Effects of S Content and Surface Finish on Pitting Corrosion of Austenitic Stainless Steels Containing Mo in Chloride and Bromide Solutions

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Pitting corrosion behavior of austenitic stainless steels with Mo was investigated in chloride and bromide solutions. The steels with higher S content as 0.009 mass% showed higher pitting potential in 1 kmol/m\(^3\) bromide solution than 1 kmol/m\(^3\) chloride solution. On the other hand, the steels with lower S content as 0.0003 mass% showed opposite results. The higher pitting potential was observed in chloride solution. This tendency became profound with passivation treatment by nitric acid. From the experimental results above, it is highly believed that chloride ions are more detrimental to sulfide inclusions induced pitting than bromide ions, whereas pitting due to breakdown of passive film other than sulfide inclusion is more easily caused in solutions containing bromide ions than chloride ions.

KEY WORDS: stainless steels; pitting corrosion; chloride ions; bromide ions; sulfide inclusion.

1. Introduction

Mo is a highly effective element in improving the pitting and crevice corrosion resistance of stainless steels in solutions containing chloride ion.\(^1\) Various models have been proposed to explain the beneficial effects of Mo. They include improving resistant of the passive film to breakdown,\(^2\)–\(^4\) enhancing repassivation characteristics,\(^5\) or reducing active dissolution rate of the bare metal inside pits.\(^6\) Bromides are also known to cause pits on stainless steel. However, additions of Mo do not always show beneficial effects. Bond\(^7\) reported that the addition of Mo improved pitting potentials of Fe–18mass%Cr–x mass%Mo in both chloride and bromide solutions. In contrast, the addition of Mo did not improve pitting potentials of austenitic stainless steel in bromide solutions.\(^8\)–\(^10\) Similar results were also reported by Guo et al.\(^11\) that austenitic stainless steels with higher Mo content showed lower pitting potentials at elevated temperatures in bromide solution than chloride solution. In the absence of Mo high purity austenitic stainless steel showed higher pitting potentials 1 kmol/m\(^3\) LiCl than in 1 kmol/m\(^3\) LiBr solutions. The differences were attributable to the difference of active dissolution rate of the bare metal in concentrated halide solution and repassivation characteristic of stainless steel.\(^12\)

The authors have studied the effect of Mo on the pitting potential, dissolution kinetics, and repassivation behavior of high purity ferritic, Fe–18mass%Cr–x mass%Mo, and austenitic, Fe–18mass%–12–15mass%Ni–x mass%Mo, stainless steels in bromide and chloride solutions.\(^13\) Large increases in pitting potential of Fe–18mass%Cr–x mass%Mo in chloride solution were found with increased Mo content, compared with distinctly smaller increases in bromide solution. The increase in pitting potentials of ferritic alloys between Fe–18mass%Cr–2mass% and 5 mass% Mo in chloride and bromide solutions were in good agreement with the increased dissolution overvoltages in the saturated solution of dissolved products within artificial pits. Austenitic stainless steels also showed larger increases in pitting potential in chloride solution than in bromide solution. Higher pitting potential were recorded for the austenitic than the ferrite steels with the same Mo content. In the case of the austenitic steels the pitting potentials in bromide and chloride solutions were merely not attributable to difference of dissolution rates or repassivation characteristic in saturated solution of dissolved products. It was concluded that initiation processes play important role in the pitting of austenitic stainless steels.

For austenitic stainless steels sulfide inclusions are favorable initiation sites for pitting,\(^14\) therefore effects of S content on pitting resistance of austenitic stainless steels with Mo were investigated in solutions containing chloride and bromide ions. Also, effect of surface finish, a passivation treatment by immersing nitric acid, on pitting resistance of the austenitic stainless steels was investigated.

2. Experimental Procedure

High purity Fe–16.5mass%Cr–15mass%Ni–3mass%Mo alloy (alloy (A)), an alloy added S of 0.009 mass% and Mn of 0.89 mass% (alloy (B)) and Fe–18.1mass%Cr–25.9mass%Ni–5.19mass%Mo (alloy (C)) were prepared by a 20 kg vacuum furnace. The chemical composition of the stainless steels used is shown in Table 1. All the alloys con-
tained higher nickel content to avoid formation of σ phase.

The ingots of the alloys were rolled hot down to sheets in thickness of 3 mm. Test specimens were mechanically cut from the sheets to a size of a length of 11 mm, a width of 11 mm and a thickness of 2 mm.

All the samples were heat treated at 1 100°C for 10 min and water quenched. They were then pickled in solutions with 0.16 kmol/m³ HNO₃ and 0.25 kmol/m³ HF, embedded in epoxy, and polished down to #600 grit on silicon carbide paper. Exposed area of test samples was 11 mm × 11 mm for measuring pitting potential. Some samples were immersed in 4.8 kmol/m³ nitric acid solution for 2 h at 323 K as a passivation treatment to examine the effect of surface finish on pitting. After the passivation treatment some of the samples were cathodically preserved at a potential of −0.7 V (vs. SSE) in sulfuric acid of 0.5 kmol/m³ just before anodic polarization measurements.

Pitting potential of the sheets was measured potentiodynamically at a scan rate of 0.33 mV/s. in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions and reported as the potential at which the current density reached 100 μA/cm². The epoxy/steel edge of the sheet was coated with a lacquer leaving 10 mm × 10 mm area to reduce crevice corrosion. All the samples were checked under a microscope to ensure crevice corrosion did not influence the results. Measurements were carried out at least more than 7 times.

In addition, anodic polarization measurements were done for alloy (C) in 10 kmol/m³ HCl and 10 kmol/m³ HBr solutions. All the measurements were carried out at 303 K and test solutions were deaerated by Ar gas bubbling.

3. Experimental Results

Figure 1 shows the pitting potentials of alloy (A) and alloy (B) in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions. Surface finish of them were #600 grit on silicon carbide paper. In both solutions alloy (A) showed higher pitting potentials than those of alloy (B). Difference in pitting potential for each alloy in the solutions was not so large, but alloy (A) apparently indicated higher pitting potential in chloride solution than bromide solution. In contrast pitting potential was apparently higher in bromide solution than chloride solution for alloy (B).

Even alloy (A) contains 3 ppm S, presumably forms sulfide inclusions in the alloy. As passivation treatment by nitric acid makes sulfide inclusions on the surface of alloy (A) dissolved,15) pitting potential of alloy (A) after passivation treatment was also measured.

Figure 2 shows pitting potential of alloy (A) after the passivation treatment. In both solutions, pitting potentials were largely increased by the treatment. Difference of values of pitting potentials in chloride and bromide solutions became larger than that for polished alloy (A) shown in Fig. 1. The passivation treatment by nitric acid solution also increases Cr content in passive film,16,17) which is considered to increase pitting corrosion resistance of alloy (A). Pitting potentials of alloy (A) passivated in nitric acid followed by cathodic polarization at potential of −0.7 V (vs. SSE) were measured. Figure 3 shows the results. Even after cathodic polarization, pitting potentials of alloy (A) were much higher in chloride solution than bromide solution. In addition, difference of values of pitting potentials in chloride and bromide became larger than that of passivated samples due to decrease of the pitting potentials in bromide solution.

Figures 4 and 5 shows typical anodic polarization curves of alloy (B) polished and alloy (A) with passivation treatment, and followed by cathodic polarization in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions. In case of alloy (B) containing 0.009 mass% shown in Fig. 4, a lot of current fluctuations were observed before reaching pitting potential. On the other hand, for alloy (A) with passivation treatment, and followed by cathodic polarization, no current fluctuation was observed in the both solutions. And corrosion potential of the specimens with cathodic polarization were apparently less noble compared to those of specimens.

Table 1. Chemical composition of specimens tested (mass%).

| Name  | C  | Si   | Mn   | P  | S  | Ni   | Cr   | Cu   | Mo   | N   | O   |
|-------|----|------|------|----|----|------|------|------|------|-----|-----|
| alloy (A) | 0.001 | <0.1 | <0.01 | <0.003 | 0.003 | 15.1 | 16.5 | <0.01 | 3.04 | 0.003 | 0.005 |
| alloy (B) | 0.001 | <0.1 | 0.89 | <0.003 | 0.009 | 15.1 | 16.5 | <0.01 | 3.06 | 0.003 | 0.007 |
| alloy (C) | 0.001 | <0.1 | 0.88 | <0.003 | 0.0004 | 25.9 | 18.1 | 0.02 | 5.19 | 0.003 | 0.007 |

Fig. 1. Pitting potential of alloy (A) and alloy (B) in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions.

Fig. 2. Pitting potential of alloy (A) with passivation treatment in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions.
Fig. 3. Pitting potential of alloy (A) with passivation treatment followed by cathodic polarization in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions.

Fig. 4. Anodic polarization curves of alloy (B) in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions.

Fig. 5. Anodic polarization curves of alloy (A) passivated in the nitric acid solution, and followed by cathodic treatment in 1 kmol/m³ LiCl and 1 kmol/m³ LiBr solutions.

Figures 6, 7 and 8 shows auger electron microscopy measurements of surface layer of alloy (A), polished, passivated and followed by cathodic polarization treated. By applying passivation treatment Cr content in oxide film was dramatically increased compared to the sample polished shown in Fig. 5. Even after cathodic polarization treatment Cr content relative to Fe content in oxide film was still high and large amount of C were detected in surface layer.

Figures 9 shows anodic polarization curves of Alloy (C) in 10 kmol/m³ HCl and 10 kmol/m³ HBr solutions. In the
HBr solution dissolution rate of Alloy (C) was increased with increase in potential. On the other hand, the rate of Alloy (C) was reached maximum values and then decreased like a passivation behavior even though current density was relatively high.

4. Discussion

It is well recognized that MnS is a favorable site for pitting in austenitic stainless steels, which is in good accordance with the results shown in Fig. 1 that alloy (A) with lower S and Mn contents showed higher pitting potentials than alloy (B) with higher S and Mn contents in both chloride and bromide solutions. In addition, it is highly possible that increase of pitting potentials of alloy (A) by passivation treatment shown in Fig. 2 is due to dissolution of MnS in addition to increase of Cr content in passive film shown in Figs. 6 and 7.

However, the opposite order of pitting potentials of the alloy (A) and alloy (B) in LiCl and LiBr solutions were not explained merely by the difference of MnS. In addition, passivation treatment, and followed by cathodic treatment enlarged the difference of pitting potentials of alloy (A) in LiCl and LiBr solutions as shown in Figs. 2 and 3. Assuming that MnS is a favorable pitting site both in chloride and bromide solutions, both alloy (A) and alloy (B) should show similar tendency. Therefore, it is highly possible that pitting corrosion due to MnS occur easier in chloride solution than bromide solution. As examples of typical anodic polarization curves of alloy (B) in LiCl and LiBr solutions were shown in Fig. 4, a lot of current fluctuation was observed in 1 kmol/m³ LiCl solution. On the contrary, for alloy (A) containing lower amount of S as 0.0003 mass% with passivation treatment these current fluctuations were not recorded as shown in Fig. 5. From these results, current fluctuation was attributable to MnS and it implies that chloride ions are more detrimental to MnS induced pitting than bromide ions.

On the other hand, it is likely that pitting corrosion due to breakdown of passive film occur easier in bromide than chloride solution, which is in good accordance with the results that passivation treatment increased the difference in pitting potentials in chloride and bromide solutions. In addition, cathodic polarization treatment decreased the pitting potential of alloy (A) in bromide solution, which enlarged the difference of pitting potentials in chloride and bromide solutions. Cathodic treatment in sulfuric acid should dissolve surface oxide film on alloy (A), which was not clearly observed by AES analysis shown in Fig. 8. However, corrosion potential, Ecorr, of alloy (A) passivated and followed by cathodic polarization was lower compared to passivated sample shown in Fig. 5, which indicate surface oxide film was dissolved. Figure 9 showed anodic polarization curves of alloy (C) in concentrated HCl and HBr solutions which was similar environment inside pits. In these solutions, it showed passivation like behavior in chloride solution, however it dissolved with increase in potential. The results indicates that a passive film of austenitic stainless steel with Mo is more susceptible to pitting in HBr solution than HCl solution, which is in good agreement with the results shown in Figs. 2 and 3.

In this study, it was not elucidated that how the passive film suffered pitting in bromide or chloride solution. However, the authors carried out in-situ observation of state of dissolved Mo ion complex in artificial crevice in chloride and bromide. And distinctive difference was observed in the solutions above. Whereas the structures near the interface showed a significancto difference near the corroding interface; in LiCl, Mo–O bonding similar to MoO₃ octahedra in MoO₃ oxide or MoO₃²⁻ ions was dominant, but in LiBr, the Mo–O–Br complex formed. Sugimoto et al. analyzed state of Mo on stainless steels in hydrochloric solutions and Mo was considered to exist in passive film improving corrosion resistance. On the contrary, based on the in-situ observation that Mo ion forms hydro-bromo complex, Mo ion in passive film might dissolve into solutions containing concentrated bromide, which imply that pitting corrosion due to breakdown of passive film occurs easier in bromide than chloride solution.

5. Conclusions

(1) Decrease of S and Mn contents increased pitting potentials of austenitic stainless steels with Mo in both 1 kmol/m³ LiBr and 1 kmol/m³ LiCl solutions.

(2) Austenitic stainless steels containing Mo with higher S content as 0.009 mass%, Alloy (B), showed higher pitting potentials in 1 kmol/m³ LiBr solution than 1 kmol/m³ LiCl solution. On the other hand, Alloy (A) with lower S and Mn contents as 0.0003 mass% and 0.01 mass%, respectively, showed opposite results, higher pitting potentials were observed in 1 kmol/m³ LiCl solution.

(3) Passivation treatment by nitric acid largely increased pitting potentials of Alloy (A) to noble direction and enlarged the difference of those in chloride and bromide solutions.

(4) Dissolution rate of alloy (C) was increased largely with increase of a potential in 10 kmol/m³ HBr solution, whereas that in 10 kmol/m³ HCl solution showed a behavior like a passivation. Current density was decreased after active dissolution peak.

REFERENCES
1) J. Sedriks: Corrosion of Stainless Steels, 2nd Ed., John Wiley & Sons, New York, (1996), 112.
2) S. Smialowska: Pitting Corrosion of Metals, NACE, Houston, (1986), 147.
3) K. Sugimoto and Y. Sawada: Corros. Sci., 17 (1977), 425.
4) Ya. M. Kolotyrkin and L. I. Freiman: Korroziiya i Zashchita otkorrozii, 5, Izd. WINITI, Moscow, (1978), 5.
5) H. Ogawa, H. Omata, I. Itoh and H. Okada: Corrosion, 34 (1978), No. 2, 53.
6) R. C. Newman: Corros. Sci., 25 (1985), 341.
7) A. P. Bond: J Electrochem Soc., 120 (1973), 603.
8) J. Horvath and H. H. Uhlig: J Electrochem Soc., 115 (1968), 791.
9) K. Shiobara: Corros. Eng. Uppn.), 24 (1975), 453.
10) W. M. Carrol and E. E. Lynskus: Corros. Sci., 36 (1994), 1667.
11) R. Guo and M. B. Ivie: Corrosion, 46 (1990), No. 2, 125.
12) M. Kaneko and H. S. Issacs: Corros. Sci., 42 (2000), 67.
13) M. Kaneko and H. S. Issacs: Corros. Sci., 44 (2002), 1825.
14) A. J. Sedriks: Int. Met. Rev., 27 (1983), No. 5, 295.
15) M. Henthorne: Corrosion, 26 (1970), 511.
16) T. Shibata and T. Takeimoto: 19th Fushoku-Boushoku Symp., JSCE, Tokyo, (1978), 23.
17) K. Asami and K. Hashimoto: Corros. Sci., 19 (1979), 1007.
18) M. Kimura and M. Kaneko: ISIJ Int., 42 (2002), No. 12, 1399.
19) M. Kimura and M. Kaneko: "In S itu Observation of Metal State in Pitting of Stainless Steel", ECS2004, ECS, Pennington, NJ, (2004).