

# Assessment of the reaction of SiC powders with iron-based alloys

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The degree of reaction and dispersion achieved when SiC powders are brought into contact with liquid iron-based alloys has been assessed by a levitation dispersion test. SiC was found to react rapidly with molten iron matrices to form iron silicides and graphite. Attempts to generate protective TiC or Al<sub>2</sub>O<sub>3</sub> coatings on SiC *in situ* in liquid iron proved unsuccessful; neither was precoating SiC and Ni and/or Cu successful in providing protection against molten iron alloys. Unprotected SiC also reacted readily with iron in the solid state (1000–1200 °C). Precoating with Ni, however, provides protection and prevents SiC dissolution and silicide formation during sintering at such temperatures.

## 1. Introduction

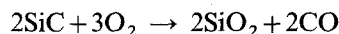
In previous publications [1, 2] the present authors have investigated the feasibility of incorporating TiC or TiB<sub>2</sub> into iron alloy matrices with the aim of producing wear-resistant metal-matrix composites. Compared with TiC and TiB<sub>2</sub>, SiC has a lower density, higher hardness value and is cheaper and more readily available. These properties make SiC an obvious candidate for use as a hard filler in tough matrix composites. However, the potential use of SiC as a filler material in iron-based matrices may be limited, as iron forms stable compounds with both silicon and carbon and, as silicon carbide, readily dissolves in liquid iron alloys.

In this investigation the reaction of SiC with liquid iron alloys has been studied. Pure iron, low- and high-carbon iron, and iron–titanium and iron–aluminium alloys were used as matrices. The overall aim of the work is to determine whether conditions can be identified where SiC can be dispersed in liquid iron alloys while preventing excessive reaction of the SiC with the iron. Such conditions could form the basis of a route for the production of Fe–SiC composites.

Initial results showed that rapid reaction occurred between SiC and the molten iron alloys studied, leading to the formation of silicides and graphite.

In the light of these initial results some time and effort was devoted to finding ways to protect the SiC from direct contact with the iron. These attempts included *in situ* protection methods where protective layers were expected to form round filler particles within the matrix metal. Precoating of SiC particles with Ni and Ni with Cu was also studied. In this area of work subsequent reactions with both liquid iron alloys at 1600 °C and solid iron alloys at 1100 °C were investigated. Previous authors have achieved some success in using Ni coating to protect particles for subsequent incorporation into aluminium matrices.

Thermodynamically SiC is very prone to oxidation. When heated in air, however, it attains a passive state after the formation of a thin, stable and impervious film of SiO<sub>2</sub>; this reaction can be represented by



Further oxidation is very slow and can only occur by the diffusion of oxygen or carbon monoxide through the oxide lattice or microcracks. Oxidized SiC was therefore used as the starting material in several of the experiments performed. It was hoped that the passive silica layer would protect the carbide from contact and reaction with iron, or would react with aluminium deliberately added to the iron matrix to form a more resilient alumina protective layer.

## 2. Experimental procedure

Assessment of the reaction and dispersion of SiC 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]. Pellets of the iron alloy containing added particles of SiC were melted and levitated. The liquid drops formed were then quenched and examined by optical and/or 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 powder, followed by premelting by induction; Ti or Al powder additions were also made where appropriate. 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 indenter and

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TABLE I Results of levitation experiments performed with SiC and various ferroalloys

Run	C in Fe (wt %)	Temperature (°C)	Time (min)	Weight of pellet (g)	Weight loss, (%)	Phase identified by X-ray diffraction	Comments
15M	0.08	1600	2	2.352	15	Fe, C <sub>gr</sub> , Fe <sub>3</sub> C, Fe <sub>2</sub> Si, FeSi	
21M	0.21	1590	2.5	1.910	23	Fe, C <sub>gr</sub> , Fe <sub>2</sub> Si	
10M	3.70	1500	2.5	3.041	7	Fe, C <sub>gr</sub> , Fe <sub>2</sub> Si, FeSi	
23M	0.08	1600	3	1.867	7	Fe, Fe <sub>3</sub> C, C <sub>gr</sub> , FeSi	SiC had been baked in air at 1000°C for 2 h
33M	0.21 (Z)	1590	2.5	1.579 (Z)	4	Fe, TiC, C <sub>gr</sub>	Pellet used was of Z alloy
R37	Fe-5.2 wt %Ti	1600	0.5	2.362	-	Fe, TiC, Fe <sub>3</sub> C (weak), Fe <sub>2</sub> Si and FeSi (possible)	Ferrotitanium alloy used; loss of some sample during experiment, so ΔW was not calculated
R20 <sup>a</sup>	Fe-1.5 wt % Al	1560	15	41.976	5	Fe, Fe <sub>3</sub> C, C <sub>gr</sub> , Al <sub>2</sub> O <sub>3</sub> (v. weak), Fe <sub>2</sub> Si (v. weak)	SiC had been baked in air at 1000°C for 2 h; mixture induction-melted in a magnesia crucible

<sup>a</sup> All except R20 were levitation experiments.

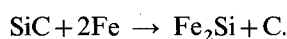
a 10 kg load. The reactions occurring during solid-state processing of Fe-based SiC composites were assessed at 1000 to 1200°C by performing heat treatments of suitable alloy-SiC mixtures in sealed argon-filled silica tubes.

A methane mixture (CH<sub>4</sub> + 10%H<sub>2</sub>) was cracked over an SiC sample to provide the sample with a fine surface layer of graphite for subsequent incorporation into the iron. SiC which had been coated with a layer of Ni or Ni and Cu was supplied by Morgan Materials Technology. The nickel coating was obtained by electroless flashing and some of the nickel-plated samples were further coated with nickel or copper using a barrel plating method [3].

### 3. Results

#### 3.1. Reaction of SiC with liquid iron alloys

Table I gives a summary of the levitation experiments performed with various iron alloys using SiC as the filler. Regardless of the carbon content of the matrix, SiC always reacted with iron to form iron silicides and graphite:



Some Si also dissolved in the iron and there was frequent evidence of the formation of other silicides such as FeSi and Fe<sub>3</sub>Si.

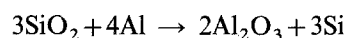
Silicon increases the activity of carbon in molten iron (Sigworth and Elliot [4] quote the value of the extraction coefficient  $e_C^{\text{Si}}$  as + 0.08, for example) and its presence in the molten iron promotes the formation of graphite. The morphology of the precipitated graphite varies greatly according to cooling rates and the amount of SiC which had reacted, as shown in Fig. 1. The morphology favoured with pure and low-carbon alloy matrices was that of a fine flake network; the high-carbon alloys had this network and also some short thick graphite stubs and even nodules (Fig. 1a and b).

#### 3.2. *In situ* protection methods

##### 3.2.1. Fe-Al alloy with oxidized SiC

In experiment R20 (Table I) pure iron and aluminium

were melted together under an argon atmosphere to produce an Fe-1.5 wt % Al alloy. Some of this alloy was then induction-melted with oxidized SiC under argon. It was hoped that the Al in the iron would react on the filler particle surface and replace the silica protective layer with a more resilient silica one according to

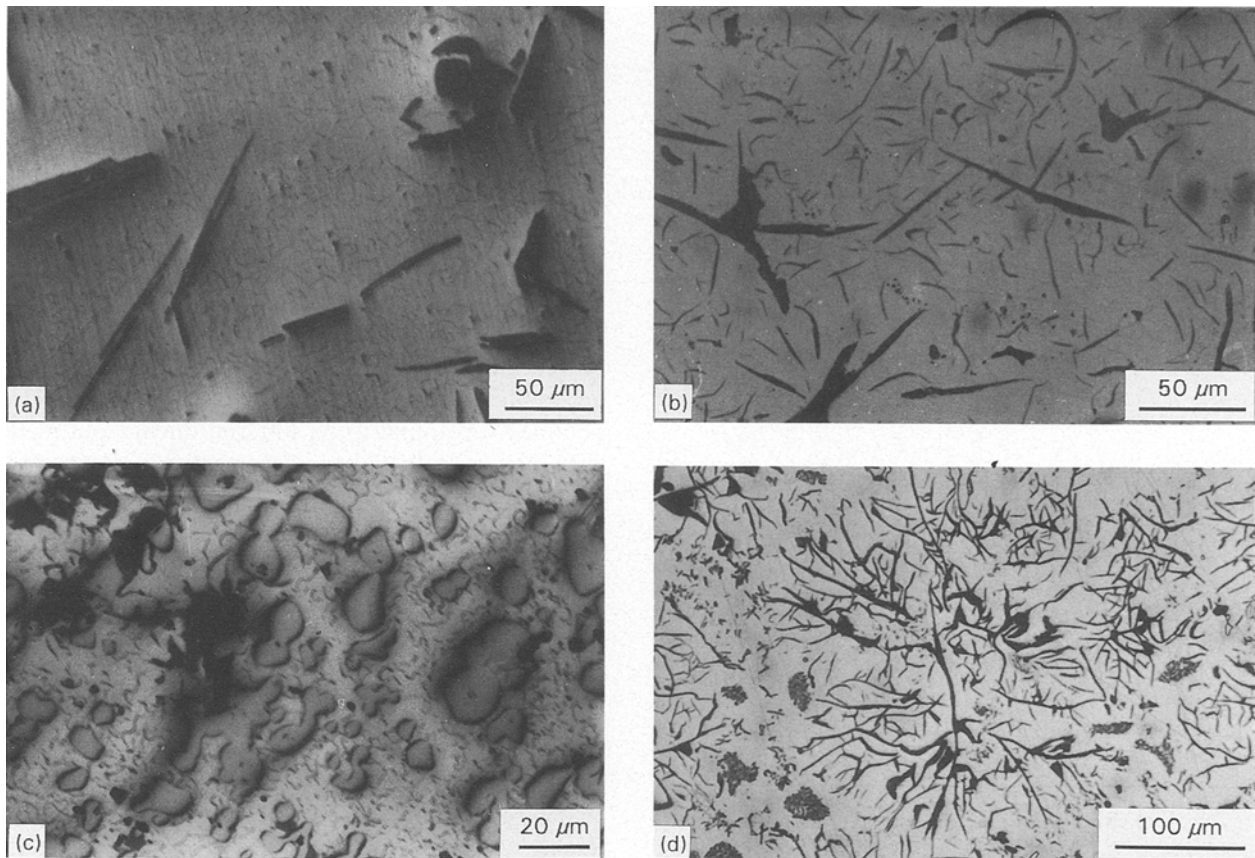


The resultant microstructure (Fig. 1d) showed large-scale graphite flake formation and some clusters of precipitates between the branching flakes. Microanalysis showed that the precipitates were rich in Al, probably alumina. The silicon was mostly dissolved in iron and the X-ray diffraction patterns for silicides were very weak. There was no dispersion of the filler phase and hence protection had not been achieved.

These results seem to suggest that the alumina did not form as a continuous film round to oxidized SiC particles but instead nucleated and grew only at selected points, leaving other areas of the filler open to attack by molten iron. It had already been demonstrated in experiment 23M that silica itself did not confer protection.

##### 3.2.2. Fe-Ti alloy with SiC

It has already been established in previous investigations [1, 5] that TiC is wetted by iron and that it can form *in situ* in ferrotitanium alloys if carbon is added. In experiments 33M and R37 it was hoped that Ti in solution in liquid iron would react with the carbon being released as the SiC decomposed, thus forming a protective layer round the filler particles. The results obtained in both cases, however, showed a fine dispersion of TiC in the matrix (Fig. 1c). There was no dispersion of SiC and in fact a fine graphite flake network was observed. It was concluded that a protective layer had not been achieved, even though TiC was formed, because of the fast diffusion of C in the iron. The fact that TiC had formed throughout the structure, including areas well away from the original SiC particles, indicates that the C had diffused away from the SiC faster than the Ti had diffused towards them.



**Figure 1** Microstructures of iron alloys levitated with SiC. (a) Most microstructures from levitated Fe + SiC samples showed a fine graphite flake network and sometimes big flakes too. (b) Typical microstructure from a high-carbon iron after levitation with SiC. (c) Rounded TiC particles, fine graphite flakes and a few large graphite modules after levitation of Z alloy with SiC. (d) Microstructure observed after levitation of Fe–Al alloy with oxidized SiC. Note clusters of alumina particles.

### 3.2.3. Fe–Ti alloy with carbon-coated SiC

In an attempt to effect protection of SiC filler material, a layer of carbon was deposited on the SiC by cracking a methane–hydrogen gas mixture (90% CH<sub>4</sub>, 10% H<sub>2</sub>) over the SiC. The SiC was then levitation-melted with Fe–5.2 wt % Ti at 1600 °C for 40 to 50 s. It was hoped that the carbon surface layer would react preferentially with the Ti of the matrix to produce a protective coating on the SiC particles by an *in situ* reaction. This, however, did not occur; the SiC particles decomposed, producing graphite flake formation in the matrix. The rapid diffusion of carbon into the matrix was again assumed to be the reason for the lack of protection.

### 3.2.4. Protection of SiC with Ni or Ni and Cu coatings

SiC coated with Ni or Ni and Cu, as previously described, was studied as a potential filler for incorporation into iron matrices. Table II details the form of protection conferred on these SiC samples. The protection available can be summarized as follows:

- (i) protection by the Ni or Ni and Cu layers,
- (ii) protection by the oxides of Ni and Cu after heating in air,
- (iii) protection by the silicides of Ni and Cu after heating under argon.

Levitation dispersion tests were performed at 1600 °C for a normal time of 1 min.

### 3.2.5. Ni and Ni–Cu protection

Protection at high temperature (1600 °C) was not achieved by this technique because both Ni and Cu melt at lower temperature (1453 and 1083 °C, respectively). This melting occurred so rapidly that the surface of the SiC was quickly left exposed to attack by the molten iron.

### 3.2.6. Protection by Ni and Cu oxides or silicides

Although the oxides and silicides of Cu and Ni were expected to be more resilient than the elements, they still did not prevent the decomposition of the SiC during dispersion at 1600 °C. In the case of experiments R24 and R26, the oxide or silicide scales were seen to be peeling off when the samples were shaken. It was hardly surprising, therefore, that they did not remain intact during the vigorous agitation of levitation melting.

### 3.2.7. Protection by Ni and Ni–Cu at low temperatures

Some sintering experiments were performed using carbonyl iron powder and coated SiC powders in the temperature range of 1000 to 1200 °C. Pellets of Fe + coated SiC were made by cold-pressing appropriate quantities of the constituent powders. These pellets were then heated in a tube furnace for various times. The experimental details are summarized in

TABLE II Protective coatings on SiC particles

Experiment	Treatment	Further treatment	X-ray analysis	Resultant coating	Comments
R23 <sup>a</sup>	Electroless Ni flash	None	SiC, trace Ni	Ni	Only a small layer of Ni deposited so not identified on the X-ray film
R23	Electroless Ni flash	Heated in air 1000 °C, 3 h	SiC, NiO, $\theta$ -Ni <sub>2</sub> Si, possibly $\delta$ -Ni <sub>2</sub> Si	Predominantly NiO	X-ray patterns of everything except SiC very weak; olive-green colour of oxide observed
R25	Electroless Ni flash	Heat in Ar 1000 °C, 3 h	SiC, $\theta$ -Ni <sub>2</sub> Si	Ni <sub>2</sub> Si	Again X-ray pattern weak but then change of colour confirms formation of silicide
R24 <sup>a</sup>	Electroless Ni followed by Cu flash	None	SiC, Cu, Ni	Ni, Cu	Cu easily detected, but for Ni only the strongest lines detected
R24	Electroless Ni followed by Cu flash	Heated in air 800 °C, 3 h	SiC, CuO, NiO?, $\theta$ -Ni, Si, possibly Cu <sub>3</sub> Si	Mainly CuO and NiO	Cu <sub>3</sub> Si lines very coincident with those of SiC; the dark grey scale on SiC peeled off fairly easily after shaking the bottle
R26	Electroless Ni followed by Cu flash	Heated in Ar 800 °C, 3 h	SiC, $\theta$ -Ni <sub>2</sub> Si, trace CuO, possibly $\gamma$ -Cu <sub>9</sub> Si	Suspect Cu <sub>3</sub> Si and Ni <sub>2</sub> Si	Small oxygen leak, giving trace oxides presence

Table III and typical microstructures of the products of sintering are shown in Fig. 2.

In experiment 43X, uncoated SiC was used and after the relatively short time of 3 h, reaction with the matrix had taken place and graphite and silicides were formed. Because of the high volume fraction of SiC used, there was usually some remanent carbide but it was surrounded by graphite and only loosely bound by the matrix. Fig. 2a illustrates clearly the graphite flake formation observed in experiment 43X.

When Ni- or (Ni + Cu)-coated powders were used, however (experiments 42X to 49X), very little reaction occurred between the matrix and the filler. The matrix obtained was found to be soft and ductile and there were no graphite flakes or cementite present. The matrix-filler interface was clearly defined (Fig. 2b-d) in most cases and there appeared to be good bonding between filler and matrix. As expected, there was a significant amount of porosity present in the matrix. It therefore appears that, although Ni is readily soluble in Fe, the rate of dissolution noted in the present study is sufficiently slow to maintain a protective coating on the SiC particles. Such dissolution could be further reduced by including Ni in the Fe matrix.

Some SiC powders were barrel-plated rather than coated by electroless flashing. This resulted in a much thicker protective layer of 80  $\mu$ m compared to 20  $\mu$ m. The degree of protection achieved in each case, however, appeared to be the same and it therefore appears that there is a little to be gained from barrel plating.

## 4. Discussion

### 4.1. SiC dissolution in liquid iron alloys

Phase equilibria in the Fe-Si-C system have recently been reviewed by Raghovan and Ghosh [6]. The solubility limit of SiC in molten Fe-Si-C alloys is well established. Without appreciable quantities of silicon initially present in the liquid iron, silicon carbide dissolution will clearly produce graphite saturation before silicon carbide saturation. The level of SiC additions made in the present study (about 10 wt %) would be expected to dissolve totally in liquid iron. The present study has shown that such dissolution occurs extremely rapidly and offers little hope of retaining undissolved SiC by the use of rapid processing in the liquid state.

### 4.2. Prospects for Fe-SiC composite production

The high reactivity between uncoated silicon carbide and iron-based alloys eliminates the possibility of forming a composite material with SiC and Fe which could be used for abrasive wear applications. Although during lower temperature (1000-1200 °C) processing some SiC remained unreacted, silicide formation and dissolution of silicon rendered the matrix brittle.

Attempts to provide protection for silicon carbide by the use of coatings have met with varying degrees of success. It has proved impossible to generate surface coatings of TiC by an *in situ* method, with TiC

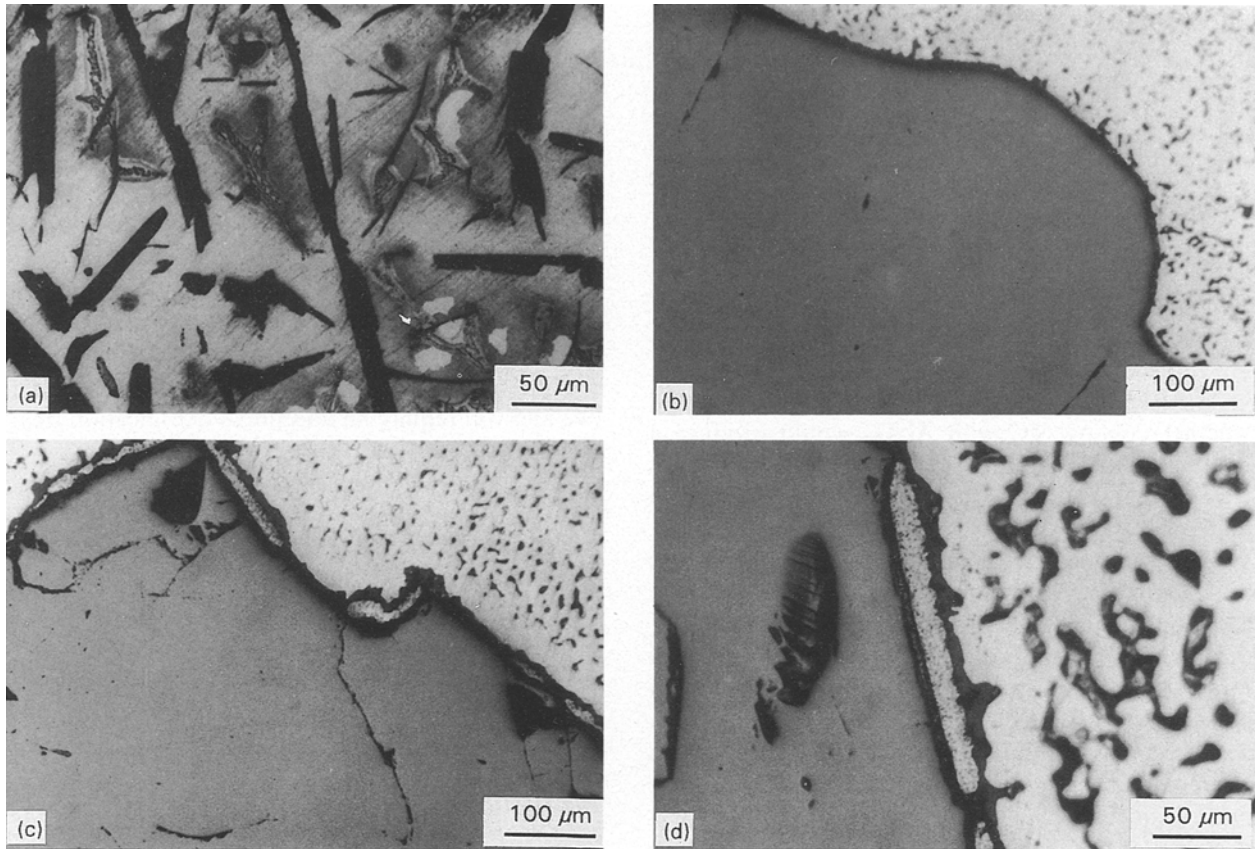


Figure 2 Microstructures of carbonyl iron sintered with Ni- or (Ni + Cu)-coated SiC particles. (a) Graphite flake formation after sintering unprotected SiC with carbonyl iron at 1200 °C. (b) Large SiC particle (dark grey) next to iron matrix (light grey) with porosity (black). The SiC was Ni-coated by electroless flashing. (c) Barrel-plated particles showing thicker interface regions. (d) Large magnification of interface after using SiC barrel-plated with Ni.

TABLE III Sintering experiments with carbonyl iron powder and coated SiC particles

Run	Filler	Weight of pellet (g)	Filler		Temperature (°C)	Time (h)	Phases identified by X-ray diffraction
			wt %	Vol %			
43X	SiC	5.62	17	33	1200	3	Fe, C <sub>gr</sub> , Fe <sub>2</sub> Si, SiC
41X	Ni-coated SiC (electroless)	6.73	12	25	1200	3	Fe, SiC, possibly FeSi, U <sup>a</sup>
46X	Ni-coated SiC (electroless)	6.12	17	33	1100	19	Fe, SiC
47X	Ni-coated SiC (barrel plating)	5.96	17	34	1100	42	Fe, SiC
48X	Ni-coated SiC (barrel plating)	6.03	17	33	1100	18	Fe, SiC
42X	Ni-coated then Cu barrel-plated SiC	4.74	18	35	1000	17	Fe, SiC
49X	Ni barrel-plated then Cu-barrel-plated SiC	5.95	17	33	1000	18	Fe, SiC, U <sup>a</sup>

<sup>a</sup> U = unidentified phase.

nucleation and growth apparently occurring preferentially in the bulk of the iron matrix. Precoating of the silicon carbide with titanium may facilitate subsequent nucleation and growth of titanium carbide on the silicon carbide surface; even then it is not clear just what degree of protection will be conferred by such a coating of titanium carbide and the economic viability of the whole process must be questionable. The pre-

coating of SiC by TiC or other carbides is almost certainly possible by a wide range of techniques, but at this stage it is difficult to see how the expense involved could be justified.

The present authors [7] have observed that an apparently continuous TiC layer forms on the surface of TiB<sub>2</sub> when brought into contact with solid iron alloys. There may therefore be scope for producing

protective TiC layers on SiC by *in situ* means during solid-state processing. Preliminary investigations are currently under way.

It has also proved impossible to produce a continuous layer of Al<sub>2</sub>O<sub>3</sub> on the surface of silicon carbide by *in situ* means. The formation and growth of metallic oxides is usually associated with volume and structural changes. Lateral constraints at interfaces can lead to descaling or microcrack formation and loss of protection. The Al<sub>2</sub>O<sub>3</sub> layer generated on the SiC during the present work is clearly incapable of providing protection against molten iron.

As Al<sub>2</sub>O<sub>3</sub> is not wetted by pure iron it is doubtful whether coating SiC with Al<sub>2</sub>O<sub>3</sub> would produce a good dispersion of SiC, unless further precautions were taken to modify the composition of the iron matrix.

Most intermetallic compounds, including silicides of Ni and Cu, tend not to be relatively stable in thermodynamic terms. It is not surprising, therefore, that they offered no protection to SiC against liquid iron in the present study. The inability to generate an adherent, continuous, protective layer of oxide which was observed with aluminium was also apparent with attempts to confer protection by the use of copper and nickel oxides.

Nickel and copper coatings have, however, proved successful in conferring protection to SiC during long-term sintering with iron at 1000–1200 °C. This offers the real opportunity of a route to Fe–SiC composite production. The material produced by such a sintering process is naturally very porous, and clearly some kind of densification procedure involving pressing or forging is essential if any useful component is to be manufactured. As some reaction of nickel-coated SiC has been observed during hot isostatic pressing with iron, there is obviously a need to keep such processing steps to minimal duration. Above all, however, the mechanical properties of the composite materials produced by such a route, and the overall economic viability of producing nickel-coated SiC, require detailed consideration as a next step.

## 5. Conclusions

The principal conclusions which can be drawn from this study are as follows.

1. Liquid iron alloys readily with SiC, resulting in silicon and carbon dissolution and iron silicide formation.
2. All attempts to provide protection for the SiC against liquid iron have proved to be unsuccessful.
3. Nickel coatings produced by electroless flashing have proved effective in preventing reactions between SiC and Fe during long-term sintering at 1000–1200 °C. The resultant product is, however, porous and will require an additional densification treatment.

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