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Simultaneous oxidation and carburization of a Fe-9Cr alloy under different oxygen pressures at 800 °C

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ABSTRACT

A model Fe-9Cr alloy was exposed to various H₂–CO₂–CH₄ mixtures providing different oxygen pressures and carbon activities at 800 °C. Three oxidation modes and three oxygen pressure ranges have been observed. At low pressures (Range I) only thin external Cr₂O₃ scales formed. An intermediate range (Range II) produced an internal precipitation of Cr₂O₃ and Cr carbide without an external scale. Higher pressures (Range III) produced external FeO_x scales plus an internal oxidation of Cr. Two critical oxygen pressures for the transitions between the three oxidation modes were observed and also calculated in reasonable agreement with the experimental results.

1. Introduction

Oxidation and carburization of alloys at high temperatures is a long-standing problem that involves huge economic and energy losses [1–5]. Carburization of alloys is a common form of high temperature degradation of alloys in practical applications, especially in petrochemical and chemical process industries and in electric power generation [6]. Combustion of fossil fuels produces complex atmospheres containing at least two basic oxidants, oxygen and carbon. On the other hand, iron is the most common metal applied in these industrial processes, while chromium additions are commonly present to provide good oxidation resistance by forming continuous external Cr₂O₃ scales [7–9]. However, carbon may still be involved in the corrosion of high temperature alloys when it is present in these mixed gas atmospheres. Thus, it is of interest to consider the nature of the simultaneous attack by oxygen and carbon with respect to binary Fe-Cr alloys, although the composition of commercial alloys is considerably more complex.

Recent studies indicated that ferritic chromium-containing steels exposed to different C-bearing gas atmospheres will suffer serious carbon corrosion by two forms, denoted respectively as internal carburization and dusting [10–12]. The formation of a complete layer of external Cr₂O₃ scale is an effective way generally adopted to relieve the carburization attack.

Two types of research have been carried to investigate the behavior of binary Fe-Cr alloys in mixed C–O atmospheres. On one side, the effect of the chromium content on the formation of external Cr₂O₃ scales has been studied. Fujii [13] reported a simultaneous oxidation

and carburization of Fe-Cr alloys containing 1–15 wt.% Cr exposed to pure CO₂ at 700, 900 and 1100 °C. All alloys remained ferritic at 700 °C and produced mixed (Fe, Cr) carbides, whose nature varied with the alloy chromium content from (Fe, Cr)₃C to (Fe, Cr)₇C₃ and (Fe, Cr)₂₃C₆, in agreement with the Fe-Cr-C phase diagram [14].

On the other side, the control of the gas atmospheres is another key factor influencing the oxidation behavior. CO₂ is the common gas used to provide mixed C–O atmospheres by its equilibrium decomposition at high temperature [6,15,16]. The oxygen partial pressures produced by mixtures with small CO₂ contents are large enough to oxidize iron, so that dilute Fe-Cr alloys readily form Fe-rich oxide scales upon exposure to CO₂ at high temperatures. Nonetheless, the available information indicates that heat resisting alloys can also be attacked by carbon from CO₂ in spite of the low equilibrium carbon activity. Relevant experimental results have been reported by several authors. Reaction of pure CO₂ with an 18Cr steel (ss304) at 704, 816 and 927 °C [17] and with an Fe-15Cr alloy at 900 °C [18] led to an internal carbide precipitation beneath the external FeO_x oxide scale. Internal carbides were also observed after exposure of a Fe-9Cr steel (P92) to an Ar-50%CO₂ mixture at 550 °C [19] and after exposure of model Fe-Cr alloys to an Ar-30%CO₂ mixture at 650 °C [20]. D.J. Young made an extensive work concerning the kinetics and mechanism of the corrosion of the Fe-Cr alloys in carbon dioxide [21–27].

This paper is focused on the effects of varying the oxygen pressure in the range from 10^{–23} to 10^{–18} atm on the thermodynamic, kinetic, structural and morphological aspects of the oxidation of a Fe-9Cr model alloy in various H₂–CO₂–CH₄ mixed gases at 800 °C. In particular, two

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theoretical models have been applied to predict the oxidation behavior of binary alloys with a single oxidant in the presence of an external scale and of binary alloys with a combination of two oxidants in the absence of an external scale. Moreover, the calculations about the critical conditions required to produce a coupled internal oxidation plus carburization have proved that the presence of carbon can affect the oxidation behavior by dissolving in the alloy and changing its phase structure. Finally, a new method to calculate the relevant kinetic parameters taking into account the low stability of chromium carbides has been developed.

2. Materials and experiments

A model Fe-Cr alloy containing 9 wt.% Cr (Fe-9Cr) was used to investigate the oxidation behavior in mixed gases containing both oxygen and carbon. The alloy ingots were cast by vacuum induction melting of mixtures of appropriate amounts of the two pure elements (99.9 wt.% Fe and 99.9 wt.% Cr) in cylinders of 5 cm diameter and 10 cm high. The ingots were subsequently annealed in 1 atm argon at 1000 °C for 36 h to remove the residual mechanical stresses and to achieve better equilibration. In terms of the ICP-AES analysis, the actual composition of the test Fe-9Cr alloy is Fe-9.6 at.% Cr (all in at.%, if not specified otherwise). These ingots were then cut into samples with a size of about $10 \times 8 \times 1.5$ mm using a line saw after which a 1 mm hole was drilled near one edge. All the specimens were mechanically ground down to 2000 grit finish and then ultrasonically cleaned in acetone and ethanol immediately before exposure.

The corroding gases providing different oxygen partial pressures and carbon activities were mixtures composed of different combinations of three pure gases, i.e. H_2 , CO_2 and CH_4 . To discover the possible oxidation patterns of the oxidation-carburization of Fe-Cr alloys, a series of gas mixtures with different oxygen pressures and carbon activities were examined. Since the region of high oxygen pressures has already been extensively explored in previous works [21–27], the experimental gas mixtures explored here have been selected in a range of low oxygen pressures and high carbon activities. The detailed composition of the twelve different gas mixtures is shown in Table 1, where they are denoted as Gases 1–12. The same table gives also the oxygen pressures and carbon activities calculated at equilibrium in the gas phase at the reaction temperature [28]. The specimens were exposed to each atmosphere at 800 °C for 20 h, except for additional tests of 8 h for Gases 5 and 7. The phase diagram of the Fe-9Cr-C system of Fig. 1 [15,29–31] shows the phase structures, α or γ , of Fe-9Cr with various contents of carbon and the areas of stability of possible chromium carbides at different temperatures. The phase boundaries in the Fe-9Cr-C system were calculated with the Thermo-Calc software and the TCFE4

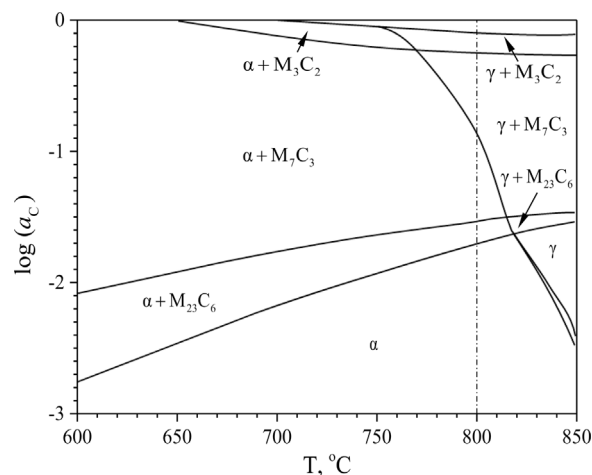


Fig. 1. Predominance diagram as function of interfacial carbon activity calculated by the Thermo-Calc software and TCFE4 database for Fe-9Cr-C system (dash-dotted line for 800 °C) [15].

database [32]. The composition of the experimental alloy falls in the field of stability of the α phase at the reaction temperature.

The oxidation experiments were carried out in a microbalance SETARAM B-92. The oxidized samples were examined by scanning electron microscopy SEM (FEI INSPECTF 50, USA) attached with energy dispersive X-ray spectrometer (EDS) (OXFORD X-MAX, UK) and by X-ray diffraction (XRD) (Panalytical X'pert PRO, Holland) to identify the morphology, the element distribution and the phase constitution of the oxide scales. All the reacted samples were etched with Murakami's etchant to reveal the presence of precipitated carbides.

3. Results

3.1. Scale morphology and microstructure

Corrosion of the Fe-9Cr alloy produced three different types of scale structure depending on the composition of the gas mixtures examined. This allows to divide the overall range of oxygen pressures into three different smaller ranges, denoted as Ranges I, II and III. In particular, corrosion in Gases 1–4 (Range I) gave rise to scale composed of a single external layer of Cr_2O_3 , while corrosion in mixtures 5–8 (Range II) produced a simultaneous internal oxidation (io) and carburization in the absence of an external scale. Finally, corrosion in mixtures 9–12 (Range III) produced a zone of internal oxidation of chromium overlaid by an external scale of FeO divided into an outer layer of pure FeO and

Table 1

Initial composition of the twelve gas mixtures and calculated values of the oxygen pressures and carbon activities after equilibration at 800 °C.

Gas Mixture	Gas Input (vol.%)			Equilibrium oxygen pressure, P_{O_2} (atm) ^a	Equilibrium carbon activity, a_C ^a		Equilibrium vapor pressure, P_{H_2O} (atm) ^a	Classification by Oxidation Model
	H_2	CO_2	CH_4					
1	0.5	0.15	0.35	2.53×10^{-22}	1		1.85×10^{-2}	Range I
2	0.55	0.2	0.25	4.76×10^{-22}	1		2.30×10^{-2}	
3	0.4	0.35	0.25	2.81×10^{-21}	0.603		4.4×10^{-2}	
4	0.9	0.1	0	5.77×10^{-21}	9.96×10^{-2}		9.27×10^{-2}	
5	0.55	0.3	0.15	7.83×10^{-21}	0.30		7.68×10^{-2}	Range II
6	0.2	0.5	0.3	8.85×10^{-21}	0.4		6.18×10^{-2}	
7	0	0.654	0.346	2.0×10^{-20}	0.296		7.17×10^{-2}	
8	0.35	0.5	0.15	5.48×10^{-20}	0.134		0.131	
9	0	0.78	0.22	1.56×10^{-19}	9.28×10^{-2}		0.114	Range III
10	0	0.8	0.2	2.6×10^{-19}	7.59×10^{-2}		0.118	
11	0.1	0.76	0.1	6.64×10^{-19}	3.38×10^{-2}		0.143	
12	0.3	0.7	0	2.09×10^{-18}	1.24×10^{-2}		0.206	

^a Thermodynamic data taken from Ref. [28].

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