

CHLORINATION OF Ni-Cr ALLOYS IN Cl_2 ENVIRONMENT AT 575 °C^①

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ABSTRACT

The chlorination of nickel-chromium alloys in chlorine environment at 575 °C was investigated using thermogravimetric analysis and examination of the corrosion products using SEM, EDS, XRD, XPS and chemical analysis. In a dry chlorine environment at high temperature, the corrosion resulted from the formation of volatile chlorides. The reaction kinetics followed a complex pattern which can be approximated by initial parabolic rate law to linear rate law after long time exposure.

Key words: chlorination chloride reaction product scale vapor pressure

1 INTRODUCTION

Corrosion of many metals in chlorine gas at elevated temperatures were greatly accelerated due to the formation of low melting point volatile chlorides by chlorination reactions. The upper temperatures for continuous service were limited^[1,2]. Several previous studies had focused on the effect of contaminated chlorine as an accelerator of oxidation^[3-5], but little has been done on the corrosion behavior of alloys in high partial pressure chlorine at elevated temperature.

In chemical industry, liquid chlorine must be atomized using over-chlorination technology to produce tetrachlorethylene and tetrachloroethane. The reaction was carried out between 500 and 600 °C. The reaction chamber and vaporizer suffered severe damage during reaction. Among metals only nickel and chromium have some importance because of the comparatively high melting

points and low vapor pressure of chloride^[6]. In this work, the chlorination processes of Ni-Cr alloys in dry chlorine at 575 °C are studied. The kinetics of chlorination and reaction product scales were also discussed.

2 EXPERIMENTAL

Ni-Cr alloys were melted and drop cast, using 99.9% Ni, 99.9% Cr in an Ar gas atmosphere. The alloy ingots were annealed at 1150 °C for 24 h. Samples were 10 mm × 10 mm × 0.5 mm in size, polished with 600 mesh silicon carbide emery paper and degreased with acetone.

The chlorination tests were carried out in the corrosion apparatus (Fig. 1). Before the chlorine gas was introduced into reaction chamber, water in chlorine was absorbed by H_2SO_4 . The gas flow rate was 1.5 cm/s. The temperature in the reaction zone could be kept at 575 ± 3 °C. In order to clean the

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reaction chamber and dry the samples before each measurement, the apparatus was introduced by N_2 gas and evacuated to about 10^{-3} Pa. Then the temperature was raised to 575 °C and the Cl_2 was introduced into the reaction chamber.

The weight change during corrosion was measured by a Cahn Model 1000 Balance. The outer scales of alloys after attack were examined by optical and scanning electron micrograph. The reaction products were analysed by XRD, EDS and XPS.

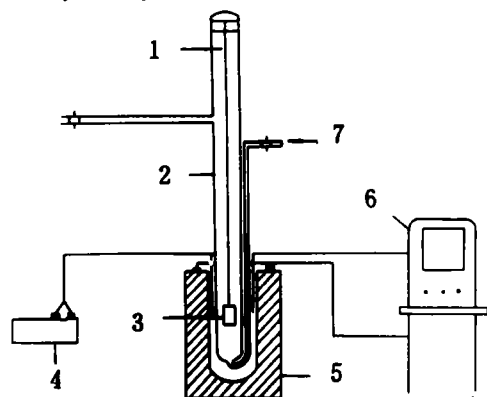


Fig. 1 Corrosion apparatus

1—quartz helix; 2—reaction chamber;

3—sample; 4—potentiometer;

5—furnace; 6—temperature controller; 7— Cl_2

3 RESULTS AND DISCUSSION

X-ray diffraction and chemical analysis data indicated reaction products formed on the alloys and deposited on the reaction chamber were same chlorides: NiCl_2 and CrCl_3 . The chlorination reaction consisted of two major processes: (1) formation of chlorides; (2) vaporization of chlorides.

Fig. 2 shows weight change of test samples of Ni-Cr alloys exposed to Cl_2 gas at 575 °C. For short time exposure, the weight of samples increased because of the formation of NiCl_2 , CrCl_3 and growth of scale. After long time exposure, the samples showed a net decrease in weight for vaporization of

NiCl_2 and CrCl_3 . At 575 °C standard condition, the vapor pressures of NiCl_2 and CrCl_3 are 2.94 Pa or 2.34 Pa^[7].

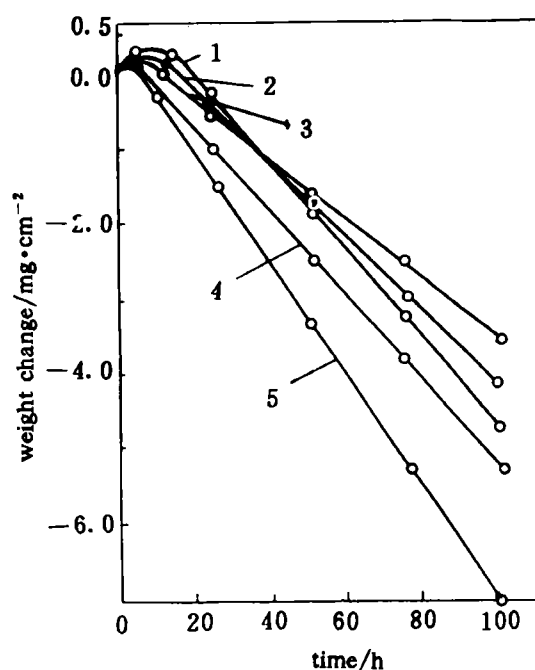
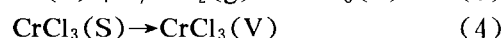
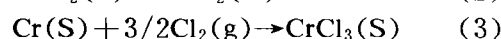


Fig. 2 Weight change vs exposure time for Ni-Cr alloys corroded at 575 °C in Cl_2 gas

1—Ni-4Cr; 2—Ni-8Cr; 3—Ni-13Cr;

4—Ni-23Cr; 5—Ni-30Cr

According to the results of thermogravimetric experiments and reaction products, the nickel-chlorine and chromium-chlorine reaction are the same process, namely,



The rate of chloride formation was controlled by Cl^- diffusion through the scale. the initial corrosion stage, the thickness of reaction product scale formed on alloy was thin, the distance of Cl^- diffusion was short, then the rate of chloride formation was rapid. In steady corrosion system, the rate of vaporization from the surface was normally considered to be constant.

$$\frac{d(Wt)}{dt} = \frac{d(\text{Ni-Cr})}{dt} + \frac{d(\text{NiCl}_2 + \text{CrCl}_3)_a}{dt} + \frac{d(\text{NiCl}_2 + \text{CrCl}_3)_d}{dt} \quad (5)$$

where $(\text{NiCl}_2 + \text{CrCl}_3)_a$ represents the chlorides on the alloy, $(\text{NiCl}_2 + \text{CrCl}_3)_d$ the chloride deposited on the reaction chamber.

Under steady state condition, the rate of scale growth equals the rate of vaporization, then

$$\frac{d(\text{NiCl}_2 + \text{CrCl}_3)_a}{dt} = 0 \quad (6)$$

Now, the weight loss is solely due to the vaporization process. Each mole of Ni-Cr alloy produces one mole chlorides, thus

$$\frac{d(\text{Ni-Cr})}{dt} = - \frac{d(\text{NiCl}_2 + \text{CrCl}_3)_a(\text{evap})}{dt} \quad (7)$$

Equation(7) can be rewritten as

$$\frac{d(\text{Ni-Cr})}{dt} = - \frac{d(\text{NiCl}_2 + \text{CrCl}_3)_a(\text{evap})}{dt} \times \frac{M_{\text{Ni-Cr}}}{M_{(\text{NiCl}_2 + \text{CrCl}_3)}} \quad (8)$$

where $M_{\text{Ni-Cr}}$ and $M_{(\text{NiCl}_2 + \text{CrCl}_3)}$ represent the mass per mole of the alloy and the chlorides, respectively.

In dry chlorine atmosphere at 575 °C ,

$$\frac{d(\text{NiCl}_2 + \text{CrCl}_3)_a(\text{evap})}{dt} = -Kv \quad (9)$$

$$\text{and } \frac{d(\text{NiCl}_2 + \text{CrCl}_3)_d}{dt} = Kd \quad (10)$$

Hence, under steady state condition,

$$\frac{d(Wt)}{dt} = - \frac{M_{\text{Ni-Cr}}}{M_{(\text{NiCl}_2 + \text{CrCl}_3)}}Kv + Kd = Ke \quad (11)$$

At time t , the weight change of the sample will be

$$\begin{aligned} \Delta(Wt)_t &= \frac{M_{(\text{NiCl}_2 + \text{CrCl}_3)} - M_{\text{Ni-Cr}}}{M_{(\text{NiCl}_2 + \text{CrCl}_3)}}x + Kdt \\ &\quad - \frac{M_{\text{Ni-Cr}}}{M_{(\text{NiCl}_2 + \text{CrCl}_3)}}Kvt \end{aligned} \quad (12)$$

where x is the thickness of the chloride

scale at t , Equations (9) ~ (12) can be combined to give

$$\Delta(Wt)_t = mx - Ket \quad (13)$$

At the initial stage, the rate of chloride formation was rapid. The thickness of chloride scale increased with increasing exposure time. The kinetics of Ni-Cr alloy—chlorine reaction nearly followed a parabolic rate law. When the rate of vaporization equaled the rate of the scale growth, the reaction reached the steady state. At the steady state, the thickness of chloride scale maintained constant. The kinetics of chlorination exhibited a linear decrease in weight as a result of the evaporation of volatile chlorides.

When the alloy was exposed in Cl_2 gas at 575 °C, the surface of the alloy was covered with a yellow reaction product scale (Fig. 3). For short time exposure, the scales exhibited spalling morphology. After long time exposure, the volatile chlorides caused mechanical damage to the growing scale. The scales exhibited blistered morphology. The blistering of scales formed on the alloys containing high chromium content appeared much severe.

At the steady state, the corrosion process was determined by the volatilization of chlorides. In Cl_2 atmosphere at 575 °C the vapor pressure data of NiCl_2 and CrCl_3 were almost the same, the transfer rates of volatile NiCl_2 and CrCl_3 produced at the scale-alloy interface through the scale were equal. Then the distribution of NiCl_2 and CrCl_3 in the scale was homogeneous.

Fig. 4 shows XPS spectra formed on Ni-13Cr alloy. The surface of scale is primarily nickel, chromium and chlorine. Oxygen on surface was absorbed by water in air. The peaks of Ni_{2p} and Cr_{2p} indicate that nickel is in NiCl_2 and chromium is in CrCl_3 . After sputter etch to remove outer surface, the Ni_{2p} and Cr_{2p} peaks did not shift. Accord-

ing to ref. [8] the products of chromium-chlorination reaction were CrCl₂, CrCl₃ and CrCl₄. But in this work, there was no evidence of CrCl₂ and CrCl₃.



Fig. 3 Scanning electron micrographs of Ni-Cr alloys after exposure to Cl₂ gas at 575 °C (a) Ni-13Cr, 10 h, 600×; (b) Ni-13Cr, 100 h, 600×; (c) Ni-30Cr, 100 h, 400×

4 CONCLUSION

(1) The chlorination of Ni-Cr alloy in

Cl₂ gas at 575 °C resulted from the formation of volatile chlorides.

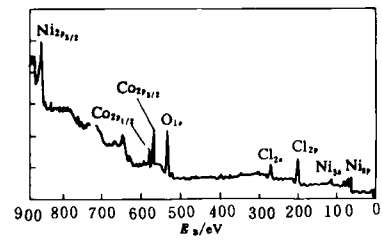


Fig. 4 XPS spectra of a scale formed on Ni-13Cr alloy

(2) At the initial reaction stage, the chlorination process was controlled by chloride ion diffusion through the scale. The kinetics of reaction followed a parabolic rate law. When the reaction reached the steady state, the chlorination process was determined by the volatilization of chlorides, and the kinetics of reaction exhibited a linear rate law.

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