

## Corrosion behavior of NiCr alloys in HCl-containing oxidation atmosphere at 700 - 800 °C<sup>①</sup>

ZHANG Ke(张 轲), NIU Yan(牛 焱), PAN Taijun(潘太军), WU Weirao(吴维叟)  
(State Key Laboratory for Metals Corrosion and Protection, Institute of Metal Research,  
Chinese Academy of Sciences, Shenyang 110016, China)

**Abstract:** Corrosion behaviors of pure Ni and three NiCr alloys were investigated in an HCl-containing oxidizing atmosphere at 700 °C and 800 °C. All materials suffer from accelerated corrosion at both temperatures. NiCr alloys show an initial mass loss due to the formation of volatile  $\text{CrCl}_3$  and  $\text{CrO}_2\text{Cl}_2$ . Some chlorides are detected at the scale/substrate interface and many voids are also found there. NiCr alloys with higher chromium content have better corrosion resistance. However, Ni50Cr is inferior to Ni25Cr due to its two-phase structure, which makes it easy for chlorine to diffuse along grain boundary and to occur inner oxidation. The relevant corrosion mechanism was also discussed.

**Key words:** NiCr alloy; high temperature corrosion; refuse incineration; chlorination oxidation; active oxidation

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### 1 INTRODUCTION

Increasing attention is given to the disposal of refuse by incineration method. However, corrosion problems have been reported in most of incineration units<sup>[1-5]</sup>. In recent years, the increase of HCl and/or chloride content in the combustion products due to increase of PVC and plastic content in refuse has been considered to be of potential problem with respect to its effect upon rapid corrosion and degradation of structural materials used in incineration equipment such as waterwall and heat exchangers<sup>[3,4]</sup>. It is reported that the amount of Cl-compounds of the flue gas in waste fired boilers is significantly higher than that of S-compounds, and Cl-compounds are more corrosive than S-compounds<sup>[5]</sup>. The corrosion rates are always enhanced and the scales formed on the materials are porous and less protective when Cl-compounds such as HCl,  $\text{Cl}_2$  and chlorides are introduced into environments whatever Cl-compounds exist as gaseous contaminations in incineration atmosphere or salt deposits in flying ashes<sup>[4,5]</sup>. Because of the higher thermodynamic stability of nickel chloride and the good protection of chromia at high temperatures, NiCr alloys are applied as substrate alloys as well as coatings to resist high temperature corrosion induced by Cl-compounds<sup>[6-10]</sup>. However, the corrosion mechanism induced by chlorine is not fully understood. Therefore, in this study, corrosion behavior of NiCr alloys with different chromium contents is studied at 700 °C and 800 °C in a HCl-containing oxidiz-

ing atmosphere that simulates the incineration atmosphere in order to elucidate the effects of chlorine on corrosion process.

### 2 EXPERIMENTAL

To simulate typical atmosphere of the most common waste incineration environments, a mixture of 5%  $\text{O}_2$ , 0.3% HCl (volume fraction) and balance  $\text{N}_2$  (supplied in premixed cylinders) was used, which was purified by removing moisture before use. The gas was then supplied to a  $\phi 60$  mm (inner diameter) silica tube by a capillary flow meter selected to provide a flow velocity of  $2.1 \times 10^{-3} \text{ m}^3/\text{s}$  under constant atmospheric pressure at desired temperature. Before the gas flowed horizontally through the reaction tube, it firstly passed through a platinum catalyst, which enabled the gases to reach thermodynamic equilibrium. The gas then past around the specimen, which was suspended on the top of a silica boat with a platinum wire. The specimen and the platinum catalyst in the reaction tube were heated at the same time by a horizontal furnace with a temperature control accuracy of  $\pm 1$  °C. The specimens were fetched out of the reaction tube at intervals, cooled and weighted by a balance with an accuracy of 0.01 mg, and then moved back into the reaction tube again.

Three NiCr alloys with nominal chromium contents of 10%, 25%, 50% (mole fraction) respectively and balance nickel were prepared by arc melting the mixtures of the pure components under a Ti-gettered

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**Correspondence:** ZHANG Ke; Tel: + 86-024-23915910; E-mail: kezhang@imr.ac.cn;

argon atmosphere using nonconsumable tungsten electrodes. The alloy ingots were subsequently annealed in argon atmosphere at 850 °C for 48 h. According to the Ni-Cr binary phase diagram, the microstructures of Ni10Cr and Ni25Cr showed single phase and their actual compositions were Ni 90.12%, Cr 9.98% and Ni 74.84%, Cr 25.16% (mole fraction) respectively. However, microstructure of Ni50Cr alloy is a matrix of NiCr solid solution ( $\alpha$  phase, bright) with a dispersion of a Cr-rich solid solution ( $\beta$  phase, dark), as shown in Fig. 1. Pure nickel and the three NiCr alloy samples were machined into size of 1.5 cm  $\times$  1.0 cm  $\times$  0.12 cm and their surface was ground

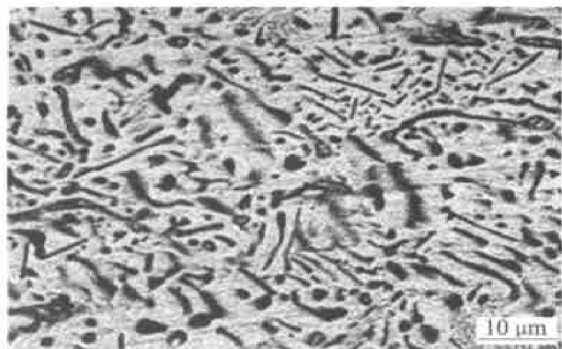


Fig. 1 Microstructure of Ni50Cr alloy

with SiC abrasive paper, cleaned with acetone and dried before experiment.

Corrosion tests were performed at 700 °C and 800 °C, respectively, for 96 h. After each test, the specimen surfaces were examined by scanning electron microscopy as well as by X-ray diffraction analysis, then were embedded in resin, sectioned, polished and finally examined by scanning electron microscopy.

### 3 RESULTS

#### 3.1 Corrosion kinetics

The corrosion kinetic curves for Ni and three kinds of NiCr alloys in the HCl containing oxidizing atmosphere at 700 °C and 800 °C are presented in Figs. 2 and 3. In order to elucidate the effect of HCl on corrosion process, parallel experiments, in which Ni and NiCr alloys are in the similar oxidizing atmosphere without HCl at the same temperatures, were carried out and the results are also shown in Figs. 2 and 3. Comparatively, the kinetic curves with HCl at both temperatures are very irregular. After an initial stage about 10 h of rapid mass gain for Ni at the two temperatures, it showed a decreasing corrosion rate.

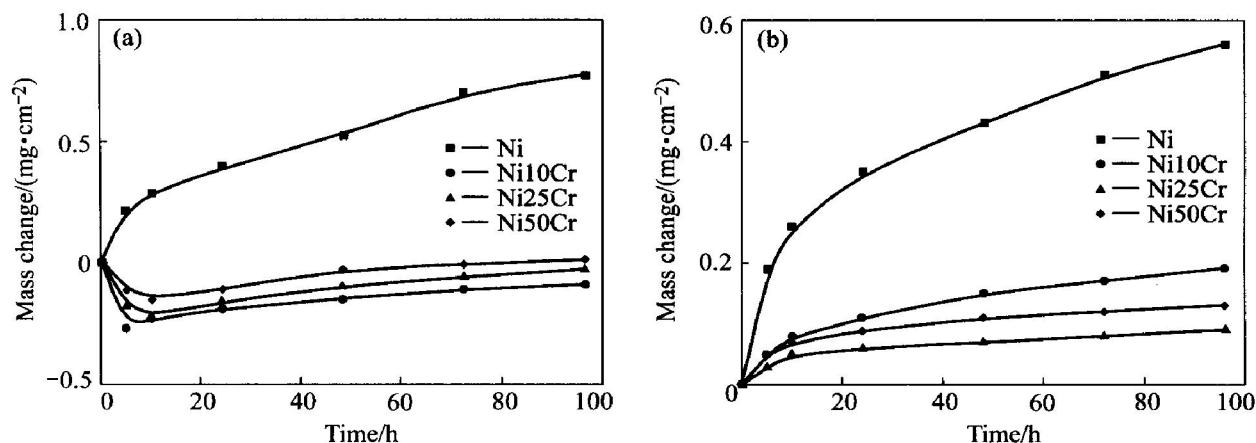


Fig. 2 Corrosion kinetic curves of pure Ni and NiCr alloys in 5% O<sub>2</sub>-0.3% HCl-N<sub>2</sub>(a) and 5% O<sub>2</sub>-N<sub>2</sub>(b) at 700 °C up to 96 h

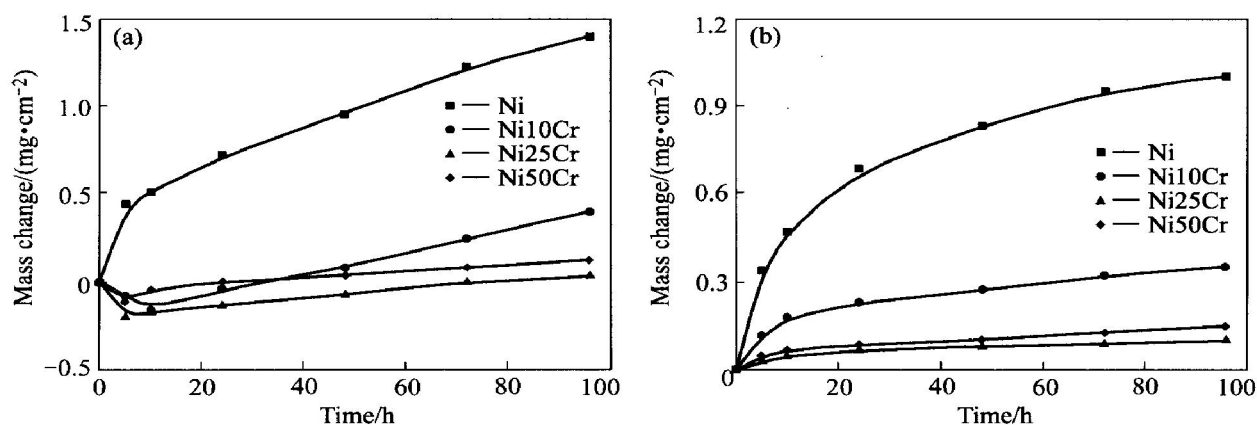


Fig. 3 Corrosion kinetic curves of pure Ni and NiCr alloys in 5% O<sub>2</sub>-0.3% HCl-N<sub>2</sub>(a) and 5% O<sub>2</sub>-N<sub>2</sub>(b) at 800 °C up to 96 h

However, for three kinds of NiCr alloys, in the initial 10 h corrosion, they underwent mass loss, and then turned to mass gain. Until the end of tests, the total mass change for those NiCr alloys was less than that of pure Ni at both temperatures. In addition, the corrosion rates of the samples at 800 °C were higher than those at 700 °C.

### 3.2 Scale structure and composition

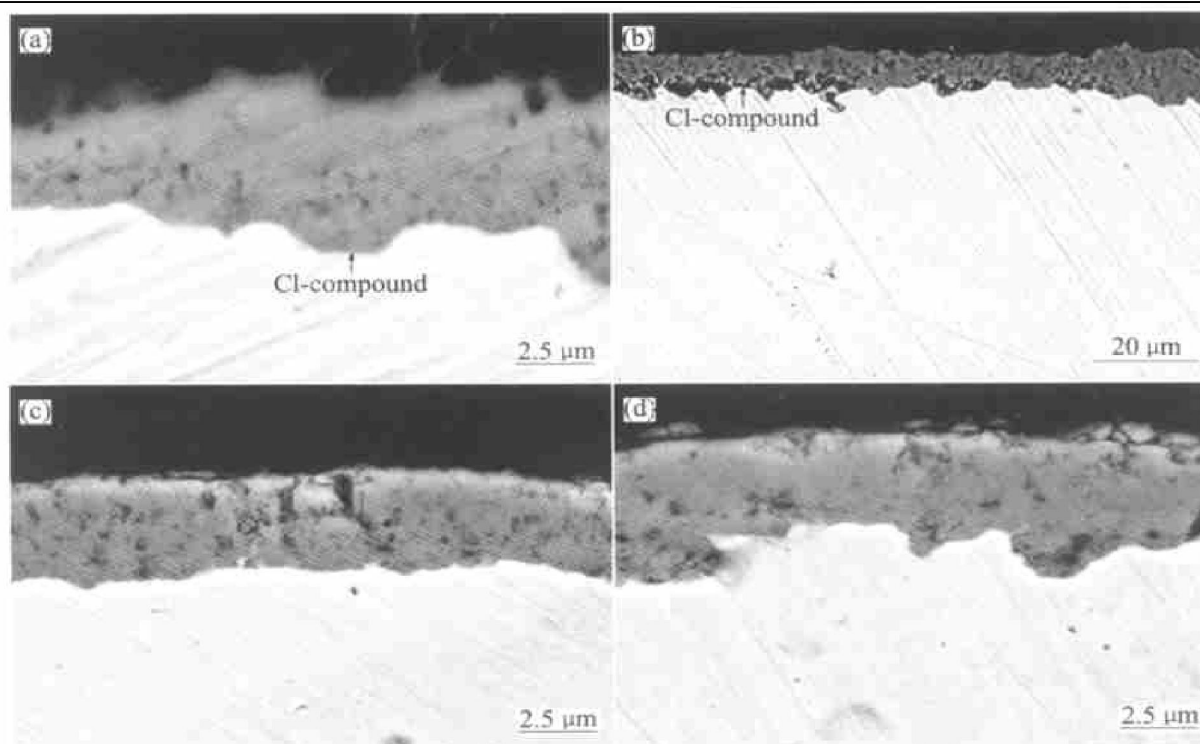
The cross sectional microstructures of the scales formed on surfaces of Ni and the three NiCr alloys in oxidizing atmosphere with and without HCl at 700 °C and 800 °C are shown in Figs. 4 – 7. In the atmosphere without HCl or with HCl, on the pure Ni a uniform scale of NiO at both temperatures formed; and on Ni10Cr a double-layer scale formed, which consisted of an outer NiO layer and an inner NiCr spinel layer; besides, on Ni25Cr and Ni50Cr a layer of Cr<sub>2</sub>O<sub>3</sub> formed. Nevertheless, obvious differences of the scales' structures were: 1) the scales formed in atmosphere containing HCl were considerably thicker than those in atmosphere without HCl under the same test condition and a small amount of chlorine was detected at the scale/metal interface; 2) some voids were also found there and the scales formed in atmosphere with HCl were apt to spalling at 800 °C; and 3) some materials underwent internal attacks by Cl such as Ni10Cr and Ni50Cr at 800 °C and Ni25Cr at 700 °C, especially along grain boundaries.

## 4 DISCUSSION

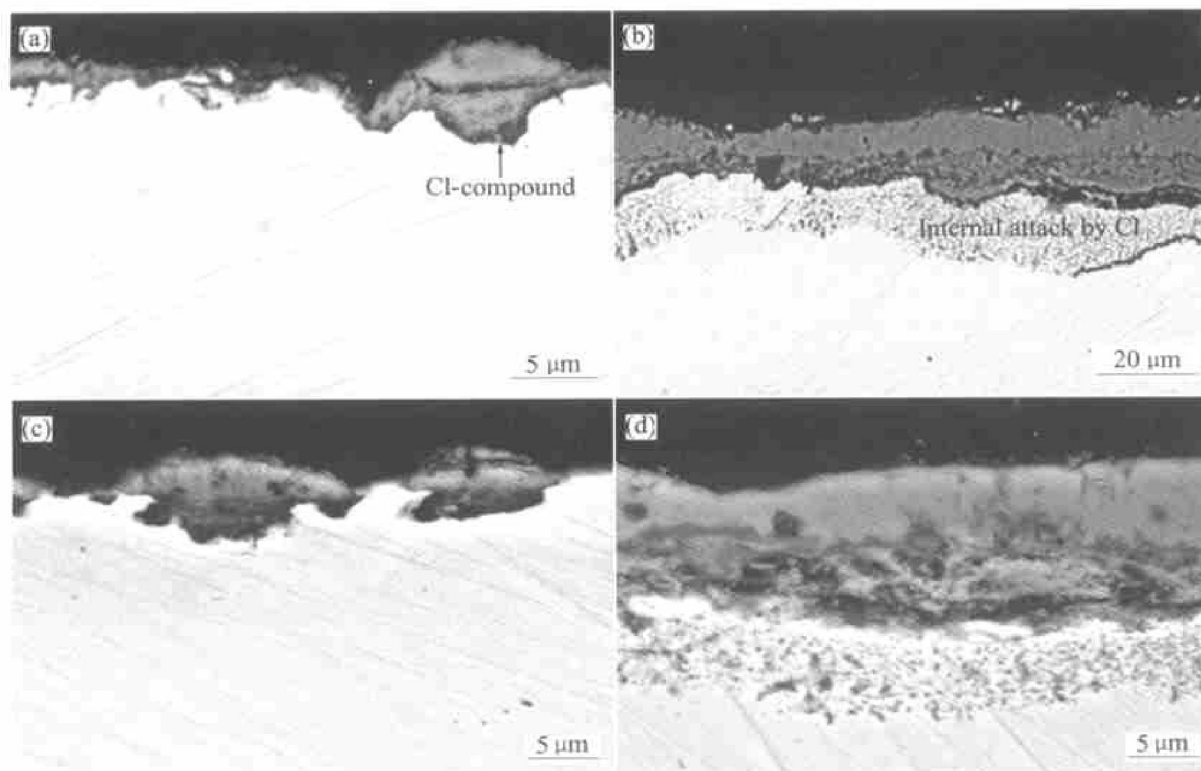
For pure Ni and NiCr alloys, the corrosion

rates in pure oxygen and air at 700 – 800 °C are relatively low. However, once HCl was introduced into the reactive gas mixture, pure Ni would undergo accelerated corrosion whereas the three NiCr alloys in this test would suffer from mass loss at the initial stage and then from mass gain. Though the total mass changes for these NiCr alloys in the atmosphere with HCl were small, the scales formed on them were thicker than those in the similar atmosphere without HCl. At the same time some chlorides were also detected at the scale/substrate interface and some internal attack by chlorine beneath the external oxide scale happened. These experimental phenomena reveal that HCl was really involved in the corrosion process.

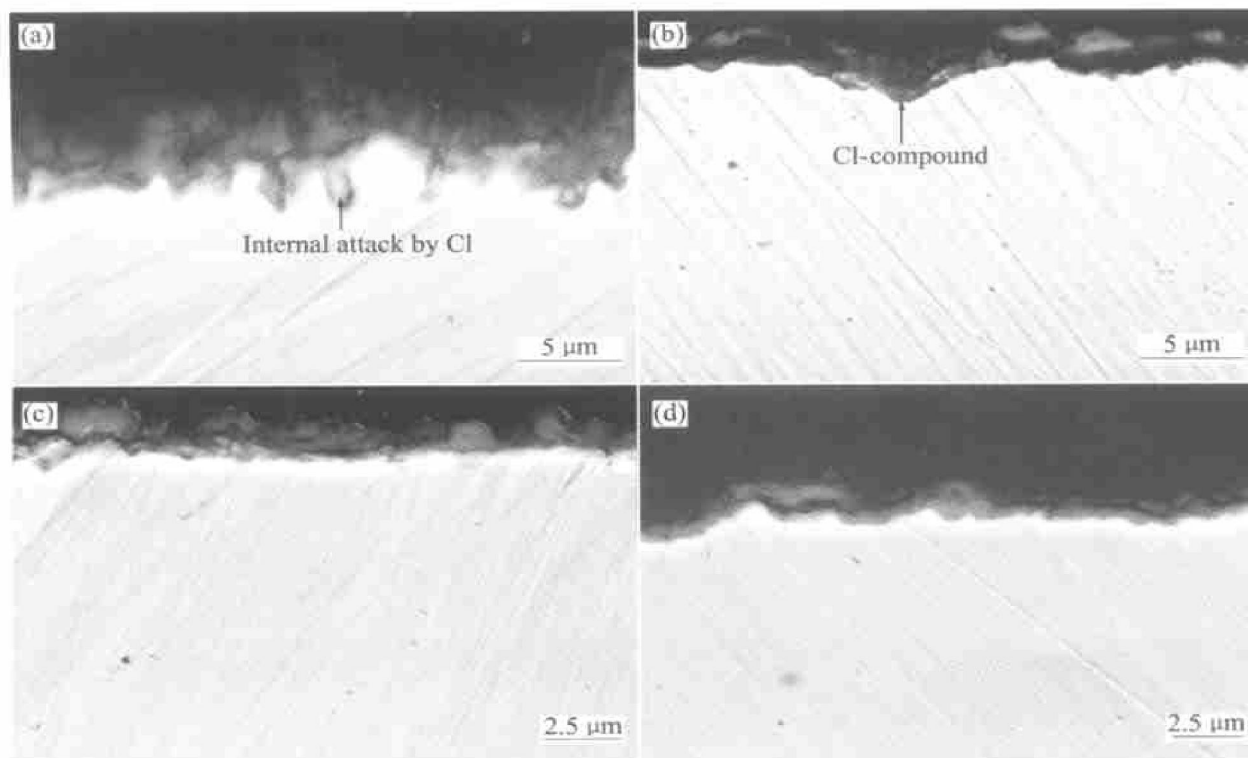
Thermodynamic phase stability diagrams can help us to ascertain the stability of corrosion products in the corrosion process and to elucidate the corrosion mechanism, further to reveal the effect of chlorine in the corrosion process. Superimposed phase stability diagrams for the Ni-Cr-Cl-O systems at 700 °C and 800 °C are plotted in Fig. 8 and the thermodynamic data are taken from Refs. [11, 12]. The assumption is made that the activities for all solids are 1 and all gases behave ideally. When the mixed gases arrive at the reaction tube at 700 °C and 800 °C, a new equilibrium is established. The calculated partial pressures of Cl<sub>2</sub> and O<sub>2</sub> of 89 Pa and 4.9 kPa at 700 °C, 63 Pa and 4.9 kPa at 800 °C, respectively, are marked as a black point in Fig. 8. Metal oxides including NiO and Cr<sub>2</sub>O<sub>3</sub> are stable oxide phases seen on the superimposed Ni-Cr-Cl-O stability phase diagrams at both



**Fig. 4** Cross-sectional micrographs (SEM/BEI) of Ni in 5% O<sub>2</sub>-0.3% HCl-N<sub>2</sub> at 700 °C (a), 800 °C (b) for 96 h, and in 5% O<sub>2</sub>-N<sub>2</sub> at 700 °C (c), 800 °C (d) for 96 h



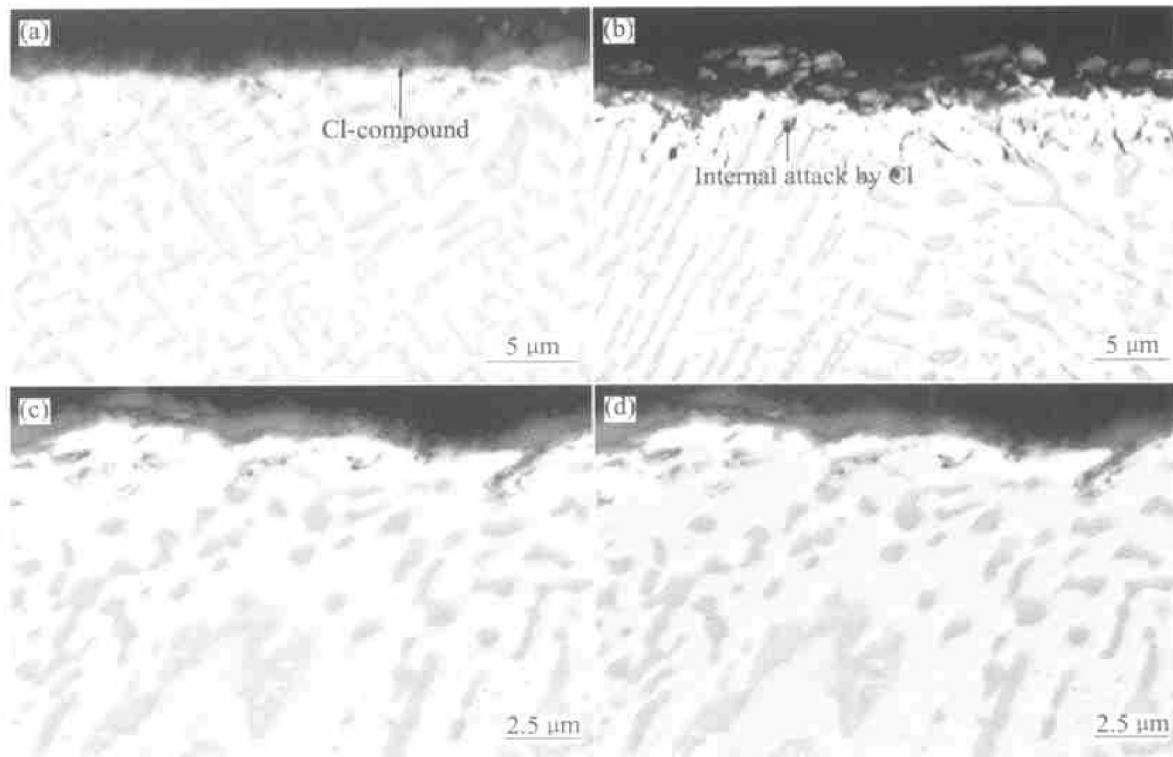
**Fig. 5** Cross-sectional micrographs(SEM/BEI) of Ni10Cr in 5% O<sub>2</sub>-0.3% HCl-N<sub>2</sub> at 700 °C(a), 800 °C(b) for 96 h, and in 5% O<sub>2</sub>-N<sub>2</sub> at 700 °C(c), 800 °C(d) for 96 h



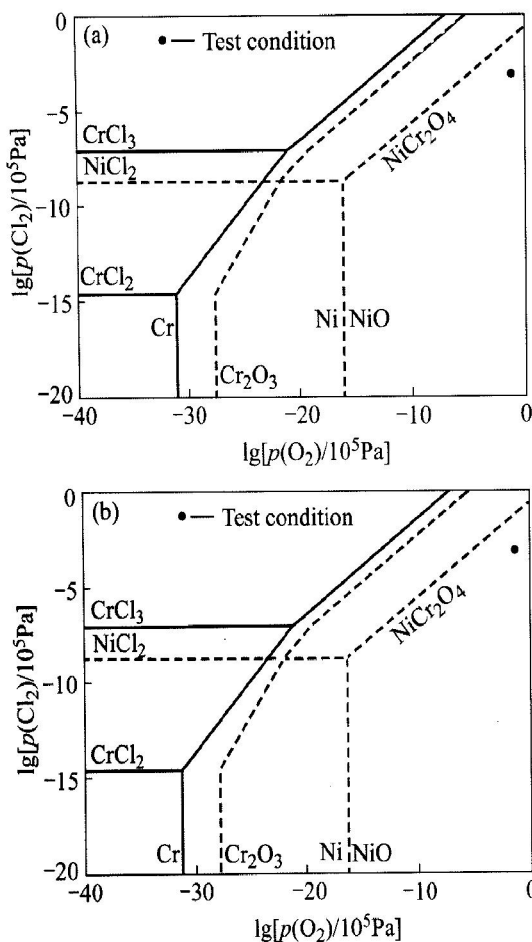
**Fig. 6** Cross-sectional micrographs(SEM/BEI) of Ni25Cr in 5% O<sub>2</sub>-0.3% HCl-N<sub>2</sub> at 700 °C(a), 800 °C(b) for 96 h, and in 5% O<sub>2</sub>-N<sub>2</sub> at 700 °C(c), 800 °C(d) for 96 h

temperatures. However, for equilibrium of the ternary oxide NiCr<sub>2</sub>O<sub>4</sub> with Ni, Cr<sub>2</sub>O<sub>3</sub> and O<sub>2</sub>, or with Ni, CrCl<sub>2</sub> and O<sub>2</sub>, or with NiCl<sub>2</sub>, CrCl<sub>3</sub> and O<sub>2</sub> has a line above the Ni/NiO and NiCl<sub>2</sub>/NiO lines in the diagrams, which indicates NiCr<sub>2</sub>O<sub>4</sub> is more stable

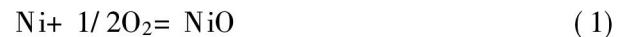
than NiO. Because the gas equilibrium for Cl<sub>2</sub> and O<sub>2</sub> in this study at both temperatures is also above the dissociative pressures for Ni and Cr chlorides and oxides in the diagrams, Ni and Cr could be chloridized and oxidized with Cl<sub>2</sub> and O<sub>2</sub> from the mixed gases



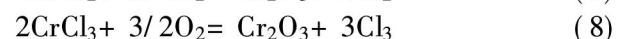
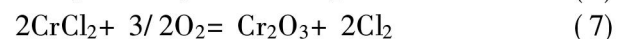
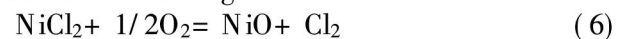
**Fig. 7** Cross sectional micrographs (SEM/BEI) of Ni50Cr in 5% O<sub>2</sub>-0.3% HCl-N<sub>2</sub> at 700 °C (a), 800 °C (b) for 96 h, and in 5% O<sub>2</sub>-N<sub>2</sub> at 700 °C (c), 800 °C (d) for 96 h



**Fig. 8** Superimposed thermal stability diagram for Ni, Cr-Cl-O system at 700 °C (a) and 800 °C (b) simultaneously when the mixed gases containing HCl was introduced at the initial stage of corrosion:



For the phase that contacts with the test gaseous atmosphere is oxide but not chloride, therefore, the metal chlorides will be transferred into the corresponding oxides as following reactions:



At the same time, NiO can combine with Cr<sub>2</sub>O<sub>3</sub> to form NiCr<sub>2</sub>O<sub>4</sub>:



Through these above reactions, an oxide scale can form on the surface of samples at the initial stage. Once the oxide scale is formed, it can separate the alloys from corrosive gas mixture, and then the corrosion rates may be reduced. However, chlorine from the gases mixture can penetrate the oxide scale and reach the scale/substrate interface due to the chlorine pressure difference between the scale/gas interface and scale/substrate interface. For example, assuming CrCl<sub>2</sub> can be in equilibrium with Cl<sub>2</sub> at scale/substrate interface, the chlorine pressure can be calculated to be  $2.34 \times 10^{-10}$  Pa at 700 °C and  $2.04 \times 10^{-8}$  Pa at 800 °C, whereas in the gases mixture, the partial pressure of chlorine is 89 Pa at 700 °C and 63 Pa at 800 °C respectively. Therefore, a chlorine pressure difference will be established between the two interfaces, which



drives chlorine to permeate from the gas/scale interface to scale/substrate interface. At the scale/substrate interface, chlorine reacts with metal to form chlorides. Generally, metal chlorides are apt to volatilization at high temperature. As listed in Table 1, for the Ni and Cr chlorides, vapor pressures of  $\text{CrCl}_3$  at 700 °C and  $\text{NiCl}_2$ ,  $\text{CrCl}_2$  and  $\text{CrCl}_3$  at 800 °C exceed 10 Pa, which is considered as the critical vapor pressure that a massive volatilization may occur<sup>[13]</sup>. Similarly, in the oxide scale, the partial pressure of oxygen falls from a high value at the gas/scale interface to a very low value at the scale/substrate interface. This helps to set up an oxygen pressure gradient opposite to the partial pressure gradient of the volatile chlorides by Eqns. (6)–(8), which is a driving force for the diffusion of chlorides vapor<sup>[14]</sup>. Therefore, chlorides volatilize and the vapor of chlorides diffuse outward through the scale to scale/gases interface. In the diffusion process of chlorides vapor in the scale, Ni and Cr chlorides can be converted into its corresponding oxides where oxygen pressure exceeds the level that the conversion by Eqns. (6)–(8) may facilitate. One of these reaction products,  $\text{Cl}_2$  could partially permeate through the scale into scale/substrate interface, where it reacts with metal to form metal chlorides again. This will produce a  $\text{Cl}_2$  cycle catalyzed by itself, which is termed as “active oxidation”<sup>[14, 15]</sup>. “Active oxidation” process can increase diffusion outwards rate of the metal ion by vapor chlorides diffusion, which accelerates corrosion rates.

**Table 1** Physical properties of Ni and Cr chlorides

Chloride	Melting point/ °C	$\theta_4$ / °C	$p_{700}$ / Pa	$p_{800}$ / Pa
$\text{NiCl}_2$	1030	607	0.182	70.8
$\text{CrCl}_2$	820	611	2.86	51.6
$\text{CrCl}_3$	1150	741	226	3 820

$\theta_4$ —Temperature at which chloride vapor pressure reaches 10 Pa;  $p_{700}$  and  $p_{800}$ —Chloride vapor pressures at 700 °C and 800 °C, respectively

From the theory of “active oxidation”, the external oxide growth can be explained by two parallel mechanisms, one based on solid diffusion, and the other on gas phase transportation of the volatile chloride compounds through the pores in the scale. According to Haanappel<sup>[16, 17]</sup>, for oxide growth by phase transportation can be written as

$$\left| \frac{dx}{dt} \right|_v = -n V_m D(\text{MCl}_y) \frac{p(\text{MCl}_y)}{x} = K''_p / x \quad (10)$$

where  $n$  is the amount of products, mol;  $D(\text{MCl}_y)$  diffusion coefficient of  $\text{MCl}_y$  in vapor phase,  $V_m$  molar volume of the product,  $p(\text{MCl}_y)$  partial pressure

of metal chloride at the scale/substrate interface,  $\varepsilon$  void fraction in the scale, and  $x$  thickness of the scale.

$K''_p$ , which corresponds to the scale growth accelerated by the gas phase transportation of chlorides, can be written as:

$$K''_p = -n V_m D(\text{MCl}_y) \Phi(\text{MCl}_y) \quad (11)$$

Generally, oxides growth by metal ion solid-state diffusion can be written as:

$$\left| \frac{dx}{dt} \right|_s = -n V_m D_i \left| \frac{dc_i}{dx} \right| \quad (12)$$

where  $D_i$  is diffusion coefficient of component  $i$  in the scale,  $\text{cm}^2 \cdot \text{s}^{-1}$ ; and  $c_i$  the concentration of component  $i$  in the scale,  $\text{mol} \cdot \text{cm}^{-3}$ .

It is known that the presence of  $\text{Cl}$ -compounds increases the oxidation rate as well as the void fraction in the oxides, especially at the scale/substrate interface<sup>[3-17]</sup>. Due to the increase of the void fraction, the oxides growth by solid diffusion diminishes by a factor  $(1 - \varepsilon)$ . Therefore, the equation describing the oxide growth by solid diffusion when taking the void fraction into account can be written as

$$\left| \frac{dx}{dt} \right|_s = -n(1 - \varepsilon) V_m D_i \left| \frac{dc_i}{dx} \right| = \frac{K'_p}{x} \quad (13)$$

where  $K'_p$  corresponds to the scale growth by solid state diffusion.

Totally, the overall modified Tedmon equation can be written as:

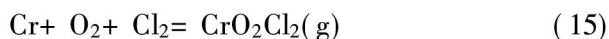
$$\left| \frac{dx}{dt} \right|_t = \left| \frac{dx}{dt} \right|_s + \left| \frac{dx}{dt} \right|_v - K_s \quad (14)$$

where  $K_s$ , which represents the decrease in mass, is time-independent. This loss is expressed by the rate constant of linear evaporation  $K_v$ , which implies the reaction between the metal and/or scale and the chlorine compounds forming volatile metal chlorides.  $K_v$  is a function of the temperature, saturated vapor pressure of chlorides and the relative activities of the aggressive gas components.

However,  $D(\text{MCl}_y)$  for many chlorides in oxides are not available, and the void fraction,  $\varepsilon$ , varies with test conditions. In addition, because the reactions for the metal and/or its oxides with  $\text{Cl}$ -compound are very complex, the mass loss constant  $K_v$  in fact cannot be calculated. However, it is very obviously shown by modified Tedmon equation that the corrosion rates were accelerated by vapor phase diffusion of metal chlorides.

In this study,  $\text{NiCl}_2$  has comparatively low vapor pressure at both temperatures, and the fact that  $\text{NiO}$  reacts with  $\text{HCl}$  from gases to form  $\text{NiCl}_2$  and  $\text{O}_2$  is not favored. Therefore, pure Ni underwent accelerated corrosion by vapor phase transportation and the mass loss is ignored. However, three NiCr alloys underwent mass loss at the initial stage due to the relative high vaporization of  $\text{CrCl}_3$ , especially Cr in alloys still reacts with  $\text{Cl}_2$  and  $\text{O}_2$  simultaneously to form

$\text{CrO}_2\text{Cl}_2^{[18]}$ :



$\text{CrCl}_4$  cannot be formed because it requires chlorine pressure about 62 kPa at 700 °C and 92 kPa at 800 °C respectively, which are far higher than the chlorine pressure supplied by the test condition. Therefore, the volatilization of  $\text{CrCl}_3$  and  $\text{CrO}_2\text{Cl}_2$  results in a mass loss at the initial stage. Once an oxide scale formed on the surface, the formation and volatilization of these two products would be hindered because the scale separated metals from corrosive gas mixture. Therefore, NiCr alloys experience mass gain after their initial mass loss.

The corrosion resistance for Ni50Cr in the HCl containing atmosphere is not better than that for Ni25Cr, and this can be attributed to its two-phase structure. Two-phase structure provides many phase interfaces, which become the rapid channel for chlorine diffusion into deep substrate where “active oxidation” can take place. For example, for Ni50Cr at 800 °C, under the depletion of chromium layer, the front of Cr-rich  $\beta$  phase is attacked by chlorine.

Finally, addition chromium into Ni can produce a chromium-rich oxide scale under NiO, with increasing the chromium content of NiCr alloys, and selective oxidation of chromium can take place to form chromia on the surface of alloys, therefore, both the Ni-Cr spinel and chromia scales can effectively diminish the “active oxidation” process and improve the corrosion resistance of alloys in the atmosphere containing HCl<sup>[7]</sup>.

## 5 CONCLUSIONS

1) NiCr alloys with higher chromium content have better corrosion resistance, however, Ni50Cr is inferior to Ni25Cr due to its two-phase structure.

2) Cl induced accelerated corrosion can be attributed to chlorides vapor phase transportation, and can be explained by “active oxidation”.

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