INTERNAL CHLORINATION OF Ni-Cr-Ce ALLOY EXPOSURE TO CHLORINE AT 575 ℃①

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ABSTRACT The kinetics of internal chlorination of Ni-Cr-Ce alloy in chlorine at 575 ℃ has been studied. Internal chlorination of Ni-Cr-Ce alloy occurred to formation of $CrCl_2$ and $CeCl_3$ solid precipitates which is thermodynamically stable and has lower vapor pressure at the temperature along grain boundaries. At initial corrosion stage, the internal chlorination rate nearly followed parabolic rate law, the internal chlorination was accompanied by the consumption of the alloy by volatilization corrosion which obeyed a linear rate equation, the thickness of the internal chlorination region would be governed by a paralinear rate equation. After a sufficiently long period of corrosion, the rate of internal chlorination would be equal to the rate of overall metal consumption, the depth of internal chlorination approaches a steady state value. Addition of Ce to Ni-Cr alloy increased the degree of internal chlorination.

Key words internal chlorination vapor pressure chloride

1 INTRODUCTION

The chlorination kinetics of alloy in containing chlorine environments has been discussed elsewhere[1-3]. In addition to the metal removal by formation of volatile chlorides, the alloys were also subject to internal chlorination near the corroding interface in chlorine gas at high temperatures. The activation energy for diffusion on grain boundary is generally lower than the activation energy for lattice diffusion. Therefore, the diffusion rate of dissolved chlorine inward through grain boundary was faster than that through the base metal matrix[4], Some active alloy elements enriched near grain boundaries and reacted with chlorine. The formation of metal chloride particles which have lower vapor pressures appeared to the phenomena of internal chlorination, which proceeded primarily along grain boundaries.

The corrosion product, $CeCl_3$ has lower vapor pressure at 575 ℃[5]. The condensed $CeCl_3$ deposits produced on the outside of the scale. The presence of condensed chlorides during chlorination can prevent the inward diffusion of chlorine through the scale and outward vapor transport. Addition of Ce to Ni-Cr alloy reduced the overall corrosion rate. Nevertheless, Ni-Cr-Ce alloy exhibited severe intergranular corrosion. This paper describes the results of experiments performed to investigate the depth of internal attack. The kinetics of internal chlorination of Ni-13Cr-0. 5Ce alloy at 575 ℃ has also been discussed.

2 EXPERIMENTAL

All of the experiments were performed in chlorine gas at 575 ℃. After exposure, the depth of internal chlorination zone and amount of precipitates were observed by optical micrograph and SEM. The chloride precipitates were examined by XRD and EDS. Because the degree and nature of the internal attack is difficult to be considered by another function, the results of the internally attacked region

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① Received Jan. 24, 1995; accepted Jul. 11, 1995

can be determined by depth measurement in this experiment.

3 RESULTS AND DISCUSSION

3. 1 *Internal Chlorination of* Ni-Cr-Ce *Alloy*

Fig. 1 shows the phenomena of internal chlorination of Ni-Cr-Ce alloy exposure to Cl_2 gas at 575 ℃. The results examined by XRD and EDS (Fig. 2) indicate that the chloride particles along grain boundaries were $CrCl_2$ and $CeCl_3$. In the temperature investigated $CrCl_2$ and $CeCl_3$ are solid with very low vapor pressure. The internal chlorination occurs formation and precipitation of the metal chlorides along grain boundaries.

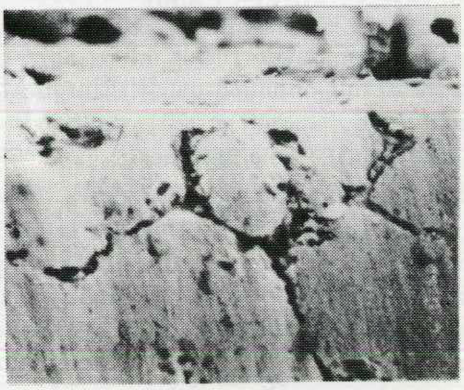

Fig. 1 Intergranular internal chlorination in Ni-Cr-Ce alloy exposure to chlorine gas at 575 ℃

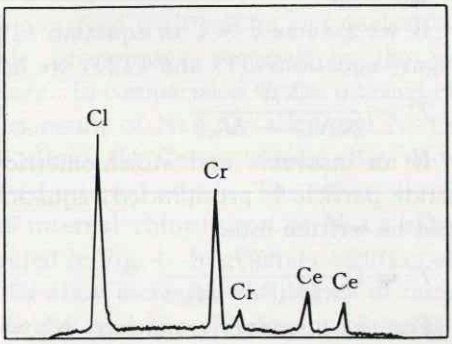

Fig. 2 EDS analysis of chloride precipitates along grain boundaries

3. 2 *Kinetics of Internal Chlorination*

Exclusive internal chlorination in the absence of external scale formation occurs in the alloy in chlorine gas at elevated temperature. The chloride ions dissolved into the alloy matrix at the alloy scale interface diffuse continuously inward through grain boundaries and combine with the outward diffusing alloy element M(Cr, Ce) to form chlorides along grain boundaries. Assuming that volatilization corrosion is to be neglected. An advancing reaction front remains essentially parallel to the external surface ($X = 0$). At the reaction front ($x = \zeta$), precipitated MCl_n chloride is produced.

Following Fick's second law, the diffusion equation for the one-dimensional diffusion of chlorine and alloying element M, namely

$$\frac{\partial N_{Cl}}{\partial t} = D_{Cl}\frac{\partial^2 N_{Cl}}{\partial X^2} \tag{1}$$

$$\frac{\partial N_{M}}{\partial t} = D_{Cl}\frac{\partial^2 N_{M}}{\partial X^2} \tag{2}$$

may be solved for the boundary conditions

$N_{Cl} = N_{Cl}^{(S)},\ X = 0,\ t > 0$

$N_{Cl} = 0,\ X \geqslant \xi,\ t = 0$

$N_{M} = N_{M}^{(0)},\ X > 0,\ t = 0$

$N_{M} = 0,\ X \leqslant \xi,\ t > 0$

where N_{Cl} is the mole fraction of chlorine in the bulk alloy, $N_{Cl}^{(S)}$ is the mole fraction of chlorinc at the external surface; N_M is the mole fraction of M, and $N_M^{(0)}$ is the mole fraction of M in the bulk alloy.

The solution of equation (1) subject to the boundary conditions will be of the form

$$N_{Cl} = N_{Cl}^{(S)} + A\mathrm{erf}\left(\frac{X}{2\sqrt{D_{Cl}t}}\right) \tag{3}$$

where $\mathrm{erf}(Z) = 2/\sqrt{\pi}\int_0^Z \exp(-\zeta^2)\mathrm{d}\zeta$

Assume the location of the advancing reaction front can be written as

$\zeta(t) = 2\gamma\sqrt{D_{Cl}t}$

where ζ is an undetermined parameter.

At the reaction front:

$N_{Cl}(\zeta) = N_{Cl}^{m}$

$N_{M}(\zeta) = N_{M}^{m}$

where N_{Cl}^{m} and N_{M}^{m} are the critical concentratrons for the nucleation of chlorides.

At the precipitation front ($x = \zeta$)

$$N_{Cl}^{m} = N_{Cl}^{(S)} + A\,\mathrm{erf}\left(\frac{X}{2\sqrt{D_{Cl}t}}\right) \qquad (4)$$

The concentration change of chloride ions in the bulk alloy becomes

$$N_{Cl}(X,\,t) = N_{Cl}^{(S)} - \frac{N_{Cl}^{(S)} - N_{Cl}^{m}}{\mathrm{erf}(\gamma)}\,\mathrm{erf}\left(\frac{X}{2\sqrt{D_{Cl}t}}\right) \qquad (5)$$

The form of the solution to equation (2) subject to the boundary conditions is

$$N_{M} = N_{M}^{(0)} + B\,\mathrm{erfc}\left(\frac{X}{2\sqrt{D_{M}t}}\right) \qquad (6)$$

where $\mathrm{erfc}(Z) = 1 - \mathrm{erf}(Z)$

At $X = \zeta$, equation (6) becomes

$$N_{m}^{m} = N_{M}^{(0)} + B\,\mathrm{erfc}\left(\frac{2\gamma\sqrt{D_{Cl}t}}{2\sqrt{D_{M}t}}\right) \qquad (7)$$

So that the concentration of alloy element M in the bulk alloy is

$$N_{M} = N_{M}^{(0)} - \frac{N_{M}^{(0)} - N_{M}^{m}}{\mathrm{erfc}[(D_{Cl}/D_{M})\gamma]}\,\mathrm{erfc}\left(\frac{X}{2\sqrt{D_{M}t}}\right) \qquad (8)$$

A given volume fraction of previously precipitatd internal chlorination particles was determined by a repeated nucleation and accompanying growth of particles of chlorides at the reaction front.

Assuming the last precipitation event occurs at $x = \zeta'$ and that the next will occur at $x = \zeta$. the amount of chlorine diffusing into the volume element at ζ' must be equal to the amount of M precipitating from this volume element plus the amount of M which diffuses into it at ζ, *so*

$$-D_{Cl}\frac{\partial N_{Cl}}{\partial X}\Big|\xi,\ \Delta t = (N_{M}^{m} - N'_{M})\Delta\xi + D_{M}\frac{\partial N_{M}}{\partial X}\Big|\xi\Delta t \qquad (9)$$

In general, the movement of the precipitation front is essentially determined by the diffusion of chlorine in the base metal.

$$\frac{D_{M}}{D_{Cl}} \ll \frac{N_{Cl}^{(S)}}{N_{M}^{(0)}} \ll 1, \text{ so that } \gamma \ll 1$$

Fig. 3 represents the concentration of chlorine in the alloy.

Fig. 3 Concentration profile of chlorine across the Ni-Cr-Ce alloy

The experiment result is in agreement with the result obtained using theoretical approach.

Equation(9) now becomes

$$D_{Cl}\frac{N_{Cl}^{(S)}}{\xi},\ \Delta t = (N_{M}^{m} - N'_{M})\Delta\xi + 2D_{Cl}\gamma^{2}\frac{N_{M}^{(0)} - N_{M}^{m}}{\xi}\Delta t \qquad (10)$$

$$\frac{\Delta\xi}{\Delta t} = \frac{1}{N_{M}^{m} - N'_{M}}\left(D_{Cl}\frac{N_{Cl}^{(S)}}{\xi'}\Delta t - 2D_{Cl}\gamma^{2}\frac{N_{M}^{(0)} - N_{M}^{m}}{\xi}\right) \qquad (11)$$

Using $\xi = 2\gamma\sqrt{D_{Cl}t}$

$$\frac{\Delta\xi}{\Delta t} = \frac{\mathrm{d}\xi}{\mathrm{d}t} = D_{Cl}^{1/2}\gamma t^{-1/2} = \frac{2D_{Cl}\gamma^{2}}{\xi} \qquad (12)$$

If we assume $\xi \approx \zeta'$ in equatian (11) and compare equations(11) and (12), we have

$$\gamma^{2} = \frac{N_{Cl}^{(S)}}{2(N_{M}^{(0)} - M'_{M})} \qquad (13)$$

If an insoluble and stoichiometric MCl_n chloride particle is precipitated, equation(13) would be written into.

$$\gamma^{2} = \left(\frac{N_{Cl}^{(S)}}{2n(N_{M}^{(0)} - M'_{M})}\right. \qquad (14)$$

For the boundary condition, $N'_{M} = 0$, equation (14) reduces to

$$\gamma = \left(\frac{N_{Cl}^{(s)}}{2nN_{M}^{(0)}}\right)^{1/2} \qquad (15)$$

The depth of internal chlorination zone gives

$$\xi = [2N_{\mathrm{Cl}}^{(\mathrm{S})} D_{\mathrm{Cl}} t / n N_{\mathrm{M}}^{(0)}]^{1/2} \tag{16}$$

At an given temperature, the product $N_{\mathrm{Cl}} D_{\mathrm{Cl}}^{(\mathrm{s})}$ and $N_{\mathrm{M}}^{(0)}$ are constant. The depth of internal chlorination zone can be written as

$$\zeta^2 = 2K_r t \tag{17}$$

In fact, the metal chlorides have higher vapor pressure at 575 ℃. At initial corrosion stage, the scale formed on the alloy was thin. The dissolution of chlorine which diffused inward through the scale into the base metal at the external surface exhibited high concentration. The rate of internal chlorination was in excess of that corresponding to volatilization corrosion. The kinetics of internal chlorination nearly followed a parabolic rate law. When the internal chlorination zone subjected to consumption of the alloy by overall corrosion which obeyed a linear rate equation, the depth of the internal chlorination region exhibited a paralinear decreasing. The depth of internal chlorination is defined as:

$$\zeta = (2K_r t)^{1/2} - Ket \tag{18}$$

where *Ke* is linear volatile rate constant.

After exposure to chlorine gas for a long period of time, the rate of internal chlorination would be equal to that of volatilization corrosion. Then the internal chlorination maintained a steady state and the depth of internal chlorination zone approached a constant value.

The free energy of $\mathrm{CeCl_3}$ formation is much negative. And cerium easily segregates to the grain boundary. The inward diffusing chlorine reacted with cerium and nucleation of chloride precipitates occurred at the grain boundary. In comparision to the internal chlorination result of Ni-13Cr alloy and Ni-13Cr-0.5Ce alloy, the Ce containing alloy showed increased internal attack. The effect of cerium on the internal chlorination of Ni-Cr alloy is illustrated in Fig. 4. In general, addition of Ce to Ni-Cr alloy increased the degree of internal chlorination and the chloride precipitates occured primarily along grain boundaries. The internal chlorination of Ni-Cr alloy was observed in the subsurface to precipitate within uniform alloy. On the basis of the EDS data of grain boundary, it is concluded the concentration of chromium at grain boundary is higher than that in metal matrix. This result indicates that cerium promote the segregation of chromium at the grain boundary.

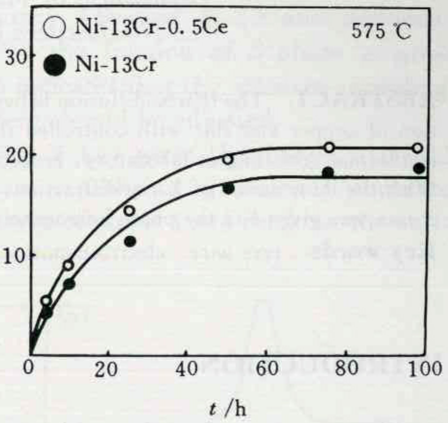

Fig. 4 Kinetics of internal chlorination of Ni-Cr-Ce alloy exposure to $\mathrm{Cl_2}$ at 575 ℃

Table 1 EDS analysis of grain boundary of the alloys (%)

	Ni-13Cr	Ni-13Cr-0.5Ce
Ni	85.949	83.743
Cr	13.942	15.420
Ce		0.837

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(Edited by Zhu Zhongguo)