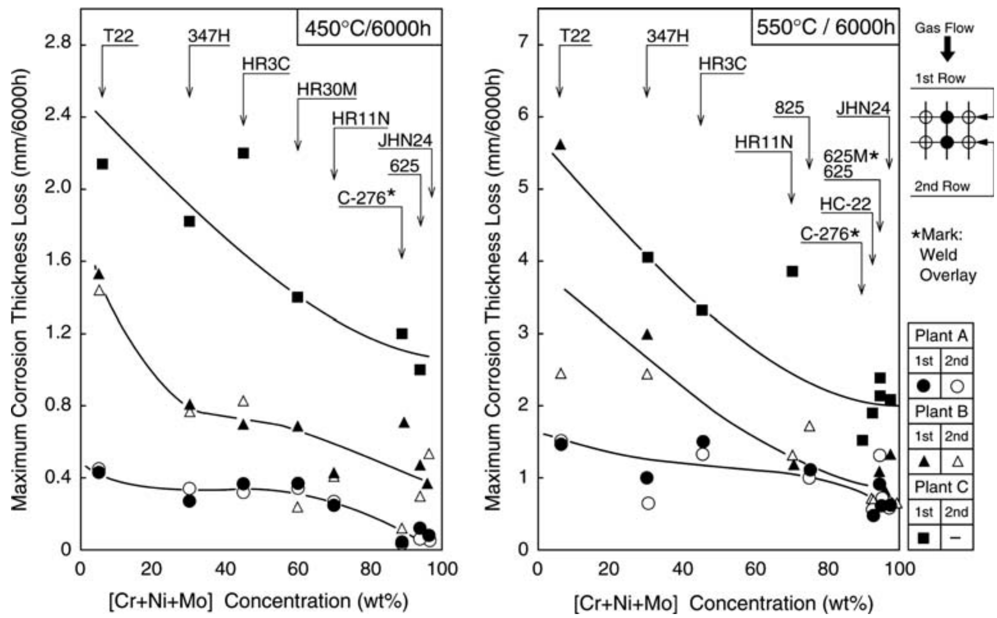

Fig. 7 Change in maximum corrosion thickness loss with [Cr + Ni + Mo] concentration of alloys in 6000 h field tests

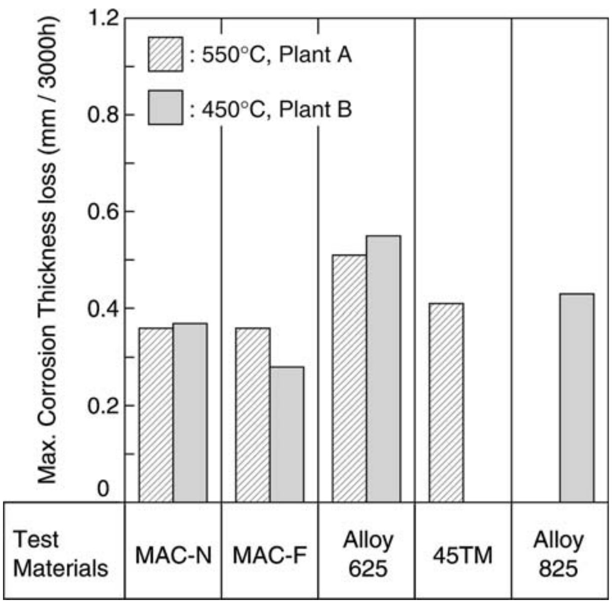

Fig. 8 Change in maximum thickness loss with time in secondary and tertiary superheater steam outlet (soot blower not affected)

4. Corrosion Mechanisms of Materials and Coatings

4.1 Corrosion Mechanisms of Materials

The effect of the main factors of combustion gas side governing the corrosion rate is described below (Ref 38). The corrosion rate depends on the metal temperature, and this type of corrosion is referred as ''molten salt induced corrosion'' because the corrosion reaction becomes active, when the amount of deposits increases and a part of deposits melts (Ref 40). The gas temperature is considered as the main factor determining deposition rate and the composition of the deposits. As the temperature gradient ΔT (gas temperature—metal temperature) is the driving force for condensation and deposition of the vapor components in the gas, the chloride concentration in the deposits is high at locations, where ΔT (gas temperature—metal temperature) is large there is a tendency for the formation of low melting deposits. Furthermore, it is known that the amounts of Cl, SO_4, alkaline and heavy metals affects the physical properties of the deposits such as molten phase amount, permeability, etc. (Ref 41). The penetration of corrosive gas through the deposits and the presence of oxidizing constituents such as O_2 are considered necessary for the maintenance of corrosion reaction, as the corrosion peak appears around 10% of chloride concentration as shown in Fig. 11. Moreover, rapid thermal cycling acts on the tube surface in the actual plants, due to gas temperature fluctuation and the use of soot blowers. The falling off and the regeneration of deposits and oxides layer are repeated. Figure 12 shows the example of crack generation of alloy 625 oxides layer due to the thermal fluctuation at the soot blow affected zone. The Cl and S partial pressures are considered to rise under the deposits due to penetration of Cl, S, etc. through the cracks onto the corrosion interface. Furthermore, if the protective oxides layer breaks down, the direct reaction with molten chlorides may occur as shown in Fig. 13(Ref 22). From the configuration of corrosion products distributing as chlorides, sulfides and oxides from the side nearest to the interface and their properties, the corrosion

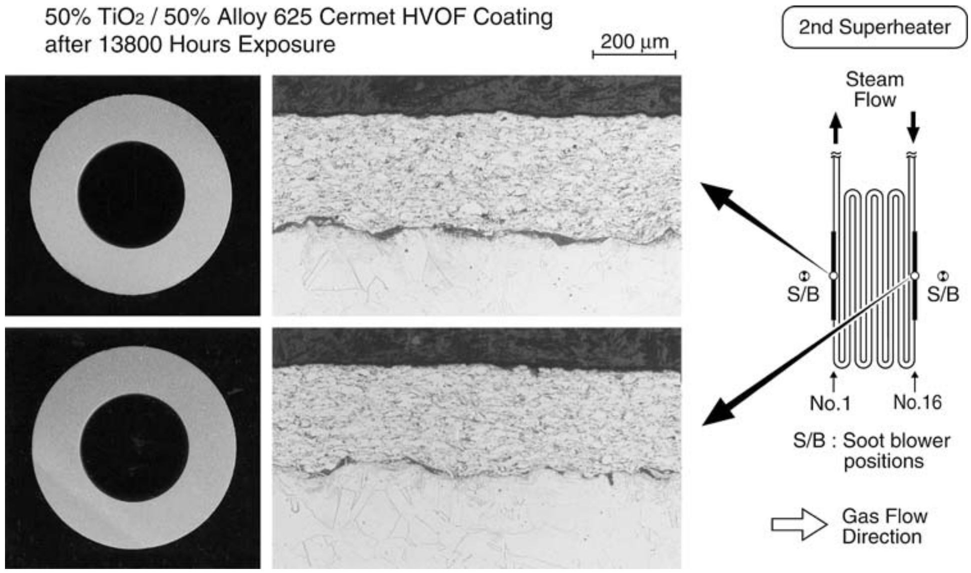

Fig. 9 Cermet spray coating on 310HCbN superheater after 13,800 h exposure

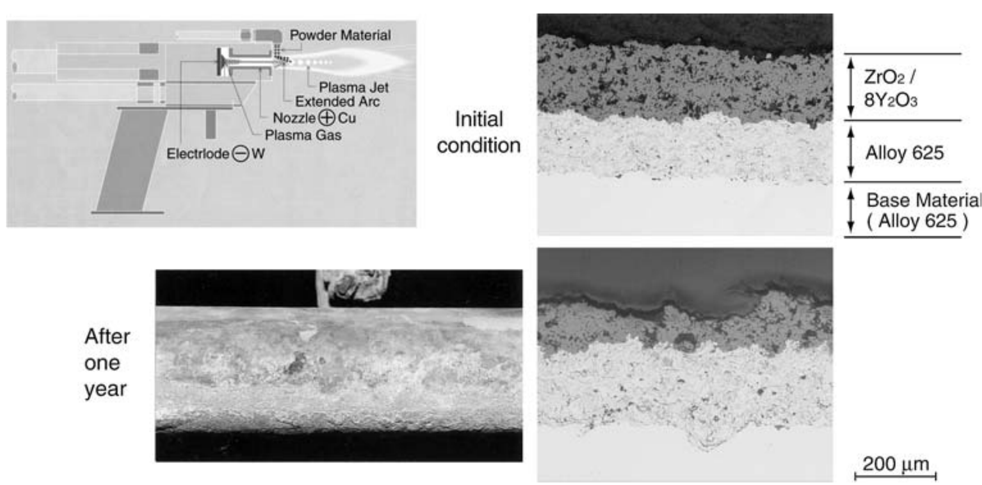

Fig. 10 ZrO_2/Alloy 625 on-site 100 kW plasma-jet spray coating for 500 °C superheaters

is considered to be mixed high-temperature gaseous reaction where reactions of chlorination/sulphidation/oxidation occur simultaneously. On the other hand, it is considered also that the molten salt corrosion occurs during the initial stage of corrosion when the oxides layer is thin. It is presumed that the corrosion by the direct reaction of molten salt changes gradually to the gas reaction as the oxides layer grows thicker. The degree of influence of major factors such as temperature gradient, temperature fluctuation, molten ash amount, etc. on the corrosion rate was examined quantitatively by recent research (Ref 42). The factors causing characteristic intergranular corrosion include both the material side (impurities, grain boundary precipitates, etc.) and the environment side (stress, molten salt, etc.) (Ref 43). This investigation will be continued.

4.2 Deterioration Mechanisms of Spray Coatings

Figure 14 shows the deterioration of the spray coating layer used for a long period. Corrosion of the base metal and deterioration of coating proceed due to the penetration of corrosive gases (HCl, etc.) to the interface of base material/coating layer. Then, ‘‘swelling’’ of the coating layer occurs, the reduction of adhesive strength is accelerated, and peeling of the layer occurs (Ref 17). Accordingly, dense coating is indispensable for improvement of lifetime, and the supersonic flame spray coating (HVOF) where the alloy powder in semi-molted state is sprayed at supersonic speed is preferable. The material factors that govern durability are the corrosion resistance of coating material, the adhesive strength with base material, the thermal properties including thermal expansion coeffi-

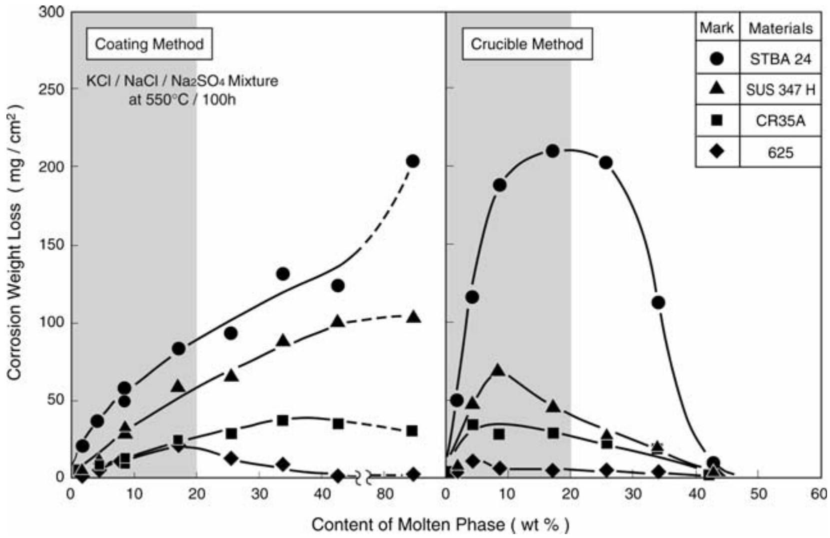

Fig. 11 Change in corrosion weight loss with molten phase content between coating test and crucible test

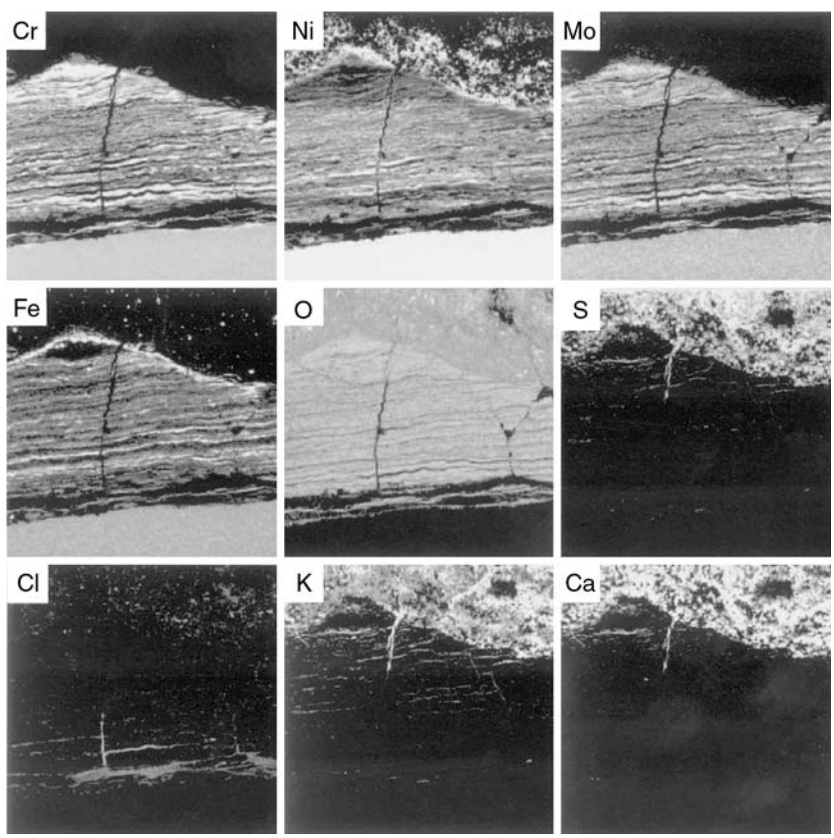

Fig. 12 Breakdown of protective oxide layer and penetration of corrosive species in Alloy 625 superheater tube influenced by soot blowing

cient, and the residual stress. As the physical properties of the coating are largely depending upon the spraying conditions, quantitative evaluation method of lifetime for coating layer is required. Research and development of life evaluation are expected in the future.

5. Summary

In recent years, the WTE plants are required to satisfy many additional requirements such as the suppression of

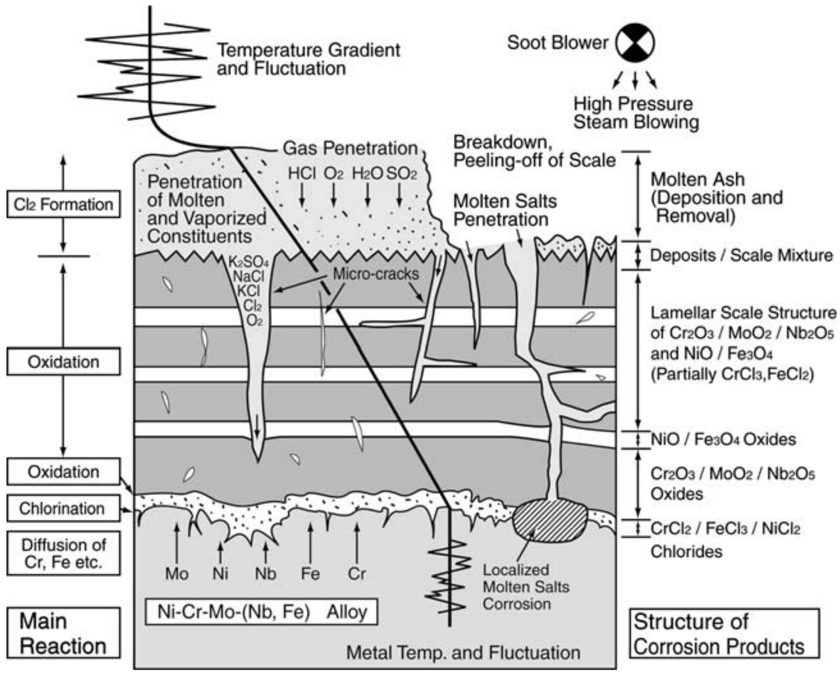

Fig. 13 Corrosion mechanisms in Ni-Cr-Mo-(Nb, Fe) alloy

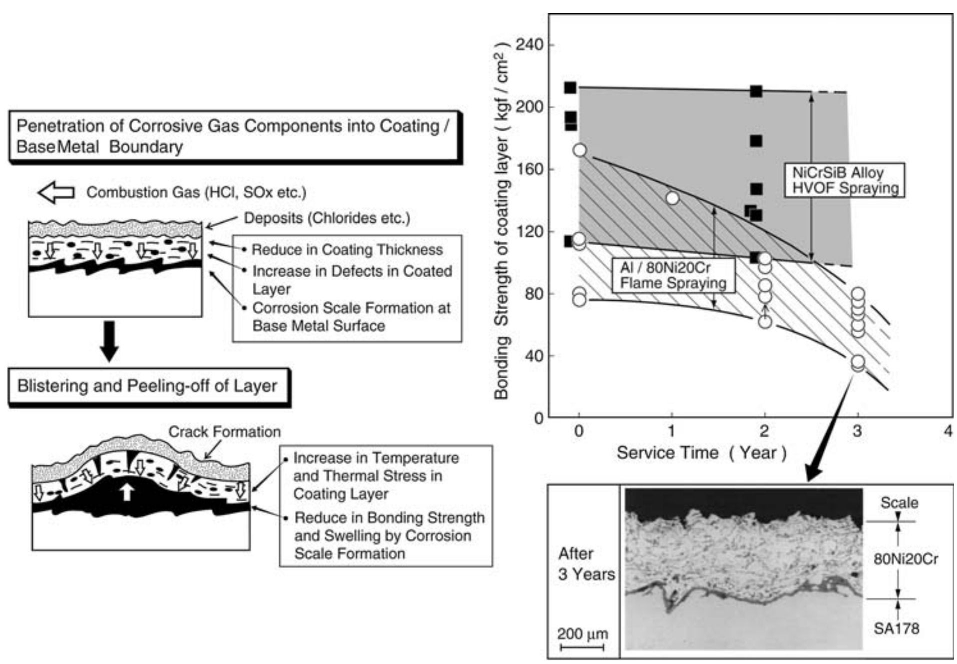

Fig. 14 Deterioration mechanisms of spray coating layer and reduce in bonding strength in severe corrosive environment

pollutants, improvement of power generation efficiency, material recycling, etc. Various combustion methods and plant systems have been adopted, and the HTC environment of the plants is becoming more complicated and diversified. It is believed that the development and application of corrosion prevention technologies aim strongly at the right material in the right place and at a reasonable cost of application. The improvement of performance and durable lifetime of the WTE plants has been supported by the development of corrosion-preventing CRM and CRC technologies. There are many subjects for future research, such as the development of software for effectively applying these corrosion prevention technologies to WTE boilers. It is expected that engineers and researchers in the field of CRMs and CRCs will meet these challenges.

References

1. Y. Kawahara, Recent Trends and Future Subjects on High-Temperature Corrosion-Prevention Technologies in High-Efficiency Waste-to Energy Plants, *Corros. Eng.*, 2005, **54**, p 213-235
2. Y. Kawahara and Y. Kaihara, Recent Trends in Corrosion-resistant Tube Materials and Improvement of Corrosion Environments in the WTE Plants, Corrosion/2001, Paper No. 1173 (Houston, TX), NACE, 2001
3. Y. Kawahara, Recent Trends in Development and Application of High-temperature Corrosion-resistant Materials and Coatings in High Efficiency Waste Incineration Boiler, *MTERE2*, 2002, **41**(3), p 190
4. Y. Kawahara, M. Nakamura, H. Tsuboi, and K. Yukawa, Evaluation of New Corrosion Resistant Superheater Tubings in High Efficiency Waste-to-Energy Plants, *Corrosion*, 1998, **54**(7), p 576
5. Y. Kawahara, N. Orita, M. Nakamura, S. Ayukawa, and T. Hosoda, Laboratory Corrosion Tests for Simulating Fireside Wastage of Superheater Materials in Waste Incinerators, Corrosion/99, Paper No. 89 (San Antonio, TX), NACE, 1999
6. Y. Fukuda, Y. Kawahara, and T. Hosoda, Application of High Velocity Flame Sprayings for Superheater Tubes in Waste Incinerators, Corrosion/2000, Paper No. 264 (Orlando, FL), NACE, 2000
7. P.Z. Kubin, Corrosion/99, Paper No. 90 (San Antonio, TX), NACE, 1999
8. D.E. Burnham, D.R. Gibbs, J.S. Gitlinger, and H.E. Johnson, *Proceedings of 1989 Conference on Municipal Solid Waste as a Utility Fuel* (Springfield), Oct. 1989, p 10-12
9. H.H. Krause, Corrosion/92, Paper No. 140 (Nashville, TN), NACE, 1992
10. I.G. Wright, H.H. Krause, and R.B. Dooley, Corrosion/95, Paper No. 562 (Orlando, FL), NACE, 1995
11. T. Yoshikawa, Spray Coating and Weld Overlay in Circulating Fluidized Bed Boiler (CFB) and Waste-to-Energy (WTF) Boilers, *Proceedings of International Symposium on High Temperature Oxidation and Corrosion/2005* (Nara, Japan), 2005, p 27
12. P.L.F. Rademakers, R.W.A. Wetzel, and E. Kokmeijer, Materials for Advanced Power Engineering, *Proceedings of the 6th Liege Conference Part II*, 1998, **5**, p 751
13. Y. Kawahara, Y. Nakagawa, M. Kira, T. Sakurada, H. Kamakura, and Y. Imaizumi, *Life Evaluation of ZrO_2/Ni Base Alloy Plasmajet Coating Systems in High Efficiency Waste-to-energy Boiler Superheaters*, Corrosion/2004, Paper No. 04535 (New Orleans, LA), NACE, 2004
14. G. Lai and P. Hulsizer, *Proceedings of Stainless Steel World/99* (Den Haag, Netherlands), Nov. 1999, p 681
15. Y. Takeuchi, Y. Kawahara, and T. Hosoda, Application of Composite Tubes Plasma-Weld-Overlayed with Ni-Cr-Mo Alloy for Superheater in Waste Incinerators, Corrosion/2000, Paper No. 261 (Orlando, FL), NACE, 2000
16. AB Sandvik Steel Technical Report
17. Y. Kawahara and M. Kira, Corrosion Prevention of Waterwall Tube by Field Metal Spraying in Municipal Waste Incineration Plants, *Corrosion*, 1994, **53**, p 241
18. Y. Yamada, M. Koyama, T. Otuka, M. Osawa, and K. Toyama, *Yosya-Gijyutu,* 1994, **14**(3), p 30
19. Y. Kawahara, X. Li, Y. Nakagawa, H. Imaizumi, T. Katoh, and H. Nakajima, Laboratory Corrosion Tests of New Weldoverlay Materials in Simulated Environment of High Efficiency WTE Boilers, *Proceedings of 48th Conference of JSCE Materials and Environments,* 2001, **C-308**, p 431
20. Y. Kawahara, N. Orita, K. Takahashi, and Y. Nakagawa, Demonstration Test of New Corrosion-resistant Boiler Tube Materials in High Efficiency Waste Incineration Plant, *Tetsu-to-Hagane*, 2001, **87**(8), p 24
21. A. Wilson, U. Forsberg, M. Lunderg, and L. Nylöf, *Proceedings of Stainless Steel World/99* (Den Haag, Netherlands) Nov. 1999, p 669
22. Y. Kawahara, High Temperature Corrosion Mechanisms and Effect of Alloying Elements for Materials Used in Waste Incineration Environment, *Corros. Sci.*, 2002, **44**, p 223-245
23. M. Yokono, A. Matsumoto, M. Noguchi, H. Yakuwa, M. Miyasaka, K. Miyoshi, K. Kosaka, and Y. Fukuda, Corrosion/99, Paper No. 87 (San Antonio, TX), NACE, 1999
24. T. Ishizuka, H. Mimura, T. Takahashi, M. Kurita, N. Hirayama, and K. Mori, *Proceedings of High Temperature Corrosion and Protection/2000* (Lusutsu, Japan), 2000
25. Y. Kawahara, M. Nakamura, H. Tsuboi, and K. Yukawa, Evaluation of New Corrosion Resistant Superheater Tubings in High Efficiency Waste-to-Energy Plants, *Corrosion*, 1998, **54**(7), p 576
26. G.D. Smith and W.G. Lipscomb, Corrosion/89, Paper No. 201 (New Orleans, LA), NACE, 1989
27. E. Haggblom and L. Nylöf, *Materials for Advanced Power Engineering, Part II,* D. Coutsouradis *et al.* Ed., Kluwer Academic Publishers, Netherlands, 1994, p 1597
28. Y. Kawahara, K. Sasaki, and Y. Nakagawa, Development and Application of High Cr-high Si-Fe-Ni Alloys to High Efficiency Waste-to-Energy Boilers, *J. Jpn. Inst. Metals*, 2007, **71**(1), to be published
29. C.M. Antony, G.Y. Lai, J.W. Tackett, and E.J. Bickel, Pressure Vessels Pipe Div., **262**, ASME, 1993, p 57
30. S. Yamamoto, A. Natori, Y. Yamadera, N. Otsuka, T. Kubo, and K. Ogawa, *Karyoku-Gensiryoku-Hatsuden*, 1996, **47**(7), p 6
31. Nippon Steel's Tubes for Boiler and Heat Exchanger and Pipes for Piping, 1998
32. U. Brill, J. Klöwer, E. Maasen, H. Richter, W. Schwend, and J. Venkateswarlu, *Corrosion*, 1994, **53**, p 1585
33. T. Matsui, H. Takizawa, S. Wakita, Y. Kawahara and T. Hosoda, *Development of Ni-Cr-Mo Alloy for Superheater Tube Applications*, Corrosion, Paper No. 262 (Orlando, FL), NACE, 2000
34. Technical Report on Special Metalls Inc., 1999
35. Technical Report of Sumitomo Metal Industries, Ltd., 1995
36. A. Shiyo, T. Isomoto, M. Yoshiba, N. Hirayama, T. Urabe, and K. Nagashima, *Proceedings of the 10th Conference of The Japan Society of Waste Management Experts*, C5-3, 1999, p 749
37. A. Shiyo, T. Isomoto, K. Toyama, T. Urabe, and M. Yoshiba, *J. Jpn. Inst. Metals,* 2002, **66**(6), p 554
38. Y. Kawahara, Basic Science and Application of High Temperature Corrosion and Protection in Energy Conversion and Environmental Equipments, JIM Seminar Text, ISBN4-88903-129-4, C3057, 2001, p 39
39. D.C. Agarwal, J. Klöwer, and G.K. Grossmann, Corrosion/97, Paper No. 155 (New Orleans, LA), NACE, 1997
40. P.D. Miller, H.H. Krause, D.A. Vaughan, and W.K. Boyd, *Corrosion*, 1970, **28**, p 274
41. Y. Kawahara and M. Kira, Effect of Physical Properties of Molten Deposits on High Temperature Corrosion of Alloys in Waste Incineration Environment, *Zairyo-to-Kankyo*, 1997, **46**(1), p 8
42. Y. Kawahara, Evaluation of High-Temperature Corrosion Life Using Temperature Gradient Corrosion Test with Thermal Cycle Component in Waste Combustion Environment, *Mater. Corros.*, 2007, **57**(1), p 60-72
43. M. Uekado, Y. Kamei, and K. Hujii, Effect of Static Stress on High Temperature Corrosion Behavior of Boiler Tubes in Waste Incineration Environment, *J. Jpn Inst. Metals*, 2002, **66**(6), p 576
44. Y. Yamada, M. Sasaki, and Y. Nakagawa, Application of Flame Spray Coatings of Ni base Alloy for Waste Incineration Boilers, *Proceedings of 43rd Conference of JSCE Materials and Environments*, *B-114*, 1996, p 195
45. Technical Report of Haynes Alloys International, Inc., 1998
46. M.S. Brennan and R.C. Gassmann, Corrosion/2000, Paper No. 235 (Orlando, FL), NACE, 2000

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