

High temperature oxidation of Fe-Cr-Mo alloys

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The Cr-Mo steels, whose microstructure was tempered martensite, were oxidized isothermally at temperatures of 800-1000°C for up to 30 h in air, and their oxidation behavior was examined. The thick scales that formed consisted mainly of Fe₂O₃. The scale spalled easily, owing to the formation of voids and cracks inside the scale. The oxides of Cr and Mo tended to be formed below the outwardly growing iron oxide scales.

Key words: Steel, Oxidation, Chromium, Molybdenum.

Introduction

Tubing, piping and headers in boilers are exposed to high-temperature oxidative atmospheres during service in high temperature plants. Service lifetimes of these parts are limited by creep, fatigue or oxidation. Traditionally, materials designed for use at high temperatures have been developed primarily for their mechanical properties, but there is now a growing realization that oxidation may limit lifetime, either directly through metal wastage or indirectly through raising local temperatures (and consequently reducing creep-controlled lifetimes) due to the lower thermal conductivity of the oxide scale.

During oxidation, carbon steels form a scale consisting of one or more layers of wustite, hematite and magnetite, depending upon the specific oxidation conditions. The addition of chromium to the alloys firstly changes the scale such that the inner layer (magnetite on plain carbon steels) is an iron-chromium spinel in low alloy ferritic (up to 3%Cr) or martensitic (9-12%Cr) steels. Further increases in chromium will eventually lead to the formation of chromia, e.g. in austenitic stainless steels [1-5].

The purpose of this study is to investigate the oxidation behavior of Cr-Mo steels that were developed as heat-resisting ones for power plants. This study is of practical importance to assure the service lifetime. The oxidation tests were performed at 800, 900 and 1000°C in air. The oxidation property strongly depends on the oxidation temperature, time, atmosphere, and alloy composition. Particular attention was paid to clarifying the oxidation products, and to discuss the oxidation characteristics.

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Experimental

Using a vacuum induction melting (VIM) furnace, 1 ton of a Cr-Mo steel ingot was melted. The ingot was remelted to 200 mmφ using an electro-slag remelter (ESR) to control the composition, cut to 5 kg lumps, heated at 1150°C for 2 h followed by hot forging to 60 mm in thickness, and heated at 1100°C for 1 h followed by hot rolling to 12 mm in thickness with a reduction ratio of 76%. The rolled plate was normalized at 1150°C for 2 h, and tempered at 700°C for 2 h to make a tempered martensitic structure. The chemical composition of the prepared Cr-Mo steel samples that are designated as #1~#5 is listed in Table 1. The alloy composition was designed to have optimum mechanical properties.

The heat-treated steel coupons were cut, polished to 1000-grit abrasive paper, ultrasonically degreased in acetone, and oxidized isothermally using a thermogravimetric analyzer (TGA) at temperatures of 800, 900, and 1000°C for up to 30 h. The coupons before and after oxidation were inspected by means of an optical microscope, an X-ray diffractometer (XRD with Cu-K_α radiation), a scanning electron microscope (SEM),

Table 1. Chemical composition of the Cr-Mo steel

Alloy	Composition (wt%)
#1	9.25Cr-1.49Mo-0.23V-0.17C-0.17Mn-0.17Co-0.14Ni-0.011N-0.06Si-0.07Nb-0.06W-0.003Al-0.0033B
#2	9.22Cr-1.45Mo-0.24V-0.17C-0.15Mn-0.17Co-0.14Ni-0.012N-0.08Si-0.09Nb-0.06W-0.003Al-0.0076B
#3	9.21Cr-1.46Mo-0.24V-0.17C-0.18Mn-0.16Co-0.21Ni-0.016N-0.012Si-0.06Nb-0.02W-0.003Al-0.0133B
#4	9.17Cr-1.53Mo-0.25V-0.17C-0.2Mn-0.17Co-0.2Ni-0.017N-0.13Si-0.08Nb-0.04W-0.003Al-0.0144B
#5	9.21Cr-1.54Mo-0.25V-0.17C-0.19Mn-0.15Co-0.21Ni-0.012N-0.1Si-0.07Nb-0.02W-0.003Al-0.0196B

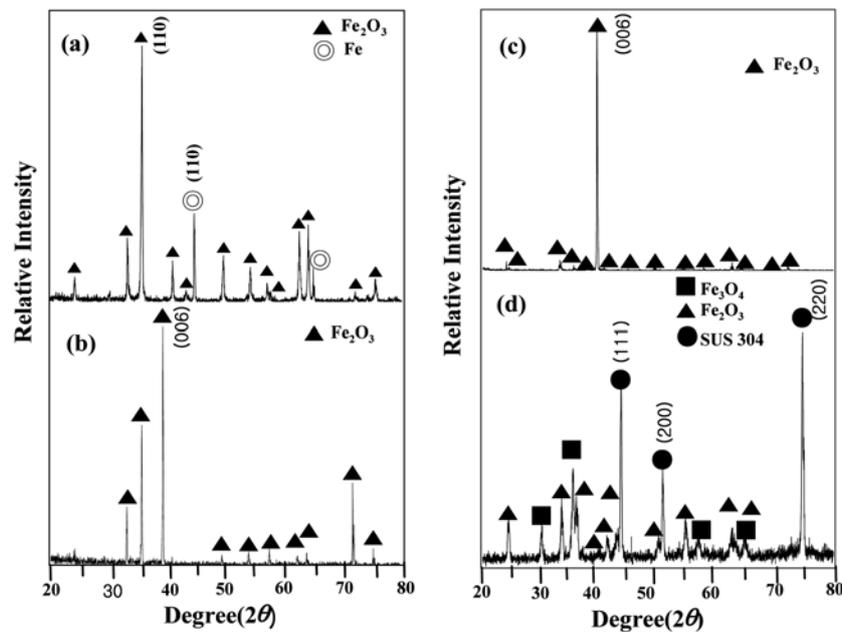


Fig. 1. XRD patterns of the oxide scales formed on Cr-Mo steel after oxidation in air. (a) at 800°C for 10 h, (b) at 900°C for 30 h, (c) at 1000°C for 30 h (this pattern was taken from the surface side), (d) at 1000°C for 30 h (this pattern was taken after removing the surface oxide scale).

and an electron probe microanalyzer (EPMA).

Results and Discussion

Figure 1 shows the XRD patterns of the oxide scale formed on the Cr-Mo steel after oxidation. It is known that the oxidation of steel leads to the formation of a multi-layered scale that consists of Fe_2O_3 , Fe_3O_4 , and FeO , from the surface. Due to the much greater mobility of defects, the wustite layer is usually very thick compared with those of magnetite and hematite [1, 2]. However, in this study, the scale was very rich in Fe_2O_3 , with a preferred orientation along (110), but without an indication of the formation of Fe_3O_4 and FeO , as shown in Fig. 1(a). Here, the tempered martensite, whose diffraction pattern is similar to that of ferrite (JCPDS #06-0696), is also seen, due to the thinness of the scale. As the oxidation temperature was increased to 900°C, the preferred orientation of Fe_2O_3 was gradually changed to (006), indicating that the growth direction of Fe_2O_3 depended on the extent of oxidation, as shown in Fig. 1(b). In Fig. 1(c), the surface scale consists primarily of Fe_2O_3 , with a preferred orientation along (006) after oxidation at 1000°C for 30 h. Fig. 1(d) shows the XRD pattern of the matrix phase, Fe_2O_3 , and Fe_3O_4 . The absence of FeO indicates that the oxygen potential around the scale-alloy interface is comparatively high. The matrix phase matched with austenitic, 304 stainless steel ($\text{Fe}_{0.7}\text{Cr}_{0.19}\text{Ni}_{0.11}$; JCPDS #33-0397). This suggests that the outward diffusion of iron to form the iron-oxides [1, 2] results in the depletion of Fe and the resultant enrichment of Cr beneath the scale-alloy interface.

The oxidation kinetics of the Cr-Mo steels between

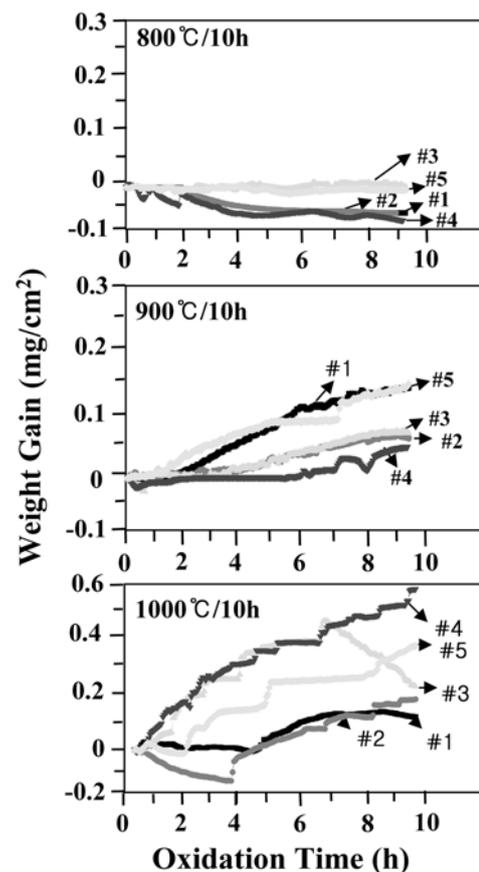


Fig. 2. Weight gain vs. oxidation time curves of Cr-Mo steels in air between 800 and 1000°C.

800 and 1000°C in air are plotted in Fig. 2. Cracking and spallation of the oxide scales occurred during oxidation, so that the data shown in Fig. 2 are not a

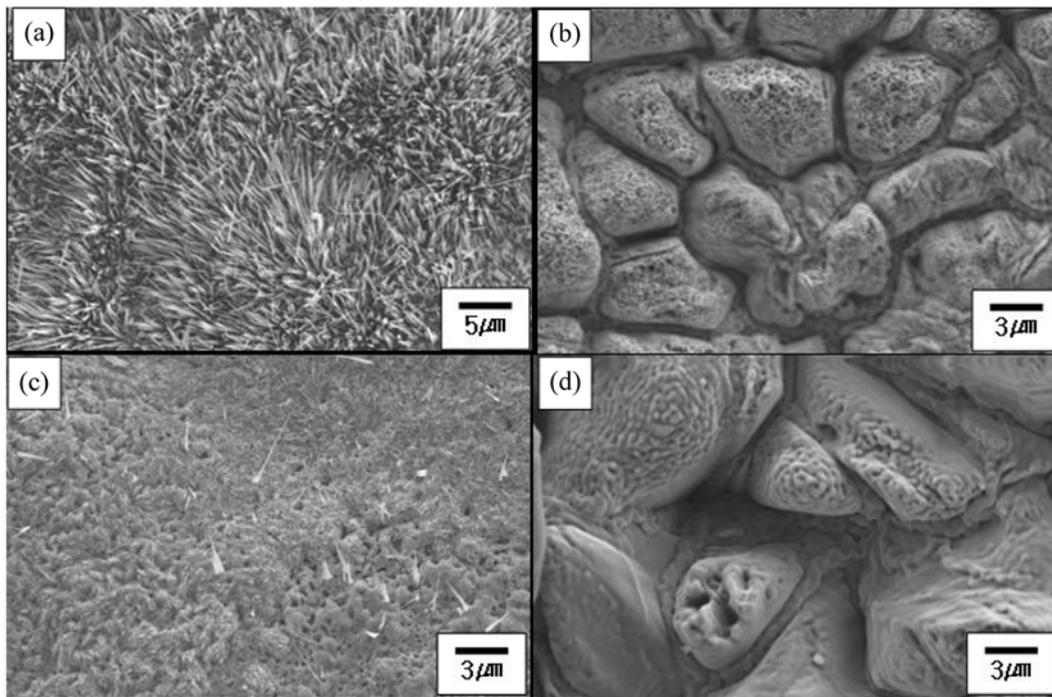


Fig. 3. SEM top views of the oxide scales formed on Cr-Mo steels after oxidation for 30 h in air: (a) sample #4; 800°C, (b) sample #1; 900°C, (c) sample #4; 900°C, (d) sample #5; 1000°C.

direction function of oxidation rates, but allow the major trends to be observed. As the oxidation temperature increased, the overall weight gains increased. There are, however, no specific tendencies in the order of the oxidation rates for specimens #1-#5. This can be attributed to scale failure such as local cracking, fracture and void formation, the amount of which would vary to a certain extent for each test run, yielding experimental scatter in weight gain curves. Scale failure can expose the fresh metal surface locally, while voids decrease the contact area between the scale and metal, thereby hindering the outward cationic diffusion. Nevertheless, the oxidation resistance of the Cr-Mo steels under the current conditions is poor.

Figure 3 shows typical SEM top views of the scales formed on the Cr-Mo steels. The oxidation at 800°C for 30 h usually resulted in the formation of numerous whiskers on the oxide surface (Fig. 3(a)). The formation of Fe_2O_3 whiskers to relieve the high residual stress that generated during scaling was previously reported from the early oxidation stage of steels [4]. The whisker-type oxides nucleate at dislocations generated by scale growth stresses, and grow by a dislocation mechanism at their tips [5]. A small amount of whiskers was also formed on the somewhat porous, rather flat surface oxide layer that formed after oxidation at 900°C for 30 h, as shown in Fig. 3(b). However, most of the area was covered with interconnected oxide nodules (Fig. 3(c)). Some cracks propagated across the oxide grains, and the outer scale was highly prone to spallation. After oxidation at 1000°C for 30 h, virtually no whiskers

were found. Instead, the surface oxide layer was covered with well grown Fe_2O_3 nodules, as shown in Fig. 3(d). Hence, growth stresses which arose during oxidation above 900°C seemed to be relieved by deformation, convolution or wrinkling of the oxide scales, instead of whisker formation that observed at 800°C. Micropores or gas holes inside the oxide nodules in Fig. 3(c) and (d) are due to the volatilization of oxides at high oxidation temperatures.

Figure 4 shows the cross sections of the scales formed on the Cr-Mo steels after oxidation for 30 h in air. Thick scales formed from as low as 800°C. They had many voids, and were highly susceptible to spallation. The formation of the layer of pores parallel to the metal substrate in the early stages of oxidation is attributed to the growth of coarser grains on the initially-formed smooth wustite layer, which leaves behind a continuous layer of trapped pores [3]. Pores and cracks can also be formed by the heterogeneous volume expansion during scaling, which deteriorates the scale adherence. The oxidation of Fe to form FeO, Fe_3O_4 and Fe_2O_3 proceeds by the predominant outward diffusion of Fe^{+2} , and Fe^{+3} ions [1]. Hence, the outwardly diffusing iron ions also can leave Kirkendall voids behind. On the other hand, the growth and thermal stresses generated during oxidation may be accommodated by scale cracking, scale spalling from the alloy surface, and the plastic deformation of the matrix and the scale [1]. The oxide may be under a considerable stress because, for example, the molar volume ratio of FeO to Fe is approximately 1.7. This resulted in the formation

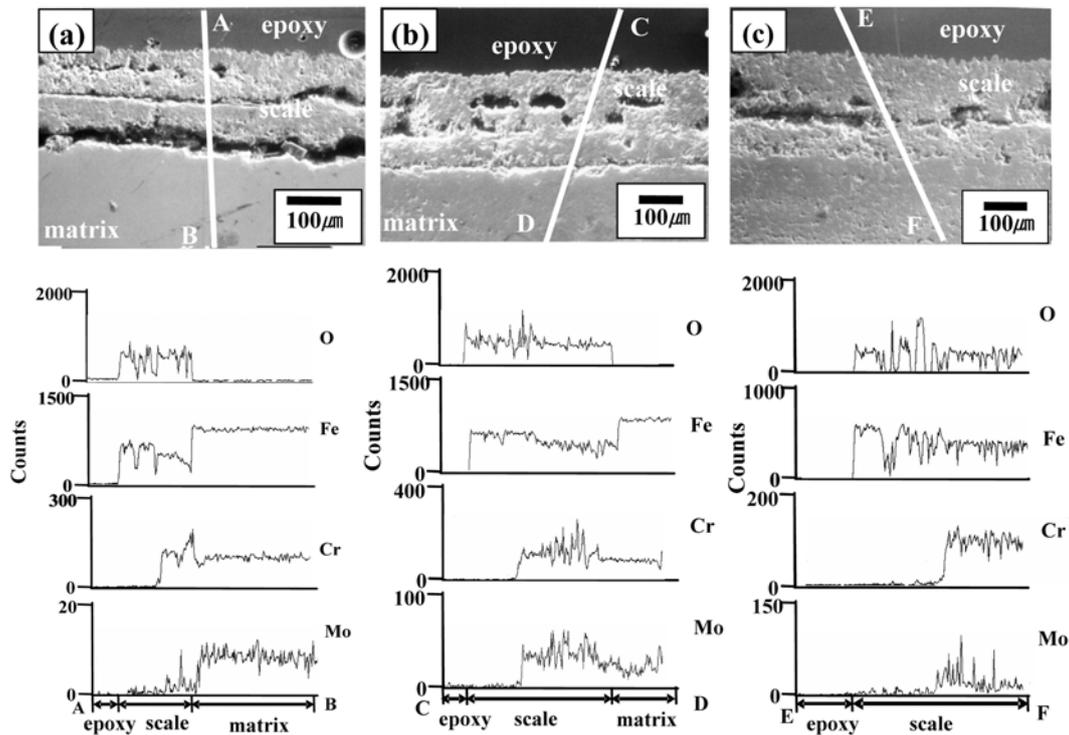


Fig. 4. EPMA images and elemental line profiles of cross sections of scales formed on Cr-Mo steels after oxidation for 30 h in air. (a) sample #1; 800°C, (b) sample #4; 900°C, (c) sample #1; 1000°C.

of whiskers that protruded above the adherent scale, and the cracking of the oxide scale around 800°C. The elemental line profiles indicate that, in Cr-Mo steels, Cr and Mo tend to be oxidized below the iron-oxides due probably to their nobility when compared to Fe.

Conclusions

The scales formed on Cr-Mo steels were thick and nonadherent. They had numerous voids and some cracks. Iron oxidized predominantly, so that the scale consisted mainly of Fe_2O_3 . Cr and Mo were mainly distributed below the iron oxides, owing to their inertness. Oxide nodules and whiskers were seen on the scale surface. Regardless of the alloy composition, the scale morphology was similar for the tested 5 different specimens.

Acknowledgements

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References

1. N. Birks and G.H. Meier, Introduction to High Temperature Oxidation of Metals, (Edward Arnold London, 1983) p. 72.
2. S. Taniguchi, K. Yamamoto, D. Megumi, and T. Shibata, Mater. Sci. Eng. A308 (2001) 250-257.
3. H.T. Abuluwefa, R.I.L. Guthrie, and F. Ajersch, Metall. Mater. Trans. A28 (1997) 1633-1641.
4. R.Y. Chen and W.Y.D. Yuen, Oxid. Met. 59[5/6] (2003) 433-468.
5. R.A. Rapp, Metall. Trans. A 15[5] (1984) 765-782.