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# HIGH TEMPERATURE CORROSION OF PREOXIDIZED Ni-Al ALLOY IN CHLORINE①

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## ABSTRACT

The chlorination behavior of preoxidized Ni-3.5Al alloy at 575 ℃ was investigated. The corrosion resistance of preoxidized alloy against chlorination had been improved due to the formation of protective $NiO/Al_2O_3$ scale. In chlorine atmosphere at high temperature, chlorine attacked the oxide scale by three mechanisms: mechanical damage by volatile chlorides, scale pitting and spalling by chlorine dissolving in the scale and oxides being displaced by chlorides.

**Key words**: chlorination oxide scale chloride vapor pressure preoxidization

## 1 INTRODUCTION

The corrosion rates of metals in high temperature environments containing chlorine are rapid because the reaction products generally have low melting points and high vapor pressures[1]. The volatile chlorides, oxychlorides produced in oxygen-chlorine mixtures played a role in the corrosion behavior of metals[2]. In many cases, the chlorine may penetrate an ordinary oxide scale, react with metal matrix to produce volatile chlorides and accelerate the high temperature corrosion. In previous work, Hauffe and Hinrichs[3] studied the chlorination behavior of Ni and NiO. They found the corrosion process was controlled by the formation of volatile $NiCl_2$. Because most metal chlorides are volatile at elevated temperatures, so that no protective scale is formed. The porous chloride scale cannot resist continuous attack of chlorine. The attempt to improve the corrosion resistance of alloys against chlorination by adding small amounts of $O_2$ to the atmosphere was not successful[4]. While oxygen did not affect the reaction at low $O_2$ pressures, it even caused on ignition-like reaction above a critical pressure[5]. At high temperatures, some oxides have high thermodynamic stability. If adding some elements such as Al or Cr, which can form a stable coherent and adherent oxide layer to Ni, which is suitable construction material for reaction in chlorine, and preoxidizing the alloy before chlorination, the Ni-base alloy would show better resistance against chlorine because of the formation of protective $NiO/Al_2O_3$ or $NiO/Cr_2O_3$ scales. This paper studied the high temperature chlorination behavior of preoxidized Ni-3.5Al alloy. The corrosion products were examined and analysed by SEM and XRD.

## 2 EXPERIMENTAL

Ni-3.5Al alloy was melted and drop cast, using commericially 99.9% Ni, 99.95% Al in an Ar gas atmosphere. The alloy ingot was annealed at 1 050 ℃ for 12h. Samples were cut 10mm×10 mm×0.5mm in size, polished with 600 mesh silicon carbide emery paper and degreased with acetone. Then the samples were oxidized in air at 700 ℃ for 10h. The oxide films formed on Ni-3.5Al alloy were compact and integral.

The chlorination tests were carried out in the corrosion apparatus. The chlorine gas was in static state. The temperature in the reaction zone was capable of maintaining to 575±3 ℃. The exposure

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time was from 1 h to 100 h. The weight changes of the samples were measured using balance in dry atmosphere. Before each experiment, the apparatus was purged with nitrogen to remove residual chlorine, evacuated to about $10^{-2}$ Pa and then heated to the experimental temperature. Following this, the chlorine gas was introduced.

The corroded surfaces were analysed and examined by SEM and XRD.

## 3 RESULTS AND DISCUSSION

### 3.1 *Reaction Kinetics*

Fig. 1 shows the mass changes of test samples of Ni-3.5Al alloy and preoxidized Ni-3.5Al alloy with exposure time in $Cl_2$ gas at 575 ℃. For Ni-3.5Al alloy, plots of weight change versus time show two stages: an increase in weight for short exposure time; and a linear decrease in weight after long time exposure. The results can be adequately described by the Tedmon equation[6]. However, the kinetic processes of preoxidized Ni-3.5Al alloy has corresponding change. The weight changes versus time represent three stages: (1) an increase in weight according to a parabolic law; (2) no change or a little decrease in weight; (3) a linear decrease in weight.

The chlorination resistance of preoxidized samples of Ni-3.5Al alloy has been considerably improved due to the formation of compact $NiO/Al_2O_3$ scales. NiO and $Al_2O_3$ have high chemical stability at 575 ℃. The $NiO/Al_2O_3$ scales could protect the attack of chlorine and reduced the corrosion rate. During the first stage of chlorination, the compact and integral $NiO/Al_2O_3$ scale blocked direct reaction of chlorine with alloy. The corrosion resulted from the diffusion of chloride ions and the formation of $NiCl_2$ and $AlCl_3$ between scale and alloy interface. The corrosion rate was controlled by diffusion of chloride ions through oxide scale and nearly followed a parabolic law. During the second stage of chlorination, oxide scale suffered damage to some extent, which exhibited reduction in integrity and declined in thickness. The distance of $Cl^-$ diffusion decreased and the reaction rate of chloride ions with metals increased. Porous scale could not hinder the transport of volatile chlorides from scale-alloy interface to gas phase effectively.

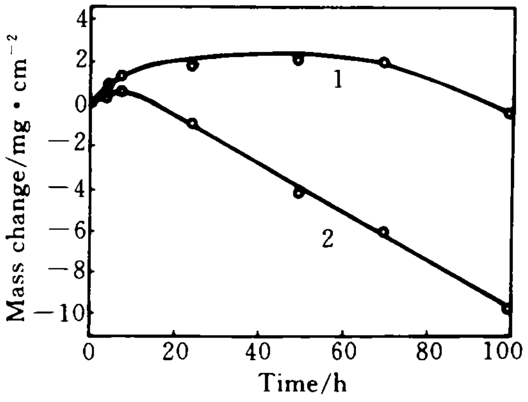

**Fig. 1 Mass changes of Ni-3.5Al and preoxidized Ni-3.5Al alloy vs time of exposure to $Cl_2$ gas at 575 ℃**

1—preoxidized Ni-Al; 2—Ni-Al

During the third stage, the protective scale was completely destroyed. The corrosion process was determined by the volatilization of $NiCl_2$ and $AlCl_3$. The corrosion was characterized by rapid, linear rate law.

### 3.2 *Damage Processes of Protective Oxide Scale*

(1) Mechanical Damage to Scale

When chloride ions diffused through oxide scale to scale-alloy interface, the chlorides would produce in this region. At 575 ℃, $AlCl_3$ is in melting state and the vapor pressure of $NiCl_2$ reaches 2.3 Pa[7]. The presence of volatile chlorides may be responsible for the loss of adhesion, formation of voids at the scale-alloy interface, and blistering of the oxide scale.

(2) Scale Pitting and Spalling by Chlorine

Chlorine altered the defect structure of the scale and increased the diffusion coefficient of chloride ions by dissolving in the oxide scale[8]. On anionic lattice sites, singly changed chloride ions may replace doubly charged oxygen ions. Considering charge and sitebalance, there is following reaction[9]:

$$Cl_2(g)+O_O^{\times}=2Cl^{\circ}_O+V^{\circ}_M+\frac{1}{2}O_2(g) \qquad (1)$$

The reaction increased the concentration of cation vacancies. The vacancies tended to precipitate as voids produced at the scale surface and interior. The voids resulted in pitting and spalling of the scale. The oxide scale could not hinder effectively diffusion of the ions chloride through scale to matrix and transport of volatile chlorides across scale to gas phase.

(3) Transformation of Oxides into Chlorides

In high temperature environments, the oxide scale formed on alloy may react with chlorine. The displacement reactions are as follows:

$$Ni(O)(s)+Cl_2(g)=NiCl_2(v)+\frac{1}{2}O_2(g) \qquad (2)$$

$$Al_2O_3(s)+3Cl_2(g)=2AlCl_3(v)+\frac{3}{2}O_2(g) \qquad (3)$$

The oxide particles on the outer layer were depleted and the scale thickness decreased. The oxide scale dissolved gradually and was displaced by the chloride layer (Fig. 2).

Table 1 indicates the structure of corrosion products observed on preoxidized Ni-3.5Al alloy after different exposure time.

**Table 1 Summary of results obtained by X ray diffraction**

| Exposure time | 0 h | 2 h | 25 h | 100 h |
|---|---|---|---|---|
| Composition of corrosion layer | $NiO$, $Al_2O_3$<br>$NiAl_2O_4$ | $NiO$, $Al_2O_3$, $NiAl_2O_4$<br>$NiCl_2$, $AlCl_3$ | $NiCl_2$, $AlCl_3$<br>$NiO$, $Al_2O_3$ | $NiCl_2$, $AlCl_3$<br>$Al_2O_3$ |

## 4 CONCLUSIONS

(1) The corrosion resistance of preoxidized Ni-3.5Al alloy against chlorination has been improved because of the formation of protective $NiO/Al_2O_3$ scale.

(2) The oxide scale was destroyed by three mechanisms: mechanical damage to scale by volatile chlorides scale; pitting and spalling by chlorine dissolving in oxide scale; and transformation of oxides into chlorides.

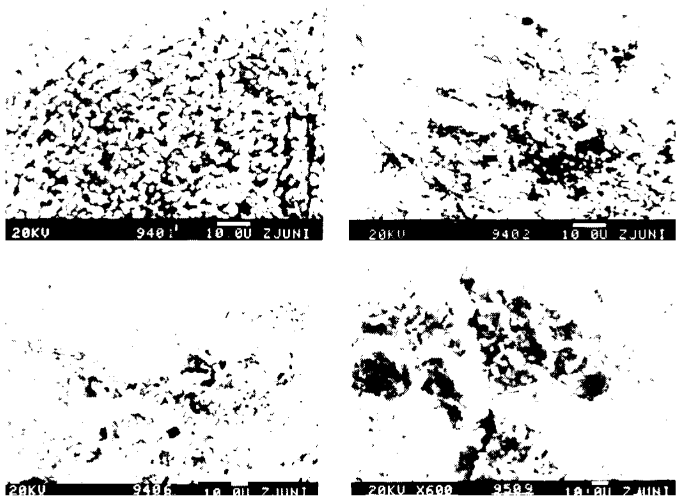

Fig. 2 SEM micrographs of surfaces of preoxidized Ni-3.5Al alloy after attack

(a) oxide scale; (b) 575 ℃, 2 h; (c) 575 ℃, 25 h; (d) 575 ℃, 100 h

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then it is easier for the metastable phase to nucleate. If the thermodynamic conditions for its formation in the overcooled melt is satisfied, the metastable phase should nucleate preferentially.

Most of the structure in Figs. 1～3 is the parent phase. This indicates that the formation of the metastable phase does not completely hinder the formation of the parent phase; and this can be explained from their difference in growth rates: although the metastable phase nucleate prior to the parent phase, the later can also nucleate and grow under the experimental conditions. Due to the fact that the free energy of the parent phase is lower than that of the metastable phase, the equilibrium temperature of free energy between the parent phase and the liquidoid is higher than that between the metastable phase and the liquidoid. Therefore, the nuclei of the parent phase has large overcooling degree; and the latent heat released from solidification has less influence on their growth rates. On the contrary, the overcooling degree of the metastable phase is smaller and the latent heat released from solidification during its growth further reduces the overcooling in the liquid- solid front edge. Consequently, the growth rate of the metastable phase is lower because of the limitation of the overcooling degree after its nucleation. The parent phase grew at a higher rate under the temperature gradient from the contact surface to free surface, then formed the morphologies as shown in Figs. 1～3.

## 5 CONCLUSIONS

(1) Under a cooling rate of about $2\times10^5$ K/s, there appears a granular *fcc* metastable phase in the Ni-Ti alloy with the lattice constant $a_0 = 4.300$ Å. This phase has the same composition as the parent phase; and it is also composed of near equiatomic Ni and Ti.

(2) The sizes of the second phase in the strip vary along the thickness. The second phase particles at positions close to the contact surface are smaller and densier. As the position moves toward the free surface, the sizes of the second phase particles become larger and their distribution gets less densified.

(3) The second phase is believed to form directly from the liqudoid by a preliminary analysis. But its formation mechanism needs to be further studied.

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