

# Interaction of metals and alloys with silicon-based ceramics

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Silicon-based ceramics have been found to interact chemically with a number of metals and alloys when the materials were placed in physical contact in air at temperatures in the vicinity of  $1000^{\circ}\text{C}$ . Among the reaction products found after 100 h were silicides, silicates and carbides and the severity of the interaction depended on the temperature and the ease of migration of free silicon from the ceramic to the metallic phase. The occurrence of these reactions may be deleterious in applications in which silicon based ceramics and alloys are in contact for extended periods at high temperatures.

## 1. Introduction

The use of structural ceramics, such as silicon carbide and silicon nitride, in gas turbine engines has received increasing attention in recent years. These silicon-based ceramics offer significant benefits for use in hot components for such engines because of their excellent high-temperature strength and oxidation resistance. Of course, their inherent brittleness requires a new design technology, and this aspect of their use for high performance applications has been the subject of several intensive investigations [1].

This paper is concerned with another aspect of the use of ceramics in high-temperature engines that has not received the same attention. For any structural ceramic component in hot machinery, at some point the ceramic must come into contact with the metal support structure. Because of the relatively high thermal conductivity of the silicon-based structural ceramics, the points of contact between metal and ceramic may be at a high temperature, probably in excess of  $1000^{\circ}\text{C}$ . The possibility of a metal/ceramic reaction at these temperatures must be considered, as well as the effect of this reaction on the material properties. These reactions, if present, might be preventable by the use of suitable barrier coatings; but because of the increased processing complexity required by the use of coatings, they should not be employed unless necessary. Consequently, some knowledge concerning the nature,

severity, and temperature ranges of metal/ceramic reactions is needed.

Probably the largest amount of information available concerning solid-state metal/ceramic reactions has resulted from the work dealing with metal matrix composites. Much of this work has recently been summarized [2, 3], and it has been shown that such reactions can occur under certain conditions, even with such relatively stable oxide ceramics as  $\text{Al}_2\text{O}_3$ , with deleterious effects to both the metal and ceramic.

The investigation to be described in this paper deals with the reaction of several metals and alloys with three ceramic materials; Si/SiC, SiC, and  $\text{Si}_3\text{N}_4$ . The latter two materials are well known and need not be discussed in detail. Si/SiC, however, is somewhat different. This material, which has been developed recently [4], is formed by the infiltration of carbon fibres by liquid silicon. The subsequent reaction between the carbon and molten silicon forms polycrystalline  $\beta$ -SiC, which retains the original fibrous distribution of the carbon. From a chemical standpoint, this material resembles self-bonded silicon carbides, such as developed by the U.K.A.E.A.'s Springfields Laboratories [5]. Silicon carbide crystals are immersed in a matrix of silicon; and in view of the aggressive nature of silicon in reacting with almost all metals at elevated temperatures, the possibility of a metal/ceramic reaction must be seriously considered.

Several different types of reaction are possible between silicon-based ceramics and alloys, depending on the chemistry of the phases in contact, the temperature, and oxygen partial pressure at the interface. In an oxidizing environment, silicon-based ceramics are normally covered with a thin surface layer of  $\text{SiO}_2$  which can interact with certain metal oxides to form silicates which may be molten at elevated temperatures (e.g.  $\text{Fe}_2\text{SiO}_4$ ). Under conditions of very low oxygen partial pressure at the ceramic–alloy interface, silicon may diffuse into the metallic phase to precipitate refractory silicides (e.g.  $\text{CrSi}_2$ ) near the alloy surface or result in penetration of molten silicide phases (e.g.  $\text{NiSi}_2$ ) deep into the alloy substrate. In addition, depletion effects due to silicide formation may cause the growth of carbide phases. Also, impurity levels of silicon are known to promote the formation of brittle Laves and sigma phases in a wide range of alloys [6]. As the net result of all these interactions is to produce deterioration in the properties of the materials, it is important to consider the possibility of chemical reactions in applications where silicon-based ceramics and alloy phases are required to be in physical contact at elevated temperatures.

## 2. Experimental

### 2.1. Heat-treatment

All heat-treatments were conducted in a still air environment using a  $1200^\circ\text{C}$  capacity, 3.2 cm diameter tube furnace with a 7.6 cm uniform hot zone. The time for all specimen treatments was the same: 120 h. Temperatures between 950 and  $1150^\circ\text{C}$  were investigated.

The arrangement for conducting the reaction experiments is indicated in Fig. 1. Rough dimensions of the stack are indicated. Prior to assembly, the metal surfaces were polished on 600 grit SiC

paper, and the ceramics on a 220 mesh diamond wheel. All pieces were cleaned in alcohol prior to assembly. The metal/ceramic couple was held together by wrapping high-temperature wire around it. The specimen assembly was placed in an alumina boat and heated for 120 h at the temperature concerned. After heat-treatment, the metal oxidation products were brushed off and the reaction zone (if any) was examined. Characterization of the reaction zone was conducted using optical and scanning electron microscopy, electron microprobe, and X-ray analysis. No attempt was made to measure any strength degradation of the metal or ceramic. The observations to be described are phenomenological in nature; no detailed thermodynamic or kinetic aspects of the reaction were attempted at this time. Such analysis will be presented at a future date.

### 2.2. Materials

The ceramic materials used were hot pressed SiC and  $\text{Si}_3\text{N}_4$ , the former made in this laboratory and the latter manufactured by the Norton Co. The Si/SiC was fabricated in this laboratory and consisted of approximately 70% SiC, 25% Si, and 5% C. The pure Si used in some experiments was manufactured by the Materials Research Corporation and designated as Marz grade.\* The  $\text{SiO}_2$  was used in the form of fused quartz plates. The metals were used in the form of rectangular coupons machined from bars of round stock and were cut and polished through 600 grit silicon carbide paper before use. The metals employed in this study were: nickel 99.98% (Fe 0.002, C 0.01, Mn < 0.001, Cu < 0.001); cobalt 99.92% (Fe 0.002, C < 0.003, Ni 0.05, P < 0.003, Si < 0.001); chromium 99.5% (Fe 0.35, Si 0.019, Al < 0.007). Binary Ni–Cr and Ni–Al alloys were prepared by induction melting and casting in argon. The actual compositions of the alloys

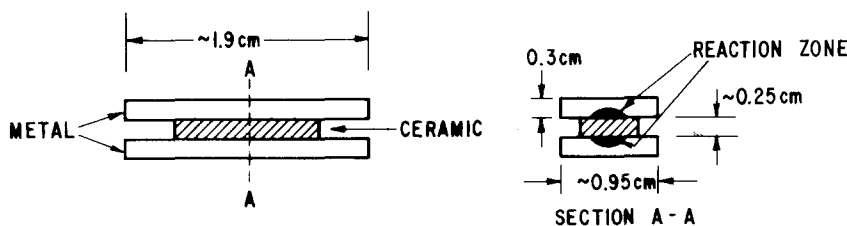


Figure 1 Schematic arrangement of ceramic/metal reaction couple and location of transverse section.

\* Oxygen:  $10^{16}\text{ cm}^{-3}$ ; metallic: non-detectable.

were Ni-49.8% (nominal Ni-50Cr) and Ni-29.3% Al (nominal Ni-30Al). The nickel-base superalloys used were IN-718 (nominal composition: Ni-19Cr-0.5Al-0.9Ti-3Mo-18.5Fe-5.1Nb) and IN-738 (nominal composition: Ni-16Cr-3.4Al-3.4Ti-8.5Co-1.7Mo-2.6W-1.7Ta-0.9Nb). The IN-718 was used as 0.292 cm thick sheet with a mill anneal; the IN-738 was solution annealed in argon at 1120°C, cooled in air, then precipitation treated for 24 h at 840°C in vacuum, and finally cooled in air again.

The majority of the work to be described in the following sections deals with Si/SiC. As will be seen, because of the presence of free silicon, the nature of the Si/SiC-metal reaction was more severe than either the SiC-metal or Si<sub>3</sub>N<sub>4</sub>-metal reaction, and indeed is governed by the presence of free Si. This, of course, should be true for any ceramic containing free silicon. In addition, it will be shown that in an air environment the reaction behaviour of SiC and Si<sub>3</sub>N<sub>4</sub> is governed by the presence of the protective SiO<sub>2</sub> surface layer, so basically these two materials react the same but in a completely different manner than those containing free Si.

### 3. Results and discussion

#### 3.1. Reactions of metals and alloys with Si/SiC composite

##### 3.1.1. Nickel

A number of reactions are possible between pure nickel metal and the Si/SiC composite, depending on the oxygen partial pressure or activity in the contact zone. The Ni-Si phase diagram [7] indicates that the silicide NiSi (m.p. 992°C) would exist in the liquid state at the reaction temperature of 1150°C, whereas other silicides, such as Ni<sub>3</sub>Si<sub>2</sub> (m.p. 1390°C), would be solid. In the presence of enough oxygen to form an SiO<sub>2</sub> layer on the ceramic, silicates might be expected to form at the metal-composite interface; however, the NiO-SiO<sub>2</sub> phase diagram [8] indicates that no liquid silicate phases would be expected below 1650°C. Nickel carbide is not stable at 1150°C.

Coupons of pure nickel heated in contact with the Si/SiC composite in air for 120 h at 1150°C developed a thick oxide scale with a glassy appearance on exposed regions of the metal surface.\* In the contact zone between metal and composite, an intense reaction had occurred.

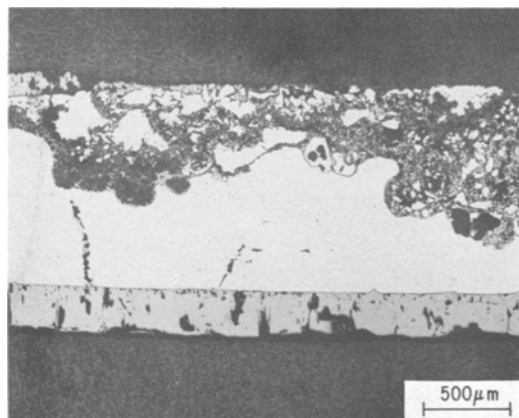
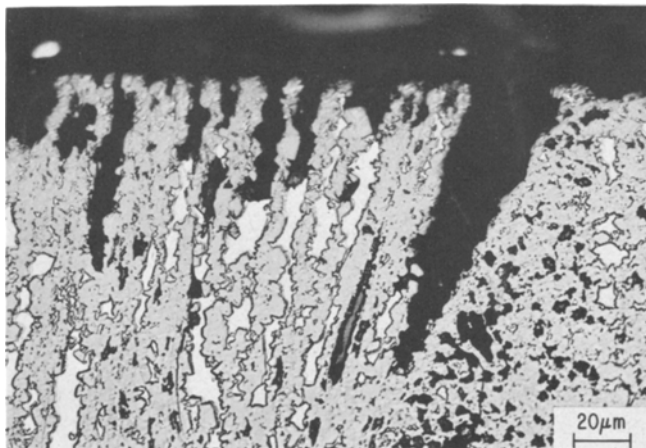


Figure 2 Section of Ni specimen after contact with Si/SiC composite for 120 h at 1150°C. Upper surface, which had been in contact with ceramic, shows deep penetration of silicides.

Fig. 2 shows a section of the metal coupon after this experiment. The thick oxide layer is clearly shown in the lower portion of the micrograph. The upper surface of the metal specimen, which had been in physical contact with the Si/SiC composite, was deeply penetrated by a dark liquid phase. A metallographic section of the Si/SiC composite in the region of contact with the metal is shown in Fig. 3. Depletion of silicon from the composite matrix is marked near the contact surface, leaving voids between the converted fibre bundles. Scanning electron micrographs of the surface regions of the nickel specimen in the contact zone are shown in Fig. 4. Crystals of NiO are shown growing beneath a fibrous mat of SiO<sub>2</sub> needles in Fig. 4a. In some localized areas, a solidified molten phase was observed beneath the NiO-SiO<sub>2</sub> surface zone (Fig. 4b). Electron microprobe scans of this molten phase confirmed that this reaction product was NiSi. The appearance of this liquid silicide is in fact very similar to that observed by Jackson [9] in SiC fibres embedded in nickel matrices after heating at 1000°C for 24 h. No evidence was found in the present work for the formation of a nickel silicate phase. X-ray diffraction examination of the nickel surface in the contact zone showed the presence of NiO, NiSi and  $\alpha$ - and  $\beta$ -cristobalite. It seems likely that the initial oxygen content of the narrow space between the ceramic and metal phases was insufficient to cover the whole Si/SiC composite surface with

\* Referring to Fig. 1, there was always a greater area of metal present than ceramic.



*Figure 3* Section of surface of Si/SiC composite after contact with Ni coupon in Fig. 1, showing depletion of Si between SiC fibre bundles.

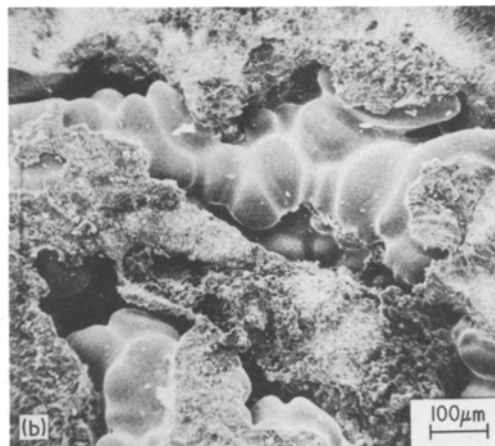
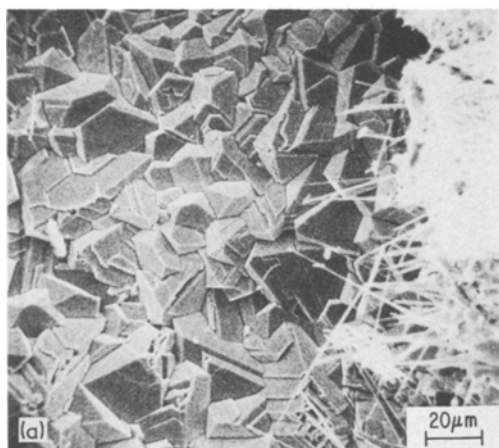
an SiO<sub>2</sub> layer thick enough to prevent silicon diffusion. Oxygen diffusion into the contact zone by gas phase transport being slow, the gettering action of surface silicon would reduce the oxygen partial pressure at contact points to very low levels. Hence, excess silicon would be free to diffuse directly into the metallic phase. It is also conceivable that silicon may migrate by a vapour phase process, perhaps as SiO (g) or SiO<sub>2</sub> (g). In general, the formation of silicide phases in the metal or alloy could be taken as an indication that very low partial pressures of oxygen were present at the ceramic–metal interface.

### 3.1.2. Cobalt

The Co–Si phase diagram [7] indicates that the silicides of cobalt all melt at temperatures above 1200° C and, in addition, no liquid silicates would be expected below 1380° C. However, the solid-

state reaction between SiO<sub>2</sub> and CoO is known to form cobalt silicate by an unusual type of surface diffusion process in which the silicate phase spreads out sideways across the CoO surface [10]. The morphology of this reaction, which is not completely understood, is shown schematically in Fig.5.

Coupons of cobalt metal held in contact with the Si/SiC composite and heated to 1150° C for 120 h in air developed a thick CoO layer over the exposed surface and were bonded firmly to the composite by a glassy reaction product in the contact zone. Detailed metallographic examination of the corrosion morphology was not carried out in this case; however, the surface of the metal in the contact zone was investigated by X-ray diffraction after the experiment and found to contain CoSiO<sub>4</sub>, Co<sub>2</sub>SiO<sub>4</sub>, CoO, α-cristobalite and silicon metal phases. No cobalt silicide or carbide was identified on the metal surface.



*Figure 4* SEM micrographs of surface of Ni specimen in Fig. 1, after contact with Si/SiC, showing (a) layers of NiO and fibrous SiO<sub>2</sub>, and (b) molten Ni silicide phase beneath oxide scale.

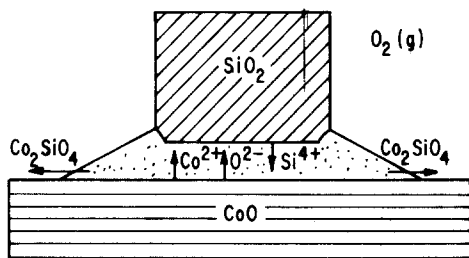


Figure 5 Schematic representation of growth of  $\text{Co}_2\text{SiO}_4$  on  $\text{CoO}$  surface during reaction with  $\text{SiO}_2$ , according to Schmalzried [10].

### 3.1.3. Chromium and Ni–Cr alloy

The complex Cr–Si phase diagram [7] shows the existence of a number of refractory chromium silicide phases, none of which melt below  $1300^\circ\text{C}$ . Chromium has a strong affinity for carbide formation, and the numerous chromium carbides are all highly refractory. Silicate-forming reactions between  $\text{Cr}_2\text{O}_3$  and  $\text{SiO}_2$  have not been identified. It would, therefore, be expected that pure metallic chromium would be relatively inert to Si/SiC at temperatures in the vicinity of  $1100^\circ\text{C}$ .

Coupons of pure chromium, when heated in contact with the Si/SiC composite in air at  $1150^\circ\text{C}$  for 120 h, showed only a slight degree of pitting at contact points, probably as a result of localized formation of chromium silicides by diffusion of silicon for short distances into the metal. The extent of interaction was, however, generally minimal.

An Ni–50Cr alloy specimen showed quite different behaviour. This alloy, which would normally be expected to form a protective  $\text{Cr}_2\text{O}_3$  scale when heated in air, showed extensive pitting

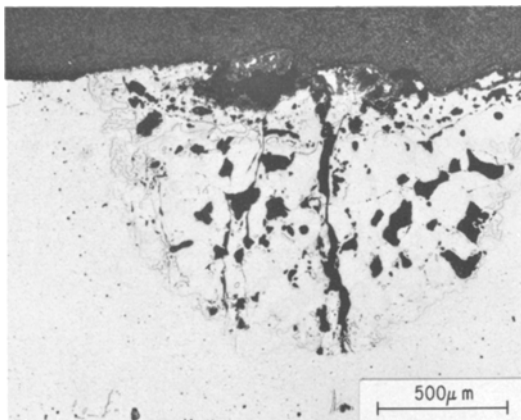


Figure 6 Section of Ni–50Cr alloy specimen in region of contact with Si/SiC composite after 120 h at  $1150^\circ\text{C}$ .

and localized attack when pressed in contact with the Si/SiC composite for 120 h at  $1150^\circ\text{C}$  in air. A section through the pitted contact zone (Fig. 6) revealed deep penetration of a liquid-like phase into the alloy substrate and extensive void formation and disruption of the surface. Scanning electron micrographs of the surface of the alloy in a pitted region are shown in Fig. 7. Typical surface features include a flaky, porous and exfoliated oxide scale (Fig. 7a), which proved to be  $\text{Cr}_2\text{O}_3$  on analysis by the microprobe. Beneath this scale a molten phase was clearly visible (Fig. 7b), which was rich in the elements Ni, Cr and Si. It appears that silicon had penetrated the disrupted  $\text{Cr}_2\text{O}_3$  surface scale to form a (Ni, Cr) silicide which was in the liquid state at  $1150^\circ\text{C}$ . It is interesting that Parratt [11] also

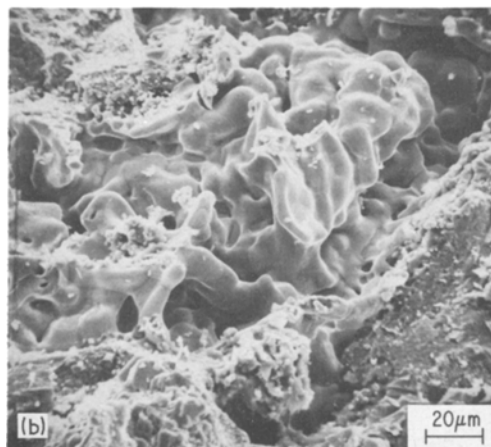
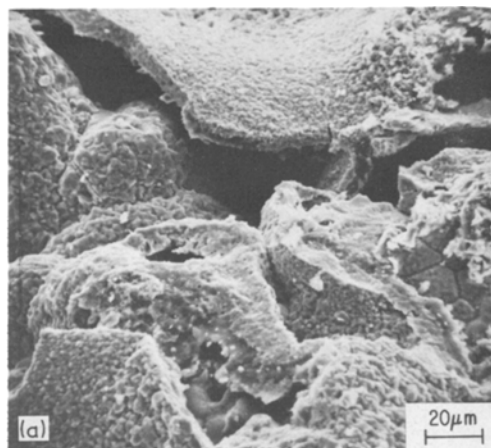


Figure 7 SEM micrographs of surface of Ni–50Cr specimen shown in Fig. 6, after contact with Si/SiC composite, showing (a) exfoliated  $\text{Cr}_2\text{O}_3$  scale, and (b) molten (Ni, Cr) silicide phase beneath oxide scale.

found SiC whiskers to be unstable in Ni–Cr alloy matrices at 1100° C.

### 3.1.4. Aluminium and Ni–Al alloys

Aluminium and silicon form a eutectic which melts at 577° C and contains 11.7 wt% Si [7], whereas Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> react only at high temperatures to form mullite, 3Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>, with a very high melting point. Also, as Al<sub>2</sub>O<sub>3</sub> is a more stable oxide than SiO<sub>2</sub>, reduction of Al<sub>2</sub>O<sub>3</sub> by metallic silicon would not be expected. However, at extremely low values of oxygen activity, aluminium metal can reduce SiO<sub>2</sub> to form free silicon.

Interactions between Al<sub>2</sub>O<sub>3</sub>-forming alloys and the Si/SiC composite were indeed found to be mild, and minimal reactivity was observed when pack-aluminided alloys of several types were heated in contact with the composite at 1150° C. An Ni–30Al (NiAl) showed some disruption of the oxide scale after this treatment, with the formation of minor amounts of a dark subsurface phase (Fig. 8) which was found to contain silicon. It is possible that diffusion of silicon metal from the composite through cracks in the Al<sub>2</sub>O<sub>3</sub> scale resulted in the formation of the low melting Al–11.7Si eutectic. With aluminided alloys in which a thick, dense and coherent Al<sub>2</sub>O<sub>3</sub> layer was present, this interaction did not occur.

### 3.1.5. Nickel-base superalloys

In actual practice, the metal support structure in contact with a ceramic will often not be a simple metal but a complex superalloy. Accordingly, a

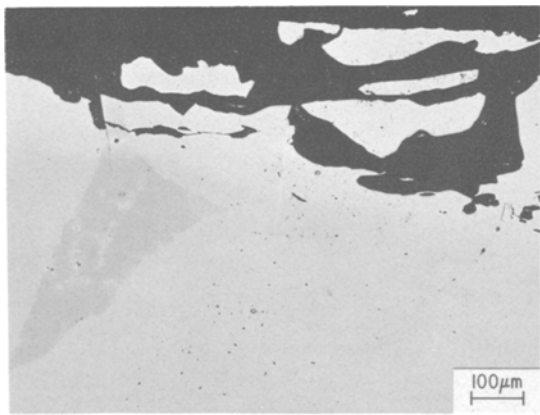


Figure 8 Section of Ni–30 Al alloy specimen in region of contact with Si/SiC composite after 120 h at 1150° C, showing fractured surface scale and penetration of Si-rich phase.

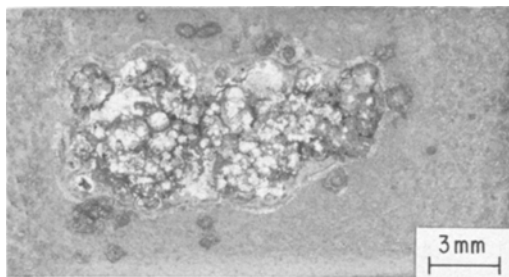


Figure 9 Surface appearance of IN-718 after reaction with Si/SiC for 120 h at 1150° C.

series of experiments at different temperatures (to determine the minimum temperature required to cause reaction) was conducted between IN-718 and Si/SiC between 950 and 1150° C.

At 1150° C severe pitting occurred on the alloy surface, as shown in Fig. 9. Pitting was also present, but much less severe, at 1050° C. At 1000° C pitting was barely detectable; at 950° C, no sign of a Si/SiC-718 reaction was found. In all cases where a reaction occurred, the Si/SiC exhibited surface depletion of Si, as shown in Fig. 3.

A transverse section of the metal reaction zone formed at 1150° C is shown in Fig. 10. The cracking probably occurred in cutting the metal. As may be seen, in addition to the normal air corrosion products, a reaction zone extends down into the metal to an extent of about 0.1 cm. The particles in the base metal, which also appear occasionally in the reaction zone, are probably titanium/niobium carbides. A more detailed section of the reaction zone some distance from the metal surface is shown in Fig. 11. Three primary phases are shown; a grey matrix phase

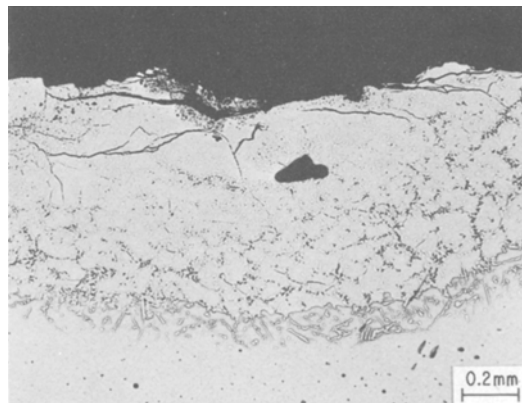


Figure 10 Section of IN-718 in region of contact with Si/SiC after 120 h at 1150° C.

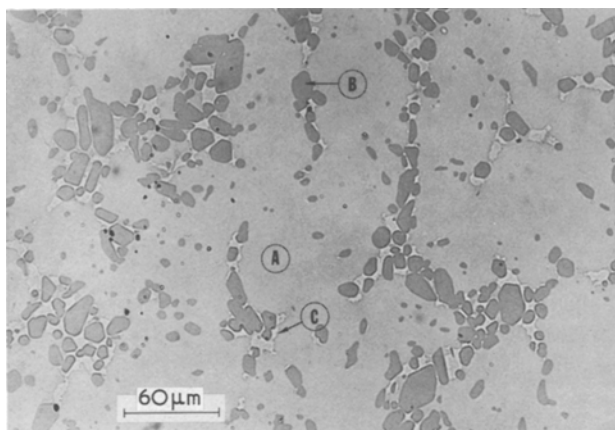


Figure 11 Reaction zone in IN-718 after exposure to Si or Si/SiC after 120 h at 1150° C. Letter identification of phases is used in Table I.

TABLE I Microprobe data for Si or Si/SiC/718 reaction products

Element	Weight concentration of indicated elements (%)				
	IN-718	A	B	C	
	Nominal*	Exp.			
Ni	50–55†	49.6	34.6	49.0	45.2
Fe	17	18.0	20.7	4.60	24.1
Mo	2.8–3.3	2.72	4.67	1.13	0.44
Si	0.35 max.	0.10	9.09	12.49	6.35
Cr	17–21	17.25	23.02	1.89	16.14
Ti	0.65–1.15	1.18	0.073	3.57	0.02
Nb	4.75–5.5‡	4.82	2.77	22.8	0.026
Ta	4.75–5.5	0.09	0	0	0
Al	0.2–0.8	—	—	—	—
P	0.015 max.	—	—	—	—
C	0.08 max.	—	—	—	—
Mn	0.35 max.	—	—	—	—
S	0.015 max.	—	—	—	—
Cu	0.1 max.	—	—	—	—
Total§	—	93.8	94.9	95.5	95.3

\* From vendor literature.

† Ni + Co.

‡ Nb + Ta.

§ Total is not 100% because there are other elements present besides those chosen for analysis.

(A), dark particles (B), and a light phase associated with the particles (C). Microprobe data for these phases, as well as the base metal, are shown in Table I. It seems clear that complex mixed silicides, some of which contain Nb and Ti, are present.

IN-738 showed somewhat similar behaviour. A coupon of this alloy, heated in contact with the Si/SiC composite for 120 h at 1150° C, developed deeply pitted regions in the contact zone, similar to that shown in Fig. 9. X-ray diffraction analysis of these corroded surface regions indicated the presence of a number of phases con-

taining silicon, including  $Ni_{16}Cr_6Si_7$ ,  $Co_2Si$  and  $Ni_2Si$ . Microprobe examination of sections of the alloy coupon beneath the pitted surface zone showed dark areas of (Ti, Nb) silicide particles which had formed in bands throughout the mm thickness of the alloy specimen. The appearance of this phase was similar to that shown in Fig. 11 for the IN-718 alloy. A liquid-like Al, Si-rich phase was also identified in the reaction zone.

To definitely establish that free silicon in the Si/SiC was responsible for the observed reaction behaviour, experiments were performed in an identical manner using pure Si in contact with IN-718 in place of Si/SiC. Precisely the same microstructure was obtained and gave identical microprobe results. Furthermore, when surface Si was removed by etching from Si/SiC, resulting in the structure as in Fig. 3, silicide formation was completely suppressed in IN-718, and the reaction zone shown in Fig. 12 was obtained. As

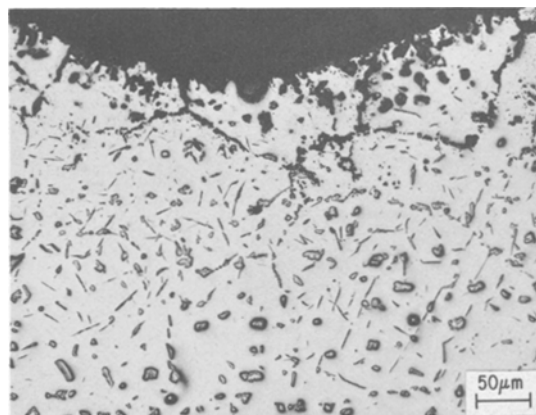


Figure 12 Reaction zone in IN-718 after exposure to Si depleted Si/SiC for 120 h at 1150° C.

will be seen in Section 3.2, this is typical of the reactions obtained with SiC and Si<sub>3</sub>N<sub>4</sub>.

It seems clear, then, that the Si present in Si/SiC is responsible for the severe attack in both simple and complex metals when the two materials are brought into contact with one another. As noted above, because of the limited access of oxygen to the contact zone, the composite surface in this region is not entirely covered with a protective layer of SiO<sub>2</sub> and hence silicon is free to diffuse into the alloy phase. It seems probable, then, that for the class of ceramics containing free silicon, protective coatings will be needed in order to prevent metal/ceramic reaction at temperature.

### 3.2. Reaction of alloys with SiC, Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>

Interaction studies involving alloys and SiC and Si<sub>3</sub>N<sub>4</sub> were carried out primarily with the IN-718 alloy. Some experiments with pure metals were also performed; and in all cases (including IN-718), the reaction with these ceramic materials was markedly less pronounced than when free silicon was present. Significant interaction did occur between SiC and strong silicide formers, such as nickel and cobalt, which showed slight pitting of the metal surface with the formation of minor amounts of liquid silicide phases, presumably formed by reactions of the type



The small extent of reaction, however, was probably an indication that much of the ceramic surface in the contact zone had been rendered inert by an SiO<sub>2</sub> layer.

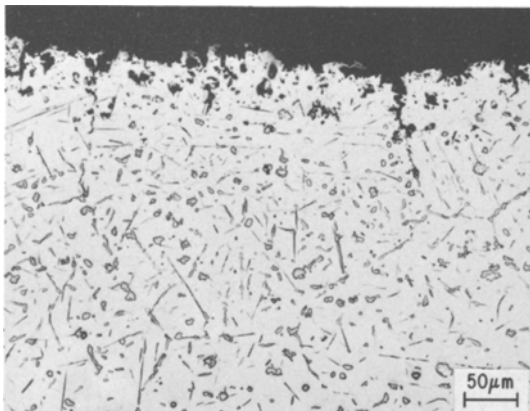


Figure 13 Section of IN-718 in region of contact with SiC after 120 h at 1150° C.

The reaction between IN-718, SiC, and Si<sub>3</sub>N<sub>4</sub> were studied at 1150° C in air. No systematic investigation of the reaction rate as a function of temperature was carried out, but experiments at 1000° C did not show any indication of an SiC/IN-718 reaction. The reaction products at 1150° C consisted of narrow zones containing fine needle-shaped particles and larger irregular-shaped precipitates, as shown in Fig. 13. The ceramic phase showed evidence of reaction at contact points and a slight discoloration of the ceramic surface was

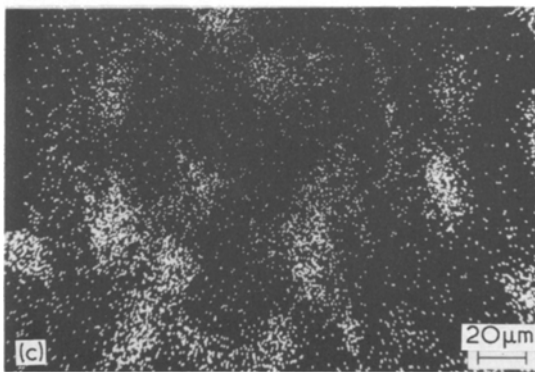
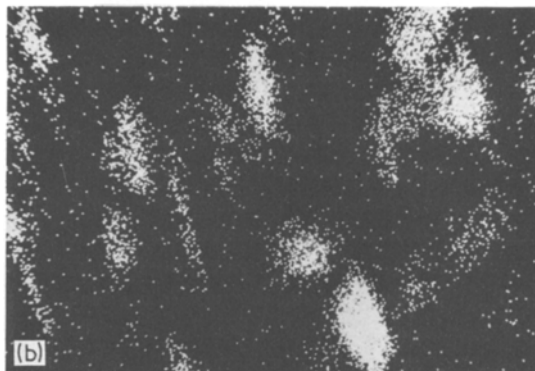


Figure 14 Electron probe photographs of SiC/IN-718 reaction zone, showing (a) specimen current image, (b) Ti X-ray image, and (c) Nb X-ray image.



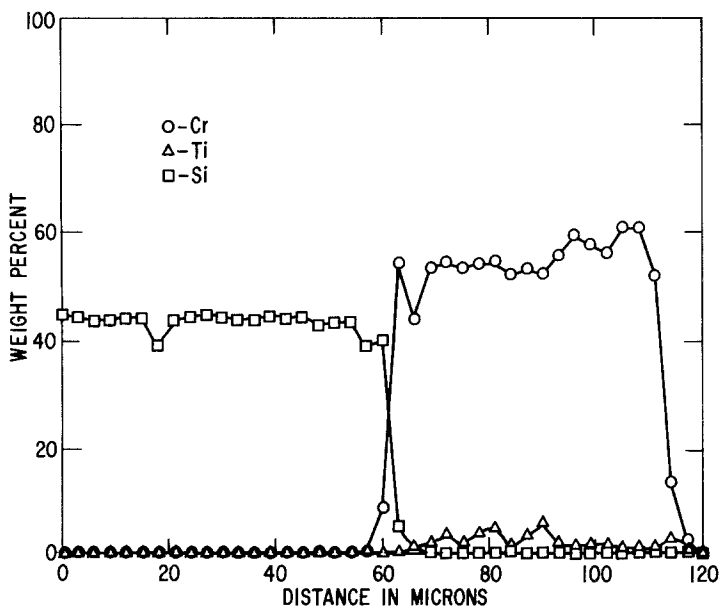
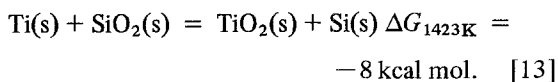


Figure 15 Electron microprobe data in discoloured region of  $\text{SiO}_2$  after exposure to IN-718 for 120 h at  $1150^\circ\text{C}$ .

noted in this region. Microprobe analysis indicated that the needles and the irregular particles in the alloy were rich in Ti and Nb, as shown in the X-ray maps in Figs. 14a, b and c. The concentrations of Si and oxygen were low in these phases, which were assumed to be carbides. Increased concentrations of Si and Cr were found in the matrix between the acicular particles, although discrete silicide particles were not identified.

Similar reaction morphologies and phase compositions to those shown in Fig. 13 were found when  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$  were used as the ceramic phase in contact with IN-718. Identical behaviour was also exhibited by the Si/SiC composite material after the surface silicon had been etched away (Section 3.1.5). Published thermochemical data [12] indicate that the vapour pressure of  $\text{Si(g)}$  over  $\text{SiC}$  is approximately  $10^{-7}$  atm at 1600 K, and it is conceivable that appreciable vapour phase transport of silicon could occur from SiC to an adjacent alloy phase even at  $1150^\circ\text{C}$  (1423 K). The mechanism by which free silicon is liberated from  $\text{SiO}_2$  is not entirely clear. Microprobe analysis of the discoloured region of an  $\text{SiO}_2$  specimen which had been in contact with an IN-718 coupon, indicated the presence of Ti, Cr, and Fe oxides, as shown in Fig. 15.  $\text{TiO}_2$  is, in fact, more stable than  $\text{SiO}_2$ , so that titanium diffusing from the alloy could form free silicon as a result of the reaction



Titanium in nickel-base superalloys is known to diffuse rapidly to the surface during oxidation at elevated temperatures [12]. The subsequent diffusion of small amounts of silicon into the alloy could result in the formation of chromium silicides in some regions and chromium-depletion and (Ti, Nb)-carbide precipitation in adjacent regions. The details of these processes are not, however, known.

Penetration of silicon into the alloy was much more marked when a low oxygen partial pressure was maintained in the environment. For example, when an SiC/IN-718 reaction couple was treated for the same time and temperature in a static vacuum ( $10^{-7}$  Torr), the reaction morphology in the alloy (Fig. 16) was similar to that found when free silicon was present (Fig. 11). Microprobe

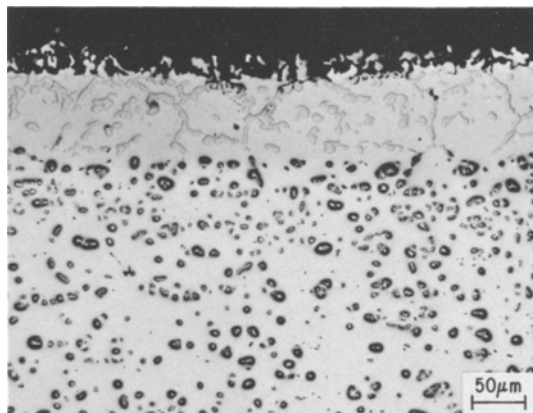


Figure 16 Section of IN-718 in region of contact with SiC in a static vacuum after 120 h at  $1150^\circ\text{C}$ .

measurements revealed high Si contents, with some of the phases being high in Ti and Nb, suggesting the presence again of complex mixed silicides. The composition of these particles was similar to that found when free silicon was present (Fig. 11). Microprobe measurements revealed high Si contents, with some of the phases being high in Ti and Nb, suggesting the presence again of complex mixed silicides. The composition of these particles was similar to but not exactly the same as for the Si/SiC. The SiC was not probed, but severe surface reaction was present, extending about 0.4 mm into the SiC. Under these conditions, SiC can decompose; and Si in the form of Si(g), or possibly SiO(g), can migrate into the metal to form silicides.

#### 4. Conclusions

From the results of this investigation, the following conclusions may be drawn:

(1) The reaction in air between metals and ceramics containing free silicon, such as Si/SiC, is governed by the presence of the silicon. Complex mixed silicides are found in the reacted metal, and the Si/SiC is depleted in silicon. The reaction does not occur appreciably at temperatures less than 950°C for the times studied ( $t \leq 120$  h). Because the SiO<sub>2</sub> protective layer is not sufficient to prevent these reactions, it will be necessary to use additional protective coatings for any ceramic containing free silicon.

(2) For the case of SiC and Si<sub>3</sub>N<sub>4</sub> in contact with IN-718 in air at 1150°C, the reaction is governed by the SiO<sub>2</sub> layer on the ceramic. Small local reactions occur, leading to the reduction of SiO<sub>2</sub> by titanium and causing particles high in titanium and niobium to precipitate from the alloy matrix. Again, it seems likely that reaction barriers will be necessary for service applications.

(3) For the same conditions in a static vacuum of 10<sup>-7</sup> Torr, SiC decomposes and silicides similar

to those in (1) above are formed on the metal surface.

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