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The oxidation of binary alloys of chromium with metals of the first long period

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Binary alloys of chromium with titanium, vanadium, manganese, iron, cobalt and nickel respectively have been oxidation-tested in air up to 1100°C. From the results the temperature corresponding to a weight change of 1 mg cm^{-2} over 4 h was determined by interpolation, and this temperature has been plotted against composition.

With the exception of a 50% cobalt alloy, alloys of chromium with either iron, cobalt or nickel withstand air oxidation at much higher temperatures than the constituent metals. Oxidation resistance in the other systems is generally lower.

An additional note describes the determination, during oxidation, of comparative electrical resistance of scales on iron, chromium, and an iron-20% chromium alloy.

1. Introduction

In a previous communication [1] the oxidation in air of metals from lithium to bismuth was studied. Samples were heated for a fixed time of 4 h at successively higher temperatures and a value termed T_p was found by interpolation, such that T_p was the temperature corresponding to a weight gain of 1 mg cm^{-2} over 4 h. This degree of weight gain was fixed arbitrarily, but as a practical guide it is probably true to say that no metal could be used continuously in air at temperatures *higher* than T_p. As a result of that work, the elements were classified into groups determined chiefly by the relation of T_p to the melting point of the appropriate metal or its oxide. For example, in the second and third long periods, a division was found between the behaviour of metals up to group IVA and those in later groups; that is, for metals of groups IA to IVA, T_p is of the order of half the melting point of the appropriate metal, whereas for groups VA and above, T_p is about half the melting point of an oxide of the metal. For the present purpose, we may refer to these two types as "metal-linked" and "oxide-linked", respectively. However, in the first long period, metals and their oxides in many instances have similar melting points and classification along these lines becomes difficult. T_p for chromium (~ 800°C) indicates that it behaves in metal-linked fashion, but chromium is exceptional in that terminal oxidation (i.e., complete loss) sets in only at a *considerably* higher temperature (~ 1050°C, which could correspond to oxide-linked behaviour). It appeared possible that this property of chromium could be turned to advantage by using it as an "indicator" in a study of the oxidation behaviour of binary alloys of chromium with its neighbours in the first long period, with a view to clarifying the above-mentioned classification. Inadequate knowledge of the chromium-scandium system, and insolubility in the chromium-copper system [2], limited the present study to systems with the metals from titanium to cobalt inclusive. Appropriate data were already available for the chromium-nickel system [3] and this is collated with the results.

2. Experimental

The raw materials were high purity metals as purchased from the suppliers. Titanium and vanadium were of approximately 99.9% purity; manganese, iron and cobalt were 99.999% pure (Koch-Light). Chromium pellets ("Specpure"; Johnson Matthey) were used to prepare Cr-Ti, Cr-V, Cr-Mn and Cr-Co alloys. Chromium-iron alloys were prepared from electrolytic chromium (Koch-Light). Alloy buttons were prepared by melting in an argon-arc furnace. Compositions were at 25 wt% intervals. The as-cast buttons were oxidation-tested by heating at temperatures of 400, 600 800, 1000 and 1100°C, as necessary, and the values for T_p determined. Details of the oxidation procedure have been given previously [1].

3. Results and discussion

The results are shown in the form of weight increase/temperature curves in Fig. 1. Composition/temperature curves for a constant weight increase, derived from Fig. 1, are shown in Fig. 2 and provide a basis for discussion.

A notable feature of the chromium-iron and chromium-nickel alloys is the temperature maximum at the 50/50 compositions coupled with high values of T_p also at the 25 and 75% compositions. The 50% cobalt alloy is exceptional, but otherwise the form of the curves is similar to that in the chromium-iron and chromium-nickel systems. The high values of T_p reached in the latter systems ($\sim$ 1050°C) is only consistent with 0.5 T_m for chromic oxide, not with 0.5 T_m for any other possible oxide or metal. It appears that unalloyed chromium is metal-linked, but that when alloyed the effect is to modify the process of oxidation in such a manner as to move T_p to $0.5\,T_m^{\text{“oxide” }(\text{Cr}_2\text{O}_3)}$. In the chromium-manganese alloys the effect of 25% manganese is to increase T_p, but higher contents drastically reduce T_p. The effect of all vanadium contents is detrimental. Oxidation in the chromium-titanium system, as in chromium-vanadium, appears not amenable to description in the same terms as applies to the group VIII systems; it may be significant that, in the latter, scales were dark green or black in appearance whereas high-titanium and high-vanadium alloys developed blue-grey scales. Probably the greater affinity of titanium and vanadium for oxygen [6] and the consequent displacement of chromic oxide as the essential scale constituent is responsible for the change in pattern of the results. If the rise in T_p with 25% addition is plotted against atomic number (Fig. 3) it will be noted that the greatest mutual advantage is possible in the chromium-iron system, with both chromium and iron as solutes.

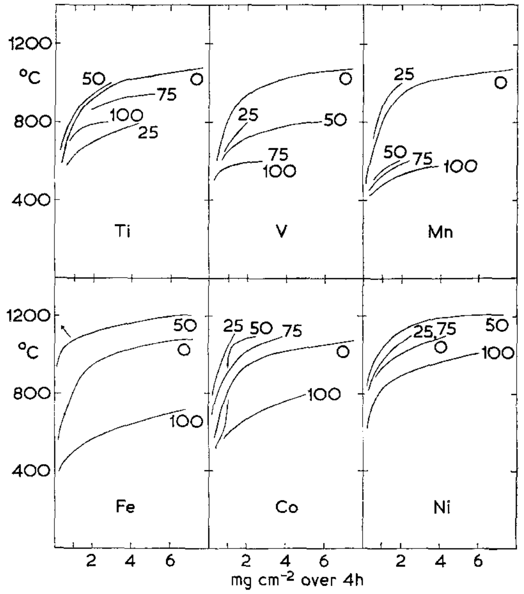

Figure 1 Weight increase versus temperature for six series of binary alloys. The curves are labelled in each case with figures representing the wt % of the component other than chromium. The arrow on the chromium-iron graph indicates that compositions with 25 and 75% iron initially behaved like the 50/50 alloy but subsequently lost weight.

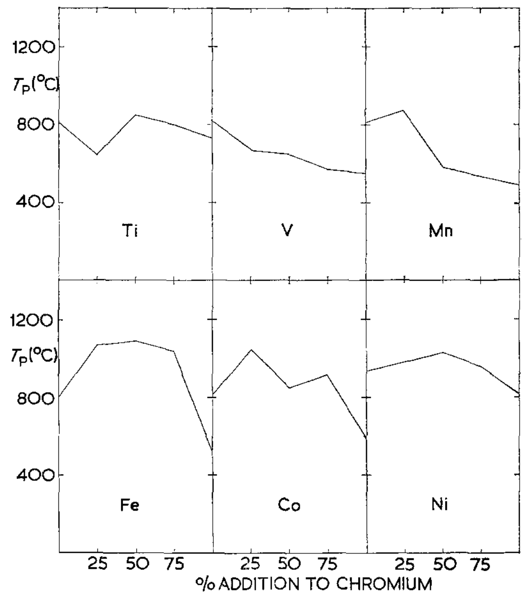

Figure 2 Composition versus T_p for six series of binary alloys. The abscissa in each case is marked with the percentage of component other than chromium.

4. The electrical resistance of scales on iron, chromium, and an iron-chromium alloy

In view of the practical relevance of the oxidation of iron-chromium alloys, and because of personal interest on the subject of the conductivity of oxide powders and compacts [4], measurements were made of the electrical resistance of the surface layers on samples of the two metals and an iron-20% chromium alloy

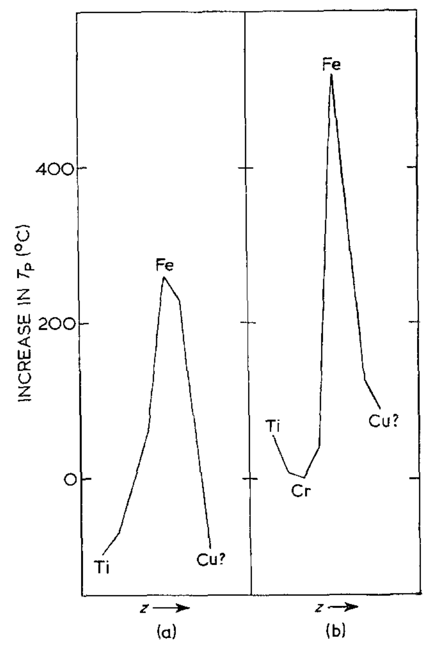

Figure 3 Atomic number versus increase in T_p with 25% addition. (a) Additions to chromium (i.e. 75% Cr-alloys), (b) additions of chromium (i.e. 25% Cr-alloys). The positions for the chromium-copper system were estimated from the proportions of the components in hypothetical alloys.

while the samples were heated in air from room temperature to approximately 1300°C. The apparatus was adapted from a standard thermocouple-in-sheath arrangement. The specimen, in the form of a small cylinder with one end metallographically polished, was pushed down the bore of an alumina sheath. An assembly of wires in four-bore alumina thermocouple insulation followed up the sample: two platinum wires provided a two-point probe for resistance measurement, and a standard platinum-platinum 13% rhodium thermocouple with tip near the probe occupied the remaining holes. Measurements, by "Avometer", were discontinuous, that is, the normal position of the probe was slightly retracted but it was pressed firmly but without excessive force every few minutes whilst a reading was taken. Provided that a sufficient pressure was applied, readings at any moment were reproducible. The results (Fig. 4) provide some additional evidence that Tammann temperatures ($\sim 0.5\ T_m$) are relevant to oxidation processes – note the sudden increase in resistance of the alloy scale at 1050°C and the rise in resistance of the chromium scale near 800°C. Extensive data on the constitution and thickness of the scales throughout the test would doubtless permit complete elucidation of the curves: a momentary change of oxygen pressure could give an indication at the oxide/gas interface of the p/n state as oxidation progressed [5].

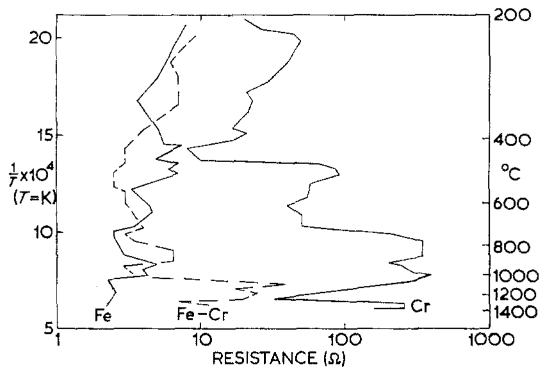

Figure 4 Electrical resistance of scales versus temperature for iron, chromium and an iron-20% chromium alloy.

Acknowledgements

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