

# SIMULATING EXPERIMENTS OF HOT CORROSION CELL<sup>①</sup>

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**ABSTRACT** The structure of hot corrosion cell was changed with the increasing of porous oxides in products during the process of hot corrosion, it was macro cell that took main role in the direction vertical to the surface of samples. Anode reaction took place at the metal/compact oxide film interface, cathode reduction reaction took place at the molten salt + porous oxide/gas interface. The interfaces of porous oxide + molten salt/gas and metal + compact oxide film/molten salt were simulated, the acidity and basicity and oxygen activity were measured at both interfaces with time. It was shown that the gradient of basicity was positive in the salt film. The oxygen activity was decreased at the metal + compact oxide film/molten salt interface with time.

**Key words** macro cell basicity gradient oxygen activity

## 1 INTRODUCTION

About the mechanism of hot corrosion, several models have been proposed<sup>[1-3]</sup>, among which, the fluxing model is more popular. Because the molten salt is electrolyte, it is necessary that the hot corrosion process is associated with the electrochemical process. Some works were done to study the mechanism of hot corrosion from electrochemistry<sup>[4-6]</sup>.

Recently, He Yedong and Zhu Rizhang have proposed a new micro cell model of hot corrosion, emphasizing that in the direction of parallel to the surface of samples the micro cell was produced by the inhomogenities and defects of oxide film formed during the process of hot corrosion, such as different kinds of oxide, sulfide.

It was considered that the process of micro cell occurred mainly in the initial stages of hot corrosion, when porous oxides were gradually increased in products, and contacted together, the electrochemical cell structure of hot corrosion was changed. In general case,

there is insufficient molten salt to fill in all pores in the porous oxide layer during the process of hot corrosion, the porous oxide can contact or sinter together locally with the compact oxide film. The situation can be proved by the hot corrosion of blade in the gas turbine. If there were not any connections between oxide particles in the porous oxide layer, which was as thick as 1 mm as reported by Moller<sup>[8]</sup>, the porous oxide layer would be thrown away under the huge centrifugal force. Because the porous oxide is a semiconductor and connects locally with the compact oxide film in high temperature, electron produced by reaction  $M \rightarrow M^{n+} + ne$  at the metal/oxide film interface could transport through the compact oxide film and porous oxide layer, reaching the molten salt + porous oxide/gas interface, so that the reduction reaction of oxidant  $O_{xi} + 2e \rightarrow O^{2-}$  could took place at this interface, so, the macro cell was constituted in the direction vertical to the surface of metals.

The reactions of cell was

Anode:  $M \rightarrow M^{n+} + ne$

Cathode:  $O_{xi} + 2e \rightarrow O^{2-}$

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## 2 EXPERIMENTAL

When the electrochemical cell, as shown in Fig. 1, was constituted, the basicity and oxygen activity at the metal + compact oxide film/molten salt interface and molten salt + porous oxide/gas interface should be changed. A simulating cell was used to measure these changes, as shown in Fig. 2.

The samples were plate of 99.8% Ni (10 mm × 10 mm × 1 mm), ground to 600 # by abrasive paper and degreased in acetone, a Ni-Cr wire used as conducting wire was welded at one end. The simulating cell device was an alumina tube, whose one end was closed by a porous sintered NiO layer. The porous sintered NiO + molten salt/gas interface and Ni sample/molten salt interface simulated porous oxide + molten salt/gas interface and Ni + compact oxide film/molten salt interface during the hot corrosion of nickel respectively. As shown in Fig. 2, a sealed alumina tube was used as reaction container, in which argon was aerated into the Ni sample/molten salt interface to exclude oxygen. To make porous NiO layer, a nickel-plating net of Pt wire was winded round the end of alumina tube, one end of Pt wire was led as conducting wire, NiO powders were painted on the net, dried in room temperature, heated to 900 °C, repeated several times until porous NiO layer was formed. Two pairs of oxygen probe and sodium sensor were fixed at two interfaces in the

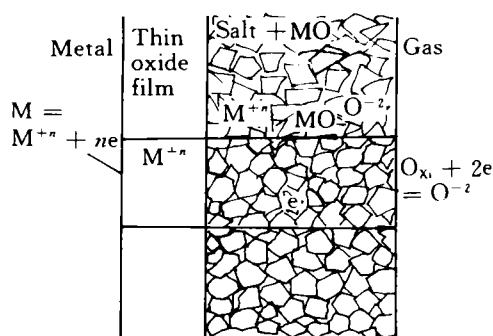


Fig. 1 The macro cell model of hot corrosion

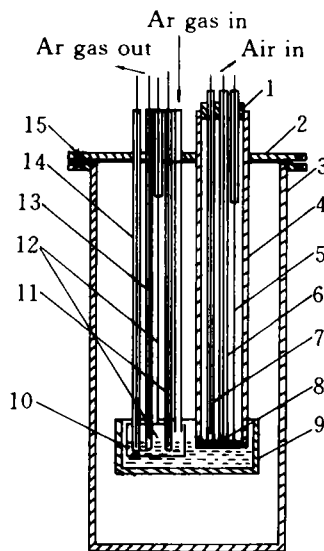


Fig. 2 The device of simulating cell

- 1—Rubber plug; 2—Flange; 3—Al<sub>2</sub>O<sub>3</sub> tube;
- 4—Al<sub>2</sub>O<sub>3</sub> tube; 5—Ni wire pre-oxidized in air;
- 6—Sodium probe; 7—Oxygen probe;
- 8—Porous NiO; 9—Al<sub>2</sub>O<sub>3</sub> Crucible;
- 10—Fused Na<sub>2</sub>SO<sub>4</sub>; 11—Thermocouple;
- 12—Ni sample; 13—Oxygen probe;
- 14—Sodium probe; 15—Rubber-O-Ring

simulating cell to measure the oxygen activity and basicity. The oxygen probe was made of partially stabilized one-end-closed zirconia tube, the inside bottom of which was painted with Pt ink and sintered, a Pt lead wire was contacted with the internal sintered Pt and air was aerated into the inside of the tube during the measurements. The sodium sensor was made of a pure silver wire dipped into a 10 mol% Ag<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub> mixture salt contained in a one-end closed  $\beta$ -Al<sub>2</sub>O<sub>3</sub> tube.

The difference of equilibrium voltage between the sodium sensor and the working electrode (WE) in molten Na<sub>2</sub>SO<sub>4</sub> at 900 °C was

$$E_1 = 1.455 + \frac{RT}{2F} \ln(a_{\text{Na}_2\text{O}}/P_{\text{O}_2}^{1/2})(\text{WE})$$

The equilibrium voltage difference between the oxygen probe and the working electrode was

$$E_{\text{II}} = \frac{RT}{2F} \ln[P_{\text{O}_2}^{1/2}(\text{air})/P_{\text{O}_2}^{1/2}(\text{WE})]$$

$E_1 - E_{\text{II}}$  was used to calculate the melt

salt basicity,

$$E_{\text{III}} = E_{\text{I}} - E_{\text{II}} =$$

$$1.494 + 0.116 \lg a_{\text{Na}_2\text{O}}(\text{WE})$$

At the interface of Ni + compact oxide film/molten salt, the working electrode was Ni, at the interface of porous NiO + molten salt/gas, NiO was used to represent the working electrode. On measuring, Pt wire was connected with Ni sample, the molten salt basicity could be inferred by measuring the voltage difference  $E_{\text{III}}$  between the sodium sensor and the oxygen probe, the oxygen activity of two interfaces could be calculated by measuring the voltage difference  $E_{\text{II}}$  between the oxygen probe and working electrode. The voltage difference was measured by digital voltmeter. The experimental temperature was controlled at 900 °C by Pt-PtRh10 thermocouple.

### 3 RESULTS AND DISCUSSION

The results of the simulating cell experiment were shown in Fig. 3. The basicity at the porous NiO + molten salt/gas was located in the regime of NiO basic dissolving, and increasing with time,  $P_{\text{O}_2}$  was generally constant. Meanwhile, the basicity at the Ni sample/molten salt interface was located in the regime of NiO acidic dissolving,  $P_{\text{O}_2}$  was decreased with time, shifting into the stable regime of nickel sulfide from NiO stable regime. It was shown that the basicity of the molten salt layer was positive during the process of hot corrosion.

According to the cell model shown in Fig. 1, the compact NiO film was formed on the surface of Ni sample during the process of experiment, anode and cathode reactions took place at the Ni/compact NiO film interface and compact NiO film/molten salt respectively, when the macro cell was constituted, polarization took place, the anodic current density was the difference between the oxidation current density of reaction  $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}$  at the Ni/compact NiO film interface and the reduction current density of reaction  $\text{O} + 2\text{e} \rightarrow \text{O}^{2-}$  at the compact NiO film/molten salt,  $\text{Ni}^{2+}$  ion could transport through the compact NiO

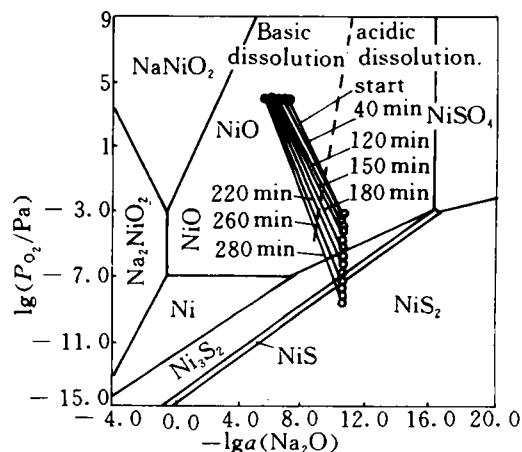


Fig. 3 Trace of basicity and oxygen activity with time

- the interface of porous NiO + molten salt/gas;
- the interface of Ni sample/molten salt

film, dissolving in the molten salt film and reacting with  $\text{O}^{2-}$  to form porous NiO. So, the basicity at the Ni/molten salt interface was lower, meanwhile, oxygen was depleted with time. Because of the equilibrium reaction  $2\text{SO}_2 = 2\text{O}_2 + \text{S}_2$ ,  $P_{\text{S}_2}$  was decreased, so that the sulfur penetrated into the compact NiO film and reacted with substrate to form nickel sulfide. The cathode reduction reaction  $\text{O} + 2\text{e} \rightarrow \text{O}^{2-}$  took place at the porous NiO + molten salt/gas interface, so the basicity increased at this interface, and because of opening to the air,  $P_{\text{O}_2}$  was generally constant. By this way, the positive basicity gradient was established in the salt film during the process of nickel hot corrosion. Because the solubility of oxide responded to a certain basicity<sup>[9]</sup>, as shown in Fig. 4, the solubility gradient of oxide was positive at the compact oxide film/molten salt interface, which was opposite to the criterion that the solubility gradient of oxide was negative at the oxide film/molten salt interface<sup>[3]</sup>.

Actually, according to the hot corrosion experiment about the pre-oxidation Ni covered with  $\text{Na}_2\text{SO}_4$  in 0.1%  $\text{SO}_2$ - $\text{O}_2$  tested by Otsuka<sup>[10]</sup>, the basicity also increased with time, but they considered that the measured value was the basicity at the interface of compact

oxide film/molten salt, so the negative basicity gradient was established in the salt film, although the measured value was a chemistry averaged over the salt film thickness. But, if analyzing their experiment device, it was shown that the probes were attached to the samples, the measured value was initially the one at the compact oxide film/molten salt interface, because  $\text{SO}_2$  and  $\text{O}_2$  were contained in the reactive atmosphere and the following reactions existed

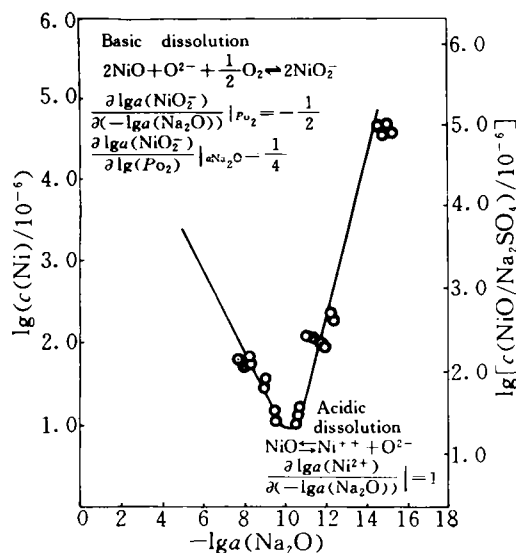
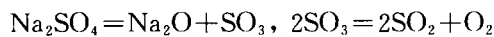


Fig. 4 Solubility of NiO in fused  $\text{Na}_2\text{SO}_4$  at 1200 K

$\text{SO}_3$  increased, the basicity decreased, the acidity was shown. But, with increasing time, because the porous oxide increased in products and the molten salt penetrated into them, the measured value was changed to the one at the porous oxide + molten salt/gas interface, where the oxygen reduction reaction took place, the measured basicity increased. It was shown that this experiment result conformed with our simulating cell situation.

## 4 CONCLUSION

With the porous oxide increasing during the process of hot corrosion, the electrochemical cell was constituted in the direction of vertical to the surface of samples, the oxidant reduction reaction took place at the porous oxide + molten salt/gas interface, the metal oxidation reaction took place at the metal/compact oxide film interface. The changes of the basicity and oxygen activity at the Ni + compact NiO film/molten salt and porous NiO + molten salt/gas interfaces were measured with time by the simulating cell device, it was shown that the positive basicity gradient existed in the salt film, which conformed with the proposed model of macro cell.

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