Investigation of the transient state of oxidation-chloridation

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Abstract. — The transient state of the simultaneous oxidation and chloridation of Fe-2.25Cr-1Mo at 773 K and Fe-25Cr-20Ni-Nb at 973 K have been studied in He-O₂-H₂O-HCl and N₂-H₂-H₂O-HCl mixtures in short term oxidation tests. The surface of the corroded samples were examined by SEM and AES. The simultaneous attack of O₂ and Cl₂ leads to the formation of metal oxides and chlorides side by side on the alloy surfaces during the early stage of reaction, although the chlorides are not in stable equilibrium with the gas phase. After longer exposure times only the thermodynamically stable oxides were detected in the outer scale, however, at the metal/oxide interface chloride layers are still present. The initial simultaneous growth of oxides and chlorides strongly affects the structure and morphology of the subsequently formed oxide scales.

1. Introduction.

In several technical applications metals and alloys are exposed to oxidizing and chloridizing environments. The presence of HCl or Cl₂ in the gas phase leads to a degradation of protective oxide scales due to formation of volatile reaction products even at relatively low temperatures (773 K). The steady evaporation of chlorides affects the structure and morphology of the oxides; they always show a porous structure and are badly adherent. The great influence of Cl₂ or HCl on the high temperature corrosion of metals and alloys was studied in many investigations [1-5]. In contrast to simultaneous oxidation-sulfidation [6-8], very few studies have dealt with the transient state of oxidation-chloridation of metals and alloys.

The studies on the transient state of the simultaneous oxidation-sulfidation showed that side-by-side growth of oxides and sulfides occurs in the initial stage of reaction even if only one of these phases can be in stable equilibrium with the gas phase. This leads to the formation of non-protective scales and breakaway corrosion as was often observed.

The study is concerned in aggravated corrosion which will take place in incineration of chlorine containing waste or coal [10,11] - especially if such fuels were used already in the very first run of the plant. The initial, transient state of simultaneous oxidation-chloridation was investigated on one low alloy steel Fe-2.25Cr-1Mo which is widely used for heat exchanger tubes in power plants up to 550 °C and a high alloy steel Fe-25Cr-20Ni-Nb which can be used at higher temperature e.g. for transporting grids. The low alloy steel was exposed at 773 K and the high alloy steel at 973 K in short term tests to an oxidizing He-O₂-H₂O-HCl mixture and a "reducing" N₂-H₂-H₂O-HCl mixture simulating incineration and gasification atmospheres respective.

2. Experimental.

The chemical compositions of the steels are listed in table I. Short term oxidation tests were performed in a He-O₂-H₂O-HCl mixture at a high oxygen partial pressure and in a N₂-H₂-H₂O-HCl mixture at a low oxygen partial pressure. In these gas atmospheres different p_{O_2} and p_{Cl_2} were established according to the following equilibria:

The oxygen and chlorine pressures at 773 K and 973 K are summarized in table II.

The condensed phases which can be in stable equilibrium with the gas phase under these conditions can be seen from the thermodynamic stability diagrams for Fe-O-Cl at 773 K (Fig. 1) and for M-O-Cl (M = Fe, Cr, Ni) at 973 K (Fig. 2) [9]. Under the experimental conditions the oxides are the only stable condensed phases in thermodynamic equilibrium with the gas atmosphere, but the formation pressure of the condensed chlorides is also exceeded.

The oxidized samples were examined after corrosion by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX) and Auger electron spectroscopy (AES).

Table I. — *Chemical composition of investigated iron based alloys (in wt %).*

	Fe	Cr	Ni	Mo	Nb
Fe-2.25Cr-1Mo	Bal.	2.21	-	0.91	-
Fe-25Cr-20Ni-Nb	Bal.	25.6	20.5	-	0.1

Table II. — *Compositions of the gas mixtures.*

T [K]	He-O ₂ -H ₂ O-HCl		N ₂ -H ₂ -H ₂ O-HCl	
	log p_{O_2}	log p_{Cl_2}	log p_{O_2}	log p_{Cl_2}
	[bar]	[bar]	[bar]	[bar]
773	-1.71	-3.46	-27.9	-16.55
973	-1.71	-4.28	-21.0	-13.93

Fig. 1. — Thermodynamic stability diagram of the system Fe-O-Cl at 773 K.

Fig. 2. — Thermodynamic stability diagram of the system M-O-Cl at 973 K (M = Fe, Cr, Ni).

3. Results.

Fe-2.25Cr-1Mo. — When a blank metallic alloy surface is exposed to a corrosive gas atmosphere at high temperatures each phase can be formed, whose formation pressure is exceeded in the gas phase [7,12-14]. Therefore during the transient state for Fe-2.25Cr-1Mo at 773 K not only Fe_2O_3 formation was expected but also Fe_3O_4 and $\text{FeCl}_2(\text{s})$ formation.

Fig. 3. — a) AES sputter profile of Fe-2.25Cr-1Mo after 1 min oxidation in He-O₂-H₂O-HCl at 773 K; b) AES sputter profile of Fe-2.25Cr-1Mo after 10 min oxidation in He-O₂-H₂O-HCl at 773 K.

Fig. 4. — a) AES sputter profile of Fe-2.25Cr-1Mo after 1 min oxidation in N₂-H₂-H₂O-HCl at 773 K; b) AES sputter profile of Fe-2.25Cr-1Mo after 10 min oxidation in N₂-H₂-H₂O-HCl at 773 K.

In figures 3 and 4 AES sputter profiles are shown obtained on Fe-2.25Cr-1Mo samples after 1 and 10 min exposure to the He-O₂-H₂O-HCl and N₂-H₂-H₂O-HCl gas mixtures at 773 K. In both gas atmospheres with high and low oxygen partial pressures, after 1 min reaction, iron oxides and chloride were detected on the surface of the sample, although FeCl₂(s) is not in stable equilibrium with the gas phase. In this early stage of oxidation the iron chloride is in equilibrium with the metal phase and the iron activity (a_{Fe}) on the scale surface is high.

After 10 minutes of oxidation, only iron oxide was detected on the sample. Upon taking

a sputter profile a significant chlorine enrichment was observed at the oxide-alloy interface. This shows that the chloride was overgrown by the thermodynamically stable oxide and that equilibrium with the gas phase was established at the gas/oxide interface, beneath the oxide layer the iron chloride remained. There the oxygen pressure is reduced. However, $\text{FeCl}_2(\text{s})$ is only stable at a low p_{O_2} , if the chlorine pressure is sufficiently high. During the early stage of reaction oxides and chlorides grow simultaneously, making the formation of a dense, protective oxide scale unlikely. The morphology of the porous oxide scale is shown in figure 5b and is different when compared with the scale formed in a HCl-free atmosphere (Fig. 5a). Through such a scale, Cl_2 and HCl have easy access to the underlying substrate, thus stabilizing the ferrous chloride. With an increasing scale thickness resulting from oxidation, the iron activity (a_{Fe}) decreases on the scale surface. If a_{Fe} at the surface becomes too low to form the chloride, the oxide can overgrow the chloride and subsequently FeCl_2 is present at the metal/oxide interface.

a)

b)

Fig. 5. — SEM micrographs of Fe-2.25Cr-1Mo after oxidation at 773 K in: a) He- O_2 ; b) He- O_2 - H_2O -HCl.

Fe-25Cr-20Ni-Nb. — In figures 6 and 7, AES sputter profiles are shown taken on Fe-25Cr-20Ni-Nb samples after 1 and 10 min oxidation in He-O₂-H₂O-HCl and N₂-H₂-H₂O-HCl at 973 K are shown. From the profiles, after 1 min exposure, can be seen that simultaneous

Fig. 6. — a) AES sputter profile of Fe-25Cr-20Ni-Nb after 1 min oxidation in He-O₂-H₂O-HCl at 973 K; b) AES sputter profile of Fe-25Cr-20 Ni-Nb after 10 min oxidation in He-O₂-H₂O-HCl at 973 K.

Fig. 7. — a) AES sputter profile of Fe-25Cr-20Ni-Nb after 1 min oxidation in N₂-H₂-H₂O-HCl at 973 K; b) AES sputter profile of Fe-25Cr-20 Ni-Nb after 10 min oxidation in N₂-H₂-H₂O-HCl at 973 K.

a)

b)

c)

Fig. 8. — SEM micrographs of Fe-25Cr-20Ni-Nb after oxidation at 973 K in: a) He-O₂; b) and c) He-O₂-H₂O-HCl.

growth of oxides and chlorides occurred in both atmospheres on this high alloy steel, although the chloride was not in stable equilibrium with the gas phase. In the early stage of oxidation, the chloride is in equilibrium with the metal phase and the metal activity is high on the surface of the reaction products.

After longer oxidation times the thermodynamically stable oxides have overgrown the chloride phase, and on the scale surface, only oxides could be detected in both gas atmospheres. Beneath the oxide layer, a chloride layer was detected. Also on this high chromium and nickel containing alloy the simultaneous growth of oxides and chlorides leads to the formation of a non-protective, porous oxide scale (Figs. 8a, b, c) different to the scale formed during oxidation in He-O₂. As mentioned previously, this allows Cl₂ and HCl species easy access to the underlying alloy substrate thus stabilizing the chloride phase beneath the oxide.

With increasing scale thickness, the metal activity (a_{Me}) on the surface decreases. If a_{Me} becomes too low, no chloride forms and the oxides overgrow the chloride and subsequently the chloride is present at the metal/oxide interface.

4. Conclusions.

The transient state of simultaneous oxidation-chloridation of Fe-2.25Cr-1Mo at 773 K and Fe-25Cr-20Ni-Nb at 973 K has been examined in He-O₂-H₂O-HCl and N₂-H₂-H₂O-HCl mixtures in short term corrosion tests.

Upon short time exposure the simultaneous growth of oxide and chloride was observed independent of the alloy composition, both in the atmosphere at a high p_{O_2} and a low p_{O_2} , although the chloride is not in stable equilibrium with the gas phase. After longer exposure times only the thermodynamic stable oxides were detected on the surface of the scales. However, at the metal/oxide interface, where the oxygen pressure is sufficiently low, a chloride layer is still present. The initial simultaneous growth of oxides and chlorides and the subsequent formation of a chloride layer at the metal/oxide interface occurs in both the oxidizing and the more reducing atmosphere on the two different alloys and strongly affects the structure and morphology of the oxide layer deteriorating the protective function of the scale as demonstrated by SEM.

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