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The action of borates as inhibitors for the high temperature oxidation of alloys*

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The oxidation of metals and alloys at high temperature is usually considered to be a diffusion limited process, controlled ultimately by the concentration of defective lattice sites in the growing oxide film. Measures for controlling rates of oxidation usually depend, therefore, on replacing the oxide phase normally formed by another with a more favourable structure, or by doping the oxide to reduce the concentration of defects. These measures require the presence of a modifying agent either as a constituent of the alloy or as a relatively thick surface coating, and very few cases are known in which useful effects have been obtained by applying traces of material to the surface. There has therefore been no effective development of inhibitors for high temperature oxidation analogous to the well known inhibitors of wet corrosion, suitable for application *ex post facto*.

Recently, however, it has been discovered that small traces of borates, or of boron itself, are highly effective in reducing the rate of oxidation of ferrous alloys containing relatively small percentages of chromium in the temperature range 600–1000 °C. The active material can be applied to the alloy by dipping in dilute solutions to leave a thin film of deposit on the surface, or by vapour-phase transfer; in the latter case, extremely small additions to the oxidizing atmosphere may be effective. There are indications that superficial deposits may be more effective than incorporating boron as a constituent of the alloy. The materials of greatest interest are binary iron–chromium alloys containing 5–20 % Cr. The oxidation of these alloys normally proceeds through the formation of a very thin (*ca.* 50 nm) duplex film with an inner layer of spinel approximating to $FeCr_2O_4$, and an outer layer of Fe_2O_3. The kinetics at this stage are approximately logarithmic, and this thin protective film survives essentially unchanged for a period of hours or days depending on the temperature and the composition of the alloy. Eventually, however, there is a sharp increase in rate, even at 600 °C, and the oxide film then thickens at a high rate, which does not decrease with increasing film thickness, until the specimen is destroyed. The action of the borate inhibitor is to maintain the protectiveness of the very thin film and prevent this transition to rapid linear kinetics.

This contribution describes a programme of research with the use of electron microscopy on stripped films to investigate the mechanisms of the oxidation reaction and of the inhibitive effect of borates. It proved extremely difficult to detect any boron in certain oxide films which had been very effectively treated with inhibitor, but this was eventually achieved by Auger electron spectroscopy and secondary ion mass spectroscopy. It is shown that the 'breakaway' oxidation is caused by a growth of stress in the oxide film produced by inward diffusion of oxide anions in the outer layer of Fe_2O_3. The films grown in the presence of inhibitor are modified in subtle ways; the most important effect is to limit the growth of stress sufficiently to prevent disruption of the protective film. It is suggested that the essential feature of this action is the

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* Extended abstract.

formation of networks of –O–B–O covalent bonds which inhibit inward diffusion of oxide anions. The diffusion of chromium cations in the oxide lattice is slow, because of the high value of the activation energy, but if the short-term development towards breakaway is prevented, time will then be available for chromium to penetrate the Fe_2O_3 layer. This provides an additional mechanism for preventing further growth of stress. Films grown on an alloy containing 10 %Cr for 28 days at 600 °C in air containing a volatile borate inhibitor are similar in appearance to those grown on the same alloy for 5 min in clean air, and to those grown on a 20 % Cr alloy for 1–2 days.

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