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The mechanical property of the oxide scale on Fe–Cr alloy steels

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ABSTRACT

In this study, we investigated the influence of the Cr content on the microstructure and interfacial adhesion of the oxide scale formed on steel alloys. The four different alloys selected for this study are stainless steels and low- and medium-carbon steels with different Cr and Si contents. The model steels were oxidized at 1100–1200 °C for 4–5 h. The types of oxide phases in the scale were analyzed by X-ray diffraction (XRD), and the results were compared with the phases predicted by thermodynamic calculations. The cross-sectional scale microstructures were analyzed by electron probe micro-analysis (EPMA). The interfacial adhesion strength of the scale with the model alloys were analyzed by a uniaxial tension test. According to our results, continuous Cr-oxide layers are formed along the interfaces; the thickness of these layers proportionally increases with Cr, while the total thickness of the scale is inversely proportional to the Cr content. The thick Cr-oxide layers seem to hinder the interdiffusion of Fe and O between the scale and the substrate, which decreases the growth rate of Fe-oxides on the top surface. The predicted phases in the scale and the minimum oxygen partial pressure at which each oxide phase is formed agree well with the microstructural analysis results. Our results also revealed that the Cr-oxide layers survived the tension test for up to 5% of the strain, whereas the scale on top of the Cr-oxides cracked and delaminated. Based on these results, the Cr content determines the adhesion strength of the scale.

1. Introduction

Most steel and metal alloy fabrication processes are performed at high temperatures and in air. Because of the oxidizing nature of the atmosphere, layers of oxide scale form on the surfaces [1,2]. Oxide films on metals serve various functions. Some serve as passive films that prevent further oxidation, while others beautify the surface [3]. In many types of steel, the descalability of the oxide films is essential to maintain the quality of the steel products [4]. As the mechanical properties of the oxide films are generally not well known, the fabrication or descaling of the films is difficult to control [4,5].

According to previous studies [4,6], the mechanical properties of the oxide films depend on various parameters, including the processing conditions, alloy compositions, and substrate surface conditions. Among the parameters, the alloy composition strongly affects the cracking and delamination behaviors of the oxide films because it determines the types and numbers of oxide phases comprising the layered film structures of the scale [6]. The oxides of some elements, such as Si and Cr, are formed as continuous layers along the interface and have good adhesion strength with steel [6]. These layers are generally not removed by the descaling process and remain as a thin scale layer on the substrate. The layers grow further if O is available and will undergo structural changes [7].

The addition of Cr to steel is very effective in improving heat-resistance and corrosion-resistance [8]. Si is also known to enhance the high-temperature oxidation resistance of steel. The continuous oxide layers of the Cr and Si are SiO_2, Cr_2O_3, and spinels of the FeX_aO_b ($X = Si, Cr$) type between the scale and the metal interface [8,9]. To maintain the surface properties, such as the resistance to corrosion, friction, and wear, that are originally designed by alloying, it is essential to understand the mechanical properties of the scale and the phase transformation of the oxides under given processing conditions [10,11]. Nevertheless, little is understood about the effect of the addition of alloying elements on the mechanical properties of oxides because the alloying elements significantly modify the morphological evolution, crystalline structure, and chemical composition of the interface, even if the concentrations of the added elements are low [8,9].

In this study, we investigated the mechanical properties of the corrosion-resistant protective oxide coating layers formed by adding alloying elements such as Cr and Si. Two stainless steels having Cr contents of more than 10 wt.% were selected, and they were compared with low and medium carbon steels. All four model alloys have high levels of Si, more than 0.25 wt.%. The model steels were oxidized at the same conditions (1100–1200 °C for 4–5 h), and the hydraulic descaling was performed once. The oxide phases

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comprising the scale were analyzed by X-ray diffraction (XRD) and electron probe micro-analysis (EPMA), and the results were compared with the predictions from thermodynamic calculations. Finally, the mechanical properties of the scale were evaluated by analyzing the fracture modes under a uniaxial tension test.

2. Thermodynamic calculation and experimental procedures

The compositions (wt.%) of the four model alloys are summarized in Table 1. LCS in Table 1. is a typical low-carbon steel for tools and structural uses. MCS is a medium-carbon steel, and it has a larger Cr content than the LCS. CR1 and CR2 are stainless steels, and CR2 has the highest Cr content among the alloys listed in Table 1. All of the model alloys have a high Si content (>0.25 wt.%), and the content is the highest in CR1. These model steels were oxidized at 1100–1200 °C for 4–5 h and were cooled down in air in a POSCO Research Center pilot plant. During the process, the descaling was performed by a high-pressure water hydraulic descaler at the exit of the furnace.

The oxide scale phases formed on each alloy were predicted using Thermo-Calc® software (SSUB4 database) [12]. The types and fractions of the phases were calculated as a function of p_{O2} (from 10–24 to 10–16) and under one atmospheric pressure (1 atm). The calculations were performed at 900 °C, not 1100–1200 °C, because the commercial database provides very limited data for the solid oxide phases above 1100 °C [12]. Because of the fast cooling in air and short reheating time of the processes, most of the scale phases are solids, but the database explains that most of them are liquids over 1000 °C [1].

The chemical and microstructural analysis of the scale remaining after descaling was performed using XRD and EPMA, and the results were compared with the thermodynamic predictions. The interfaces between the scales and substrates are analyzed by EPMA. After the analysis, the uniaxial tension test was performed using an Instron™ machine. The uniaxial tension tester and the size of the test specimen are presented elsewhere [6]. The strain rate is 2.5×10^{-5}/s. After the tests, the surface and cross sections of the fractured specimens were analyzed by field emission scanning electron microscopy (FE-SEM) and EPMA.

Table 1
Model alloy compositions (wt.%) and the thickness of the scale formed on the alloys.

Sample alloy names	C	Cr	Si	Mn	Average thickness of the scale (μm)
LCS	0.2	0.2	0.37	1.0	88
MCS	0.5	1.0	0.25	0.9	72
CR1	0.004	10.0	0.6	0.3	35
CR2	0.04	15.0	0.3	0.4	31

3. Results and discussion

The thermodynamic calculation results are summarized in Fig. 1(a)–(d). The phase fractions in Fig. 1 are weight-based, excluding the fractions of Fe. The scale generally consists of a stack of different oxide layers [11], and there are compositional gradients of the elements from the top surfaces to the substrates [5]. Considering these, the phase that appeared at a lower p_{O2} in Fig. 1 can be assumed to exist closer to the interface with the substrate than that formed at a higher p_{O2}; the diffusion of elements cannot be considered in the thermodynamic calculations.

According to the calculation results in Fig. 1, the major phases over 0.001 in the phase fraction are $Fe_{1-x}O$ (wűstite of iron protoxide), a gas phase (CO and CO_2), FeX_aO_b-type spinel structure phases (Fe_2SiO_4 and $FeCr_2O_4$), Mn_2SiO_4, SiO_2, and Cr_2O_3. $Fe_{1-x}O$ becomes

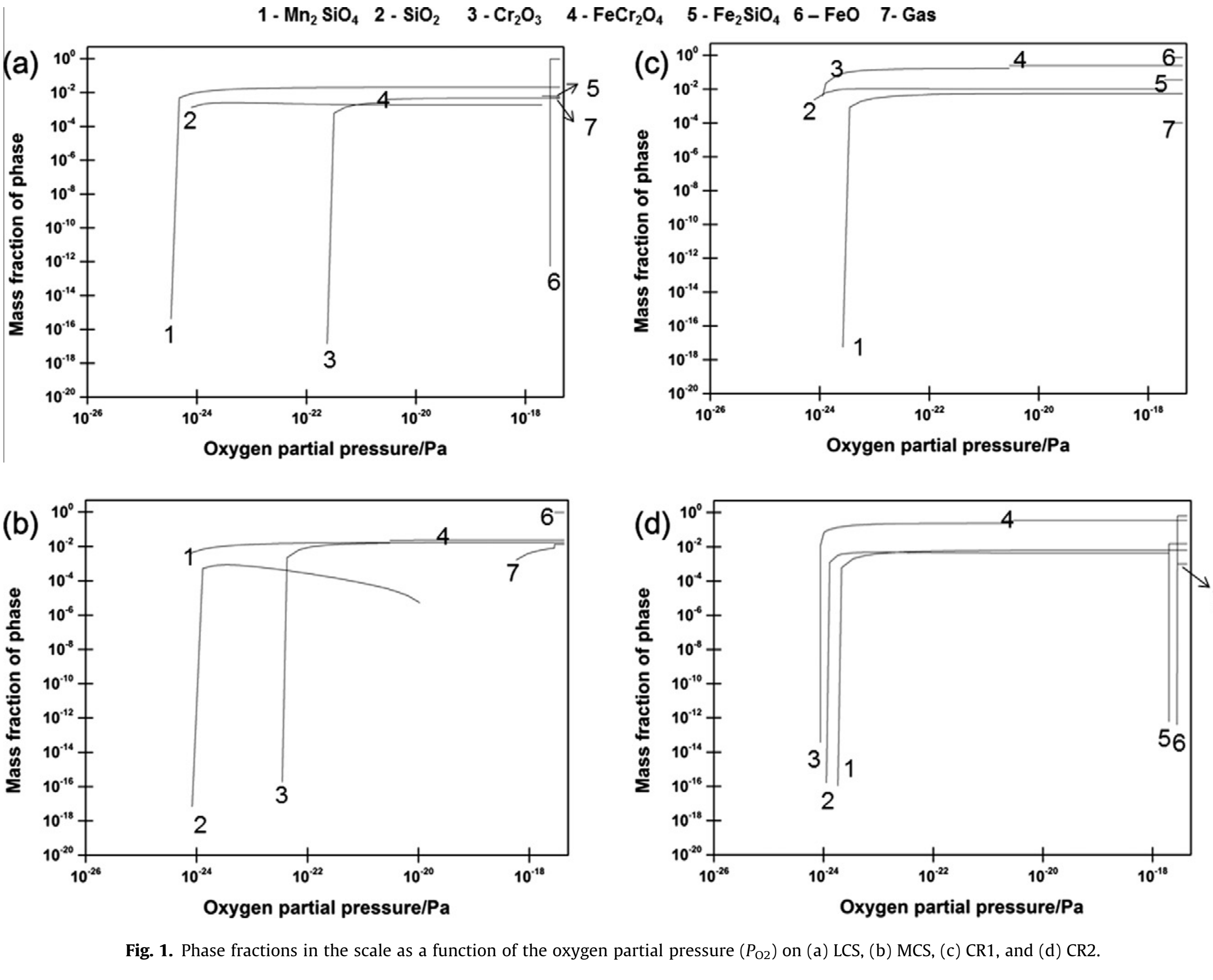

Fig. 1. Phase fractions in the scale as a function of the oxygen partial pressure (P_{O2}) on (a) LCS, (b) MCS, (c) CR1, and (d) CR2.