The Effect of the Third Element Cr on Oxidation Behavior of Fe-xCr-10Al (at. %) Alloys at 900°C

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Abstract: Alloys Fe-(0, 5, 10)Cr-10Al (all in at.%) were oxidized at 900°C in 1 atm oxygen to study the effect of Cr additions on the oxidation behavior. The oxidation kinetics was recorded with a thermal microbalance. The morphologies and microstructures of the oxide scales were examined using SEM, EDS, and XRD. Fe-10Al developed an Al2O3-rich scale during the initial stage of oxidation, and a non-protective scale containing oxides of Fe and Al formed. Mixed oxides of Al and Fe formed firstly on Fe-5Cr-10Al, but an externally dense and continuous Al2O3-rich scale formed. The initially formed Fe oxides were locally reduced to Fe-rich particles. Fe-10Cr-10Al formed an Al2O3-rich scale from the onset of oxidation and this slowly growing scale was protective up to 50 h. The Cr additions to Fe-10Al were beneficial for restraining the oxidation of Fe, but that did not promote the transition from metastable Al2O3 to α-Al2O3.

Keywords: Iron-based alloys, high temperature oxidation, third element effect, metastable Al2O3.

INTRODUCTION

Iron-based alloys are commercially important high-temperature materials, among which the Fe-Al [1-7] and Fe-Cr-Al [7-17] alloys are of very great interest in the studies of high temperature oxidation. Fig. (1) schematically shows the oxide map of Fe-Al alloys, which directly correlates oxidation products with oxidation conditions. The data points in Fig. (1) were obtained during the oxidations performed in oxygen of 1 atm (0.1 MPa) or in air. Al2O3 forms more easily at higher temperatures. The oxygen pressure did not exert much effect on the scale development on Fe-Al when it was higher than 160 Torr (2.13×10^6 Pa or 0.21 atm) [4], but lower oxygen pressure promoted formation of Fe oxides [18-20]. The existence of water vapor was reported to promote the growth of Fe-rich nodules [4] or to lead to internal oxidation [7].

Many oxidation studies of Fe-Cr-Al alloys have concentrated on those of commercial compositions. Fig. (2) is the isothermal oxide map, constructed by summarizing the results of relative papers, for the oxidation of Fe-Cr-Al alloys in oxygen of 1 atm or in air at 1000°C. Most of the alloys with commercial compositions are Al2O3 formers, and oxidant pressure did not affect the oxidation properties very much. A systematic study of the oxidation behavior of high-purity Fe-Cr-Al alloys, containing 0–27 wt.% Cr and 1–10 wt.% Al, at 800°C in oxygen of 200 Torr was carried out by Tomaszewicz and Wallwork [21]. Four major types of scaling behaviors were encountered, and an “oxide map” was constructed by superposing morphological features onto a phase equilibrium diagram at 800°C. Additions of Cr did not reduce the concentration of Al, where the transition from a bulky, continuous, and stratified scale to a thin Al2O3 scale interspersed with Fe-oxide nodules occurred; however, the prevention of nodule growth was directly attributed to Cr additions [21]. A study on the cyclic oxidation, in oxygen at 1 atm over temperature 950–1050°C, of Fe-10wt.%Cr alloys containing 2–8 wt.% Al was carried out [22], both oxidation resistance and scale adhesion were improved with increasing Al content.

Addition of Cr to the binary Fe-Al alloys reduces the concentration of Al required to establish the Al2O3 scale [7, 8, 10, 11]. Fe-Cr-Al alloys offer an example of the so-called third element effect (TEE), by which the critical content of a most reactive component C needed to establish exclusive external scales of its oxide on ternary A-B-C alloys, where A is the most noble component, is reduced with respect to binary A-C alloys by the addition of an element B with an oxygen affinity intermediate between those of A and C [23]. The mechanism of TEE is not yet clear, but the explanations proposed so far, following the initial suggestion by Wagner [24], attribute the beneficial effect of B to its ability to induce a transition between the internal and external oxidation of C on ternary alloys under lower C levels than for binary A-C alloys [23]. The mechanism of the Cr effect on Fe-xCr-10Al (at.%) alloys is apparently different from those considered in the classical explanations of TEE because Fe-10Al does not suffer internal oxidation at high temperatures [2, 4]. Since this kind of TEE involving transition from external oxidation of both Fe and Al to exclusive oxidation of Al has not been the object of specific investigations, thus the oxidation behavior of the Fe-10at.%Al alloy with different Cr additions is studied by focusing on the Cr effect.

EXPERIMENTAL PROCEDURE

The alloys used in this investigation were prepared by vacuum arc-melting using appropriate mixtures of high pu-
The composition of each alloy was analyzed using energy dispersive spectroscopy (EDS). The nominal and the actual compositions of the alloys in atom percent are listed in Table 1. The alloys in this study are always represented by nominal composition in atom percent.

Before oxidation, the specimen was suspended with quartz filaments, and the reaction chamber was flushed using sufficient oxygen. After the temperature reached 900°C, the vertical furnace was elevated to locate the specimen in the hot zone. It was a hermetical system with an inlet and an outlet of oxygen. The mass change of the specimen was continuously recorded with a thermal microbalance (SETARAM MTB 10-8).

The phase analysis was performed by X-ray diffraction (XRD, Rigaku D/max-2500pc). Surface morphologies of oxidation products were examined with a scanning electron microscope (SEM, Philips XL30). The specimen was mounted in a cold-setting epoxy resin for examining the
cross-section. EDS were used to determine distributions of elements in the various solid phases.

### Table 1. Chemical Composition of the Experimental Alloys

<table>
<thead>
<tr>
<th>Nominal</th>
<th>Analysis (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Fe-10Al</td>
<td>90.2</td>
</tr>
<tr>
<td></td>
<td>(n = 18, s = 0.69)</td>
</tr>
<tr>
<td>Fe-5Cr-10Al</td>
<td>85.1</td>
</tr>
<tr>
<td></td>
<td>(n = 18, s = 0.60)</td>
</tr>
<tr>
<td>Fe-10Cr-10Al</td>
<td>80.1</td>
</tr>
<tr>
<td></td>
<td>(n = 12, s = 0.55)</td>
</tr>
</tbody>
</table>

Note: \(n\) presents measuring times, and \(s\) is standard deviation.

### RESULTS

#### Oxidation Kinetics

The two ternary alloys, Fe-5Cr-10Al and Fe-10Cr-10Al, were oxidized at 900°C in 1 atm oxygen for both 10 h and 50 h respectively, whereas the alloy Fe-10Al underwent two 50 h runs. The mass gain curves of the 10 h runs were in reasonable agreement with those of the starting stage of the 50 h runs. The mass gain curves of the three alloys are presented in Fig. (3); the corresponding parabolic plots are given in Fig. (4).

None of these curves adheres to a single parabolic relation. During the first 1.0 h, Fe-10Al showed a slow initial stage with a parabolic rate constant of about \(1.9 \times 10^{-14}\) g^2·cm^{-4}·s^{-1}, but this initial parabolic kinetics was immediately substituted by a linear kinetics corresponding to linear rate constant of about \(4.7 \times 10^9\) g·cm^{-2}·s^{-1} until 50 h. In the first oxidation duration from about 0.4 to 2.0 h, Fe-5Cr-10Al showed an approximate linear stage with rate constant of about \(4.9 \times 10^{-8}\) g·cm^{-2}·s^{-1}, after which the instantaneous parabolic rate constant promptly decreased, and after 4.7 h it became nearly constant up to the end. The Fe-10Cr-10Al had a low initial stage oxidation rate and then subsequently reached the second stage with rate constant of about \(2.6 \times 10^{-14}\) g^2·cm^{-4}·s^{-1} from 5 h to 50 h.

Fe-10Cr-10Al had the lowest mass gain after 50 h oxidation, and the two successive parabolic rate constants were adjacent in value. For Fe-5Cr-10Al, the oxidation was very fast at initial stage, but slowing down during oxidation and eventually reached a very slow rate. The mass gain curve of alloy Fe-10Al seems a linear relationship (Fig. 3), and the

![Fig. (3). Oxidation kinetics of Fe-10Al, Fe-5Cr-10Al, and Fe-10Cr-10Al at 900°C in 1 atm oxygen. (a) Plot for the total oxidation duration, (b) expended plot for oxidation duration of the initial 4 h.](image)

![Fig. (4). Parabolic plots of oxidation kinetics of Fe-10Al, Fe-5Cr-10Al, and Fe-10Cr-10Al at 900°C in 1 atm oxygen. (a) Plot for the total oxidation duration, (b) expended plot for oxidation duration of the initial 9 h.](image)
mass gain steadily increased with oxidation time. Values of the parabolic rate constants for the initial and steady state stages of the three alloys are given in Table 2.

Table 2. Approximate Parabolic Rate Constants ($k_p$) for Oxidation at 900°C in 1 atm Oxygen

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Oxidation Duration (h)</th>
<th>$k_p$ (g²·cm⁻⁴·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-5Cr-10Al</td>
<td>0.4 to 2.0</td>
<td>linear</td>
</tr>
<tr>
<td></td>
<td>4.7 to 50</td>
<td>$2.9 \times 10^{-14}$</td>
</tr>
<tr>
<td>Fe-10Cr-10Al</td>
<td>0.5 to 4.7</td>
<td>$1.0 \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>5 to 50</td>
<td>$2.6 \times 10^{-14}$</td>
</tr>
<tr>
<td>Fe-10Al</td>
<td>0 to 1.0</td>
<td>$1.9 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>1.0 to 50</td>
<td>linear</td>
</tr>
</tbody>
</table>

Morphology of Scales

Figs. (5, 6) show the surface and cross sectional morphologies, respectively, of alloy Fe-10Al after 50 h oxidation at 900°C in oxygen at 1 atm. The oxide scale was very wrinkling and occasionally localized Fe-rich nodules formed, while the cross section revealed that the scale was composed of mixed Al and Fe oxides. The XRD analysis (Fig. 7) indicated that this scale was a mixture of hematite (Fe₂O₃), α-Al₂O₃, and a small amount of magnetite (Fe₃O₄).

Fig. (5). Micrograph of surface morphology of oxides on Fe-10Al after 50 h oxidation at 900°C in 1 atm oxygen.

Fig. (6). Micrograph of cross section of Fe-10Al after 50 h oxidation at 900°C in 1 atm oxygen.

Fig. (7). XRD analysis of alloy Fe-10Al and oxides formed on the alloy after oxidation at 900°C in 1 atm oxygen.

The surface and cross sectional morphologies of alloy Fe-5Cr-10Al after 10 h oxidation are shown in Figs. (8, 9), respectively. Protrusions of Al-rich oxide distributed uniformly on the oxidized surface of the alloy, and no convolution of oxides was found (Fig. 8a). About 20% of the surface was covered by a layer of oxide with plate-like structure (Fig. 8b). In addition, many Fe oxide nodules formed on the specimen edge, and the nodules are much bigger than those on Fe-10Al. The cross sectional micrograph reveals the exis-
existence of inclusions of Fe oxide (Fig. 9). α-Al₂O₃, θ-Al₂O₃, and Fe₂O₃ were identified in the 10 h scales using XRD analysis (Fig. 10). After 50 h oxidation, the alloy developed a convoluted scale, and Fe oxide nodules are also found on the edge of the specimen (Figs. 11, 12). The existence of Fe₂O₃ was not identified with XRD analysis (Fig. 10) for the 50 h scales although parts of the scales contains small amount of Fe-rich oxides (Fig. 12b).

DISCUSSION

The additions of Cr to alloy Fe-xCr-10Al led to the transition of oxidation kinetics, i.e. from linear relationship (Fe-10Al) to parabolic relationship during steady oxidation stage (Fe-5Cr-10Al), and then to parabolic relationship during whole oxidation stage (Fe-10Cr-10Al).

The alloy Fe-10Al formed a convoluted and layered scale after 50 h oxidation at 900°C. The XRD analyses indicated that the oxides are mixtures of α-Al₂O₃ and Fe₂O₃, but a small amount of Fe₃O₄ was also detected. The XRD pattern for the 50 h scale shows a strong component from the alloy substrate (Fig. 7). Al₂O₃ or Al₂O₃-rich oxides formed during the initial stage of oxidation, which was corresponding to the parabolic rate constant, 1.9×10⁻¹⁴ g²·cm⁻⁴·s⁻¹, of the typical value for the growth of Al₂O₃ on Al-containing alloys [25] at 900°C. However, the slow-growing scale was replaced later by a layered scale containing mixtures of Fe and Al oxides.
Because only a few localized Fe-rich nodules formed, the formation of these nodules did not play an apparent role on the total mass gain during oxidation. The formation of Fe-rich nodules has been noted in several investigations on the oxidation of binary Fe-Al alloys [2, 4, 6]. It seems that the nodules apt to form on the alloys containing 3–6 wt.% Al at temperatures 750 to 900°C, as presented by the loop of dashed line in Fig. (1). The nodular formation was suggested to result from the depletion of Al beneath the cracks in the Al2O3 film [4]. There should be other factors responding to the formation of oxide nodules, such as the corner effects [2], composition of oxidant [4], and surface conditions of the specimens. The present authors have studied the roughness effects on the oxidation properties of Fe-xCr-10Al alloys containing 0–10 at.% Cr [26], and the results indicated that the alloy surface conditions played important roles on the formation of nodular Fe-rich oxides.

Duplex or triplex scales were found to form on Fe-Al alloys after oxidation at high temperatures [1-3]. The cross section of the oxidized Fe-10Al alloy revealed that layered scales composed of the mixture oxides of Fe and Al were developed during the oxidation. It seems that the alloy Fe-10Al developed an Al2O3 or Al-rich scale during the initial stage of oxidation. However, this initial scale was not thick and dense enough, and some cracks and/or defects occurred. The Al oxide and Fe oxide formed alternately after the initial oxidation stage, and the stratified scale became thick steadily. Although the oxidation rate may present local fluctuations, the average kinetics may become reasonably regular presented by a linear relationship (Fig. 3).

The compound Fe2O3·Al2O3 (FeAlO3) is known to be stable only at temperatures above 1300°C [27], so there should be no FeAlO3 in the layered scales on Fe-10Al. However, the existence of magnetite (Fe3O4) is expectable [4], and the spinel phase FeAl2O4 maybe exists due to the reaction between Fe2O3 and Al2O3 [6], but the Fe-Al-O equilibrium oxygen pressure diagram at 900°C [28] illustrated that the spinel phase could exist only at oxygen pressure below 1.4×10⁻¹⁸ atm. Therefore, the content of Fe2O3 and FeAl2O4 is probably lower than the detection limit, but a weak diffraction peak of Fe2O3 was found (Fig. 7).

The kinetics of Fe-5Cr-10Al at 900°C is presented by a fast linear oxidation during initial stage, and the oxidation rate was rapidly decreased at middle stage, and then a slow parabolic oxidation reached at final stage. The growth rate of Fe-rich nodules is very rapid because of their huge volume in comparison with the scale thickness, but their growth was undercut by an Al2O3-rich healing layer with time (Fig. 12c). Since the oxide of Cr was not detected, the fast oxidation during initial stage is attributed to the simultaneous growth of oxides of Fe and Al, especially the formation of Fe-oxide nodules on the specimen edge.

The surface morphologies of the scales formed on Fe-5Cr-10Al after 10 h reveals that around 20% of the area was covered by fast-growing 0-Al2O3 (in comparison with α-Al2O3). The other parts of the alloy surface uniformly developed outwards growing Al2O3 protrusions (Fig. 8a), which did not coalesce into an integral Al2O3 layer. The development of plate-like structure and protrusions suggested outwards transport of cations. However, the scales displayed convolute top-view morphology after 50 h, and the oxide with plate-like structure disappeared (Fig. 11a). The cross-sectional morphology after 50 h indicates most of the alloy surface was covered by a duplex scale composed of an outer Al2O3 layer and an inner Al-rich layer (Fig. 12a). The Al2O3 protrusions (Figs. 8a, 9a) have coalesced into a dense and integral scale, i.e. the outer Al2O3 layer. The plate-like structures or whiskers of metastable Al2O3 (0-Al2O3) could be transformed to the α-crystal structure with the oxidation time. The thickness of the scales did not increase much with time from 10 h to 50 h, which was consistent with the kinetics of the second stage. The XRD analysis did not identify the existence of Fe2O3 in the 50 h scale as it did for the 10 h scale (Fig. 10), so the content of Fe2O3 of the 50 h scale should be lower than the detection limit, which implied that Fe got much less opportunity to form Fe oxide than Al did during the oxidation time from 10 h to 50 h. Since the XRD pattern from the substrate was not detected (Fig. 10), it is

![Fig. (12). Micrographs of cross sections of Fe-5Cr-10Al after 50 h oxidation at 900°C in 1 atm oxygen. (a) General morphology, (b) local morphology, (c) morphology of a Fe oxide nodule formed on the specimen edge.](image-url)
probably that the existence of small amount of Fe oxide near the scale/substrate interface was not identified. However, Al$_2$O$_3$ is the prevailing oxide formed on Fe-5Cr-10Al after a transient oxidation period in which the alloy components, mainly including Fe and Al, were simultaneously oxidized. Fe-5Cr-10Al is more sensitive than Fe-10Al to surface conditions of the investigated alloys for the Fe-oxides nodules formation during initial stage oxidation [26]. Therefore, the Cr addition at level of about 5 at.% to binary Fe-Al alloy restrained the growth of Fe oxides after a transient stage despite it actually promoted the simultaneous oxidation of Fe and Al in the initial stage of oxidation (in comparison with Fe-10Al).

It is not possible for Al and/or Cr to reduce the Fe oxides when the oxygen pressure is higher than the decomposition pressure of Fe oxides. However, the existence of inclusions that are very rich in Fe but poor in oxygen (Fig. 12b) implies that localized displacement reaction between Al (or Cr) and Fe oxide occurred, and the oxygen pressure at such locations is lower than the decomposition pressure of Fe oxide.

The alloy Fe-10Cr-10Al formed a protective Al$_2$O$_3$-rich scale during the oxidation at 900°C, which is in agreement with the parabolic oxidation kinetics shown in Table 2. However, the scale formed at 900°C was not as dense and integral as that formed at 1000°C [29] after corresponding oxidation time. There existed a small amount of Fe-containing oxide on the gas/scale interface (Fig. 14b), which was not identified by the XRD analysis (Fig. 15) because of the low content. The scale after 50 h became flatter than that after 10 h oxidation and more metastable Al$_2$O$_3$ formed; the surface morphology was consistent with the results of XRD analysis. The parabolic rate constant of about $10^{-14}$ g$^2$·cm$^{-4}$·s$^{-1}$ is characterized by the Al$_2$O$_3$ formation at 900°C [25], so the $k_p$ about ten times big as the typical value during the first oxidation stage (Table 2) is attributed to the formation of the Al-rich oxides containing Fe from the onset of the oxidation. The formation of oxide whiskers was due to the outwards diffusion of Al.
Metastable $\alpha\text{-Al}_2\text{O}_3$ ($\alpha\text{-Al}_2\text{O}_3$) was identified on both Fe-5Cr-10Al and Fe-10Cr-10Al using XRD analysis but not on Fe-10Al, which indicated that addition of Cr to Fe-Al could not have promoted the transition from $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$. This is not in agreement with has been proposed that addition of Cr promotes such a transition [20]. The reason is probably that $\theta\text{-Al}_2\text{O}_3$ is easier to form under Cr existence, and the transition from $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ was not finished within the oxidation duration.

CONCLUSION

The oxidation of alloys Fe–(0, 5, 10)Cr-10Al (all in at.%) has been carried out at 900°C in 1 atm oxygen. Fe-10Al developed an $\alpha\text{-Al}_2\text{O}_3$-rich scale during the initial stage of oxidation, and a non-protective scale containing oxides of Fe and Al formed. Mixed oxides of Al and Fe formed firstly on Fe-5Cr-10Al, but an externally dense and continuous $\alpha\text{-Al}_2\text{O}_3$-rich scale finally developed. Fe-10Cr-10Al formed protective $\alpha\text{-Al}_2\text{O}_3$-rich scale from the onset of oxidation and this slowly growing scale was protective up to 50 h. The Cr additions to Fe-10Al promoted transition from the formation of external scale composed of Fe and Al oxides to the formation of protective $\alpha\text{-Al}_2\text{O}_3$-rich scale, but that did not promote the transition from metastable $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$.

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