METALLURGY

Influence of Impurities on the Oxidation of Fe–26Cr Alloys

MOST research on the oxidation of alloys has been done using commercial materials. In recent years, however, there has been a great deal of effort to work with pure alloys in order to obtain a better understanding of the mechanism of oxidation of these materials[1]. This laboratory has been investigating the oxidation of Fe–26Cr alloys and comparing the results with those obtained using stainless steels. This communication describes the high-temperature oxidation behaviour of three vacuum-melted alloys and one commercial steel. The compositions of the materials are given in Table 1.

Table 1

	C	Mn	Si	Ni	Cr
Fe–Cr	0·022	0·003	0·02	0·02	26·2
Fe–Cr–Si	0·022	0·004	0·55	0·02	26·2
Fe–Cr–Mn	0·012	1·00	0·01	0·02	25·7
Type 446	0·18	0·75	0·86	0·32	25·9

The specimens were first mechanically polished to produce a flat surface, and electro-polished in perchloric–acetic acid to remove surface contamination. They were then annealed at 1,100° C in argon, re-electropolished, and finally etched to remove the film left after electropolishing. Oxidation was carried out in a stream of dry oxygen. Continuous weighings were made on an automatic balance.

Typical weight-gain/time curves at 1,090° C are shown in Fig. 1. It can be seen that the Fe–26Cr and Fe–26Cr–0·5Si pure alloys oxidize at a similar rate and appreciably more slowly than the commercial alloy and the pure alloy containing manganese.
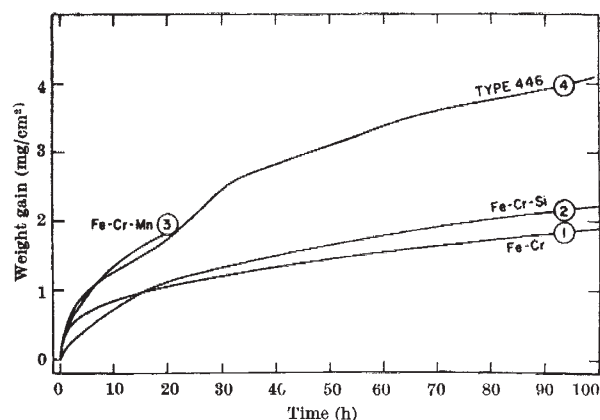

Fig. 1.　Oxidation of Fe–26Cr, Fe–26Cr–0·5Si, Fe–26Cr–1 Mn and type 446 in 1 atm. dry oxygen at 1,090° C

After these oxidation runs the samples were examined metallographically and the scales analysed by X-ray diffraction and spectrographic analysis. Typical cross-sections of the oxidized specimens are shown in Fig. 2. The only oxide phase formed on the binary Fe–Cr alloy was α-Cr_2O_3 containing a small amount of iron. (Pure chromium formed a similar single-phase scale under comparable conditions[2].) The scales formed on the other three alloys are quite different. In the Fe–Cr–Si ternary, the silicon oxidizes preferentially to form a silica sub-scale under a layer of 'Cr₂O₃' indistinguishable from the oxide on the Fe–Cr binary. The reason the oxidation rate is not affected is because a continuous layer of silica does not form. The protectiveness of the 'Cr_2O_3' layer remains unchanged. In the Fe–Cr–Mn ternary, the Mn also oxidizes preferentially but forms an Mn–Cr spinel as a continuous layer at the expense of some of the 'Cr_2O_3'. No scale section of the commercial steel is shown but, because of its manganese content, it forms a similar scale of spinel
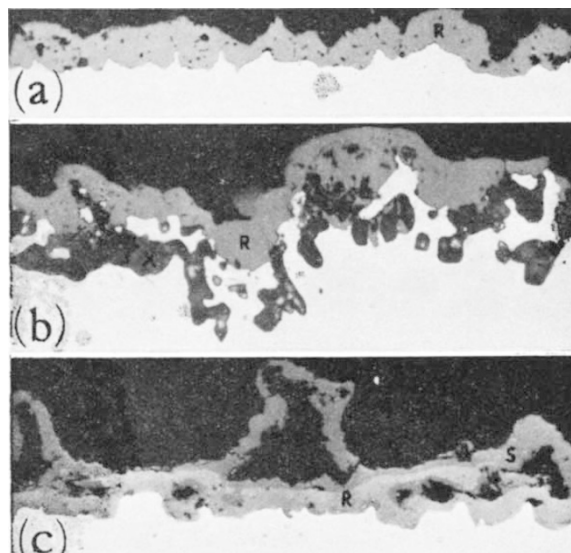

Fig. 2.　Metallographic sections through oxide layers formed at 1,090° C. Wrinkled oxide and rugged metal surface are caused by compressive stress that develops continuously in the thickening oxide. R, rhombo-hedral (Cr,Fe)₂O₃; S, MnO.Cr₂O₃ spinel; X, cristobalite silica. (a) Fe–26Cr alloy (curve 1). (Cr,Fe)₂O₃ is only phase formed. (× c. 375). (b) Fe–26Cr–0·5Si (curve 2). Islands of silica have formed below (Cr,Fe)₂O₃ layer. (× c. 750). (c) Fe–26Cr–1 Mn (curve 3). Light grey oxide is (Cr,Fe)₂O₃; darker grey is MnO.Cr₂O₃ spinel (× c. 750)

and 'Cr_2O_3' layers. Silica occurs again as a sub-scale. The high oxidation rate of the two alloys containing manganese is the result of the presence of the MnO.Cr₂O₃ spinel.

These results indicate that manganese is a deleterious additive to FeCr alloys from the point of view of high-temperature oxidation. The addition of 0·5 per cent silicon does not improve oxidation resistance. It would appear that the investigation of the pure alloys is not only useful for elucidation of the oxidation mechanisms but may also lead to the development of materials with higher oxidation resistance. This investigation indicates that the pure binary alloy is the most oxidation resistant. Further work is in progress.

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[1] Wood, G. C., Corrosion Sci., 2, 173 (1962).
[2] Caplan, D., Harvey, A., and Cohen, M., Corrosion Sci., 3, 161 (1963).

CHEMISTRY

Hydrolysis of Ferrous Ions : a Kinetic Method for the Determination of the Fe(II) Species

WE have recently shown[1] that the increase in the rate of the reaction of Fe(II) with hydrogen peroxide obtained by the addition of anions, X^{n-}, such as Cl⁻, SO_4^{2-}, $P_3O_9^{3-}$ and $HP_3O_9^{2-}$, is due to the species FeX^{2-n} reacting more rapidly with hydrogen peroxide than the hexa-aquo-ferrous ion. Following Hardwick's single observation[2] in perchlorate media that the rate at [H⁺] = 5·3 × 10⁻⁴ M is slightly greater than at lower pH, we have extended our investigation to higher pHs. We find that the observed bimolecular rate constant k_0 in perchlorate media under nitrogen remains constant over a wide range of acidity, and then changes quickly over a narrow pH range to a higher limiting value which remains unchanged when the acidity is decreased further. Such a plot of k_0