JOURNAL OF MATERIALS SCIENCE 14 (1979) 2787–2790

# Hardness, oxidation and constitution in chromium–iron alloys

H. E. N. STONE
*Blackett Laboratory, Imperial College, London, UK*

Data on the room-temperature hardness and high-temperature oxidation of chromium-containing alloys with up to 50 at % iron are presented, and the relation of these to the electronic constitution briefly discussed.

## 1. Introduction

Much work has been carried out in recent years with the object of elucidating the magnetic structure of chromium-rich chromium–iron alloys. The situation is intriguing. It is well known that the body-centred solid solutions based on alpha iron are ferromagnetic to quite low concentrations of iron, also that pure chromium is antiferromagnetic. To the question as to what happens in more detail over the critical intermediate concentration range, it would appear [1] that the Curie point of iron-rich solid solutions decreases to zero Kelvin at approximately 19% iron in chromium, whilst the Néel temperature of chromium is depressed monotonically until the antiferromagnetism disappears at liquid helium temperatures at about 16% iron, so that we have a concentration range of width 3% in which at the lowest temperatures alloys are always paramagnetic. These changes are indicated in the phase diagram (Fig. 1). Since the system has been referred to as magnetically inhomogeneous [1], that is "two phase" with separate regions of the order of 100 Å across, we may perhaps describe it as an electronic eutectic, with the eutectic horizontal, extrapolated from the falling critical temperatures for the magnetic states, being a virtual one, lying below zero Kelvin (E, Fig. 1).

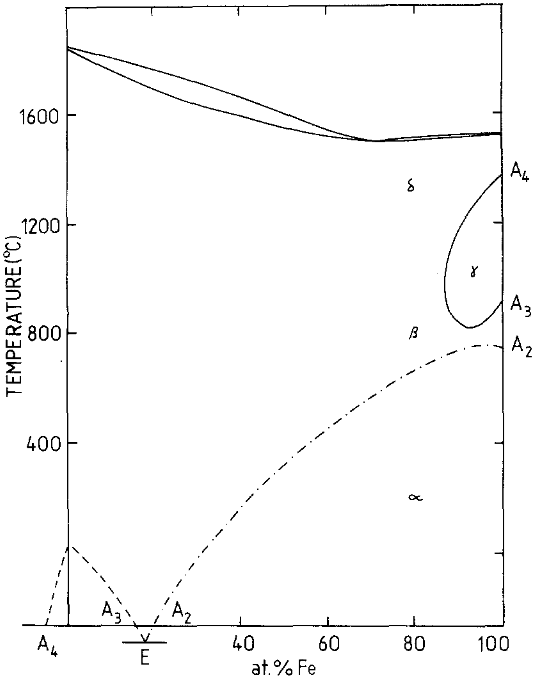

*Figure 1* The chromium–iron phase diagram [8]. The dotted and dashed line shows the variation of the Curie point, and the dashed line the variation of the Néel temperature with composition [1]. The abscissa is drawn at 0 K. The $\alpha + \gamma$ phase field is narrow and has therefore been omitted for clarity. The sigma equilibria are omitted also. The lower left-hand portion represents a small extension into the adjoining V–Cr system, with vanadium content increasing to the left.

Concurrent with the above work, which was carried out by neutron techniques, a more metallurgical-type investigation was in progress, which had the object of establishing if other changes took place at or near critical compositions for the magnetic states. This consisted, in outline, of preparing a set of samples with compositions in the range 0 to 50% iron, subsequently conducting (a) room-temperature hardness and (b) high-temperature oxidation tests on each sample. Whilst the principal motivation for the work was correlation with the low-temperature physical properties, one may remark that it becomes evident from this and previous work [2, 3] that the alloys

0022–2461/79/122787–04$02.40/0

have useful engineering properties, and it is hoped that this account will *inter alia* serve to stimulate renewed interest in them.

## 2. Experimental details

Compositions are nominal and in atomic per cent unless otherwise indicated, and a few points outside the range $2\frac{1}{2}$ to 50% iron inclusive are repeated from previous work [3, 4].

The appropriate weights of the basis materials (Johnson Matthey "Specpure" chromium and iron) were melted together in an argon-arc furnace and were cast [5, 6] into sticks about 30 mm long of section approximately $1\frac{1}{2}$ mm and weight 1 g. These were sealed in evacuated quartz capsules ($5 \times 10^{-5}$ mm Hg), heated for $2\frac{1}{2}$ days at 1050° C, followed by cooling the capsule in water and subsequent cold extraction of the relatively brittle sample. The homogenized sticks were spark cut and a metallographic specimen from a standardized position in the upper part was mounted, ground, polished and tested at 50 g load using a Vickers microhardness attachment. Five impressions were made on each specimen and the average plotted; the scatter per specimen was of the order ± 10 points.

Attention was given to the possibility that sigma phase may have been present, but no indications were found by conventional etching or from electromechanical polishing/etching [7]; also no treatments which may be expected to initiate sigma formation were required or employed in processing. The microstructure consisted of essentially uniform largely equi-axed grains. It is therefore thought that the present results refer to the sigma-free metastable system. The 40 and 50% iron specimens were magnetic at room temperature as-cast and after homogenization, the remainder not so, as would be expected from the published data [8]. The oxygen content of the chromium base was about $1\frac{1}{7}$%, estimated by making a separate set of small alloy buttons containing controlled small additions of aluminium, determining the aluminium content of the chromium matrix with the microprobe, and extrapolating backwards on a plot of actual versus nominal content. However, metallurgical evidence and the literature [2] indicate that oxygen in chromium occurs as discrete insoluble (and therefore probably inert) particles after melting. Probably oxygen content is also responsible for the manner in which chromium and chromium–iron alloys (those with less than about 15% iron) rise in "volcano" fashion as they solidify, since the rising is killed by aluminium or carbon additions; a critical addition of the latter gives buttons with the smoothest free surfaces [9]. The hardness samples for the 13 and 15% compositions were subjected to microprobe analysis for iron content, and these showed that the nominal 13 was estimated at 14.4% and the 15 at 17.9%. The estimated iron contents are therefore higher by approximately 2% than the nominal, probably due to preferential volatilization of chromium in preparation.

The cast and homogenized sticks were tested for 4 h at each of the temperatures 640, 780, 940, 1040 and 1100° C with the object of interpolating or extrapolating the temperature (called $T_\text{p}$) [10] corresponding to a weight gain of 1 mg cm$^{-2}$/4 h. The choice of these particular temperatures is not significant, although the grouping of the higher figures was deliberate. Although the generality of the $T_\text{p}$ results are above 1100° C (confirming [4]), the principal finding from the oxidation tests is not affected by the use of extrapolation, as will become evident. The temperature/weight gain curves were similar in form, so that $T_\text{p}$ gives an accurate indication of merit, although there may have been a tendency to a "chromium curve" variant [10] around 15% iron. Green oxide flare on the alumina substrate was markedly reduced for contents greater than about 16% iron.

## 3. Results

The room temperature hardness results are plotted in Fig. 2b. The general shape of the hardness/composition variation shows a maximum at 20% iron with fallaway on either side, in conformity with earlier results [3]. However, there is a sharp though shallow minimum near 15% iron, which, when allowance is made for the drift from nominal to analysed content, may be equated with the 16 to 19% range in the magnetic properties. Perhaps a mixture of ordered and disordered parts in the microstructure (the magnetically inhomogeneous conditions with either less than 17% or more than 18% iron) produces an increased resistance to the hardness indenter. Data for the V–Fe system [3] are also consistent with an inference of two maxima, with an intervening minimum likewise at an average Group number [11] of 6.25 to 6.30.

The high-temperature oxidation data are given

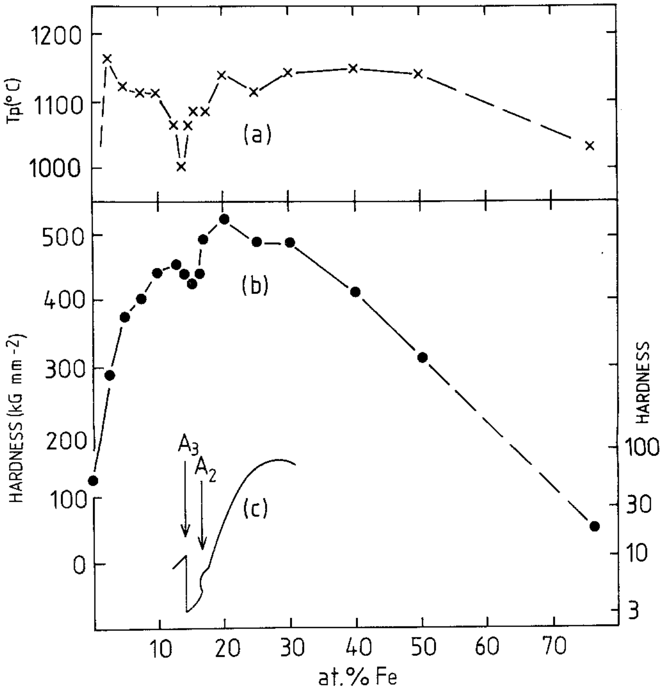

*Figure 2* The variation of (a) the oxidation parameter $T_p$ and (b) the microhardness with composition. Data on the hot hardness of pure iron from [15] are reproduced at (c); the logarithmic ordinate scale on the right applies for this, and the particular method of scaling on the abscissa is described in the text.

in Fig. 2a. All compositions showed a high level of oxidation resistance, the parameter $T_p$ nowhere falling below 1000° C. The previous cursory survey [4] indicated $T_p$ values at 25, 50 and 75 wt% iron of approximately 1150° C, and most of the points in Fig. 2a are in keeping with this. The interesting departure which is shown in the present results is the minimum at the 14% nominal iron composition, which, making allowance again for composition drift, coincides with the paramagnetic regime, so that the latter is slightly inferior in oxidation resistance (cf. magnetism and oxidation relationships in [12]).

## 4. Discussion

Let us consider the dispositions and extents of the various phase fields in the Cr–Fe phase diagram (Fig. 1). Starting from the low-temperature 100% iron corner (lower right) we have a large ferromagnetic field, which extends upwards to 768° C on the temperature ordinate and to the left to the point Cr–Fe 19%. Beyond these limits we have a large and continuous paramagnetic zone, narrow at its extremities (between 768 and 910° C, and 19 and 16% iron respectively), and further away again, two separate antiferromagnetic [13] phase fields. The extent of these two fields is approximately equal – 14% of chromium in iron and 16% of iron in chromium, respectively. A particular kind of symmetry is, therefore, evident in the diagram, and, to emphasize this, the customary designations for the allotropic change points in iron ($A_2$, $A_3$, $A_4$) have been repeated going leftwards along the abscissa in Fig. 1. Note that a few per cent of vanadium suppresses the antiferromagnetism of chromium [14], and this fixes the position of the analogue of the $A_4$ point. There is good scaling of the ($A_2$–$A_3$) and ($A_3$–$A_4$) distances along ordinate and abscissa.

In view of the symmetry and scaling of the phase changes, it was natural to consider if changes in hardness of the room-temperature alloys had counterparts in the hot hardness of iron. It so happens that the latter has been studied by Geach [15] and Petty and O'Neill [16]. The curve of the former is reproduced (Fig. 2c) in a special way, so that an analogy with hardness/composition is brought out; it is scaled so that the $A_2$ and $A_3$ change points are equated with the compositions at which ferromagnetism is lost and antiferromagnetism acquired, at 0 K, with increasing chromium content, that is, the abscissa distance 3% (the difference between 16 and 19%) is made equivalent to 142° (the difference between 910 and 768° C). (It is regretted that the method of plotting reduces the work of these authors to such modest proportions.) In the hot hardness tests, only a slight disturbance [16] in the smooth fall of the curve at

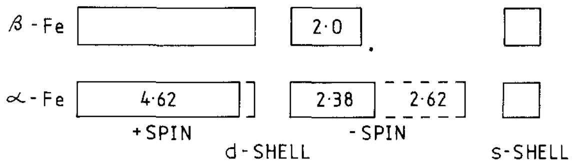

*Figure 3* Band-box diagrams for two allotropes of iron.

the magnetic transition ($A_2$ in Fig. 2c) was reported, but there was a marked increase at the $A_3$ alpha–gamma transformation at 910° C; in the alloy (room-temperature) case the intensity of the maxima are in reverse order. However, if allowance is made for the fact that for the alloy effect it is necessary first to subtract an estimated hardness for a simple dome-shaped curve, whereas for rising temperature one must subtract a basis curve for a steeply falling nil-transformation function, a parallel between the temperature effect and the alloy effect becomes credible.

Finally, it is of some interest to speculate on the changes in electronic structure that must occur as we move from one side of the phase diagram to the other, although it would be inappropriate to do so here at length, and the reader is referred to previous work [17, 18] for fuller background. Such a description starts conveniently with that of alpha iron. This is indicated in Fig. 3 in a mixed "band/spin box" type of representation. Here from left to right we have rectangular blocks representing respectively the d majority spin, d minority spin and s occupations. It is accepted that the presence of the small hole in the majority spin shell is an essential condition for ferromagnetism; we also assume that s–d resonance [17] occurs and that the occupation values may be systematized in terms of phi-related [18] quantities (where phi is the golden ratio, approximately 1.62). The beta form of iron (non-magnetic b c c) differs from alpha in that the majority half shell is filled up, and, also, integral electron occupancies replace phi-related probabilities. The delta iron electronic structure will perhaps be similar to beta, but with increased but integral s occupation. The gamma form will contain phi-related occupations but without the hole in a d shell characteristic of ferromagnetism, and this will also be true of the counterpart antiferromagnetic phase field based on chromium at the other side of the diagram. (Perhaps slightly less than half a half-shell is typical of antiferromagnetism.) A complete interpretation of the structures, more especially at the chromium-rich end, would need to take into account the magnetic moments of the components there, but this task may be simplified since present indications [1, 19] are that these quantities tend to be either integral or phi-related.

## Acknowledgements

The author is indebted to Professor B. R. Coles for laboratory facilities, Mr S. K. Burke and Dr B. D. Rainford for communicating some of their results prior to publication and for interesting discussions, and to the Analytical Services Laboratory of the College for the microprobe analyses.

It would be inappropriate to conclude without referring, with sadness but coupled with an expression of gratitude for past help, to the recent death of Dr Arthur Sully, well-known for his work on chromium-base alloys and transition metal science generally, and the writer of the standard monograph on chromium.

## References

1. S. K. BURKE and B. D. RAINFORD, *J. Phys.* (*F*) 8 (1978) L239.
2. A. H. SULLY and E. A. BRANDES, "Chromium" (Butterworths, London, 1967).
3. H. E. N. STONE *J. Mater Sci.* **12** (1977) 1416.
4. *Idem, ibid* 8 (1973) 1009.
5. *Idem, J. Phys.* (*E*) 4 (1971) 1058.
6. *Idem, Metallurgia and Metal Forming* 44 (1977) 105.
7. *Idem, Metallography* **11** (1978) 105.
8. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) and supplements edited by R. P. Elliott (1965) and F. A. Shunk (1969).
9. H. E. N. STONE, unpublished work ca. 1957.
10. *Idem, J. Mater. Sci.* 7 (1972) 1147.
11. W. HUME-ROTHERY, R. E. SMALLMAN and C. W. HAWORTH, "The Structure of Metals and Alloys" (The Metals and Metallurgy Trust, London, 1969) p. 156.
12. H. E. N. STONE, *J. Mater. Sci.* **10** (1975) 923.
13. B. R. COLES, R. H. TAYLOR, B. V. B. SARKISSIAN, J. A. KHAN and M. H. BENNETT *Physica* **86-88B** (1977) 275.
14. B. LEBECH and K. MIKKE, *J. Phys. Chem. Solids* **33** (1972) 1651.
15. G. A. GEACH, *Int. Met. Rev.* 19 (1974) 255.
16. E. R. PETTY and H. O'NEILL, *J. Iron Steel Inst.* **197** (1961) 141.
17. H. E. N. STONE, *J. Mater Sci.* **11** (1976) 1576.
18. *Idem, ibid* **12** (1977) 201.
19. S. K. BURKE and B. D. RAINFORD, unpublished work.

Received 29 January and accepted 10 May 1979.