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EFFECT OF Mo ON PITTING CORROSION OF FERRITIC STEELS IN BROMIDE AND CHLORIDE SOLUTIONS

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M. Kaneko* and H. S. Isaacs

Brookhaven National Laboratory
Upton, NY 11973, USA

*Steel Research Laboratory
Nippon Steel Corp.
20-1 Shintomi Futtsu Chiba, , Japan

ABSTRACT

A model for pitting corrosion of stainless steels, independent of changes of passive film properties, was tested using Fe-18%Cr-x%Mo alloys in bromide and chloride solutions. In 1M LiCl the pitting potential improved from -50 $\mathrm{mV_{sce}}$ to about 1200 $\mathrm{mV_{sce}}$ on increasing Mo from 2% to 10%. In 1M LiBr the pitting potential increased from 125 to only 560 $\mathrm{mV_{sce}}$. Active dissolution kinetics of these steels in saturated solutions in a simulated pit were measured. Tafel lines for dissolution moved to more noble potentials with increases in Mo, indicating Mo inhibited dissolution rates. The potential increases were found to be equal to the increases in pitting potential for both halides. Agreement was interpreted in terms maintaining high halide concentrations in the pit by high rates of active metal dissolution. Bromide was less effective suggesting it interacted with Mo adsorbed on the dissolving surface.

INTRODUCTION

Mo is one of the most effective elements in improving the pitting or crevice corrosion resistance of stainless steels in Cl containing solutions(1,2). Many models have been proposed to explain beneficial effects of Mo on localized corrosion. Most propose that improvements are due to changes in the passive film (2,3,4) More recent models have attributed changes to enhanced repassivation of the steel, (5) or to reduced active dissolution rates of the bare metal inside pits (6-12). Other models have emphasized the necessity for maintaining the high chloride concentration within an actively growing pit which was critical to pit propagation(7,8) and it has been shown experimentally that below a critical concentration the active surface repassivated(9,10)

Br is also known to cause pitting in stainless steel. However, Mo is not always beneficial in Br solutions. Although Bond (12) reported that the addition of Mo improved pitting potentials of Fe-18%Cr-x%Mo in both Cl and Br solutions, the addition of Mo did not improve pitting potentials of austenitic stainless steel in Br solutions (13-16). Similar results were also reported by Guo et. al (17) who showed that austenitic stainless steels with high Mo content had lower pitting potentials at elevated temperature in Br solution than Cl solution..

The authors have studied pitting behavior of stainless steel in Cl and Br solutions(18,19). They found that the higher pitting potentials in Br solutions without Mo, may be attributed to difference of active dissolution rate of the bare metal and its repassivation characteristics in these solutions. The effect of Mo on pitting of ferritic and austenitic stainless steels is now being studied in both Cl and Br solutions. The present paper reports on the behavior of ferritic steels. The more complex behavior of austenitic steels will be reported in the future.

EXPERIMENTAL ASPECTS

High purity Fe-18%Cr alloys containing 2% Mo, 5% Mo and 10% Mo and less than 0.005% C, 0.001% S and 0.005% N were used. Sheet samples 11 mm x 11 mm x 3 mm were used for pitting potential measurements. Wires with a diameter of 0.5 mm were used as lead in pencil type artificial pits. All the samples were heat treated at 1100°C for 10 min., water quenched, given a final surface preparation in a 15% HNO3 + 5% HF solution to remove oxides or mechanically deformed layers and were then embedded in epoxy.

Regent grade LiBr and LiCl and 18 MΩ-cm distilled water was used to prepare test solutions. Pitting potentials of sheet samples abraded to #600 grid paper with the edge between metal and epoxy coated with a lacquer, were measured by potentiodynamic polarization at a scan rate of 1.0 mV/s. Pitting potentials are reported as the potential at which the current reached 100 µA.

Pencil type wire electrodes were used to determine the active dissolution rates of the stainless steels in solutions saturated in the dissolution products of the steel (10,11). The wire was first dissolved at high potentials to depth of about 0.44 mm with a salt layer and a saturated solution adjacent to the dissolving interface. After the current was noted the potential was dropped, allowing the salt film to dissolve, and then slowly increased to obtain the same current density observed prior to dissolving the salt layer. This procedure was adopted to produce a saturated solution at the dissolving metal interface but without a salt layer (11). The potential was then stepped to lower values for 3s to measure the active dissolution rate. This procedure was repeated many times to measure the variation of the active dissolution current as a function of potential. All the measurements were carried out at room temperature, about 298K.

RESULTS

Fig. 1 shows pitting potentials of Fe-18%Cr-x%Mo alloys in 1 M LiCl and 1 M LiBr solutions. The addition of Mo increased the pitting potentials of the ferritic stainless steels in both solutions, but a much larger improvement was observed in LiCl than LiBr solutions. In LiCl the pitting potential increased from about -50 to 1200 mV_{sce} on increasing Mo content from 2% to 10%. For the same alloy it increased from 125 to only 560 mV_{sce} in Br solution.

Fig. 2 shows active dissolution rates of steels with 2% and 5% Mo in ion saturated Cl^- and Br^- solutions after correcting for resistance polarization. (The 10% Mo alloy could not be maintained in the active state in chloride solutions and was excluded in these tests.) The rates were found to follow a Tafel behavior. In both solutions the higher (5%) Mo content reduced the current at each potential, or increased the overvoltage at a particular current. The increase in Mo content from 2 to 5% increased the overvoltage by about 700 mV in Cl solution and only about 130 mV in Br solution which were about the same as the changes in pitting potentials for these alloys.

DISCUSSION

Pitting corrosion of stainless steels has predominantly been attributed to changes in the passive film as a result of interactions of chloride with the film. Many models based on properties of the passive film e.g. rupture or dissolution have been developed to account for the onset of localized corrosion and have been reviewed by Strehblow (20). Based on these models it would be expected that simple disruption of the passive film and exposure of the bare steel would lead to localized corrosion. In general, however, scratching the passive surface in a dilute chloride solution does not produce localized corrosion and a more complex series of events are necessary. Alternatively the onset of corrosion can be accounted for by the action of inclusions that are more susceptible to dissolution than the bulk metal and their attack produces an environment in which dissolution of the metal can take place in the active state (21,22).

In contrast to the difficulties in the direct demonstration of changes in passive oxides by alloying elements, changes in the conditions required for the propagation of localized corrosion can be directly demonstrated and quantified. The halide ion concentration inside pits has been shown to be a key factor in the stability of pits (7-10). The concentration of is determined by the balance between dissolution rate of the bare metal inside the pit and diffusing away from the pits. Propagation depends on maintaining the concentrated localized environment in contact with the active metal at a level above that at which repassivation takes place (7-11). Methods for determining the critical concentration at which repassivation takes place have been developed (10-11). The concentration within the pit is maintained by the dissolution of the active metal and decreases by diffusion under the high concentration gradients around the site of corrosion. Increasing active dissolution rates by increasing the applied potential produces stable pitting and alloying elements that reduce the kinetics of dissolution produce alloys that require higher potentials to maintain localized corrosion.

Comparison of the pitting potentials and active dissolution rates of Fe-18%Cr-x%Mo in Cl and Br solutions in Fig. 1 and 2 shows that the difference in pitting potentials are in very good agreement with the difference in active dissolution rates in ion saturated solutions. The increase in Mo from 2 to 5% shifted the Tafel curves in a noble direction by about 700 mV in Cl solution but only about 100 mV in Br solution. These potential increases are in good accordance with the difference of pitting potentials measured in 1.0M LiCl and 1.0M LiBr solutions respectively. It is also interesting to note that at a current density of 0.1 Acm^{-2} the potential for the Tafel lines agree with the pitting potentials observed. It is intersting to note that this current was predicted by Sato based on a somewhat different assumptions (9).

Reduction of the active dissolution rate of the bare metal by adding Mo has been attributed to formation of a submonolayer surface enrichment of Mo (6). Even though there have not been direct observation of surface concentration of Mo, it is considered that Mo might not be enriched at the surface in Br solution. Mo might form complexes with Br and reduce its activity and hence its concentration at the surface. Alternatively, the Br may adsorb competitively on actively dissolving steel and thereby displace the inhibiting Mo atoms on the surface

CONCLUSIONS

Pitting potentials of Fe-18%Cr-x%Mo were increased by 1200 mV by increasing Mo content from 2% up to 10% in 1M LiCl solution while only a 400 mV increase was achieved in 1M LiBr solution. This behavior is well explained by the difference observed in the active dissolution rates of the bare metal in ion saturated Cl^- and Br^- solutions.

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REFERENCES

1. A. J. Sedriks, *Corrosion of Stainless Steels* , 2nd Edition, John Wiley & Sons, New York, p. 112, (1996).
2. Z. Szklarska Smialowska, *Pitting Corrosion of Metals*, National Association of Corrosion Engineers, Houston, TX, p. 147, (1986).
3. K. Sugimoto, Y. Sawada, *Corrosion Sci.*, **17**, 425 (1977).
4. Ya. M. Kolotyrkin, L. I. Freiman, *Korroziya i Zashchita ot Korroziy*, Izd. WINITI, Moscow, Vol. **5**, p.5, (1978).
5. H. Ogawa, H. Omata, I. Itoh, H. Okada, *Corrosion*, **34**, 52 (1978).
6. R. C. Newman, *Corrosion Sci..*, **25**, 341 (1985)
7. Isaacs and Kissel, *J. Electrochem. Soc*, **119**, 1628 (1972).8. Y. Hisamatsu, in *Passivity and Its Breakdown on Iron and Iron Base Alloys* , Edts R. W. Staehle and H. Okada, National Association of Corrosion Engineers, Houston, TX, p. 99, (1976).
9. N. Sato, in *Corrosion and Corrosion Protection*, Edts R. P. Frankenthal, F. Mansfeld, The Electrochemical Society Inc., Proceedings Vol. 81-8, p. 101, (1981).
10. G. T. Gaudet, W. T. Mo, T. A. Hatton, J. W. Tester, J. Tilly, H. S. Isaacs and R. C. Newman, *AIChE J.* **32**, 949 (1986).
11. U. Stainsmo and H. S. Isaacs, *J. Electrochem. Soc*, **140**, 643 (1993).
13. A. P. Bond, *J. Electrochem. Soc* 120, p.603, (1973).
14. J. Horvath and H. H. Uhlig, *J. Electrochem. Soc*, **115**, 791 (1968).
15. Kunio Shiobara, *Boshoku Gijyutsu*, **24**, 453 (1975).
16. W. M. Carrol and E. E. Lynskey, *Corrosion Sci.*, **36**, 1667 (1994).
17. R. Guo and M. B. Ives, *Corrosion*, **46**, 125 (1990).
18. M. Kaneko and H. S. Isaacs, Extended Absracts., San Antonio, TX, Oct. 6-11, 1996, The Electrochemical Society, Inc **Vol. 96-2**, Abs. 188, (1996)
19. M. Kaneko and H. S. Isaacs, to be published.
20. H. H. Strehblow, in *International Congress of Metalic Corrosion* , Toronto, Canada, June 3-7, Proceedings **Vol. 2**, p. 99, 1984..
21. M. A. Baker and J. E. Castle, *Corrosion Sci.*, **34**, 667 (1993).
22. P. C. Pistorius and G. T. Burstein, *Phil. Trans..* **341A**, 531 (1992)

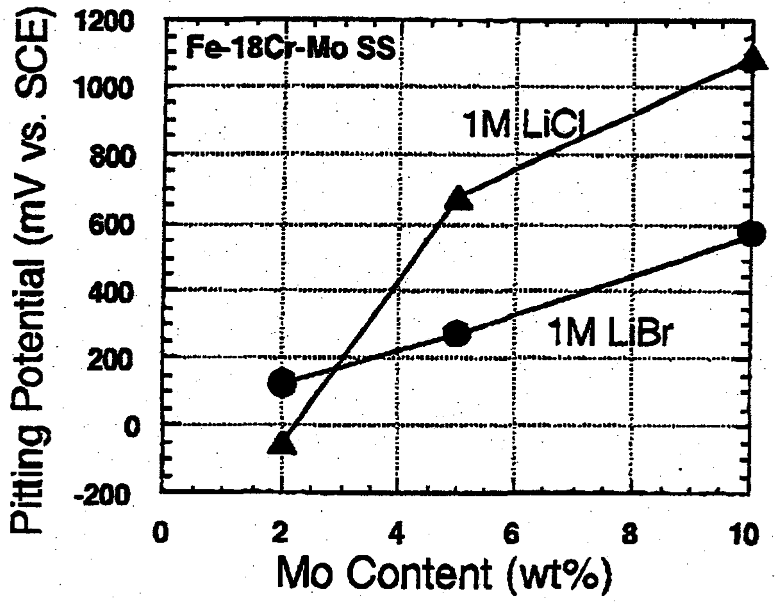

Figure 1. Effect of Mo on pitting potential of Fe 18%Cr-Mo alloys in 1M LiCl and 1M LiBr (scan rate 1mV/s, stable pit criteria = 100 μA).

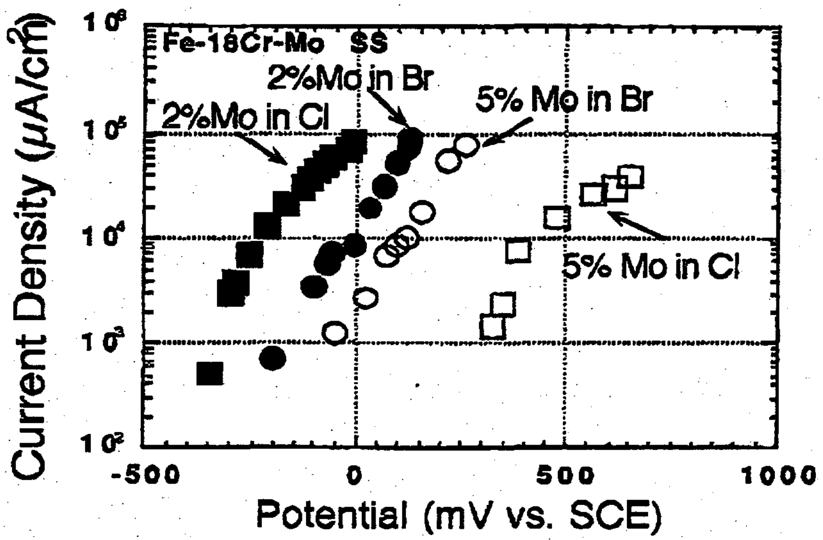

Figure 2. Dissolution rates of Fe 18% Cr alloys with 2 and 5% Mo in saturated solutions of their chloride or bromide dissolution products.