

Historical Understanding of Acid Chloride Passivity Breakdown on Fe-Cr Alloys and New Insight Derived from Artificial Passivation Film Experiments

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1. Introduction

Pitting processes on Fe-Cr alloys have been divided into two processes, that is, the first passive film breakdown and the consecutive matrix alloy dissolution. In this paper, historical understanding on the roll of Cr in the inhibition of passive film breakdown and then new insight on the roll are given. Although nonmetallic inclusions such as MnS act an important roll in pitting processes on industrial alloys, the influence of nonmetallic inclusions is excluded because this paper is intended for pitting on high purity alloys.

2. Historical understanding

Historical review on the anodic polarization curves of high purity Fe-Cr alloys shows that the alloy becomes immune against pitting in 1M HCl when the Cr content of the alloy exceeds 30mass% (Sugimoto 1977,1982, Hashimoto 1979). Concerning to the roll of Cr in the inhibition of passive film breakdown on Fe-Cr alloys in acid chloride and other electrolyte solutions, many theories have been proposed: (1)Micro-pore repassivation model (Hashimoto 1979), (2)Bipolar model (Clayton 1986), (3)Percolation model (Newmann 1986, Fujimoto 1993, Ryan 1998, Davenport 2001), (4)Point defect model (Macdonald 1992), (5)Cr-oxide enriched barrier layer model (Marcus 1994), (6)High crystallinity oxide model (Sugimoto 1999), (7)Fe₂O₃-component-reduction suppression model (Sugimoto 2001). The last model has been proposed by the authors using artificial passivation films which are the analogue of passive films on stainless steels. It provides a quantitative and functional explanation for the suppression of passive film breakdown by the Cr addition.

3. New insight

This time, the potentiostatic dissolution behavior of Fe₂O₃-Cr₂O₃ artificial passivation films, which were formed by the ion-beam sputtering technique, has been examined in 1M HCl. The dissolution rate of the films as a function of potential was measured by *in-situ* ellipsometry. The dissolution rate of the films as a function of potential obtained (Fig. 1) was compared with the dissolution rate of Fe-Cr alloys as a function of potential obtained in the same solution (Fig. 2). The films show the reductive dissolution (Region I) and the transpassive dissolution (Region III), but no pitting dissolution (Region II) (Fig. 1). It was found that pitting dissolution of the alloys occurs in the reductive dissolution range of the films (Region I) in which the Fe₂O₃ component of the films suffers from cathodic reduction (Fig. 2). When the Cr content of the passive films on Fe-Cr alloys exceeds the critical value at which the Fe₂O₃-Cr₂O₃ artificial passivation film attains no reductive dissolution, no pitting occurs on the Fe-Cr alloys. The critical value of the cationic mass fraction of Cr, X_{Cr} , was ca. 0.6 and the X_{Cr} value of the passive films formed on the Fe-30Cr alloy in 1M HCl was estimated to be X_{Cr} = ca. 0.6. In the potential range between the reductive dissolution and the transpassive dissolution of the Fe₂O₃-Cr₂O₃ artificial passivation films (Region II), the

Fe-Cr alloys become immune against pitting.

4. Conclusion

It can be concluded that the attainment of X_{Cr} = ca. 0.6 of passive film is very important for the attainment of immunity against the passive film breakdown in 1M HCl. If there is a locally Cr-depleted part, of which Cr content is less than X_{Cr} = 0.6, in the passive film with the X_{Cr} value higher than 0.6, the part suffers from the reductive dissolution and then pitting occurs by the anodic dissolution of matrix alloy at the part.

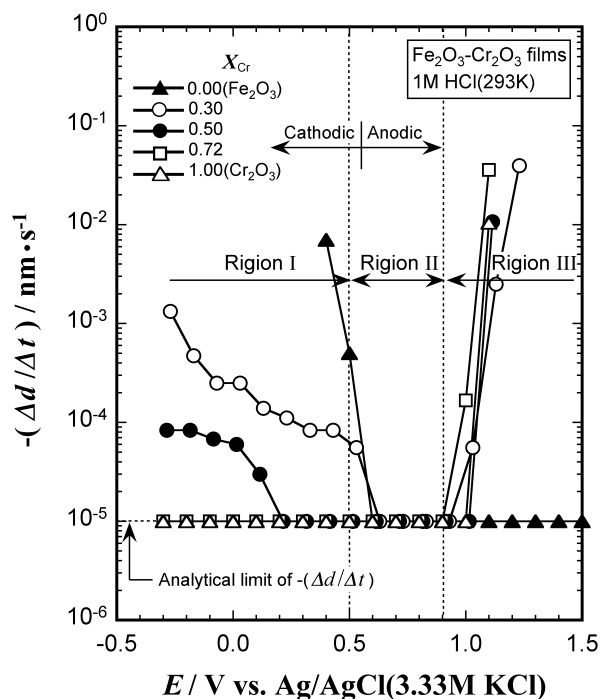


Fig. 1 Thinning rate of film thickness as a function of potential for Fe₂O₃-Cr₂O₃ artificial passivation films.

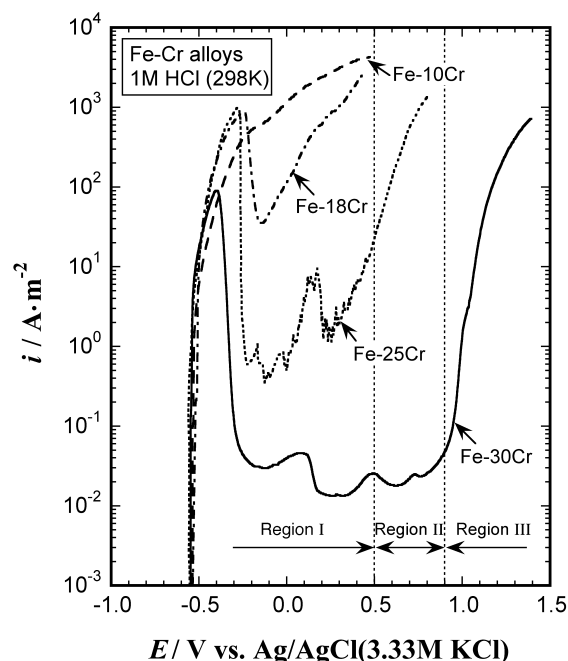


Fig. 2 Anodic polarization curves for Fe-Cr alloys in 1M HCl at 298K.