Effect of rare earth additions on high-temperature oxidation resistance of V and Mo alloyed steels

Rare earths (RE) have been used to improve the high temperature oxidation resistance of low alloy steel containing elements like Cr, Al, V and Mo. Further, the RE can be added either to the alloy or by applying as an oxide coating to the alloy surface. In this study the high temperature oxidation resistance of rare earth (RE) oxide coated 1Cr-0.3Mo-0.25V alloy was determined. This paper presents the influence of surface additions of nanocrystalline oxides CeO2 on the isothermal oxidation behavior of 1Cr-0.3Mo-0.25V alloys at temperatures ranging from 600 °C to 900 °C. The oxidation rate of RE oxide coated1Cr-0.3Mo-0.25V was significantly lower than that of the uncoated alloy. The improvements in oxidation resistance are the reduced oxidation rates and the increased oxide scale adhesion. Scanning electron microscopy (SEM), X-ray diffractometry (XRD), and electron probe micro analyzer (EPMA) were employed for these analyses. The scale formed in the presence of RE oxides was very thin, fine grained and adherent.

Introduction

Chromia scales that form on low-chromium content Fe-Cr alloys at elevated temperatures grow relatively slowly and usually provide good oxidation resistance. Addition of small amounts of elements or their chemical compounds, such as, cerium or their oxide dispersions to these alloys greatly increases their oxidation resistance under isothermal conditions. These so-called reactive element effects have been extensively reviewed by Whittle and Stringer [1] and more recently by Moon and Bennet [2]. Oxidation resistance is also improved if reactive element oxides are applied to the surfaces of the alloys [3...7] or introduced by ion implantation [8; 9]. Rahmel et al. [10] showed that additions of 0.5 - 5.5 %Mo decrease the oxidation rate of iron by almost the power of ten in the temperature range 500 - 1000 °C; Fig. 1 schematically shows that the oxidation of iron proceeds with increasing temperature, different layers of oxide scales, i.e., FeO, Fe3O4 and Fe2O3 are formed. In case of iron, wustite is formed above 600°C which is a most ionic defective oxide. [11]

Very few definite conclusions can be drawn as to the usefulness of the oxides of the rare-earth lanthanide series. The thermodynamic properties of many of these compounds have never been ascertained. Others have been only estimated or assigned tentative values based on qualitative or incomplete investigations. The lanthanide series’ oxides, in general, appear to have quite high melting points. Those known with some degree of certainty are La2O3 (2305 °C), CeO2 (2600 °C), Nd2O3 (2270 °C), Sm2O3 (2300 °C), Eu2O3 (2050 °C), Gd2O3 (2300 °C), and Dy2O3 (2340 °C) [12] Very favorable free energies of formation at high temperatures (about – 418.4 KJ at 2000 K) [13] indicate that these lanthanide oxides range among the most stable oxides. Carbides of this series are also known to exist, but data on the stability of these compounds have not been reported. It is known that they have dicarbide stoichiometry and that they are decomposed by water vapor [14]. The use of reactive elements is well known, especially rare earths (RE) to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys. The improvements are in the form of reduced oxidation rates and increased scale adhesion [15; 16].

Figure 1: Schematic representation of the diffusion processes and phase boundary reactions during the oxidation of iron in oxygen, according to Hauffe [11]
In aqueous solution both vanadium and cerium oxides can form ionic species:

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\text{Ce}^{4+} + \text{H}_2\text{O} \leftrightarrow (\text{CeOH})^{+3} + \text{H}^+ \quad [17] \\
2 (\text{CeOH})^{+3} \leftrightarrow (\text{Ce}^{2+} - \text{Ce}^{6+}) + \text{H}_2\text{O} \quad [17] \\
\text{V}_2\text{O}_5 \leftrightarrow \text{V}^{4+} \leftrightarrow \text{V}^{4+} - \text{OH} \quad [18]
\]

Starting from CeO2 and V2O5, a new phase CeVO4 is formed via an intermediate state V2O5-X/CeO2-y in which an unpaired electron is trapped at high temperatures being responsible for the reducibility of Ce4+ to Ce3+ and for the active sites on a ceria supported vanadia catalyst [19...21].

**Material and Methods**

Boiler quality low alloy steel i.e. 1Cr-0.3Mo-0.25V were hot rolled to 2.5 mm thickness. The plates were obtained from RDCIS, SAIL plant for oxidation tests. These plates were descaled and cut to the size of 2.5 • 15 • 25 mm3, approx. The percentage of chemical composition of steel is Fe-97.63, C-0.12, Mn-0.5, Si-0.20, S-0.015, P-0.018, Cr-0.99, Mo-0.28, V-0.24. Both the surfaces of the specimens were mechanically polished using SiC papers of up to 600 grit. The prepared samples were thoroughly washed in distilled water and rinsed with acetone, then dried and stored in desiccators. 2.5 g of cerium oxide powder (ASTM mesh size -230 +325) were mixed with 50 ml ethyl alcohol to prepare the slurry. The samples were dipped into the slurry to be coated and the slurry was constantly stirred to prevent the reactive oxide particles from sedimentation. The samples were dried in air at a temperature of 100 °C. The dipping and drying process was repeated for 10 to 15 times until a uniform thickness of the coating layer was achieved on both the surfaces. The difference between the initial and final mass of the samples was measured and the coating thickness was calculated to range between 5 • 10-3 and 7 • 10-3 cm. Isothermal oxidation tests were carried out in dry air under atmospheric pressure by hanging all the specimens with and without coating in a vertical quartz tube reactor. The reactor tube was closed with glass wool. The temperature accuracy in the reactor tube was ±5°C. The atmosphere in the reaction zone was natural air. A Pt-Pt13%Rh thermocouple was inserted from the top of the furnace to measure the temperature of the reaction zone. This thermocouple connected to a PID controller was placed inside the annular space between the furnace and reactor wall. Electronic digital balance having an accuracy of ±0.1 mg was used for measuring the mass changes of the sample during oxidation. A timer was used for a fixed time interval to continuously record the weight gain of the sample during oxidation.

**Evaluation of the results**

Kinetic studies. The oxidation kinetics data for 1Cr-0.3Mo-0.25V low alloy steels with and without cerium oxide coatings were conducted in the temperature range of between 600 °C and 900 °C for 24 h. The weight gains as a function of time for the above mentioned three steels were plotted for different temperatures. Figs. 2, 3 show the curves for 1Cr-0.3Mo-0.25V steel without coating and CeO2 coated in the temperature range from 600 °C to 900 °C, respectively. Further, the data were plotted as log (weight gain per unit area) vs. log t at temperatures 600 °C to 900 °C, respectively, which is shown in fig. 4. Further, the slope vs. 1/T plot of steel at 700°C, 750 °C and 800 °C is shown in fig. 5. The kinetics data and rate constants for the above mentioned steels are also...
When an oxidant comes into contact with a metal, the reactions proceed by forming a stable scale at the metal-gas interface due to combination of metal ions with oxidant ions. The growth of scale at the interface was found to be rate controlled process. The mechanically polished samples were improved oxidation resistance in the presence of CeO2 coatings. In all cases, the rate of weight gain was initially fast but after a certain time, it was observed to increase at a steady rate. This can be seen in the plots of weight gain vs. time as shown in fig. 2 - 3. The weight gain vs. Time plot for 1Cr-0.3Mo-0.25V steel at 800 °C temperature shows the kinetics of oxidation and slope were changed. However, the curve was observed to be of parabolic nature. In the presence of RE it grows at the metal/oxide interface. The result of Gibb’s free analysis shows that the stability of different oxides depends on their standard Gibb’s free energies of formation (ΔGoMO), oxygen partial pressure pO2 and temperature. It is possible to evaluate the stabilities of different oxides in different atmospheres by calculating the oxygen partial pressure where the oxide dissociates. Dissociation oxygen partial pressure (pO2)dissoc for the metal oxide (MO) is calculated by the equation:

$$\log (pO_2)_{dissoc} = \frac{2\Delta G_0MO}{(2.303RT)}$$

The oxygen partial pressure under atmospheric pressure is greater than the dissociation oxygen partial pressure; therefore, the oxide is thermodynamically stable. Gibb’s free energy analyses clearly show the marked increase in the oxidation resistance of the molybdenum and vanadium alloyed steels compared to those coated with RE oxides. For each oxide, care has been taken to optimize the RE oxide grain size and shape, to consequently increase coverage and also to optimize the chemical potentials of those two RE oxides having ionic radii very close to each other.

SEM, EPMA and XRD investigation. Figs. 6 – 8 schematically show the oxide growth in the presence of...
RE. SEM and EPMA clearly suggest that the scales formed on the bare steel were of coarse-grained, non-uniform character and depleted the substrate, whereas fine-grained, compact, well adherent and uniform scales were found to be formed on the CeO2 coated steel. XRD analysis of the scales showed the presence of simple, complex and mixed oxides (spinals), including CeO2, Fe2O3, FeCe2O4, (FeO•CeO3), CeFeO3, Fe21.34O32, Cr2O3 and FeO•Cr2O3 for ceria coated oxidized 1Cr-0.3Mo-0.25V steel samples. The formed FeO•Ce2O3 is thermodynamically more stable than CeO2 under the present testing conditions. A comparison of XRD analysis of steel showed that the steel coated with cerium oxide shows superior oxidation resistance compared to the others investigated here.

Conclusions

[1] In the above-mentioned steel, the kinetics of oxidation were faster for an initial period of 100 min after which it was decreased. This showed that the diffusion of anions and cations were also decreased due to the formation of a certain scale thickness;

[2] SEM studies showed that the outer layer of the oxide scale was compact and the micrograph of fractured interface showed the crystalline structure;

[3] the Mo and V alloyed steels coated with CeO2 exhibited higher oxidation resistance compared to the uncoated alloys;

[4] the effect of CeO2 coating on the oxidation behavior of 1Cr-0.3Mo-0.25V showed that the CeO2 coating prevents scale formation in the temperature range from 600 °C to 900 °C;

[5] X-ray diffraction patterns for the CeO2 coated steel showed the presence of CeO2 in the scale.

References


Figure 8: XRD micrograph of 1Cr-0.3-Mo-0.25V steel at 800 °C