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Assessment of B_4C reaction with liquid iron alloys

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The degree of reaction achieved when B_4C powders are brought into contact with liquid iron alloys has been assessed by a levitation dispersion test. Reaction occurs rapidly, leading to boron carbide dissolution and iron boride formation. In carbon-free iron alloys borocarbide, $Fe_{23}(C, B)_6$, also forms and in low-carbon iron alloys free graphite was also formed. High-carbon alloys reacted to form both $Fe_3(C, B)$ and free graphite. Attempts to provide protection for the B_4C by forming a TiC coating on its surface by *in situ* reactions with liquid Fe–Ti and Fe–Ti–C alloys proved unsuccessful, with TiC forming as a dispersed phase throughout the iron matrix

1. Introduction

As a potential filler material in the manufacture of abrasive wear-resistant composites B_4C has attractive properties including a high hardness (4500 H_V) and a low density (2.52 $g\,cm^{-3}$) and a high melting point (2350 °C). B_4C is however known to be reactive with iron-based alloys, forming brittle iron borides and graphite.

In this study the reaction of B_4C with liquid iron alloys has been investigated. Pure iron, low carbon iron, high carbon and ferro-titanium alloys were used as matrix alloys. The overall aim of the work was to determine whether conditions could be identified where B_4C could be dispersed in liquid iron alloys without the formation of iron boride. The identification of such conditions could then form the basis of a liquid route for the production of Fe–B_4C composite materials with the added advantage of producing near net-shaped components.

2. Experimental procedure

Assessment of the reaction and dispersion of B_4C in liquid iron alloys was performed using the levitation dispersion test procedure developed by the present authors and described in detail in a previous publication [1]. Essentially pellets of the iron alloy containing added particles of B_4C were melted and levitated. The liquid drops formed were then quenched and examined by optical and electron microscopy to provide a visual assessment of the degree of dispersion achieved. The phases present in the sample after the test were identified by X-ray diffraction to assess matrix–filler reactions.

The iron alloys were prepared by the addition of carbon in the form of specpure graphite to carbonyl iron, followed by premelting by induction. B_4C powders were obtained from E.S.K. (Germany). In order to provide a crude assessment of mechanical properties, macrohardness measurements were carried out on the products of the levitation test using a Vickers machine with a diamond indentor and using a 10 kg load.

3. Results

Table I provides a summary of the results obtained after the levitation of iron alloys with boron carbide filler material. Figs 1 and 2 illustrate some of typical microstructures which were observed.

3.1. Pure iron and low-carbon iron matrices

In virtually every case the boron carbide reacted with iron to form iron boride (Fe_2B) and some graphite. With carbon-free alloys, e.g. pure (run R28) and Fe–5 wt % Ti alloy (run R38), $Fe_{23}(C, B)_6$ borocarbide was also formed. This phase seemed to form in preference to the cementite observed in the reaction of B_4C with iron–carbon alloys. Its formation had previously been noted during the heat treatment of Fe–TiB_2 powder mixtures [2]. This phase seemed to form in preference to cementite which was observed with iron–carbon alloys, probably because of the lower carbon activity prevailing in the presence of B_4C.

In addition to Fe_2B and graphite, low-carbon iron experiments also resulted in the formation of cementite and sometimes FeB. Previous studies [3, 4] have shown that in the formation of cementite in the Fe–B–C system, boron commonly substitutes for carbon, leading to the formation of the so-called borocementite, $Fe_3(C, B)$. Nicholson [3] reported that up to 80% of the carbon atoms in cementite can be replaced by boron to give $Fe_3C_{0.2}B_{0.8}$, the limiting formula at 1000 °C. The extent of substitution decreases with temperature and is about 60% ($Fe_3C_{0.4}B_{0.6}$) at 600 °C.

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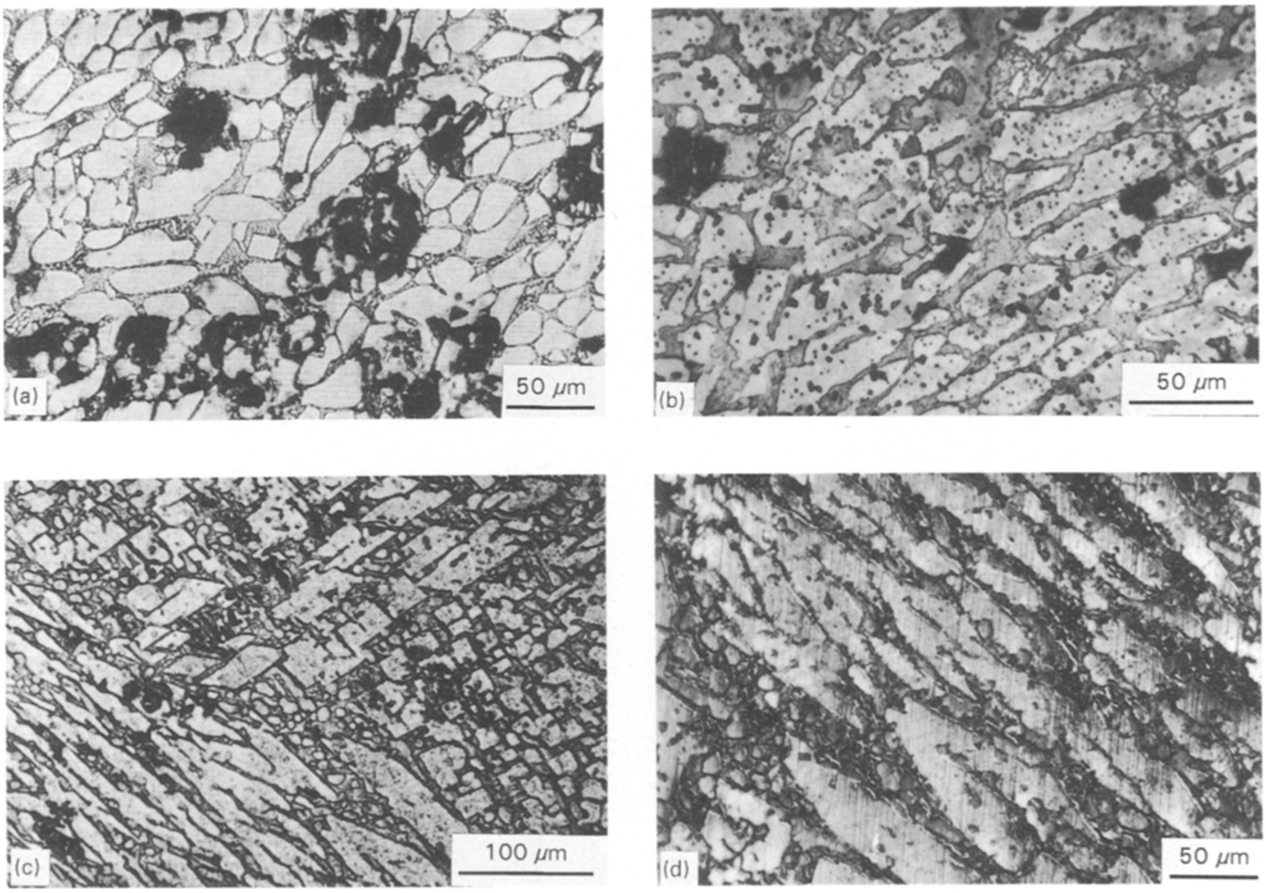

Figure 1 Microstructures observed after levitation of pure and low-carbon iron alloys with B_4C. (a) Graphite is formed as a result of B_4C decomposition and was observed even when pure iron was used. (b) The "dirty" appearance of most micrographs was due to discrete particles of precipitated graphite. Relatively slower cooling led to more rounded grains in (a) and (b). (c) Grains have sharp defined edges as with TiB_2 samples after fast cooling of low-carbon iron and B_4C. (d) Nomarski photomicrograph of the sample in (c).

In experiments using low-carbon iron as the matrix alloy, B_4C was frequently detected by X-ray analysis. The phase could not however be identified microstructurally, which suggests that the B_4C consisted of very fine particles. It was interesting to note that very high hardness values were recorded for these samples, suggesting that the remanent B_4C made a significant contribution.

3.2. High-carbon iron matrices

In experiments with high-carbon iron as the matrix alloy (27M, 9M), Fe_2B and $Fe_3(C, B)$ were formed and free graphite was precipitated. In some cases there was too little graphite to show up in X-ray diffraction analysis but it was always clearly identifiable microstructurally.

The ease of formation of graphite is a result of the increase of the activity coefficient of carbon by boron in molten iron–boron–carbon alloys and the consequent decrease in solubility. Sigworth and Elliott [5] give the first-order interaction E_C^B as $+0.24$.

3.3. Protection of B_4C

In view of the apparent ease of dissolution of B_4C in liquid iron alloys and the resultant iron boride formation, it seems apparent that it is necessary to impart some form of protection to B_4C if it is to be contacted with liquid iron. In a previous publication [6] by the present authors a number of possible ways were considered in which SiC particles could be protected from iron alloys.

In the present study experiments R38 and 34M were performed in an attempt to impart protection to B_4C particles *in situ* in liquid iron. It was hoped that by using an Fe–Ti or Fe–Ti–C alloy as the matrix, *in situ* protection of the B_4C by a layer of TiC would be effected. As B_4C started to dissolve it was hoped that the Ti in solution would react with the graphite being released to form thin TiC layers round the rest of the B_4C; since it has already been established [1] that TiC is well wetted by iron–titanium–carbon alloys, particle dispersion could be achieved in this way.

The results obtained indicated that significant reactions between B_4C and iron were still occurring as X-ray analysis failed to reveal the presence of any B_4C; Fe_2B and TiC were found in the final material. The TiC formed dispersed throughout the structure, often in a long thin plate-like morphology (Fig. 2), ruling out the possibility of its having formed round B_4C particles.

These observations seem to suggest that the reaction between iron and boron carbide was very fast one and that to form TiC as protection was much slower. This can be explained by the fact that carbon diffuses

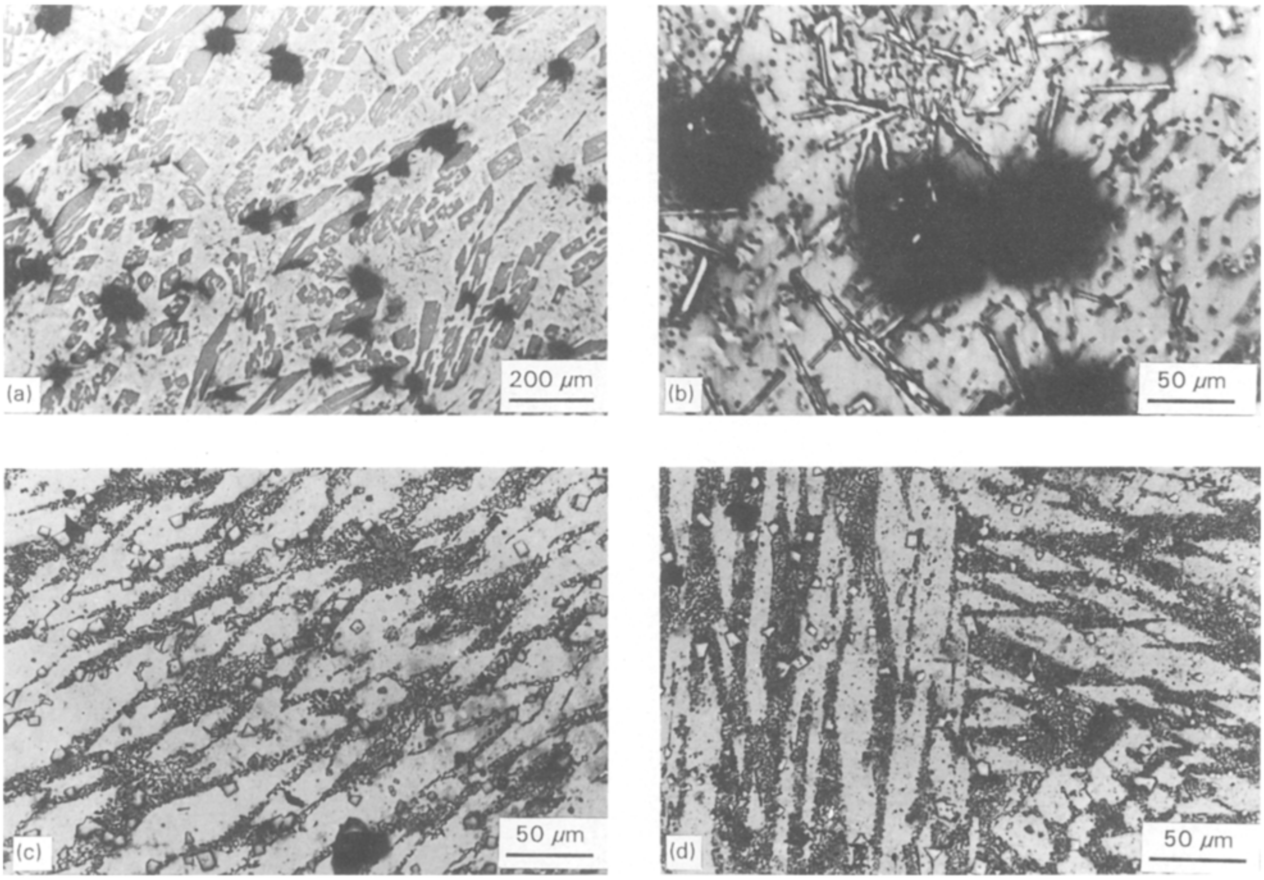

Figure 2 Microstructures observed after levitation of Fe–Ti and high-carbon iron alloys with B_4C. (a) High-carbon iron and B_4C, showing well-defined Fe_2B grains and graphite after etching in nital. (b) Large graphite modules and TiC platelets after levitation of Z alloy with B_4C. (c) Structure observed after levitation of Fe–Ti alloy with B_4C. The prominent particles are TiC. (d) Same as in (c), different area.

much more easily in liquid iron than Ti and so TiC can be nucleated and precipitated well away from decomposing B_4C particles.

3.4. Iron boride formation

The iron boride (Fe_2B) formed in all the experiments did so as large plates running parallel in a common direction. This was also true for the Fe_2B formed in our previous study of iron–TiB_2 reactions [2]. This directionality gave rise to X-ray diffraction patterns which had lines characterized by non-uniform intensities, i.e. broken rather than strong solid lines. In some cases the columnar grains formed were quite sharp and faceted (Fig. 1c and d) whereas in others they were rounder, although the directionality was always unmistakably present (Fig. 1a and b). It is thought that this slight difference in morphology may be attributed to small differences in cooling rates, with the former having been somewhat faster than the latter.

3.5. Hardness values

Very high hardness values were recorded for most of the samples produced in the present study. This was probably because most of the major phases formed after experimentation were characteristically hard phases such as Fe_2B, Fe_3C, $Fe_3(C, B)$ and $Fe_{23}(C, B)_6$. The ease with which the products could be crushed in preparation for X-ray diffraction analysis was however an indication of their inherent brittleness.

4. Discussion

4.1. B_4C dissolution in liquid iron alloys

Raghavar and Ghosh [6] have recently provided a comprehensive review of phase relationships in the boron–carbon–iron system. The ready solubility of B_4C in liquid iron alloys is clearly evident. The present study has shown that unprotected B_4C dissolves rapidly in liquid iron alloys. The extremely low solubility of iron borides in iron results in their subsequent formation during cooling and solidification.

4.2. Prospects for Fe–B_4C composite production

The ease and speed with which B_4C reacts with liquid iron alloys to form iron borides clearly militates against the development of a liquid-based route for the production of iron-based B_4C composites. Clearly if any progress is to be made, some form of protection needs to be imparted to the B_4C. Attempts to provide such protection in the form of TiC generated by *in situ* reactions have not proved successful in this study. Similar attempts at generating TiC and Al_2O_3 protection on SiC by *in situ* means have previously been unsuccessful, and precoating SiC with Ni and/or Cu coatings did not provide protection against liquid iron alloys. The prospects for developing an inexpensive means of protection for B_4C against attack by liquid iron alloys do not therefore appear to be very promising. Our previous work on SiC reactions with iron does however offer some encouragement, in that SiC reaction with solid iron has been successfully prevented by the use of Ni coatings. The application of such procedures to the solid-state processing of iron–B_4C composites appears to be a natural extension of the current work.

5. Conclusions

The principal conclusions to be drawn from this work are the B_4C reaction dissolution with liquid iron alloys is so rapid that a liquid-based route for the production of Fe–B_4C composite materials is not viable. There may however be some scope for the development of a solid-state processing route, provided that some form of protective coating is applied to the B_4C.

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