Dissolution and Film Formation of Fe-Cr-Ni Alloys in Boiling Magnesium Chloride Solution in Relation to Stress Corrosion Cracking

Toshio Shibata and Taro Takeyama

*Metals Research Institute, Faculty of Engineering, Hokkaido University**

High speed straining electrode technique has been applied for measuring the current for dissolution and film formation at newly created surfaces of iron, nickel, and several kinds of Fe-Cr-Ni alloys in boiling 46% MgCl₂ solution. Nickel content of alloys changes keeping chromium content between 15% to 19%. It is found that the maximum current density observed upon straining for a given amount at the corrosion potential decreases with the increase of nickel content. The film formation kinetics is described as $i = k/(Q - Q_0)^m$, where i is the current density, Q is the amount of charge involved and Q_0 , k and m are constants. The value, m , also decreases with the increase of nickel content, exhibiting the highest value for 304 type steel. The higher susceptibility of alloys to stress corrosion cracking is closely connected with the higher maximum current density corresponding to the higher dissolution rate at fresh surfaces and also the larger value of m which indicates the higher inhibitive action of film against successive dissolution.

1. Introduction

Several mechanisms have been proposed to explain stress corrosion cracking (SCC) phenomena. Rhodes¹⁾, Nielsen²⁾, and others assumed that hydrogen produced in the course of corrosion causes the embrittlement of given steels. But the most controversial observation concerning this mechanism is that cathodic polarization, which promotes the hydrogen evolution reaction, can stop the propagation of cracks, whereas anodic polarization accelerates the rate of propagation. Hence the active path corrosion might be a controlling reaction in SCC of stainless steels. Smith and Staehle³⁾ demonstrated that the anodic dissolution takes place preferably at slip steps, penetration of which is supposed to be an essential process in crack propagation. According to Latanision and Staehle⁴⁾, "restricted lateral dissolution" is a criterion for penetration of slip step dissolution. It is assumed that restriction of lateral dissolution is induced by a film formation or a noble metal enrichment onto surface.

In order to obtain quantitative data about dissolution and film formation, which are necessary to prove the criterion, a high speed straining electrode technique⁵⁾ has been developed and applied to analysis of repassivation process of

various metals and alloys at newly created surfaces in borate buffer solution. It was found that the susceptibility of various alloys to SCC in boiling magnesium chloride solution is related to their repassivation behavior in borate solution through following equation (1),

$$T_f = k(i_{100}/i_{max})^n \quad (1)$$

where i_{100} is the current density at 100 seconds after straining, i_{max} is the maximum current density observed upon straining. T_f is the time to fracture in boiling magnesium chloride solution, and k and n are constants. However, the current in equation (1) should be measured in the same environment as stress corrosion cracking tests. In this study the repassivation behavior of Fe-Cr-Ni alloys containing various amount of nickel in boiling magnesium chloride solution is analyzed by using the high speed straining electrode method, and compared with their susceptibility to SCC in the same environment.

2. Experimental

Detailed description of the high speed straining electrode method had been reported elsewhere.^{5,6)} The schematic illustration of the system is shown in Figure 1. A constant amount of elongation to the wire specimen is given by releasing a compressed spring with the straining rate of about 900%/sec. Electrolytic cell containing 46% boil-

* Nishi 8-chome, Kita 13-jo, Kita-ku, Sapporo, 060, Japan

Fig. 1. Apparatus for measuring the anodic current and elongation by spring loading. a) wire specimen, b) carbon rods for counter electrode, c) saturated calomel electrode for the cell (wire/boiling MgCl_2 /solid MgCl_2 /sat. sol. MgCl_2 /sat. sol. KCl /sat. calomel electrode).

ing magnesium chloride solution is equipped with a condenser to keep the composition of the solution constant, carbon rod counter electrodes, and a capillary connected to outside saturated solution of magnesium chloride at room temperature. Saturated magnesium chloride solution at room temperature is in contact with saturated potassium chloride solution and saturated calomel electrode through saturated potassium chloride salt bridge. Electrode potential of the wire specimen in the solution of $154 \pm 0.5^\circ\text{C}$, is, thus, measured against saturated calomel electrode at room temperature with no correction. Table 1 shows the chemical composition of iron, nickel, and other alloys used in these experiments. Nickel content of alloys changes keeping chromium content approximately constant from 15% to 19%. Wire specimens of 0.3 mm in diameter are obtained by cold drawing from as-received wire of 2 mm in diameter. Solution annealing of alloys is carried out at $1,100^\circ\text{C}$ for 15 min in vacuum followed by water quench-

ing. Iron and nickel are annealed at 800°C for 10 min and quenched in water. The surface of wire specimen is coated with silicon rubber sealant except the both ends of the wire for holding and the central part of 20 mm in length exposing the surface area of 0.188 cm^2 to the solution. Vacuum annealed surface is used as a starting surface without any surface treatment such as mechanical polishing. Steady corrosion potentials of test specimens are attained after 1 hr, and within $-350 \pm 20 \text{ mV}$ (vs.SCE) except the potential of iron of -600 mV . The potential of the specimen is kept at the corrosion potential by means of potentiostat, and a small amount of strain from 1% to 3% is given. The change of the current due to straining is recorded by an electromagnetic oscillograph or a chart recorder. The change of strain is recorded simultaneously on the same oscillographic paper.

Assuming a constant volume of the wire specimen, the increased area, ΔS , by the strain can be estimated by using equation (2)

$$\Delta S = S_0 \Delta l / l_0 \quad (2)$$

where S_0 is the original surface area, l_0 , the original length and Δl , the elongation given. Current density, i , is obtained by dividing the total current, ΔI , by the increment of surface area estimated from equation (2).

3. Experimental Results and Discussion

Figure 2 shows the change of current density with time in $\log i$ vs. $\log t$ plots for various metals and alloys upon straining at their corrosion potential. Maximum current density, i_{max} , is observed when the straining is stopped at given strain. Magnitude of i_{max} is in the range of ampere per square centimeter for 304, and J4 alloys, and in the range of some hundreds of miliampere per square centimeter for other specimens. Alloys of 304, J4, NTK330, and Inconel

Table 1. Chemical composition of specimens.

	Fe	Cr	Ni	C	Si	Mn	P	S	others
Fe	99.92	.0021	.0038	.002	.0015	.0015	—	.004	Co: .0104 N: .0017
304	69.54	18.70	9.79	.06	.34	1.45	.019	.022	Cu: .08
J4	66.33	17.80	13.25	.07	.58	1.45	.013	—	Mo: < .01
NTK 330	47.39	15.53	34.70	.12	.50	1.84	.016	.012	—
Inconel									Ti: .22 Mg: .004
600	7.68	15.22	76.41	.032	.17	.18			Al: .05 N: .0015 B: .005
Ni	.13	—	99.42	< .001	< .001	< .001	—	.015	Cu: .009

Fig. 2. Change of the current density with time after sudden loading.

600 exhibit similar type of decay curves but the curves for pure iron and pure nickel are different and irregular although the decay tendency can be seen in the same manner. The instability of current for pure iron is likely to be due to a vigorous evolution of hydrogen. The decay behavior of nickel and stainless steels are similar to those which had been observed in borate solution.⁵¹

It can be stated that the decay in current density is caused by film formation because the natural corrosion state of stainless steel in boiling magnesium chloride solution is in the passive potential region as discussed by Wilde.⁷¹ Several kinetics for film growth processes on passive metals have been presented: for instance, the inverse logarithmic rate law or direct logarithmic rate law is observed near room temperature. None of these, however, have been found to fit the present data and the following equation is proposed to explain the decay of current density as indicated in Figure 3,

$$i = k / (Q - Q_0)^m \quad (3)$$

where k and m are constants. The amount of charge, Q , at time t is calculated by numerical integration of i vs. t curves. Q_0 is the charge involved during the initial or transient part of straining, and can be determined by the integration of i vs. t curves from time zero to the time required to attain to $i_{\max}$. This charge might be equivalent to the amount of charge associated with dissolution, because the current density observed during the transient part of straining is independent of the amount of charge, and the

Fig. 3. Current density vs. the amount of charge involved.

process is considered to be limited by diffusion in solution. The slope of the linear portion in $\log i$ vs. $\log(Q - Q_0)$ curve in Figure 3 gives the value of m , and the current density on the horizontal line is equal to $i_{\max}$.

The integration of equation (3) gives

$$Q - Q_0 = K t^p \quad (4)$$

where K and p ($=1/m+1$) are constants. Based on equation (4), the data for 304 steel is plotted (closed circles) in terms of corrosion loss converted using Farady equivalent in Figure 4, and the corrosion weight loss measured by Kowaka⁸¹ for a similar alloy is also plotted (open circles).

Fig. 4. Corrosion loss of 304 steel vs. immersion time.

Closed circles: estimated from the amount of charge.

Open circles: determined by weight loss.

It is clearly seen in Figure 4 that both data are on the same line and the slope, p , is about 0.3. The value coincides with the one calculated from m 's value of 2.40 which is obtained in Figure 3. The above result indicates that the change in corrosion loss with time can be determined precisely by measuring the amount of charge involved through the newly created surface at corrosion potential.

Figure 3 demonstrates that the value of m and $i_{\max}$ depends on the chemical composition of specimens, the highest value being found for 304 steel and the lowest value for Inconel 600, and nickel. The curve for iron is too irregular to determine the precise slope, but the same slope as nickel is expected since both metals show the similar slope in borate solution.⁵⁾ The values of m and $i_{\max}$ are plotted in Figure 5 in terms of nickel content. The upper small figure in Fig. 5 indicates the corrosion potentials of specimens against their nickel contents. It is interesting to note that the corrosion potentials of the nickel containing alloys are almost constant regardless of change in the nickel content as Staehle and others⁹⁾ have already shown. This condition of constant corrosion potential is helpful to examine the effect of nickel content on the anodic behavior of the alloy because the change of cathodic reac-

Fig. 5. Effect of nickel content on the corrosion potential, E_{corr} , the maximum current density, $i_{\max}$, the current density at 1 sec, i , and the kinetic parameter, m , for the film growth.

tion could be neglected. The maximum current density increases rapidly with increase of nickel below 10%. Scully and Hoar¹⁰⁾ observed a similar steep increase in anodic current below 10% nickel in the case of the slow straining of iron-nickel alloys in flowing solution. It is also interesting to note that the critical current density is known to increase largely below 10% nickel for passivation of iron-nickel alloys in sulfuric acid solutions.¹¹⁾ The above facts suggest that the maximum current density is proportional to the intrinsic anodic dissolution at non-filmed surface. Extrapolation of the curve to pure iron would give a high current if its corrosion potential were not different from other alloys. But less noble value of the corrosion potential for pure iron results in the low value of current density due to decrease in anodic polarization. It is found in Figure 5 that the value of m gradually changes with nickel content from 2.40 to 1.0. Limiting value of 1.0 seen for pure nickel and pure iron corresponds to the parabolic rate law for film growth processes. The physical meaning of the value of m higher than 1.0 is not clear at present, but definitely indicates a higher inhibitive action on anodic reaction or corrosion. The highest inhibitive action of the film is seen for 304 steel.

According to restricted lateral dissolution criterion⁴⁾, high dissolution rate at a tip of crack and also high inhibition of anodic reaction on the wall due to film formation would help the crack propagate rapidly into alloy. This condition could be rationalized by equation (1), where i_{100} is the current density attained after 100 sec in decay, indicating a measure for the inhibitive action of the film, and $i_{\max}$ represents the dissolution rate at fresh surfaces. In this experiment the same equation could be applied and compared with time to fracture, T_f , as in Figure 6, where i_{100} is replaced by i_1 because of its accurate value.

The data of time to fracture by Staehle, *et al.*, on nickel alloys in boiling magnesium chloride solution are shown in Fig. 6 instead of well known Copson's data¹²⁾ because their experimental conditions are similar to those of this experiment. The general trend of both curves of $i_1/i_{\max}$ and T_f against nickel contents is similar as expected. However the use of current density at certain times in decay to represent the inhibitive action is arbitrary. It seems much more direct and definite to use the value of m instead of i_1 for expressing

Fig. 6. Effect of nickel content on the ratio of $i_1/i_{\max}$ and $i_1/i_{\max} \cdot m$, and time to fracture, T_f , of various stainless steels.

the inhibitive action of the film since the value of m is a constant independent of time. In this case the favourable condition for the crack propagation could be expressed by the ratio of $i_1/i_{\max} \cdot m$. That is, the higher values of $i_{\max}$ and also of m are expected to correlate with the shorter time to fracture. It is demonstrated in Fig. 6 that the curve of $i_1/i_{\max} \cdot m$ is closer and more parallel to the curve of T_f compared with the curve of $i_1/i_{\max}$ and the relation analogous to equation (1) is seen between T_f and $i_1/i_{\max} \cdot m$ as

$$T_f = k(i_1/i_{\max} \cdot m)^n \quad (5)$$

where k and n are constants.

The condition for the crack propagation expressed by equation (5) is included in the general conditions which have been discussed recently by Lees, Ford, and Hoar¹³⁾ on guide lines to the development of stress-corrosion-resistant alloys. They point out that much higher rate of repassivation inhibits the dissolution at bare surfaces

and results in lowering the rate of propagation. But decrease in the rate of propagation due to high rate of repassivation is not found for nickel alloys in this experiment. The highest repassivation is observed for 304 steel and this steel is most susceptible to stress corrosion cracking in boiling magnesium chloride solution.

Acknowledgment

One of the authors (T. Shibata) is indebted to Professor R. W. Staehle of Ohio State University for helpful suggestions and discussions.

(Received March 25, 1974)

References

- 1) P. R. Rhodes: *Corrosion*, **25**, 462 (1969).
- 2) N. A. Nielsen: *J. Mater.*, **5**, 794 (1970).
- 3) J. J. Smith & R. W. Staehle: *Corrosion*, **23**, 117 (1967).
- 4) R. M. Latanision & R. W. Staehle: *Fundamental Aspects of Stress Corrosion Cracking*, p. 214, NACE, Houston (1969).
- 5) T. Shibata & R. W. Staehle: *Proc. 5th Int. Congress on Metallic Corrosion*, in press.
- 6) T. Shibata & T. Takeyama: *J. Japan Inst. Met.*, **38**, 124 (1973).
- 7) B. E. Wilde: *J. Electrochem. Soc.*, **118**, 1717 (1970).
- 8) M. Kowaka & H. Fujikawa: *J. Japan Inst. Met.*, **34**, 1047 (1970).
- 9) R. W. Staehle, J. J. Roreula, T. L. Raredon, E. Serrate, C. R. Morion & R. V. Farrar: *Corrosion*, **26**, 451 (1970).
- 10) J. C. Scully & T. P. Hoar: *Proc. 4th Int. Congress on Metallic Corrosion*, p. 184, NACE, Houston (1966).
- 11) K. Shiobara, Y. Sawada & S. Morioka: *J. Japan Inst. Met.*, **28**, 1 (1964).
- 12) H. R. Copson: *Physical Metallurgy of Stress Corrosion Fracture*, Interscience, p. 247, New York (1959).
- 13) D. J. Lees, R. P. Ford & T. P. Hoar: *Metals and Materials*, **7**, 231 (1973).