The Effect of Alloying Elements on Pitting Resistance of Ferritic and Austenitic Stainless Steels in Terms of Pitting Resistance Equivalents (PRE)

Jae-Bong Lee and Suk-Won Kim

School of Metallurgy and Materials Engineering, Kookmin University
861-1 Jeongneung-dong, Sungbuk-ku, Seoul 136-702, Korea

The alloying elements, such as Cr, Mo, and N of stainless steels play important roles in their resistances to pitting corrosion. The pitting resistances of stainless steels have long been characterized in terms of electrochemical parameters such as pitting potentials. However, in order to better understand the resistances to pitting of stainless steels, Pit Propagation Rate (PPR) and Critical Pitting Temperature (CPT) tests were carried out in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution. The effect of Cr, Mo, and N alloying elements on the pitting corrosion resistances of both ferritic Fe-Cr, Fe-Cr-Mo stainless steels and austenitic stainless steels was examined by performing polarization, PPR, and CPT tests. The comparison between test results was made in terms of the Pitting Resistance Equivalent (PRE). Results showed that PRE values are the good parameters representing the extents of pitting corrosion resistance on a single scale regardless of both kinds of alloying elements and types of ferritic or austenitic stainless steels.

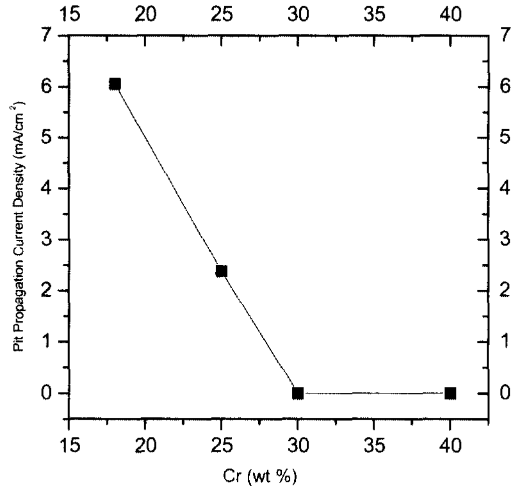
Keywords *: pitting resistance equivalent(PRE), pit propagation rate(PPR), critical pitting temperature(CPT), stainless steel.*

1. Introduction

The resistance to pitting corrosion is one of the most important properties of stainless steels, that is roughly correlated with the resistance to other forms of localized corrosions such as crevice corrosion and stress-corrosion cracking. The electrochemical parameter such as the pitting potential obtained from the potential-current behavior have long been used with some limitations due to the differences in pitting resistance of stainless steels. In terms of the engineering view point, large difference in pitting resistance between stainless steels makes it difficult to compare on a single scale. In order to characterize the pitting resistances of stainless steels by the other parameters besides the pitting potential, the concepts of Pit Propagation Rate (PPR) and the Critical Pitting Temperature (CPT) were introduced by Syrett[1] and by Brigham and Tozer,[2] respectively. PPR is related to the determination of the current density produced due to the pit propagation divided by the pit area whereas CPT is associated with the temperature indicating the critical pitting current density obtained by increasing temperature at the specific applied potential within the passive potential range. The influence of alloying elements such as Cr, Mo, and N on pitting resistance can be investigated in terms of the Pitting Resistance Equivalent (PRE). The concept of PRE was originally introduced by Lorentz and Medawar[3] who found good correlation between the pitting potential of a wide range of stainless steels and the sum of %Cr + 3.3 x (%Mo). Recently PRE was more developed by Jargelius-Pettersson (4) as the following equation.: PRE=Cr + 3.3 x [%Mo] + 36 x [%N] + 7 x [%Mo][%N] -1.6 x [%Mn], including the synergistic effect of Mo and N. In this study, the effect of Cr, Mo, and N alloying elements on the pitting resistance of both ferritic Fe-Cr, Fe-Cr-Mo alloys and austenitic stainless steels was examined by the comparison between polarization, PPR and CPT test results in terms of PRE values.

2. Experimental

Fe- x Cr (x=18. 25. 30. 40 and 100 wt%) and Fe-18 %Cr-x Mo (x=0, 1, 4, and 6 wt%) alloys were prepared by melting in vacuum arc melting furnace back-filled with subsequently by remelting numerous times to ensure proper mixing. Austenitic stainless steels (types 304, 304LN, 316L and 316LN) with the variation of N concentrations from 0 to 0.15 wt% were prepared in the form of ingots by melting in vacuum induction furnace. 0.1N H_2SO_4 + 0.1N NaCl acidic solution (pH=1.6) was prepared with distilled water and the reagent grade H_2SO_4 and NaCl. The solution was de-aerated with high purity Ar before testing and kept under Ar atmosphere during testing. A very high density graphite and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. Cyclic polarization experiments were carried out on specimens by using a Gamry Model CMS105B potentiostat controlled by a computer software (CMS 105). PPR tests were performed by using a potentiostat and a computer following the Syrett's[1] anodic potential cycle. In order to evaluate the resistance of stainless steels to pitting corrosion, CPT tests were performed, based on the ASTM Designation G 150-99.[5] Specimens were installed at the bottom of the flushed port cell before the cell was filled with electrolyte. CPT in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution at a preselected potential between Epit and Eprot was measured by raising the temperature 5℃ every 500 sec. by using the TDC1 temperature controller and potentiostat (a Gamry Model CMS105B) controlled by a computer software(CMS 110). CPT was, for practical reasons, defined as the temperature at which the current density exceeded 300 uA/cm^2 for 600 sec. Based on the cyclic polarization test in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution, applied potentials located between Epit and Eprot were chosen as -1.0 Vsce for ferritic alloys and 0.4Vsce for austenitic stainless steels, respectively for PPR and CPT tests.



(a)

(b)

Fig. 1. (a) Pit propagation current densities for Fe-Cr steels with increasing Cr content at the applied potential of -0.1Vsce in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution, (b) pit morphology of Fe-18%Cr alloy after PPR test

3. Results and discussion

3.1 Effect of Cr on the resistance to pitting corrosion

Fig. 1 (a) shows the PPR test result that the pit popagaion current density for Fe-Cr stainless steels increases with increasing Cr content at the applied potential of -0.1 Vsce. Pit propagation current densities were calculated by dividing the pit propagation current by the pitted area (Fig. 1 (b)). However since Fe- the above 30% Cr alloys did not show the any pitted area, pit propagation current cannot be determined. This fact that Cr decreases pit propagation current density has much to do with Lee's recent work (6) that Cr facilitates the repassivation, improving the stability of the passive film on stainless steels.

Fig. 2 shows the results of CPT measurements carried out to evaluate the stability of passive films formed on Fe-18%Cr and Fe-25%Cr alloys. In the same manner of PPR tests, CPT tests were also performed in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution at the applied potential of -0.1 Vsce within the stable passive potential range. Fe-18%Cr alloy shows that pits can grow below 35℃ while Fe-25%Cr still displays the stable passive current density even at 80℃. Fe-Cr alloys with the above 25% Cr were found to have the superior resistance to pitting corrosion, maintaining the stable passive film, even at the higher temperature.

3.2 Effect of Mo on the resistance to pitting corrosion

Fig. 3 is the PPR test result representing that the pit propagation current density linearly decreased with increasing Mo content. Compared with the Fe-18%Cr alloys without any Mo, the Fe-18%Cr-x%Mo ($x \geq 4$) alloys showed the very low pit propagation current density. Fe-18%Cr-6%Mo alloy did not show any pitted areas.

Fig. 4 is the result of CPT tests carried out in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution at the applied potential of -0.1 Vsce, in order to evaluate the stability of the passive films. Fe-18%Cr-1%Mo alloy shows the pit growth occurred below 45℃ while Fe-18%Cr-4%Mo and Fe-18%Cr-6%Mo alloys display the stable passive current density even at 80℃.

Various mechanisms have been put forward to account

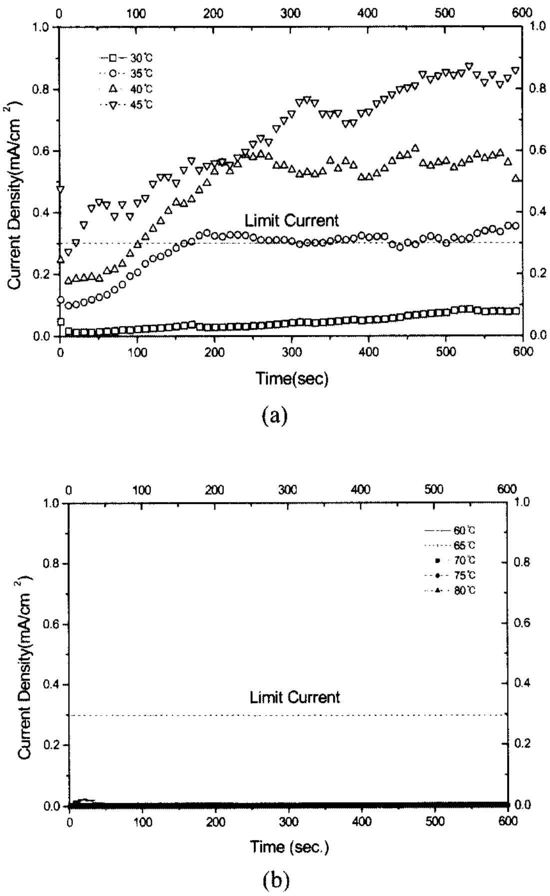


Fig. 2. CPT test results for Fe-18%Cr and Fe-25%Cr alloys in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution at the applied potential of -0.1Vsce ; (a) Fe-18%Cr , (b) Fe-25%Cr.

for the role of Mo in the resistance to pitting corrosion. These include the enrichment of Mo in the internal region of the passive film,[7-10] the formation of Mo-oxide-chloride salt films,[7] the inhibition of pit growth by the adsorption

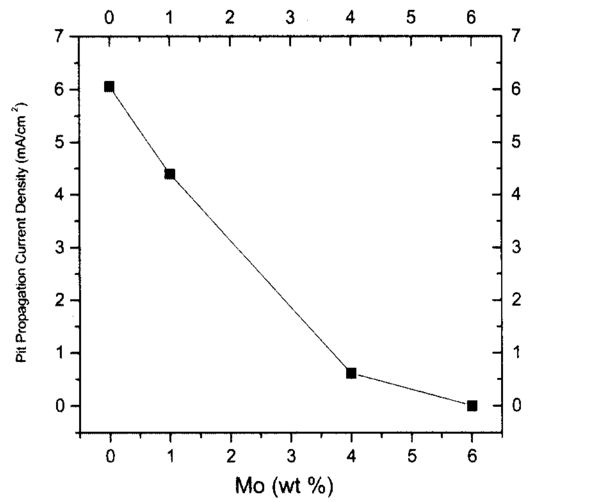


Fig. 3. Pit propagation current densities for Fe-18%Cr-x%Mo steels in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution with Mo content at the applied potential of -0.1Vsce

of MoO_4^-,[11] and the molybdate incorporation into the outer layer of the passive film.[12] Macdonald et al.[13-15] have suggested that the effect of Mo was accounted for by the solute vacancy interaction model. According to their model, Mo causes the enrichment of Cr inside of the passive film due to the accelerated dissolution of Fe, and solute(Mo^{+4}, Mo^{+6})/cation vacancies,(VFe^{3+}, VFe^{2+}) pairing hinders the shift of cation vacancies, having strong inhibitory effect on the passivity breakdown.. Olefjord et al.[16),17] proposed that the role of Mo is the formation of both stable soluble oxo-chloro complexes and insoluble salts. Thus, Mo can lower the activity of Cl^- ion in the passive film so that initiation of pitting can be obstructed.

3.3 Effect of N on the resistance to pitting corrosion

Fig. 5 is the PPR test result that the pit propagation

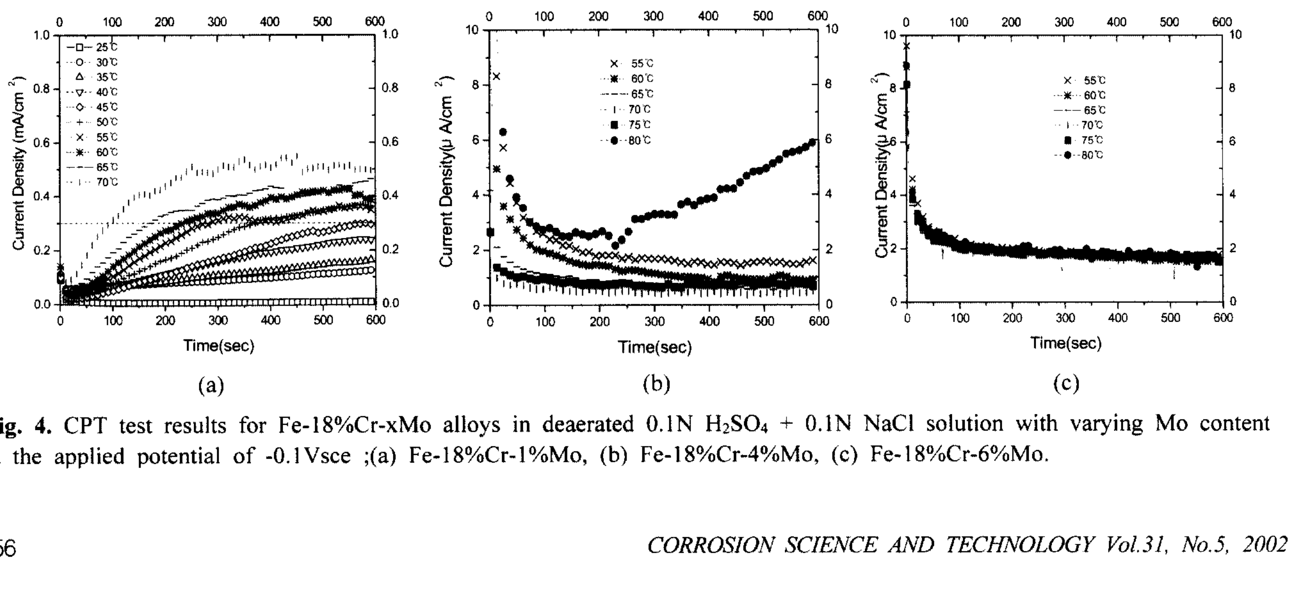


Fig. 4. CPT test results for Fe-18%Cr-xMo alloys in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution with varying Mo content at the applied potential of -0.1Vsce ;(a) Fe-18%Cr-1%Mo, (b) Fe-18%Cr-4%Mo, (c) Fe-18%Cr-6%Mo.

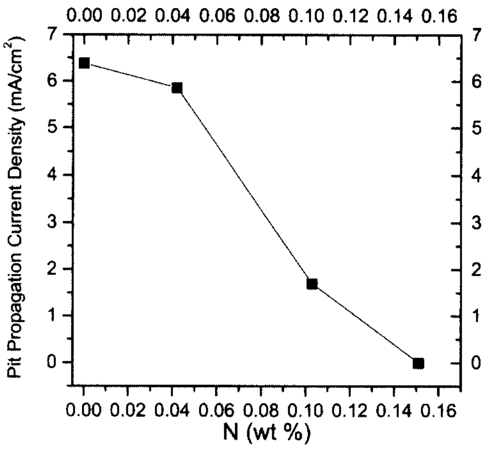


Fig. 5. Pit propagation current densities for type316L and type316LN(N=0, 0.042, 0.103, 0.151 wt%N) stainless steels in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution with varying N content at the applied potential of 0.4Vsce

current density decreased with increasing N content. Compared with type 316L without N, type 316LN with N (0.103%N) showed the much lower pit propagation current density as well as type 316LN with N (0.151%N) did not show any pitted areas.

Fig. 6 is the result of the CPT tests for type 316L and type 316LN stainless steels carried out in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution at the applied potential of +0.4 Vsce, in order to evaluate the stability of the passive films. CPT values also were found to increase with increasing N content.

The addition of N to stainless steels is known to improve the pitting corrosion resistance like as Mo does. Several mechanisms for the role of N in stainless steels have been suggested.[18-24] Osozawa and Okata[18] suggested that N may be to form NH_4^+ within the active sites, to increase the local pH, and to enhance repassivation. Newman and Shahrabi[19] reported that N and H^+ ion generated NH_4^+ and N accumulation in the passive film surface inhibits the active dissolution. Jargeilus-Pettersson[20] also suggested that N is accumulated beneath the passive film and buffers the local pH by NH_4^+ formation. Olefjord and Wegrelius[21] found that during passivation N is enriched in the oxide/metal interface. Mudali et al.[22] attributed the improvement of pitting resistance to the dissolution of N at the pit sites to form ammonium ions and subsequently inhibiting nitrate compounds. Lu et al.[23] pointed out that the synergistic effect o N with Mo exists and is more effective than N alone. In addition, Kobayashi et al.[24] observed in their microelectrochemical studies on metastable pitting of type 304 and type 316 with or without N that Mo- and N-content in stainless steels leads to a significant decresase in the transient heights, indicating an earlier start of repassivation of metastable pits.

3.4 Relationship between PRE index and the resistance to pitting corrosion

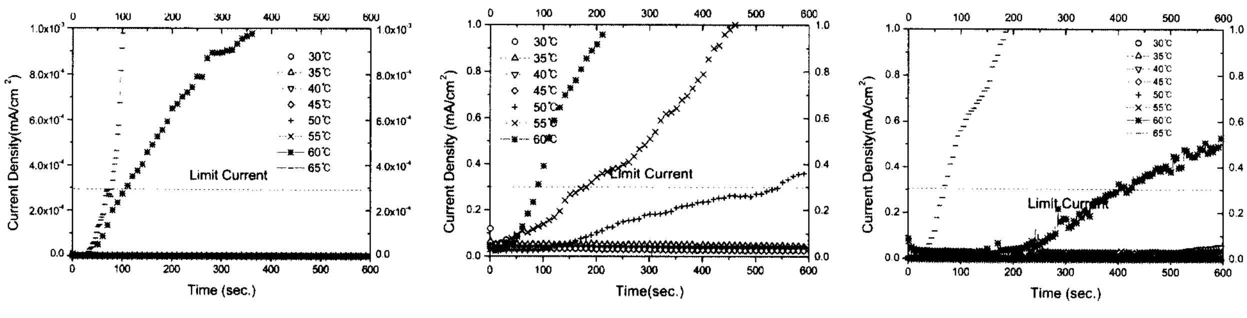
The effect of alloying elements such as Cr, Mo, and N of stainless steels on pitting resistance can be estimated in terms of a Pitting Resistance Equivalent (PRE). The general expression for PRE was also reported as follows:

$$PRE = \%Cr + a \times (\%Mo) + b \times (\%N). \quad (1)$$

Recently PRE equation including the synergistic effect of Mo and N was more developed by Jargelius-Pettersson [4] as follows:

$$PRE = Cr + 3.3 \times [\%Mo] + 36 \times [\%N] + 7 \times [\%Mo][\%N] - 1.6 \times [\%Mn]. \quad (2)$$

In the present work, pitting resistance of Fe-Cr, Fe-Cr-Mo ferritic alloys and austenitic stainless steels with and without N were evaluated by measuring pitting potentials



(a) (b) (c)

Fig. 6. CPT test results for type316L and type316LN stainless steels in deaerated aqueous 0.1N H_2SO_4 + 0.1N NaCl solution with varying N contents at the applied potential of 0.4Vsce in case of (a) type316L, (b) type316LN(0.042wt%N), and (c) type316LN(0.151wt%N) stainless steels

(Epit) and passive potential range (ΔE=Epit-Epp) with PRE index given by Eq.(2). Results showed that Epit increases with increasing PRE index, representing the stable value for stainless steels whose PRE index is above 25 (Fig. 7) while ΔE linearly increases with increasing PRE index (Fig. 8). Fig. 9 showed the relationship between CPT and PRE index for both ferritic stainless steels at applied potential of -0.1Vsce (Fig. 9(a)) and austenitic stainless steels with and without N at applied potential of 0.4Vsce (Fig. 9(b)) in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution. Increasing PRE index increased CPT for both ferritic and austenitic stainless steels. Ferritic alloys with PRE ≥25 at -0.1Vsce did not show the critical pitting temperature even at above 80℃ while austenitic stainless steels including N, especially, with PRE ≥25 at 0.4Vsce, showed that the critical pitting temperature approached to 60℃. Fig. 10 showed the relationship between PPR and PRE index for both ferritic stainless steels at applied potential of -0.1Vsce (Fig. 10(a)) and austenitic stainless steels with and without N at applied potential of 0.4Vsce (Fig. 10(b)) in deaerated 0.1N H_2SO_4 + 0.1N NaCl acidic solution. Increasing PRE index decreased PPR for both ferritic and austenitic stainless steels. Ferritic alloys with PRE index ≥25 had the pit propagation current density less than 1mA/cm^2 or no pitted area. Austenitic stainless steels with PRE index ≥25 also showed the pit propagation current density less than 2mA/cm^2 or no pitted area.

Jargelius-Pettersson (4) reported that based on the concept of PRE, increasing N for steels with < 0.25% N increased CPT, demonstrating the synergistic interaction between and N and Mo. Ujiro et al. (25) found that the pitting and crevice corrosion resistance of ferritic and austenitic stainless steels were improved as PRE index increased in various corrosive environments by anodic

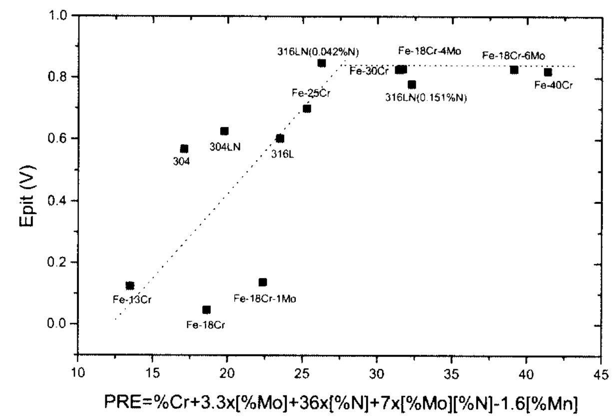


Fig. 7. Relationship between pitting resistance equivalent (PRE) and pitting potentials(Epit) of alloys used in this study deaerated 0.1N H_2SO_4 + 0.1N NaCl solution

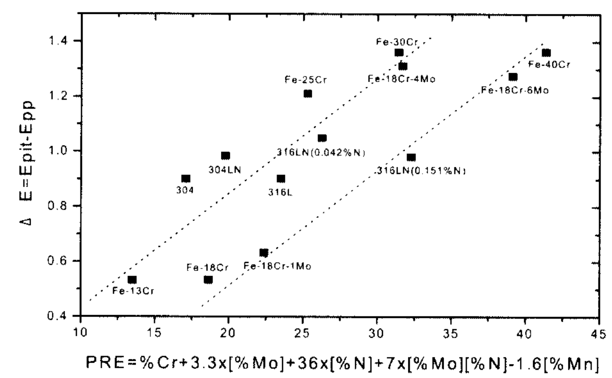


Fig. 8. Relationship between pitting resistance equivalent(PRE) and passive potential region(ΔE=Epit-Epp) of alloys used in this study in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution.

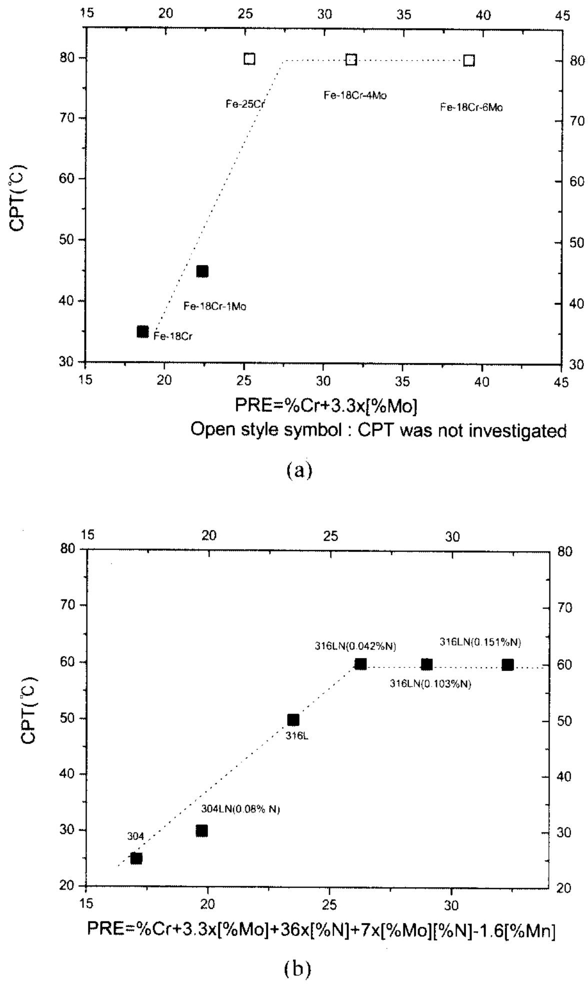
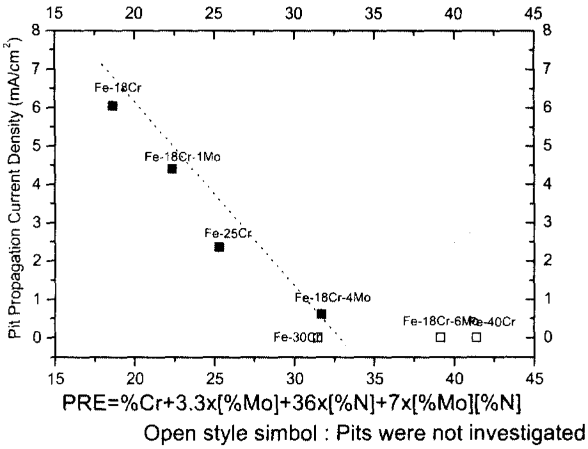
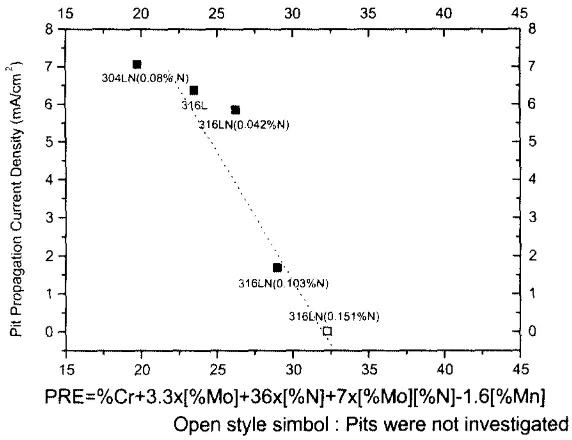


Fig. 9. Relationship between pitting resistance equivalent(PRE) and critical pitting temperatures(CPT) of various alloys in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution, (a) ferritic stainless steels at the applied potential of -0.1Vsce ; (b) austenitic stainless steels at the applied potential of 0.4Vsce



(a)



(b)

Fig. 10. Relationship between pitting resistance equivalent(PRE) and pit propagation rate(PPR) of various alloys in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution, (a) ferritic stainless steels at -0.1Vsce ; (b) austenitic stainless steels at 0.4Vsce

polarization measurements for the stainless steels. In this study, stainless steels with PRE $\geq$25 showed the superior pitting corrosion resistance, indicating that PRE index can be the good parameter to evaluate the extents of their pitting resistance on a single scale, regardless of types of stainless steels (ferritic or austenitic stainless steels) and the content of alloying elements.

4. Conclusions

The results of investigation of the pitting corrosion resistance of ferritic and austenitic stainless steels by measuring PPR and CPT in deaerated 0.1N H_2SO_4 + 0.1N NaCl solution indicate the following:

1) PPR values for ferritic and austenitic stainless steels decreased with increasing PRE index.

2) CPT results showed that ferritic alloys with PRE $\geq$ 25, at the applied potential of -0.1 Vsce did not show the critical pitting temperature even at the above 80℃ while austenitic stainless steels including N, with PRE $\geq$ 25, at the applied potential of 0.4Vsce, showed that the critical pitting temperature approached to 60℃.

3) Pitting potential (Epit) increases with increasing PRE index, approaching the stable value for stainless steels whose PRE index is above 25 while passive potential range (ΔE=Epit-Epp) linearly increases with increasing PRE index.

4) PRE is the good parameter to estimate the extents of the pitting resistance on a single scale regardless of alloying elements and types of ferritic or austenitic stainless steels.

Acknowledgement

Authors gratefully acknowledge the financial support from Korea Science and Engineering Foundation (KOSEF) under the contraction number of 2000-1-301-012-3.

References

1. R.C. Syrett, *Corrosion*, **23**, 221 (1977).
2. R. J. Brigham, E. W. Tozer, *Corrosion*, **29**, 33 (1973).
3. R. Lorentz, G. Medawar, *Tyssenforschung*, **1**, 97 (1969).
4. R.F.A. Jargelius-Pettersson, *Corrosion*, **54**, 162 (1998).
5. Annual Book of ASTM Standards, Designation G150-99, pp.1-12.
6. Jae-Bong Lee, Dong-Ho Ham and Suk-Won Kim, in 7th International Symposium on Electrochemical Methods in Corrosion Research, EMCR2000, Budapest Hungary, Paper No. 067 (2000).
7. K. Sugimoto, Y. Sawada, *Corros. Sci.*, **17**, 425 (1977).
8. C. Leygrat, G. Huktquist, I. Olefjord, B. O. Elfstrom, V. M. Knyaheva, A.V. Paskeyer, Y. M.. Kolotykin, *Corros Sci.*, **19**, 343 (1979).
9. I. Olefjord, B. O. Elfstrom, *Corrosion*, **38**, 347 (1982).
10. M.W. Tan, E. Akiyama, A. Kawashima, A. Asami, K. Hashimoto, *Corros. Sci.*, **37**, 1289 (1995).
11. K. Sugamoto, Y. Sawada, *Corrosion*, **32**, 347 (1976).
12. C. R. Clayton, J. C. Lu, *J. Electrochem. Soc.*, **133**, 2465 (1986).
13. M. Urquidi-MacDonald, D.D. MacDonald, *J. Electrochem. Soc.*, **136**, 961 (1989).
14. D.D. MacDonald, *J. Electrochem. Soc.*, **139**, 170 (1992).
15. D.D. MacDonald, *J. Electrochem. Soc.*, **139**, 3434 (1992).
16. L. Wegrelius, F, Falkenberg, I.. Olefjord, *J. Electrochem. Soc.*,**146**, 1397 (1999).
17. F. Falkenberg, I. Olefjord, , in Passivity and Localized Corrosion, An International Symposium in Honor of Professor Norio Sato, Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan, Hawaii (1999), M. Seo, B. MacDougall, H.

Takahashi, and R.G. Kelly, eds., The Electrochemical Society, PV 99-27, Pennington, NJ, pp.404-413 (1999).
18. K, Osozawa and N. Okata, in Passivity and its Breakdown on Fe and Fe-base Alloys, USA-Japan Seminar, Honolulu, (1975), R. W. Staehle and H. Okada, eds., NACE, Houston, TX, p.135 (1976).
19. R.C. Newman, T. Shahrabi, *Corros. Sci.*, **27**, 827 (1987).
20. R.F.A. Jargelius-Pettersson, *Corros. Sci.*, **41**, 1639 (1999).
21. I. Olefjord and L. Wegrelius, *Corros. Sci.*, **38**, 1203 (1996).
22. H. Kamachi Mudali, R. K. Dayal, J. B. Gnanmoorthy and P. Rodriguez, *Materials Transactions, JIM*, **37**, 1568 (1996).
23. Y.C. Lu, M.B. Ives and C. R. Clayton, *Corros. Sci.* **35**, 89 (1993).
24. Y. Kobayashi, S. Virtanen, and H. Bohni, in Passivity and Localized Corrosion, An International Symposium in Honor of Professor Norio Sato, Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan, Hawaii, (1999), M. Seo, B. MacDougall, H. Takahashi, and R.G. Kelly, eds., The Electrochemical Society, PV 99-27, Pennington, NJ, pp.533-540 (1999).
25. T. Ujiro, K. Yoshioka, R.W. Staehle, *Corrosion*, **50**, 953 (1994).