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Corrosion Behavior of 2205 DSS Base Metal and ER 2209 Weld Metal in a Deposited Ash/Water Suspension

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The corrosion behavior of 2205 duplex stainless steel (DSS) base metal (BM) and ER2209 weld metal (WM) in an ash/water suspension composed of deposited ash on the flue gas side of a low-temperature heat exchanger in a waste-to-energy plant and water was studied by polarization curve analysis, electrochemical impedance spectroscopy (EIS), localized electrochemical measurements, microscopic surface morphology observation, and metallographic analysis. The results showed that the corrosion resistance of both the BM and the WM decreased with the increase in immersion time. After 4 h of immersion, active sites where the current density increased suddenly appeared on the surface of the WM, and the surface roughness increased significantly, indicating the beginning of pitting on the WM surface. However, it took 8 h for the active sites to appear on the BM, and the pitting corrosion on the BM surface was obviously less than that of the WM surface under the same immersion time. The pitting corrosion resistance of the 2205 DSS BM was obviously better than that of the WM. According to the metallographic analysis results, the high proportion of dendritic ferrite in the metallographic structure of the WM may be the reason for its poor corrosion resistance.

Keywords: waste-to-energy plant; ash/water suspension; pitting; 2205 DSS base metal; ER2209 weld metal

1. INTRODUCTION

Duplex stainless steel (DSS) has a unique structure formed by a certain proportion of ferrite (δ) and austenite (γ). The properties of DSS depend on the microstructure ratio of γ -austenite (facecentered cubic, FCC) and δ -ferrite (body-centered cubic, BCC) [1]. The performance advantages of 2205 DSS are mainly attributed to the balance of ferrite and austenite phases [2]. The comprehensive performance of DSS is excellent. When the content of ferrite is about 51% [3], the high strength of ferrite stainless steel (FSS) and the good plasticity and uniform corrosion resistance of austenitic

stainless steel (ASS) enable DSS to exert its optimal performance. Therefore, it has been widely used in power generation, petroleum, the chemical industry, nuclear energy, the marine industry and other

fields [4]. In some highly corrosive engineering environments, DSS is usually used instead of ASS. The intercrystalline corrosion resistance of DSS is better than that of ASS [5, 6]. However, if the wrong welding method or parameters are used, the corrosion resistance of the DSS welded joint may be reduced [7]. The toughness and corrosion resistance of the DSS weld metal (WM) mainly depends on the ratio of ferrite phases to austenite phases. Generally, DSS with the same proportion of austenite and ferrite has the best corrosion resistance [7, 8]. The microstructure of the DSS weld zone depends largely on the heat input, cooling rate, and composition [9]. If the welding method or parameters are inappropriate, the joint will form a new metallographic structure at high temperature [10–12], and the precipitation of intergranular brittle phases will reduce the corrosion resistance of the joint [13]. Changes in the microstructure increase the susceptibility of the welding zone to local corrosion and stress corrosion cracking [13–15]. The filler metal used for welding 2205 DSS must be similar and compatible with the base metal (BM) and must have the same proportions of austenite and ferrite [16]. Therefore, 2209 is usually used as a welding wire material [17]. According to the literatures [18], an incorrect welding process will result in an imbalance of ferrite and austenite phases in the WM, and excessive ferrite content in the welded joints will reduce the impact toughness and fatigue resistance, resulting in a large number of cracks. In some special power plants, such as waste-to-energy plants and biomass incinerators, the operating environment is more complicated than ordinary thermal power plants [19, 20]. In this environment, the welded joints are required to have better performance to ensure safe operation of the equipment. In a waste-to-energy plant in China, condensate appears on the flue gas side at the end of the low-temperature heat exchanger and forms an ash/water mixture with the ash deposited on the metal surface, which is highly corrosive and causes serious corrosion of the heat exchanger. In the above environment, various stainless steels, such as 316L SS, are not resistant to corrosion, and the 2205 DSS welded pipe is ready to be used. In this paper, the corrosion behavior of 2205 DSS BM and ER2209 WM in a deposited ash/water suspension composed of the deposited ash from this waste-to-energy plant and water was investigated. In addition, the corrosion resistance of the BM and the WM in this deposited ash/water suspension was compared and analyzed.

2. EXPERIMENTAL

2.1. Experimental medium and materials

2.1.1. Preparation of the deposited ash/water suspension for the experiment

The ash deposit was taken from the flue gas side of the low-temperature heat exchanger of a waste-to-energy plant in China, and the ash deposit was mixed with deionized water in a ratio of 1:1 to form a deposited ash/water suspension for the experiment. The experimental temperature was 80 °C. The main soluble ions of the deposited ash/water suspension were measured and are listed in Table 1.

Conductivity $ms \cdot cm^{-1}$	pН	${f K^+} {f g} \cdot {f L^{-1}}$	Ca^{2+} g·L ⁻¹	Na^+ g·L ⁻¹	Cl^{-} $g \cdot L^{-1}$	NO_3^- $g \cdot L^{-1}$
125	4.5	25.74	43.67	5.75	100.78	15.78

Table 1. The main soluble ions of the experimental deposited ash/water suspension.

2.1.2. Preparation of the experimental materials

The experimental materials came from a welded plate with a thickness of 5 mm, in which 2205 DSS was the BM and ER 2209 was the filler metal, as shown in Figure 1. The chemical compositions of the 2205 DSS BM and the ER2209 WM are given in Table 2. The white frame area in Figure 1 was cut to obtain the BM and WM specimens. The dimension of all specimens was 10 mm \times 10 mm \times 5 mm. All specimens were polished step by step with sandpapers from 800 to 2000 mesh and were then degreased with ethanol and cleaned with distilled water.



Figure 1. The welded plate and the sampling location of the base metal (BM) and the weld metal (WM).

Table 2. Chemical composition of the BM (2205 DSS) and the WM (ER2209) (wt.	.%	6)
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Element	С	Si	Mn	Р	S	Cr	Ni	Mo	Ν	Cu	Fe
2205 DSS	0.025	0.6	1.5	0.026	0.001	22.5	5.8	3.0	0.16	/	Bal.
ER2209	0.023	0.56	1.57	0.022	0.001	23.02	8.65	3.02	0.15	0.10	Bal.

2.1.3. Etching of the specimen

After grinding, cleaning and degreasing, a specimen polished with 0.5 μ m diamond paste was used as the etching anode, and a 304 SS sheet was used as the cathode. The etching medium was 10 wt.% oxalic acid solution. The anodic current density of the etching was controlled at 1 A/cm² by a DC power supply, and the etching time was 90 s. A new oxalic acid solution was used in each experiment. After etching, the specimen was rinsed with deionized water and dried.

2.2. Testing methods

The polarization curve and electrochemical impedance spectroscopy (EIS) of the materials were measured by an electrochemical workstation (CHI604E). A Pt electrode was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. A specimen of BM or WM was soldered on the back with copper wire, and then sealed with epoxy resin to form a working electrode with a working surface area of 10 mm \times 10 mm. Each working electrode was polished step by step with sandpapers from 800 to 2000 mesh and then degreased with ethanol and cleaned with distilled water before experiment. The scanning rate of the polarization curve measurement was 1 mV·s⁻¹. The frequency range of EIS was 100 kHz to 0.01 Hz, and the amplitude was 10 mV. The results of the EIS were fitted by the Zview software.

The pitting sensitivity and localized electrochemical inhomogeneity of the electrode surface were measured by Princeton Applied Research's M370 Scanning Vibrating Electrode Technique (SVET). The scanning probe was a Pt-Ir microelectrode with a diameter of 20 μ m. The distance between the probe and the sample was adjusted to 100 μ m. The probe vibrated above the working electrode in a direction perpendicular to the surface of the working electrode, with an amplitude of 30 μ m, a vibration frequency of 80 Hz, a scanning step of 100 μ m, and a scanning area of 4 mm × 4 mm.

The surface micro-morphology and metallography of the materials were characterized by German ZEISS Axio GSM 700 white light confocal microscope. The area fractions of ferrite and austenite phases were quantitatively analyzed and evaluated with Axio CSM 700 Software.

Three parallel samples were set for each group of experiments.

3. RESULTS AND DISCUSSION

3.1. Electrochemical analysis

3.1.1. Polarization curve analysis



Figure 2. Polarization curves of the BM and the WM after immersion in the deposited ash/water suspension for 1 h at 80 °C.



Figure 3. Polarization curves of the BM and the WM after immersion in the deposited ash/water suspension for 12 h at 80°C.

Firstly, the polarization curves of the BM and the WM were measured after being immersed in the deposited ash/water suspension for 1 h and 12 h. The results are shown in Figure 2 and Figure 3.

The polarization curves in Figure 2 and Figure 3 show that after 1 h of immersion the pitting potential (E_b) of the BM and the WM was 0.127 V and 0.034 V, respectively. After immersing for 12 h, the E_b of the BM and WM negatively shifted to -0.172 V and -0.240 V, respectively. According to the above results, under the same immersion time, the E_b of the BM was higher than that of the WM. Take the passive current density at the polarization value of 0.25 V for comparison. After immersing for 1 h, the passive current densities of the BM and the WM were 2.01 μ A·cm⁻² and 4.93 μ A·cm⁻². respectively. However, after 12 h of immersion, the passive current densities of the BM and the WM increased to 16.37 μ A·cm⁻² and 41.21 μ A·cm⁻², respectively. There are similar reports [21,22] that in some harsh corrosive media, the corrosion current density of metals increases with time, indicating that the corrosion damage of materials is intensified. The results in Figure 2 and Figure 3 show that under the same immersion time the passive current density of the WM and its increase are greater, indicating that the corrosion resistance of the passive film on the WM surface was relatively poor. The passive current density of the WM fluctuated greatly after immersion for 12 h, implying poor stability of the passivation film. It may be that the surface of the WM electrode was in a metastable state [23], and the passivation film was more susceptible to damaged. By comparing the E_b values for 1 h and 12 h, it is seen that the E_b of both the BM and the WM gradually decreased with the increase in immersion time, while the passive current density gradually increased with the immersion time, indicating that with the extension of the immersion time the corrosion resistance of both the BM and the WM decreased. In addition, the corrosion potential (E_{corr}) of the two materials shifted negatively with the extension of the immersion time, indicating the deterioration of the performance of the passivation film on the electrode surface.

3.1.2. Analysis by electrochemical impedance spectroscopy (EIS)

To further compare the performance of the passive film on the surface of the BM and the WM, EIS of the two materials was performed in the deposited ash/water suspension after immersing for 1 h, 4 h, 8 h, and 12 h. The results are shown in Figure 4 and Figure 5.



Figure 4. Electrochemical impedance spectroscopy (EIS) of the 2205 DSS BM immersed in the deposited ash/water suspension for different times at 80 °C. (a) Nyquist plot. (b) Bode plot.

The deposited ash/water suspension used in the experiment was a highly corrosive solution, with a chloride ion concentration of 100.78 g/L, a conductivity of 125 ms \cdot cm⁻¹, and a pH of 4.5, as shown in Table 1. In such a relatively harsh medium, the passivation film on the surface of polished stainless steel is not easy to form, and the formed passivation film can also be easily damaged. Figure 4 and Figure 5 show that, for both the BM and the WM in the deposited ash/water suspension, the capacitive arc diameter in the Nyquist plot was reduced with the increase in the immersion time, indicating that the corrosion resistance of both materials was reduced, as described by Sinhmar et al. [24].



Figure 5. EIS of the ER2209 WM immersed in the deposited ash/water suspension for different times at 80 °C. (a) Nyquist plot. (b) Bode plot.

When the immersion time reached 8 h (for the BM) and 4 h (for the WM), two capacitive arcs appeared in the Nyquist plot, indicating that the electrode surface was in the developmental stage of pitting corrosion at this time [25]. The EIS before and after pitting were fitted with the equivalent circuits in Figure 6(a) and Figure 6(b), respectively, where R_s is the solution resistance, R_i is the interface resistance, Q_i is the interface capacitance, Q_{pit} is the electric double layer capacitance in the corrosion hole, and R_{pit} is the charge transfer resistance in the corrosion hole. The fitting results are shown in Table 3.



Figure 6. Equivalent circuits for fitting.

Motorial	t	Rs	$Q_{\rm i}$		D.	$Q_{ m pit}$		D	D
typo			Y_o	п	Λ_1	Y_o	n	Apit	Atotal
type	h	$k\Omega \cdot cm^2$	$\mu F \cdot s^{n-1} \cdot cm^{-2}$		$k\Omega \cdot cm^2$	$mF \cdot s^{n-1} \cdot cm^{-2}$		$k\Omega \cdot cm^2$	$k\Omega \cdot cm^2$
	1	0.0037	137.10	0.79	25.33	/	/	/	25.33
2205	4	0.0035	168.20	0.76	15.84	/	/	/	15.84
DSS	8	0.0022	197.10	0.80	11.62	6.02	0.84	2.37	13.99
	12	0.0041	188.90	0.77	5.53	13.76	0.95	1.54	7.07
	1	0.0023	342.40	0.72	19.81	/	/	/	19.81
ER2209 -	4	0.0041	188.90	0.77	5.53	13.76	0.95	1.54	7.07
	8	0.0043	153.50	0.79	2.49	8.77	0.88	1.31	3.80
	12	0.0039	145.90	0.79	2.40	18.62	0.97	0.87	3.27

Table 3. Fitting results of EIS.

The total resistance, R_{total} ($R_{\text{total}} = R_i + R_{\text{pit}}$), was used to compare and analyze the fitting results. The R_{total} value of the BM and the WM in Table 3 decreased with the increase in immersion time. When the immersion time increased from 1 h to 12 h, the R_{total} of the BM decreased from 25.33 k $\Omega \cdot \text{cm}^2$ to 7.07 k $\Omega \cdot \text{cm}^2$, and the R_{total} of the WM decreased from 19.81 k $\Omega \cdot \text{cm}^2$ to 3.27 k $\Omega \cdot \text{cm}^2$. Under the same immersion time, the R_{total} value of the BM electrode was always higher than that of the WM electrode. After immersing for 12 h, the R_{total} value of the WM dropped by 6.05 times, while that of the BM electrode dropped by 3.58 times, indicating that the weld metal suffered more severe corrosion than that of the BM. Zhai et al. [26] also found the lower impedance value of the WM electrode, and believed that the surface film on WM was less protective.

3.2. Scanning Vibrating Electrode Technique (SVET) analysis







(c)



(d)

Figure 7. Scanning Vibrating Electrode Technique (SVET) results of the 2205 DSS BM after immersion in the deposited ash/water suspension for different times at 80 °C. The immersion times were (a) 1 h, (b) 4 h, (c) 8 h, (d) 12 h.

SVET measurements were carried out on specimens immersed in the deposited ash/water suspension for different times to obtain the pitting corrosion sensitivity and the localized electrochemical inhomogeneity of the 2205 DSS BM and the WM. The results are shown in Figure 7 and Figure 8.

Figure 7 shows that the surface current density of the BM gradually increased with the increase in immersion time. After immersing for 1 h, the surface current density distribution of the BM was comparatively uniform, most of which remained between 5.2 and 5.6 μ A·cm⁻², indicating that there was no obvious pitting corrosion at this time. When the immersion time was 4 h, most of the surface current density remained between 6.8 and 7.4 μ A·cm⁻². As the immersion time in the deposited ash/water suspension increased from 4 h to 8 h, most of the surface current density reached 15.0 – 16.0 μ A·cm⁻². However, there were several active sites on the metal surface where the current density suddenly increased to about 17.0 μ A·cm⁻² [27]. According to Mena et al. [28], these active sites with a sudden increase in current density are anode sites where the nucleation of a corrosion pit begins. As the immersion time was extended to 12 h, the surface current density increased to 19.0 – 20.0 μ A·cm⁻², and the current density of those active sites increased to 20.5 – 21.0 μ A·cm⁻². After immersing for 12 h, the number of active sites on the electrode surface did not increase significantly, but the current density of the active sites increased markedly, indicating that the pits became deeper and no obvious new pits appeared on the surface of the BM.





(b)



Figure 8. SVET results of the WM after immersion in the deposited ash/water suspension for different times at 80 °C. The immersion times were (a) 1 h, (b) 4 h, (c) 8 h, (d) 12 h.

The SVET results of the WM in the deposited ash/water suspension in Figure 8 show a similar trend as that of the 2205 DSS BM. With the increase in immersion time, the surface current density and the number of active sites gradually increased. However, the surface current density of the WM increased faster than that of the BM, and the active sites appeared earlier. After immersing for 4 h, most of the surface current density of the WM electrode increased to $8.5 - 9.5 \,\mu\text{A}\cdot\text{cm}^{-2}$, and the current density of the active sites increased to $10.0 - 10.5 \,\mu\text{A}\cdot\text{cm}^{-2}$. However, there was no obvious active site on the surface of the BM under the same immersion time. After immersing for 8 h, the surface current

density of the WM increased to about 21.0 μ A·cm⁻², which was higher than that of the BM that of immersed for 12 h. After 12 h of immersion, the current density of the active sites on the WM surface increased to about 25.0 μ A·cm⁻², and the number of active sites was significantly more than that for the 8 h immersion, indicating that the density and depth of the pits further increased [29]. Compared with the BM under the same immersion time, there were more active sites on the WM surface and the current density was higher, indicating that the pitting corrosion resistance of the WM was obviously poorer than that of the BM in the deposited ash/water suspension.

3.3. Surface morphology analysis

Figure 9 and Figure 10 show the surface morphology of the BM and the WM specimens immersed in the deposited ash/water suspension for different times. The surface roughness (Ra) of various specimens is summarized in Table 4.





Figure 9. Surface morphology of the 2205 DSS BM immersed in the deposited ash/water suspension for different times at 80 °C. The immersion times were (a) 1 h, (b) 4 h, (c) 8 h, (d) 12 h.





Figure 10. Surface morphology of the WM immersed in the deposited ash/water suspension for different times at 80 °C. The immersion times were (a) 1 h, (b) 4 h, (c) 8 h, (d) 12 h.

Table 4. Surface roughness (*Ra*) of the BM and the WM immersed in the deposited ash/water suspension for different times at 80 °C.

t / h		1	4	8	12	
Ra / µm	BM	0.733	0.775	0.875	0.957	
·	W WI	0.739	0.830	0.980	1.094	

The results in Figure 9, Figure 10, and Table 4 show that as the immersion time increased pitting corrosion gradually occurred on the surfaces of the BM and the WM, and the *Ra* value gradually increased. Corrosion can lead to an increase in the roughness of the metal surface, and the occurrence of pitting can cause a rapid increase in the *Ra* value [20, 30, 31]. After immersion in the suspension for 1 h and 4 h respectively, no obvious pits appeared on the BM surface, and the *Ra* value increased from 0.733 μ m to 0.775 μ m. After immersing for 8 h, pitting corrosion appeared on the BM surface, and the *Ra* value increased to 0.875 μ m. When the immersion time reached 12 h, the *Ra* value increased to 0.957 μ m, and the pit width increased from 15 μ m (8 h) to about 50 μ m, and the pit depth increased from about 12 μ m (8 h) to about 20 μ m.

The change in the surface morphology of the WM in the deposited ash/water suspension with time was similar to that of the BM, and pitting corrosion gradually appeared with the increase in immersion time. After immersing for 1 h, there were no obvious pits on the WM surface, and the value of *Ra* was close to that of the BM. As the immersion time increased the corrosion severity of the WM was significantly greater than that of the BM. After 4 h of immersion, pits appeared on the WM surface, and the *Ra* value increased from 0.739 μ m to 0.830 μ m. After immersing for 8 h, the pitting corrosion of the WM surface was more serious, and the *Ra* value was close to that of the BM immersed for 12 h. The pitting corrosion and roughness of the WM surface further increased when immersed for 12 h. The above results were consistent with the EIS and SVET results.

3.4. Metallographic analysis

The microstructure of the etched BM and WM was observed, and the results are shown in Figure 11. In addition, the surface microstructure of the WM after the measurement of polarization curve was also observed. The result is shown in Figure 12.



Figure 11. Surface morphology after etching for the (a) 2205 DSS BM and (b) ER2209 WM.

Figure 11(a) shows the metallographic structure of the 2205 DSS BM, which presents a typical two-phase structure. The dark grey ferrite was the matrix, and the light grey part was austenite. The two phases have clear grains and boundaries.

Figure 11(b) shows the metallographic structure of the WM, which was also composed of ferrite and austenite phases. However, compared with the BM, its metallographic structure was very different. In the metallographic structure of the WM, the phase area of ferrite with dendrites was much larger than that of the austenite, covering almost the entire surface. Through analysis software, it was calculated that the austenite content was 49.9% in the BM, which was very close to the optimal corrosion resistance ratio of DSS [3]. The austenite content in the WM was only 39%, that is, the WM had a high proportion of ferrite. However, the good corrosion resistance of DSS welded joints mainly depends on the equal area proportion of ferrite and austenite phases [7]. The area proportion of the austenite phase in the WM was quite different, which should reduce its corrosion resistance.

Figure 12 displays the microstructure of the WM etched after measurement of the polarization curve. It can be seen that pitting corrosion mainly occurred in the phase boundary between austenite and ferrite phases, and some of the pitting corrosion occurred in ferrite. The above results indicated that pitting corrosion was prone to occur on the two-phase boundary and preferentially developed along the ferrite. Other researchers have obtained similar results [32, 33], and have proposed that this type of corrosion is caused by the electrochemical difference between austenite and ferrite phases [33]. In the corrosion process, the ferrite was the anode and the austenite was the cathode [34]. The ferrite content of the WM was about 61%, which was obviously higher than that of the BM. This may be why

the corrosion resistance of the WM is lower than that of the BM. Geng et al. reached a similar conclusion [35].



Figure 12. The etched microstructure of the WM after measurement of the polarization curve.

4. CONCLUSION

With the increase in the immersion time, the corrosion resistance of the 2205 DSS BM and the WM decreased in the deposited ash/water suspension composed of deposited ash from a waste-toenergy plant and water at 80 °C. The results of the electrochemical measurements showed that for both the BM and the WM, with the increase in immersion time, the passive current density increased and the pitting potential decreased. The total resistance (R_{total}) of the two metals also decreased with the immersion time. Compared with the BM, the passive current density of the WM was higher, and the pitting potential and the R_{total} were lower under the same immersion time. The localized electrochemical measurement results showed that the surface current density of the BM and the WM increased with the increase in immersion time. The time for active sites to appear on the surface of the WM was shorter (4 h) than that of the BM (8 h). The surface roughness (Ra) of both the BM and the WM gradually increased with the immersion time, and the Ra value of the BM was smaller than that of the WM under the same immersion time. Pitting corrosion appeared on the surface of the BM and the WM after immersion for 8 h and 4 h, respectively. The results of metallographic analysis showed that the proportions of ferrite and austenite phases were almost equal in the BM, but the ferrite content in the WM was obviously higher than the austenite content. Pitting corrosion mainly occurred in ferrite phase and the two-phase boundary. After comparing the corrosion behavior of the BM and the WM in the deposited ash/water suspension, it was found that the WM was more prone to pitting corrosion than the BM.

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