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The Influence of the Rare Earth Element Ce on the High-Temperature Oxidation Kinetics of Low-Cr Steels

Vicente Braz Trindade, Ulrich Krupp, and Hans-Jürgen Christ

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The oxidation behavior of steels containing low-Cr concentrations (0.5-2.25 wt.%) has been studied in laboratory air in the temperature range of 400-550 °C. The oxidation rate of the steels was lower than that of pure iron, but higher than that of pure iron when a small amount of rare earth element cerium (0.03 wt.%) is added to the 2.25Cr1Mo steel. The mass change follows a nearly parabolic law for the case of pure iron and the steel without Ce addition, while linear behavior describes the oxygen uptake for the case of the 2.25Cr1Mo+0.03Ce steel. SEM cross-section observations and thermodynamic calculations confirm that there is no wustite (FeO) formation during oxidation of pure iron and low-Cr steels at 550 °C, whereas FeO might be formed in the oxide scale of 2.25Cr1Mo+0.03Ce at the same oxidation conditions (temperature, atmosphere, and exposure time). By investigating the temperature for FeO stability, this study reveals that the temperature for FeO formation on pure iron is 568 °C, for the 2.25Cr1Mo steel 589 °C, and 471 °C for the 2.25Cr1Mo+0.03Ce. This low value for the FeO stability temperature found for the steel 2.25Cr1Mo+0.03Ce steel explains why this steel oxidizes very fast at 550 °C.

Keywords Ce effect, high-temperature oxidation, low-Cr steels, wustite stability

1. Introduction

Low-alloy steels are used as part of boiler components for non-heated exit areas in superheater tubes and reheater tubes. The external surface of these tubes is exposed to air at temperatures between 500 and 600 °C, which lead to a thickness loss of the tubes as a consequence of oxide formation. In spite of the numerous investigations on the oxidation of iron-alloys, basic questions concerning the oxidation mechanisms are still open. Some studies reported that oxides on low-alloy steels grow mainly by outward Fe diffusion (Ref 1-3), because the diffusion coefficient of Fe in iron oxides is much higher than that of oxygen (Ref 4-6). Even with lower diffusivity of oxygen within the bulk oxide, some investigations (Ref 7-10) pointed out that inward oxidation may take place due to fast oxygen diffusion along grain boundaries of oxides. Other studies (Ref 11-14) proposed the possibility of molecular oxygen permeation through microcracks and/or pores within the oxide scale, which leads to inward oxide growth.

Some classical investigations have been performed on the high-temperature oxidation of pure Fe in air or oxygen (Ref 15-17). Chen et al. (Ref 18) give a detailed review. It is well established that the high-temperature oxidation kinetics of Fe follows basically the parabolic rate law. A two-layer scale composed of magnetite (Fe_3O_4) and hematite (Fe_2O_3), with the thickness ratio being about 4:1, forms up to about 570 °C, and a three-layer scale composed of wustite (FeO), magnetite, and hematite, with the thickness ratio being 95:4:1, is observed at higher temperatures. The formation of the thick wustite layer upon higher temperature exposure is due to the higher diffusion coefficient of Fe and O in FeO as a consequence of a high vacancy concentration compared with hematite and magnetite (Ref 19-22).

The main objectives of the present study are to understand and quantify the effect of the grain size of the substrate on the oxidation behavior of pure iron and low-alloy ferritic steels, and to investigate the effect of cold working, thermal cycling, and the addition of Ce on the oxidation kinetics of low-Cr steels.

2. Materials and Experimental Procedure

In this study the oxidation behavior of three low-Cr steels and pure iron at high temperature was investigated. In addition to the standard compositions listed in Table 1, 2.25Cr1Mo steel was modified through the addition of 0.03 wt.% of the rare earth element cerium.

The grain sizes of the three commercial steels were modified by applying a heat treatment at 1050 °C in inert gas atmosphere for different times. Figure 1 shows the change of the grain size with heat treatment for the 2.25Cr1Mo steel. The microstructure consists basically of ferrite. Carbides are also present, but the volume is small due to the low carbon content. The grain size was measured using the mean linear intercept technique.

In order to investigate the effect of cold working on the oxidation behavior of the low-alloy steel 2.25Cr1Mo, different rolling steps were performed on annealed specimens. Four cold

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Vicente Braz Trindade and **Hans-Jürgen Christ**, Institute for Materials Science, University of Siegen, Siegen, Germany; and **Ulrich Krupp**, University of Applied Sciences, Osnabruck, Germany. Contact e-mail: vicentebraz@yahoo.com.br.

working states were studied (thickness reduction: 4, 12, 20, and 70%).

Samples with dimensions $10 \times 10 \times 3$ mm^3 were used for the thermogravimetric study. The samples were ground using SiC paper down to 1200 grit. They were finally cleaned ultrasonically in ethanol prior to oxidation. A 1-mm-diameter hole was used for hanging the samples in a thermobalance by means of a quartz thread. Isothermal and thermal cycling thermogravimetry was carried out using a microbalance with a sensitivity of 10^{-5} g in combination with an alumina chamber and a SiC furnace. The exposure temperature was varied from 400 to 800 °C. After oxidation, the specimens were embedded in epoxy and carefully polished using diamond paste down to 1 μm and cleaned ultrasonically in ethanol. Analysis of the oxide structure and thickness measurements of oxide layers was performed using scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD).

3. Results and Discussions

Figure 2(a) shows the oxidation kinetics of pure iron exposed at 550 °C to laboratory air. The oxides formed on pure iron at 550 °C are those expected by the thermodynamic calculation, i.e., Fe_3O_4 in contact with the substrate and Fe_2O_3 in the outer region. Figure 2(b) shows a scanning electron micrograph of the two layers on the sample surface.

The effect of Cr content and grain size of the steels are shown in Fig. 3. The parabolic rate constant (k_p) was calculated from thermogravimetrical measurements using Eq 1.

$$\left(\frac{\Delta m}{A}\right)^2 = k_p t \qquad \text{(Eq 1)}$$

As shown in Fig. 3(a) the oxidation kinetics decreases strongly as the grain size of the substrate increases. The decrease in the oxidation kinetics can be attributed to the reduction of the inner oxide layer growth kinetics (see Fig. 3b) (Ref 23, 24). For the three low-Cr steels the thickness of the inner scale differs considerably after 72 h of oxidation in laboratory air at 550 °C as a function of the grain size of the substrate changing from 4 to 100 μm. Measurements of the total scale thickness revealed a very small change in the thickness of the outer layer. The increase in Cr content from 0.5 wt.% (71518 steel) to 2.25 wt.% (2.25Cr1Mo steel) has a strong beneficial effect on the oxidation resistance.

Table 1 Nominal chemical composition (in wt.%) of the low-Cr steels used

Steel	Cr	C	Si	Ni	Mn	Mo	Al	Cu	Fe
71518	0.55	0.07	0.36	0.21	1.01	…	0.04	0.39	Rest
X60	1.43	0.06	0.22	0.04	0.69	…	0.05	0.01	Rest
2.25Cr1Mo	2.25	0.09	0.23	0.44	0.59	0.96	0.01	0.15	Rest

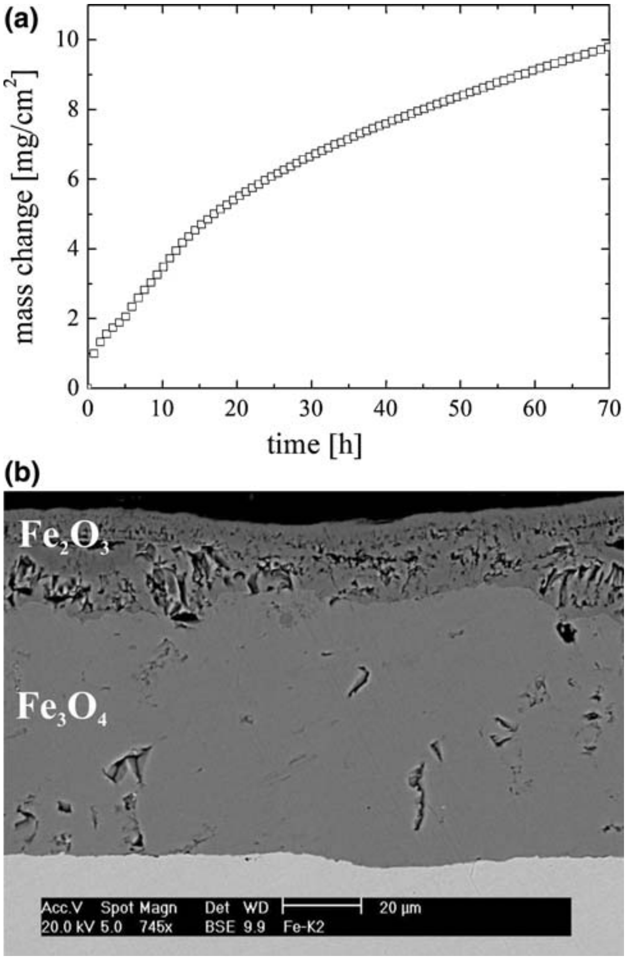

Fig. 2 (a) Mass change as a function of time for pure iron at 550 °C for 72 h; (b) cross section of the scale formed on the surface of pure iron at 550 °C for 72 h

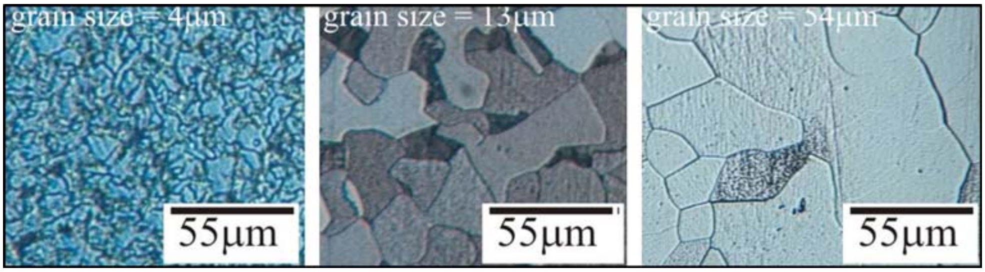

Fig. 1 Optical microscopy observation of the microstructure of the 2.25Cr1Mo steel before and after annealing in inert atmosphere for grain size change

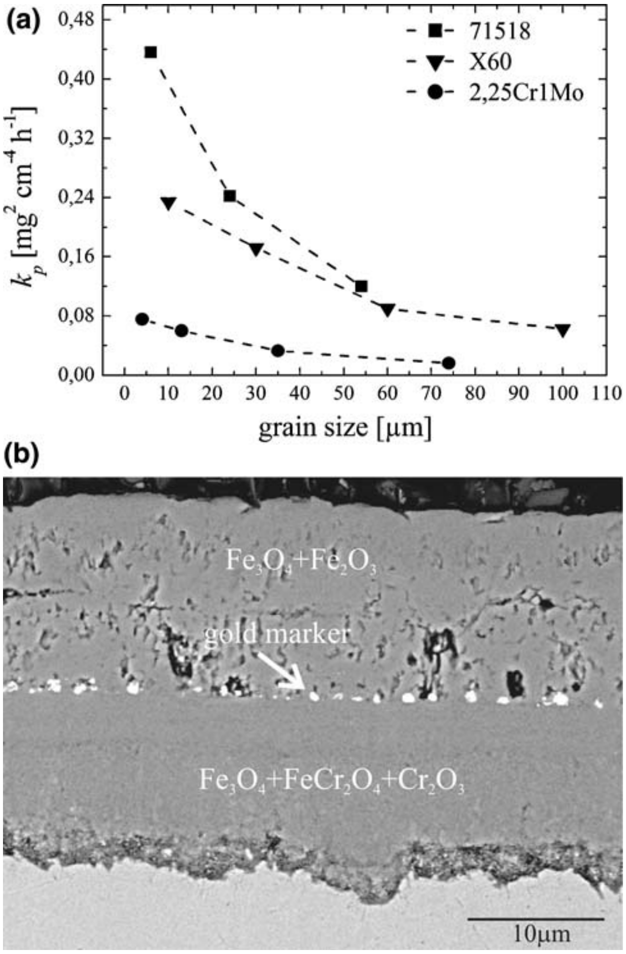

Fig. 3 (a) Effect of the grain size of the substrate and the Cr content on the oxidation kinetics of the low-Cr steels oxidized at 550 °C in laboratory air for 72 h; (b) oxide scale structure showing the gold marker within the scale separating the outer and the inner layer

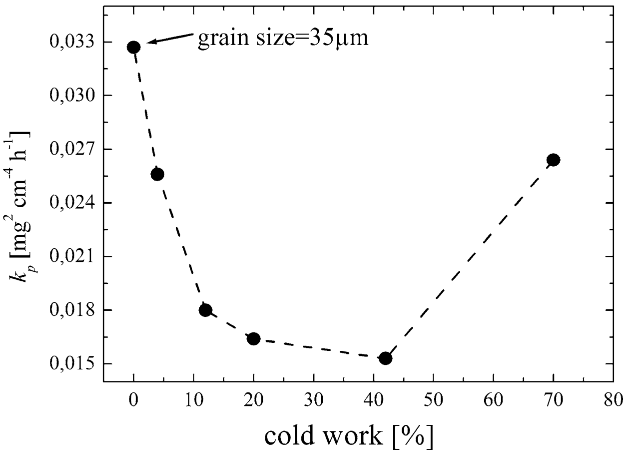

Fig. 4 Effect of the cold working on the oxidation kinetics of the 2.25Cr1Mo steel oxidized in laboratory air at 550 °C for 24 h

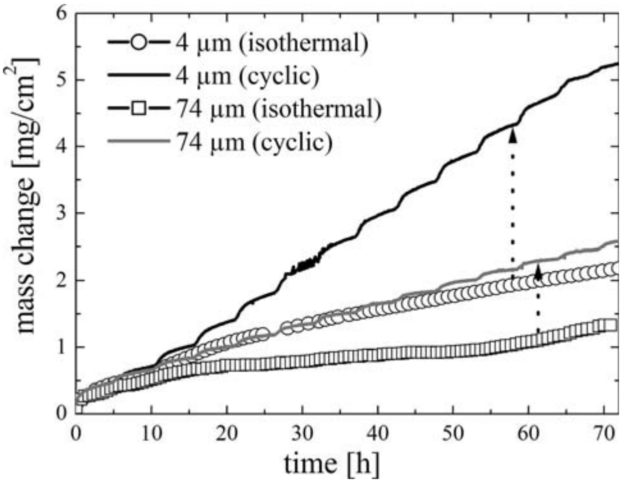

Fig. 5 Oxidation of the 2.25Cr1Mo steel with two different grain sizes at 550 °C in laboratory air under isothermal and thermal cycling conditions

Figure 4 shows the effect of cold working on the oxidation kinetics of 2.25Cr1Mo steel after oxidation in laboratory air at 550 °C for 24 h. The oxidation kinetics decreases obviously with increasing degree of cold working. Cold working increases the dislocation density and therefore increases the amount of fast diffusion paths (dislocation pipes) in the sample (Ref 25, 26). Consequently, fast diffusion of chromium to the inner scale can be expected. It was shown (Ref 27) that the increase of chromium concentration in the spinel phase decreases the diffusion coefficient of iron and oxygen in this spinel phase considerably, and therefore reduces the growth kinetics of the outer and the inner oxide layer.

For samples submitted to cold working higher than 42%, recrystallization took place, which causes a reduction in the dislocation density and the formation of very small new grains giving rise to a high inward transport of oxygen into the substrate and therefore higher oxidation kinetics was observed.

Under thermal cycling oxidation conditions, the oxidation kinetics of the 2.25Cr1Mo steel is dramatically accelerated as shown in Fig. 5. No spallation was observed as usually occurs for NiCrAl alloys. The formation of the inner oxide scale and the preferential oxidation along grain boundaries (see (Ref 10, 23)) probably acts as pegging, increasing the oxide scale adherence. However, the formed oxide scales have a high tendency of cracking during cooling permitting easy access of oxygen to the substrate/oxide interface leading to higher oxidation kinetics during the next hot cycle.

A small addition of Ce (0.03 wt.%) in the 2.25Cr1Mo steel affects oxidation kinetics strongly. The evidence is presented in Fig. 6(a), showing that the mass change of the sample during exposure to laboratory air at 550 °C reached a very high value of 15 mg/cm^2 after 72 h. This value is even higher than that of pure iron oxidation (ca. 10 mg/cm^2). Oxygen uptake follows a linear behavior with time exhibiting a constant oxidation rate k_l ($k_l = 6.3 \times 10^{-5}$ mg/cm^2 s), whereas in the previous cases (pure iron and the low-Cr steels) the mass change followed a nearly parabolic behavior. The oxide scale formed on 2.25Cr1Mo+Ce in laboratory air is shown in Fig. 6(b). Chromium is present in the FeO layer and in a small concentration in the Fe_3O_4 layer.

The presence of FeO in the 2.25Cr1Mo+Ce steel is responsible for the linear oxidation kinetics observed (see Fig. 6a). It is well known in the literature that due to the high defect concentration in FeO, iron diffuses very fast though this oxide (Ref 12, 13, 17). However, according to the thermodynamic equilibrium, FeO is stable only at temperature higher

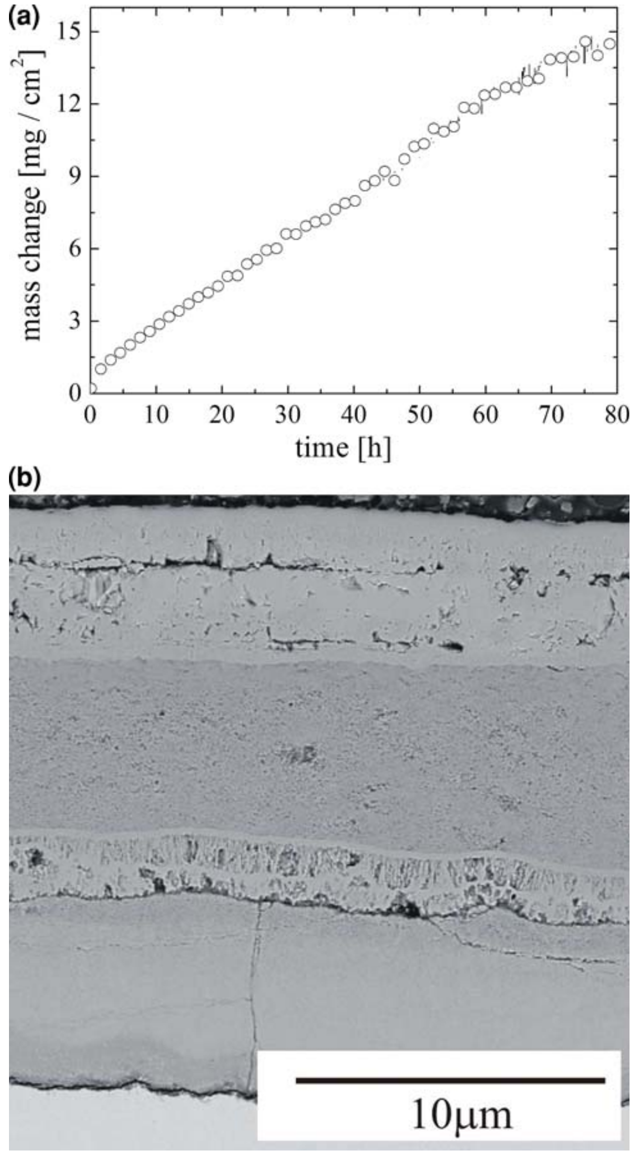

Fig. 6 (a) Oxidation kinetics of the 2.25Cr1Mo+Ce steel at 550 °C exposed to laboratory air and (b) structure of the oxide scale after 72 h

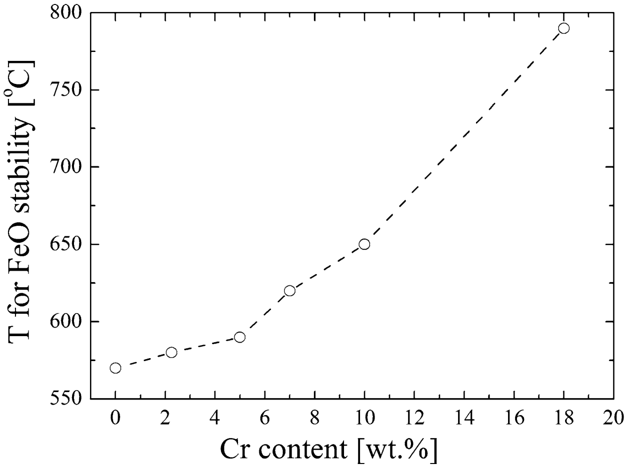

Fig. 7 Calculation of the minimum temperature for FeO (wustite temperature) stability using the thermochemistry software FactSage

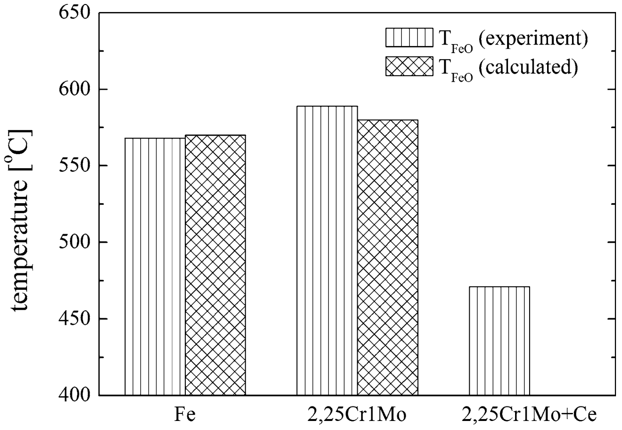

Fig. 8 Experimental and calculated temperature for FeO stability during oxidation of pure iron, the 2.25Cr1Mo steel, and the modified 2.25Cr1Mo+0.03Ce steel

than 570 °C for pure iron and this temperature increases when the Cr content increases (see Fig. 7). Since FeO forms already at 550 °C on the 2.25Cr1Mo+Ce steel, Ce can be assumed to reduce the minimum temperature of FeO stability.

In order to understand the influence of Ce on the stability of FeO (temperature for FeO formation) in the system Fe-Cr-Ce-O better, experiments were carried out in which the oxidation of samples were performed at different temperatures and the mass change as well as microstructural changes were determined. The oxidation constants measured for the three materials investigated (pure Fe, the 2.25Cr1Mo steel and steel 2.25Cr1Mo+Ce) showed that FeO is formed at (i) 568 °C on pure Fe, (ii) 589 °C on the 2.25Cr1Mo steel, and (iii) 471 °C on the 2.25Cr1Mo+0.03Ce steel. Figure 8 shows the experimentally observed and the calculated temperatures for the beginning of FeO formation. Excellent agreement exists between the simulated values and those obtained in laboratory tests. Unfortunately, thermodynamic data for Ce are not included in the thermochemistry databank used in this work.

These results confirm that Cr increases the temperature of FeO formation, and Ce seems to decrease the temperature of FeO stability to 471 °C. Steels containing Ce at temperatures higher than 471 °C are strongly discouraged, since FeO grows very fast.

4. Conclusions

This study revealed that oxide scales on pure iron and on the low-alloy ferritic steel 2.25Cr1Mo grow outward as well as inward at 550 °C. Increased oxidation was observed with decreasing grain size due to higher oxygen transport along substrate grain boundaries. The decrease in the oxidation kinetics for steel samples cold worked up to 42% can be explained by the higher Cr diffusion along dislocation-pipes leading to a higher Cr-concentration within the inner oxide layer. This reduces the outward iron diffusion and the inward oxygen diffusion. For samples cold worked, recrystallization took place causing a reduction in the dislocation density, and for very high deformation, small new grains appeared. Therefore, high degrees of cold work accelerate oxidation kinetics of low-alloy steels. Thermal cycling strongly increases the oxidation kinetics of the 2.25Cr1Mo steel due to the formation of cracks within the oxide scale during cooling.

The FeO stability was experimentally determined in the present study for each material. For pure iron the minimum temperature of FeO stability was found to be 568 °C, for the 2.25Cr1Mo steel 589 °C and for the 2.25Cr1Mo+Ce steel only 471 °C. Experimental observation and thermochemistry calculation show an excellent agreement for the cases of pure iron and 2.25Cr1Mo steel, while the experimental result for the 2.25Cr1Mo+Ce steel indicated a strong reduction of the FeO stability temperature.

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