Effects of Solution Temperature on Electronic Properties of Passive Film on Fe in pH 8.5 Buffer Solution

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As one of the major environmental parameters, it is well known that the increase in solution temperature has significantly detrimental effect on the corrosion properties of Fe and Fe-based alloys. However, understanding of these phenomena based on the electronic properties and defects structure of passive film is not yet clear.

In this study, we examined effects of solution temperature on the electronic properties and defect structures of the passive film on Fe by Mott-Schottky analysis and photocurrent measurement and discussed the results based on the Point Defect Model.

It was revealed that with increasing solution temperature from 30 ^{o}C to 80 ^{o}C, passive current density of Fe increased (Fig. 1), and the concentration of oxygen vacancy in the passive film also increased (Fig. 2).

Fig. 3 shows the effects of solution temperature on the photocurrent spectra for the passive film on Fe. There are two types of electronic excitation processes; the d-d transition, i.e. the electronic excitation from Fe^{3+} band to Fe^{2+} band, and the p-d transition, i.e. the excitation from the valence band (O-2p) to the conduction band (Fe-3d). The peak at about 2.7 eV is due to an electronic transition in γ-FeOOH hydroxide layer formed on γ-Fe_2O_3 passive film. By photocurrent measurement we showed that the increase in solution temperature induced the increase in the concentration of Fe^{2+} ion in the film which is correlated to that of oxygen vacancy.

Based on the Point Defect Model, it was concluded that the main reason for the increase in the passive current density of Fe with increase in the solution temperature was due presumably to the increase in the concentration of oxygen vacancy in the passive film. The correlative change in the concentration of oxygen vacancy and Fe^{2+} ions in the passive film could be interpreted by a charge neutrality reaction in γ-Fe_2O_3 passive film.

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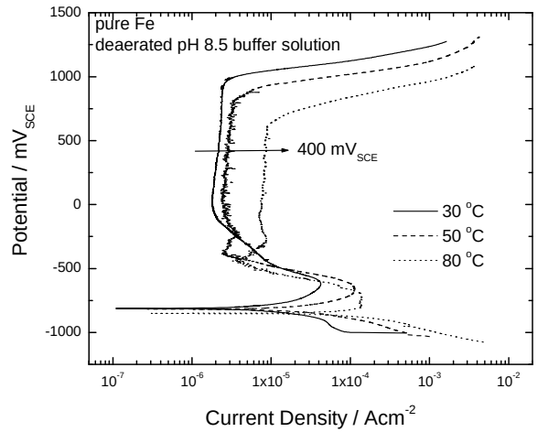

Fig. 1 Potentiodynamic polarization curves of Fe in pH 8.5 buffer solution at various solution temperatures. Scan rate was 0.5 mV/sec.

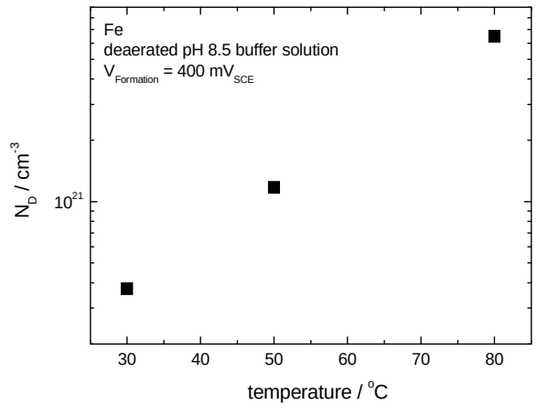

Fig. 2 Donor density in the passive film on Fe as a function of solution temperature.

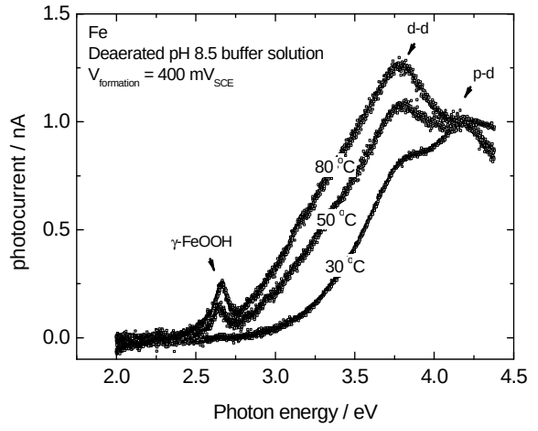

Fig. 3 Photocurrent spectra for the passive films formed on Fe for 20 h at 400 mV$_{SCE}$ in deaerated pH 8.5 buffer solutions with different solution temperatures.