

Electrochemical Properties of Fe₂O₃-Cr₂O₃ Thin Films and Pitting Behavior of Fe-Cr Alloys in Neutral NaCl Solutions

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Introduction

In our previous studies on the electrochemical nature of Fe₂O₃-Cr₂O₃ thin films in 1M HCl, the films with low Cr cationic fraction, X_{Cr}, show the reductive dissolution at low potentials and the films with high X_{Cr} the oxidative (transpassive) dissolution at high potentials [1, 2]. The films never show pitting dissolution irrespective of their X_{Cr} values. From these facts, the reductive dissolution of locally low X_{Cr} parts in the passive films on Fe-Cr alloys was presumed to be concerned with the passivity breakdown leading to pit initiation [1, 2].

The objectives of the present study are to make clear the effect of pH on the reductive dissolution of Fe₂O₃-Cr₂O₃ thin films in chloride-containing solutions and to consider the role of passive films in the pitting mechanism of Fe-Cr alloys in neutral NaCl solutions.

Experimental

Fe₂O₃-Cr₂O₃ thin films with various X_{Cr} were prepared by ion-beam sputter deposition. The thinning rate of the films in chloride-containing solutions with various pH was measured in-situ by using an automatic ellipsometer. The pitting behavior of vacuum induction melted Fe-Cr alloys with 10-30% Cr was also measured in chloride-containing solutions. The composition of passive films formed in the solution was analyzed by AES coupled with Ar⁺ sputtering. Initiation sites of pitting on the alloys were observed by SEM. The composition of non-metallic inclusions in the alloys was analyzed by EPMA.

Results and Discussion

The X_{Cr} value of passive film formed on Fe-20Cr alloy at 0V(vs. Ag/AgCl, 3.33M KCl) in 1M NaCl for 10.8ks was about 0.4. Based on this result, Fe₂O₃-Cr₂O₃ thin film with X_{Cr} = 0.5 was formed and its thinning rate as a function of potential was measured in 1M H₂SO₄ containing 0.1M Cl⁻ at pH 0.2. The film showed no dissolution between -0.3V and 1.0V, above which transpassive dissolution occurred. This suggests that the passive film with X_{Cr} = 0.5, that is, the most part of passive film, on the alloy has no susceptibility to pitting in the solution.

The start potentials of reductive dissolution of Fe₂O₃ thin film, which is a model for low X_{Cr} parts in the passive film, were measured in buffer solutions containing 1M Cl⁻ with pH from 0.2 to 8.0. The start potentials were at 0.5, 0.4, 0.2, 0.0, -0.1, and -0.3V for pH 0.2, 1.9, 4.1, 5.9, 6.9, and 8.0, respectively.

The pitting potentials of Fe-Cr alloys containing 10-30% Cr were measured in 1M NaCl with pH 5.9. The pitting potentials were at -0.4, -0.1, 0.2, and 0.7V for 10, 15, 20, and 25% Cr. No pitting occurred on the 30% Cr alloy. This suggests that the initiation of pitting becomes harder with increasing X_{Cr} value of passive film.

Then, the change in pitting potentials of Fe-20Cr alloy with pH was measured in chloride solutions containing 1M Cl⁻. The pitting potentials were at -0.2, 0.1, 0.35, and 0.3V for pH 0.2, 1.9, 3.9, and 5.9, respectively. This suggests no contribution of reductive dissolution of Fe₂O₃ rich parts in the passive film to the initiation of pitting in the solutions of pH 3.9 and 5.9, because the start potentials of reductive dissolution of Fe₂O₃ are lower than the pitting potentials in the solutions. In solutions of pH 0.2 and 1.9, however, the reductive dissolution of Fe₂O₃ rich parts should contribute to the passivity breakdown. SEM observations on the pitting sites on Fe-20Cr alloy held at 0.5V in 1M NaCl with pH 6.9 for 3.6ks showed that pitting started at non-metallic inclusions. The analysis by EPMA revealed that the inclusions were Cr₂O₃ partly covered by MnS. This finding suggests that pitting should start by the dissolution of MnS, accompanying with decrease in pH inside a pit around a Cr₂O₃ inclusion [3, 4]. If the X_{Cr} value of repassivation film formed on the pit inside is high enough to suppress the reductive dissolution of Fe₂O₃ rich parts in the repassivation film, pitting will decrease but, if not so, pitting will grow.

Conclusion

Pitting on vacuum induction melted Fe-20Cr alloy starts at Cr₂O₃ inclusions partly covered by MnS. The X_{Cr} value of repassivation film formed on the pit inside should determine the repassivation of the pit through the suppression or no suppression of the reductive dissolution of the film.

References

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