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Influence of temperature on the electrochemical and passivation behavior of 2507 super duplex stainless steel in simulated desulfurized flue gas condensates

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1. Introduction

Corrosion of chimney lining materials by residual high humidity gases after flue gas desulfurization (FGD) threatens the safe operation of thermal power plants [1–5]. The residual gases after FGD are easy to form concentrated acidic condensates, containing sulfuric acid as the most abundant corrosive agent. The chlorides, fluorides, and other contaminants can also be present and aggravate corrosion further [1].

Many materials have been used in the FGD system ranging from austenite and duplex stainless steels to nickel-based alloys. Austenite stainless steels (316, 317 and 904L) were found to experience pitting and crevice corrosion, and some of the nickel-based alloys (Alloy 400, Alloy 825, Alloy 20) cannot bear the combination attack of sulfuric acid and halides [2]. Recently, pure titanium was suggested as the lining materials but it suffered severe attack when the fluoride concentration exceeded a critical value [4,5].

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ABSTRACT

Influence of temperature on the electrochemical and passivation behavior of 2507 super duplex stainless steel in the simulated desulfurized flue gas condensates in thermal power plant chimney are investigated. Cathodic reactions are enhanced with temperature, accompanying with the involvement of oxygen reduction when the temperature is raised to 60 °C or higher. The unchanged semiconductor type, enrichment of Cr and thickening of the passive film are observed as the temperature increases. The temperature-induced variations of film structure and doping concentrations are responsible for the degradation of protective ability of the passive film.

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Super duplex stainless steel (SDSS) was found have good resistance against halides [6–8]. Moreover, it was reported to have outstanding corrosion resistance and faint pitting tendency in the high acidified chloride solution [9]. So SDSS with much lower cost than nickel-based alloys might be potential substitute for chimney lining material. However, the performance of SDSS in the concentrated acidic condensates in the chimney after FGD has not been properly understood, the environmental limits for the conditions under which they could perform were still unknown [2].

Many conditions contribute to the corrosivity of the acidic condensates in chimney including temperature, acidity, halide concentration and flow velocity [1]. Jin et al. [9] reported that there exists obvious passive region in the anodic polarization curve and minor passive current density for type 2507 SDSS in a 0.53% sulphate and 12.2% chloride containing solution. Compared with super austenite stainless steel 254SMo, duplex stainless steel 2205 and 825 nickel-based alloy, 2507 SDSS exhibited lower corrosion rate. However, Shoemaker [2] found that 2507 SDSS corroded at a much greater rate than super austenitic stainless steel and nickel alloys in an aggressive FGD solution containing 60% H₂SO₄ + 0.5% HCl + 0.1% HF + 0.1% HNO₃. Whether it is suitable for the 2507 SDSS to be used





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in chimney where the concentration of the formed condensates is different from previous studies needs further research.

The variation of temperature has great impact on corrosion behavior of chimney lining materials in the condensates with sulfuric acid and halides. The temperature of the condensates always ranges between 40 and 80 °C [4], which can affect the electrode kinetic process and passive film properties of stainless steels significantly [10-20]. Antón and co-workers suggested that passive film of Alloy 31 in phosphoric acid was compact and protective [10], and its stability was found to decrease as temperature increased [11]. Carranza et al. [12] reported that the passive film of alloy 800 in sulfate and chloride containing solution become porous with temperature increasing but no effect of temperature on the defect structure of the semiconductor oxide film was found. Wu et al. [13,14] concluded that effect of temperature on the property of oxide film could be mainly attributed to the temperature-induced variation of the composition and protective ability of the barrier layer. While Cardoso et al. [15] proposed that passive film degradation was related to the drastic oxidative dissolution of the film at high anodic potentials, independent of its semiconductor characteristic, chloride presence and increased temperature. Recently, Shoesmith et al. [16] found that increase of the passive film thickness and depletion of the alloying elements were responsible for the temperature-independent behavior of Alloy C-2000 in NaCl. Based on the above works, the composition, thickness, structure and electronic properties of the passive film should be considered to elucidate the influence of temperature on the passivation behavior of stainless steels. However, only limited information appears available on the corrosion and passive behavior of SDSS in the condensates polluted with various aggressive ions including sulphate, chloride, nitrate, and fluoride ions. Therefore, an investigation concerning on the temperature-affected corrosion behavior of SDSS in simulated condensates of the chimney in FGD is useful to provide a guide for the maintenance of the flue gas temperature and dew point temperature in thermal power plants.

In the present work, the corrosion kinetics and passivation behavior of SAF 2507 SDSS in the polluted condensates, simulating lining conditions of chimney in FGD system, are investigated. The influence of temperature on the electrochemical behavior, passive film properties (composition, thickness, structure and electronic properties) are evaluated. The temperature-dependent passivation behavior and the critical temperature are discussed.

2. Experimental

2.1. Materials and solution

The test material was a commercial standard 2507 (UNS S32750) SDSS with a thickness of 3 mm, supplied by Nippon Steel & Sumikin Stainless Steel Corporation. The alloy was provided in the form of hot-rolled and solution-annealed at 1100 °C for 20 min, followed by water quenching. The normal chemical composition (wt.%) were: C 0.03, Cr 25.15, Ni 6.74, Mo 3.43, N 0.27, Si 0.8, Mn 1.2, S 0.02, P 0.035, and Fe balance. The specimens were machined into square sheet with a dimension of $10 \times 10 \times 3$ mm, and then wet ground sequentially to 2000 grit SiC paper, polished with 0.1 µm alumina polishing power, degreased with alcohol, cleaned in water, and then dried in cold air.

Table 1

Chemical composition of the actual and simulated desulfurized fuel gas condensates.



Fig. 1. Microstructure of 2507 SDSS used in this work: (a) Optical microscope observation, (b) SEM observation. (α : ferrite, γ : austenite).

The microstructure of the 2507 SDSS was observed by optical metallography and scanning electron microscopy (SEM, Quanta 250) after the polished specimen was etched by Behara reagents for 10 s [21]. The results shown in Fig. 1 revealed that the interface between the two-phases had been clearly etched, and the austenite phase (γ) is embedded in the continuous ferrite matrix (α). The volume fractions of ferrite and austenite were 51.8% and 48.2%, respectively.

The test solution was the simulation solution of the desulfurized flue gas condensates obtained from the chimney of a power plant in China. The condensates were first collected in the chimney and then analyzed in laboratory. The chlorides, sulfates, nitrate, total fluorine and pH were detected and the results were listed in Table 1. The simulation solution was made from analytic grade reagents including H_2SO_4 , HCl, HNO₃, NaF and ultra-pure water. The actual amount of these reagents were also included in Table 1. The pH of the solution was about 1.98.

2.2. Electrochemical measurements

For electrochemical tests, the specimens were encased in epoxy powder coating at 220 °C with adhesion force more than 80 MPa to avoid crevice corrosion before being embedded in a Polyvinyl chloride (PVC) tube using epoxy resin [22]. Electrochemical measurements were performed with a CHI660 electrochemical workstation in a conventional three-electrode cell, using a platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Prior to test, the working electrodes were initially potentiostatically at $-1.0 V_{SCE}$ for 5 min to remove air-formed oxides.

Anions	SO4 ²⁻	Cl-	NO_3^-	F-	pН
Concentration (mg L ⁻¹)	494	261	49	43.4	1.98
Analytic grade reagent	H ₂ SO ₄ (98%)	HCl (37%)	HNO ₃ (68%)	NaF	
Concentration (mg L ⁻¹)	514.6	715.1	73.2	95.9	

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