Evidence for the occurrence of electrochemical reactions and their interaction with chemical reactions during the corrosion of pure Fe with solid NaCl deposit in water vapor at 600 °C

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1. Introduction

Marine corrosion of turbine blades in planes or ships is very serious because of the synergistic effect of solid NaCl and water vapor at medium and high temperatures [1–8]. From the results of a systematic investigation of this corrosion it has been suggested that there may be a “dynamic water film” with H2O molecules continuously being absorbed on, and evaporating from, the surface of the material and that electrochemical corrosion occurs in this water film, which accelerates the metal dissolution [3]. However, this hypothesis is very controversial and is not accepted by many scientists. It is therefore necessary to study the relevant electrochemical reactions.

In earlier studies, Liu et al. used EIS to investigate the corrosion behavior of pure Fe and pure Cr with solid NaCl deposit in water vapor at 600 °C [8]. Although the electrochemical reactions were not studied in detail, this work proved that electrochemical techniques, and in particular EIS, are effective methods for studying the corrosion process in this environment.

The present work focuses on: (1) to determine whether electrochemical corrosion occurs on the surface of pure Fe with a solid NaCl deposit in water vapor at 600 °C; (2) if electrochemical reactions do occur, to clarify their role in the corrosion process. It is necessary to understand the corrosion mechanism of metals/ alloys in this environment in order to develop effective protection techniques.

2. Experimental

Pure Fe (99.9%) specimens were used, the preparation of which has been reported elsewhere [8]. A special three-electrode system was built for the electrochemical measurements in this particular environment. The top and cross-section view of the electrode arrangement is shown in Fig. 1a and b. To decrease the resistance of the solution and get a uniform electric field, the reference electrodes consisted of four platinum wires with a diameter 0.4 mm, and the counter electrode was a circular strip of platinum foil about 2 mm wide. The Fe working electrode was a rod 10 mm long and 5 mm diameter. The three electrodes were in quartz tubes, which acted as insulators. All the gaps were sealed by high temperature inorganic glue.

A PAR2273 Electrochemical Measurement System manufactured by EG&G was used for electrochemical measurements. In chronopotentiometry measurements, a 0.5 mA cathodic current was applied to detect the transition times. The resistance between reference and working electrodes was compensated during measurement. In EIS measurements, the perturbation was 0.1 V because of the low conductivity of NaCl at 600 °C [9] and the frequency was swept from 10 kHz to 10 mHz.

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3. Results and discussion

3.1. Electrochemical corrosions

Fig. 2 shows the variation of galvanic corrosion current \( I_g \) with time for two couples: one is iron–platinum and the other is platinum–platinum under the synergistic effect of solid NaCl deposit in water vapor at 600 °C. The results show that \( I_g \) of the platinum–platinum couple was near to zero with some fluctuating points, while the \( I_g \) of the iron–platinum couple was about 10⁻⁵ A/cm². It is believed that no corrosion reactions occurred on the inert Pt electrode [8] and its current should be a measure of the background current of this system. The current on the pure Fe electrode was higher because of the electrochemical reactions which were occurring on it.

For pure Fe in this corrosion environment, the anodic reaction is simple \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \), but the cathodic reactions are complicated. The chronopotentiogram of the cathodic reaction (Fig. 3) showed that there was only one transition time for this cathodic reaction. Therefore, there is only one cathodic reaction on pure Fe.

Authors think that the corrosion of pure Fe in this environment includes chemical and electrochemical corrosion reactions. After calculation, the percentage of electrochemical corrosion reaction to total whole corrosion reactions is about 8.0%. However, the corrosion rate was dramatically increased when electrochemical reaction occurred. The corrosion rate is controlled by the consuming of iron and the consuming of iron produced by electrochemical reaction is limited. Therefore, the cathodic electrochemical reaction accelerated the consuming of iron produced by chemical corrosion reaction, which lead to the increase of corrosion.

Fig. 1. Schematic diagram of three-electrode cell: the top view (a), the cross-section view (b).

Fig. 2. The galvanic current of a pure Fe electrode and a pure Pt electrode with a solid NaCl deposit in water vapor at 600 °C.

Fig. 3. Chronopotentiometry curve for pure Fe with a solid NaCl deposit in water vapor at 600 °C.

Fig. 4. Frequency dependence of phase angle of pure Fe with a solid NaCl deposit in water vapor at 600 °C at open circuit potential.
3.2. The interaction between electrochemical reaction and chemical reaction

According to Smith [10], a plot of $\cot \Phi$ vs. $\omega^{1/2}$ ($\Phi$ = phase angle, $\omega$ = frequency) can be used for mechanistic diagnosis. When the preceding or following chemical reaction has varying balance constant and chemical reaction rate constants, the plot of $\cot \Phi$ vs. $\omega^{1/2}$ will show different shape. For example, an electrochemical reaction coupled with either a preceding chemical reaction (ce) or a following chemical reaction (ec) will show a maximum in a plot of $\cot \Phi$ vs. $\omega^{1/2}$. However, for a chemical reaction ($k_1 \neq k_2$), the ce mechanism, the $\cot \Phi$ decreases with $(E - E_{1/2})$ increasing; whereas for an ec mechanism, the $\cot \Phi$ increases with $(E - E_{1/2})$ increasing. Thus Fig. 6 shows that the corrosion mechanisms in this work are type ce, which means the electrochemical reaction is coupled with a preceding chemical reaction. According to Eq. (1), the plot of the potential $E$ vs. $\ln[1 - (t/\tau)]$ gives a straight line of slope $RT/\alpha F n$. The number of electrons involved in the cathodic reaction can therefore be obtained from the slope which, from Fig. 5, has a value of 0.17. Therefore the value of $a \times n$, from Eq. (1), is 0.40. According to the reactions which have been proposed [1], the cathodic reaction may involve the reduction of HCl to H2. Therefore, the cathodic reaction proceeds via one-electron transfer. The transfer coefficient (a) is 0.40.

4. Conclusion

(1) Electrochemical corrosion occurs on a pure Fe electrode with solid NaCl deposit in water vapor.

(2) The corrosion of pure Fe in this environment follows a ce mechanism: Fe first reacts chemically with NaCl and water vapor, then the following electrochemical reactions take place: the anodic reaction is Fe $\rightarrow$ Fe$^{2+}$ + 2e and the cathodic reaction involves the decomposition of HCl via a one-electron reduction to form H2.

Acknowledgments

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Reference