

Degradation of oxidized SiC-Si₃N₄ in molten aluminium

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Silicon nitride-bonded silicon carbide ceramic tubes are used to provide indirect immersion heating in non-ferrous foundries. Samples of such tubes have been oxidized for varying lengths of time and then immersed in liquid aluminium. Long-term prior oxidation renders the ceramic susceptible to wetting by aluminium with subsequent degradation of mechanical properties. Samples not oxidized before immersion were stable in the liquid metal.

1. Introduction

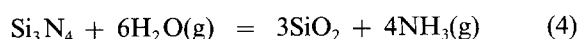
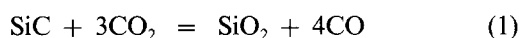
Modern non-ferrous foundries require clean, thermally efficient systems for melting and holding the casting material. Recently, indirect heating using immersion tubes has been applied to this situation [1].

Traditional methods of melting and holding require large refractory-lined bath structures and high energy inputs, reducing thermal efficiency. Because an immersion tube heats the melt by conduction rather than radiation, it can operate at temperatures close to that of the molten metal. The resultant reduction of required heat input increases efficiency, in some cases to ~65% [1].

The aggressive nature of the molten metal prevents the use of most metal tubes, so that ceramic materials must be used. Silicon carbide (SiC) ceramics have been found to exhibit excellent thermal conductivity and thermal shock resistance, and are relatively easy to fabricate. They have proved very successful in several applications [2].

British Gas is developing this technology using a silicon nitride-bonded silicon carbide ceramic for the immersion tubes. This material was chosen because it is easily fabricated and is considered to be resistant to attack by molten aluminium, one of the metals to be processed using the new system. The compatibility of SiC with aluminium has allowed the manufacture of SiC fibre-reinforced aluminium composite materials [3].

During service, tube performance was inconsistent, with many tubes failing prematurely. Preliminary work revealed the following points. The heater operates by gas combustion inside the tubes, and the CO₂ and H₂O formed can oxidize the ceramic. Possible reactions are



The silica is then wetted by, and can react with, molten

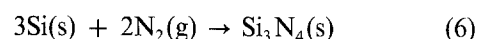
aluminium, according to



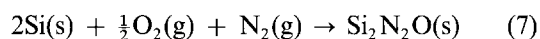
In this paper we report the investigation of the oxidation with subsequent degradation by liquid aluminium of the nitride-bonded silicon carbide ceramic, and propose mechanisms of interaction.

2. Materials

The ceramic was produced by a reaction-bonding process. A mixture of silicon and silicon carbide grit was nitrated at 1400°C to produce silicon nitride-bonded silicon carbide.



Admission of oxygen causes further reaction, giving silicon oxynitride (Si₂N₂O) which also bonds the SiC.



Silicon oxynitride has also been found to possess excellent refractory properties [4].

The heat exchanger tubes are then trimmed and shaped before installation. A large section of such a heat exchanger tube was supplied by British Gas, Midlands Research Station.

3. Experimental procedure

Samples of the ceramic were cut using a low-speed saw fitted with a diamond-edged blade. They were ultrasonically cleaned and mounted in conducting bakelite. Grinding and polishing were carried out slowly using successively decreasing SiC paper and diamond paste finishing at 0.5 μm. This careful preparation eliminated grain pull-out.

Samples for the oxidation test were also cut on the low-speed saw to approximate dimensions of 18 mm × 13 mm × 6 mm and ground and polished on all faces with 180 SiC paper. This was felt to reproduce the surface finish of the ceramic tubes in their industrial application. The specimens were then ultrasonically cleaned to remove any further contamination. This did not, however, remove some machine oil (from the manufacturing process) still

present in the surface pores. Thus the samples were heated for approximately 10 sec at 1000° C to burn off this impurity.

The degree of oxidation was measured by determining the mass change per unit surface area of coupon after oxidation for a set period of time. Coupons were oxidized in air in a resistance-heated tube furnace. A series of coupons were oxidized at 1000° C for times of 1, 2.5, 4, 8, 20, 48, 72 and 138 h. One coupon was oxidized in air at 1365° C for 72 h.

After weighing, coupons which had been oxidized for 20, 72 and 138 h at 1000° C were sectioned, and a portion mounted for scanning electron microscopy. A segment of the coupon oxidized at 1365° C was similarly mounted.

In order to monitor the progress of oxidation with time, certain of the coupons' compositions were investigated using X-ray diffraction (XRD). The analysis was carried out on four samples: (a) as-cut, (b) after 8 h oxidation at 1000° C, (c) after 20 h oxidation at 1000° C, (d) after 72 h oxidation at 1000° C. Three specimens were prepared as previously for exposure to molten aluminium. One sample was left unoxidized whilst the other two were oxidized in air at 1000° C for 48 and 138 h respectively. All three were then held immersed in molten LM6, an Al-12 wt % Si casting alloy at 750° C for 1 wk. At the end of this period the samples were removed from the melt, excess aluminium ground from the surface and specimens prepared for SEM and optical examination.

4. Results and discussion

4.1. Initial microstructure

The macro appearance of the ceramic showed a light grey silicon nitride matrix containing darker grains of silicon carbide of approximately 0.5 mm in size (Fig. 1a).

Reflected light microscopy showed the carbide grains to contain a distribution of very fine pores (Fig. 1b) and some larger (~ 150 μm) pores which are usually open, as nitride phase can be seen within them (Fig. 1c).

A scanning electron micrograph shows the nitride binder phase to have high porosity (Fig. 1d). A density of 83% theoretical was measured, i.e. 17% porosity. Reaction-bonded ceramics typically have porosity values of ≈ 20% [5].

4.2. Oxidation

Initial results showed a mass loss after oxidation. This effect has been noted before, due to the formation of volatile SiO. However, SiO exists in appreciable quantities only at temperatures above 1600° C [6] and/or low partial pressures of oxygen [7, 8], and it seemed unlikely that these reactions could be occurring in this case. It was found that an impurity was burning out of the bulk of the ceramic, igniting about 30 sec after insertion of the coupon into the furnace.

After removing this impurity the weight gain upon oxidation was measured up to 138 h at 1000° C (Fig. 2). It can be seen that very rapid initial oxidation occurs with most of the increased weight being gained within the first 10 h, the coupon thereafter being protected by the film formed. The one result for the higher temperature testing indicates a lower overall weight gain. When removed from the furnace, coupons had a thin layer of silica on the SiC grains, visible by interference tints and the macro appearance was that the coupon was slightly darker. Optical microscopy revealed little difference. The degree of porosity was similar, and some carbide grains were cracked, probably due to thermal shock (Fig. 3a). In the SEM, the surface relief was seen to be very similar to the unused sample (Fig. 3b).

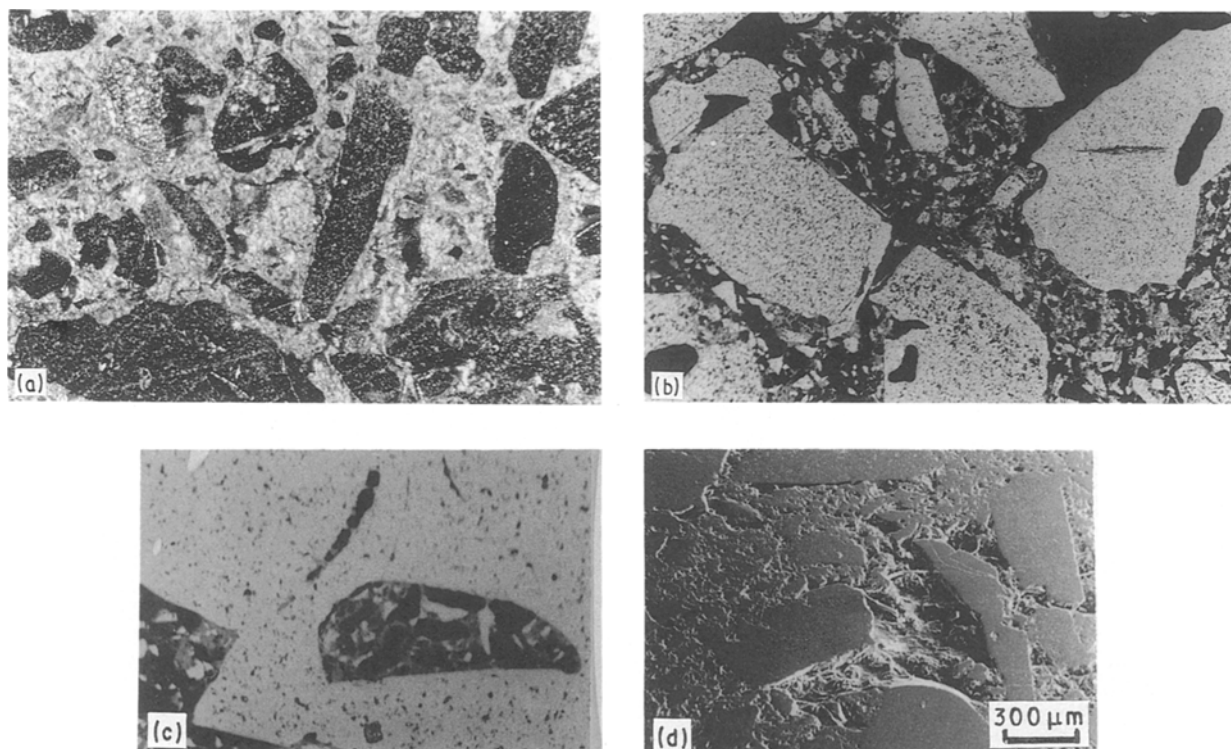


Figure 1 Optical and scanning electron micrographs of SiC-Si₃N₄ microstructure.

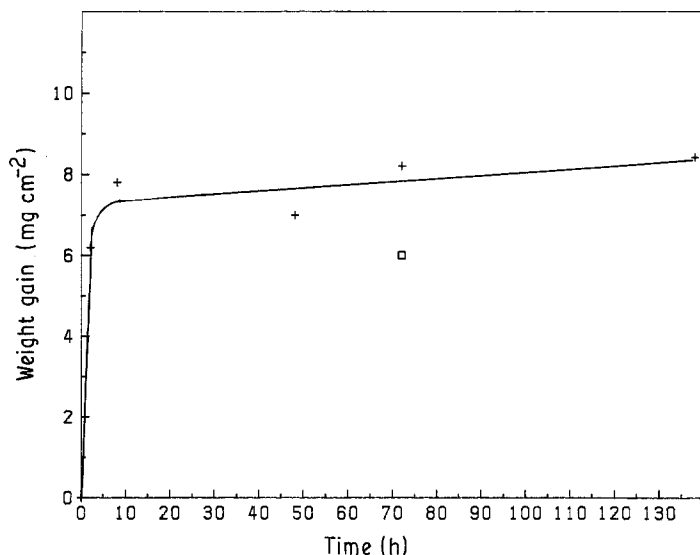
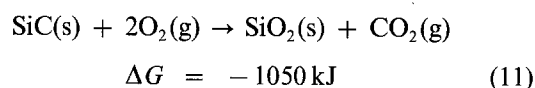
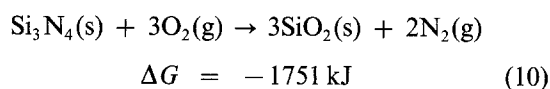
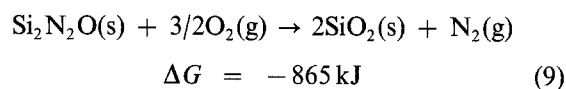
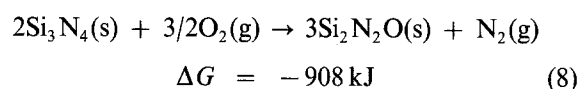


Figure 2 Weight gain plotted against time of oxidation for the ceramic. Oxidative weight gain of SiC/Si₃N₄. (+) 1000 C, (□) 1365 C.

The reproducibility of the weight gain data was not good although it has been noted elsewhere that due to the complex oxidation behaviour of non-oxide ceramics, the reproducibility of oxidation data for these systems is poor [9]. The method of sample preparation and type of furnace used can also affect the results obtained [10–12].

The data approximated parabolic behaviour although with decreased weight gains at longer times. Parabolic oxidation kinetics are typical of a diffusion-controlled reaction and previous work has found that parabolic oxidation occurs for both silicon carbide and silicon nitride [13] and it has been concluded that diffusion through a surface layer of silicon oxide is the rate-determining step. It has been suggested that, in a furnace without a flow of oxygen, this surface layer could be gaseous SiC [10], but most other authors agree that the oxide is solid silica, SiO₂. There is evidence that when sintering aids such as magnesia, MgO, or calcia, CaO, have been used, diffusion of Mg²⁺ or Ca²⁺ ions through the silica controls the reaction [7, 14]. For ceramics prepared without sintering aids, oxygen diffusion through the silica film is rate-determining [7, 15–17]. Some success has been had in linking oxidation kinetics of Si₃N₄ to asymptotic closure of pores by silica, a process which gives slightly altered behaviour [18]. Good agreement existed between this work and the previous literature.

The four possible oxidation reactions, with their free energy values at 1000° C, are shown below. Free energy data was obtained from standard sources [19–21].



All the reactions are strongly favoured by thermodynamics, yet it was found that more oxidation occurs on the silicon nitride. This behaviour is due to the differing porosities of the carbide and nitride phases.

The silicon carbide had little porosity, and oxidation occurs on the exposed surface of the grains. The kinetics of this reaction are parabolic, so that once the surface is sealed (when the oxide film is ~ 1 μm thick) the reaction slows.

The silicon nitride/oxynitride is very porous, and this gives a large surface area on which reaction can occur. Initial reaction occurs mainly within the pores

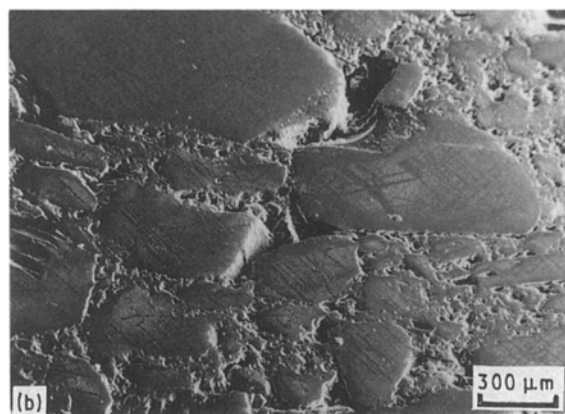


Figure 3 Optical and scanning electron micrographs of SiC-Si₃N₄ microstructure after oxidation.

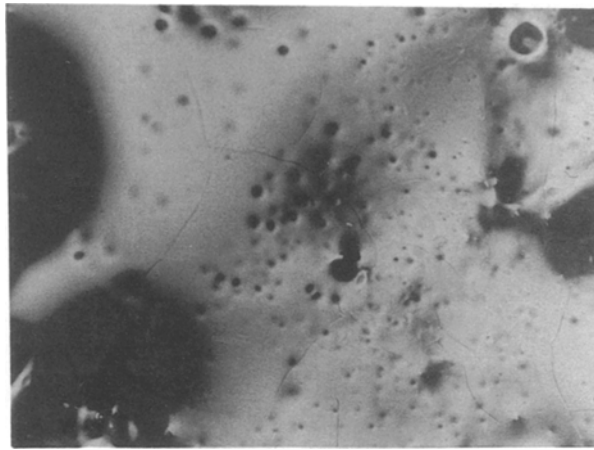
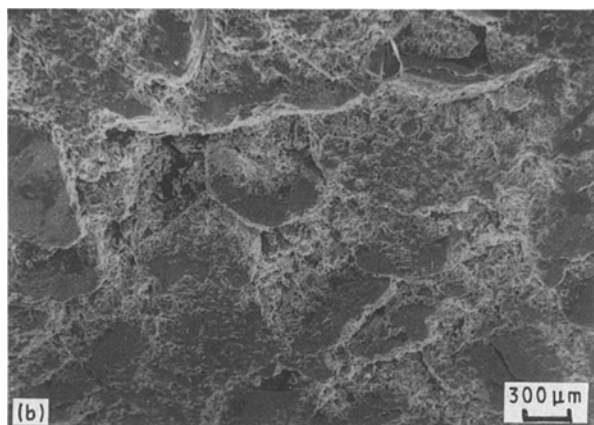
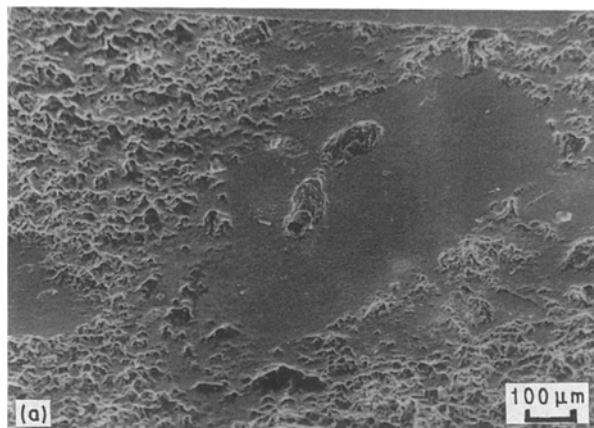


Figure 4 Cracking in the silica layer formed on the ceramic after oxidation at 1365°C for 100 h and subsequent cooling.

(internal oxidation), depositing SiO_2 on pore walls until the channel radius is too small for effective oxygen diffusion. Oxidation then occurs on the surface (external oxidation) at a reduced rate. The extent of internal oxidation depends on porosity and pore radius [16, 18]. X-ray diffraction results showed that the initial ceramic contained SiC , Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$ (silicon oxynitride) and a small amount of tridymite (formed during tube manufacture). At 1000°C the Si_3N_4 oxidized to form SiO_2 (cristobalite) the amount of cristobalite increasing with increasing time at temperature. A similar result has been reported [17]. This oxidation occurs within the pores of the silicon nitride, with little external reaction, because the ceramic surface relief is retained.



The intensity of most of the XRD peaks due to $\text{Si}_2\text{N}_2\text{O}$ fell as oxidation time increased, although some increased after a longer time. This could be attributed to texturing effects, but it is possible that at longer times, when external oxidation operates, the oxygen flux through the silica layer is reduced so that the complete oxidation of Si_3N_4 does not occur, and formation of the oxynitride takes place instead.

At high temperature (1365°C) both external and internal oxidation are important and occur more rapidly, so that the material surface is quickly sealed. Thus, the mass gain is less than at 1000°C. The silica must again exist as cristobalite. It is presumably formed as β -cristobalite, and transforms to α cristobalite on cooling through the range 270 to 200°C. This transformation has an associated 1% volume change, which causes the observed cracking of the silica layer (Fig. 4).

The coupon oxidized at 1365°C had a thick coating of silica when removed from the furnace. The silica covered the coupon, sealing most pores in the nitride phase. Microscopic examination showed the silica to be cracked in an irregular network with an average crack spacing of $\sim 150 \mu\text{m}$ (Fig. 4).

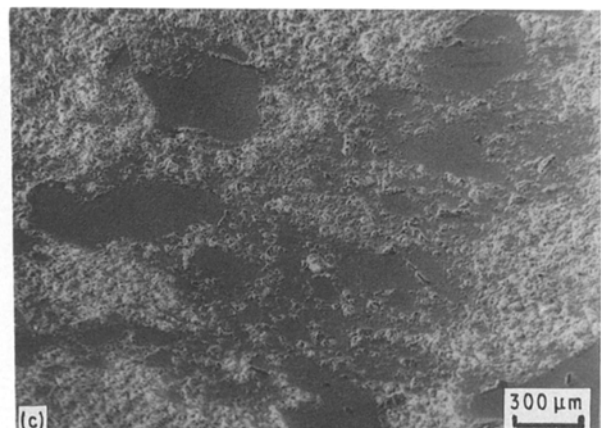
As at lower temperatures, reaction has occurred principally in the nitride phase. The formation of silica involves a volume increase, so that the SiO_2 expands across the surface, including the carbide grains. Scanning electron microscopy of coupons oxidized for 20, 72 and 138 h shows that reaction occurs mainly on the silicon nitride (Fig. 5). The extent of reaction is only slightly greater at longer times than at 20 h. There is little damage to the silicon carbide grains, and it appears that a thin ($\sim 1 \mu\text{m}$) protective layer of SiO_2 forms.

Scanning electron micrographs show the silica sealing all but the largest pores (Fig. 6a). The SiO_2 layer is $\sim 20 \mu\text{m}$ thick. Again, it can be seen that reaction has occurred primarily in the nitride phase (Fig. 6b).

4.3. Degradation in liquid aluminium

The coupon which had not been pre-oxidized but had been aluminium dipped only was not damaged by this contact. The aluminium had not wet the ceramic surface and no attack had occurred (Fig. 7).

Figure 5 Scanning electron micrographs taken after (a) 20, (b) 72 and (c) 138 h showing oxidation primarily in the nitride phase.



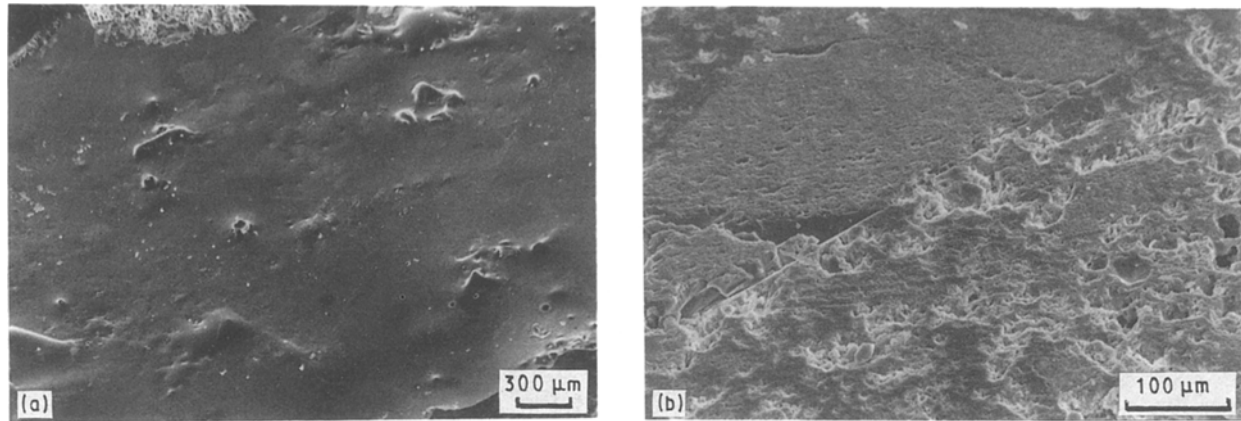


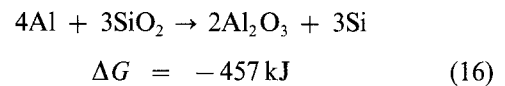
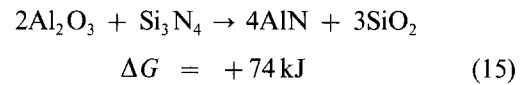
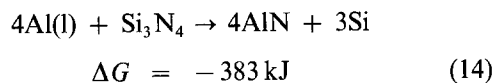
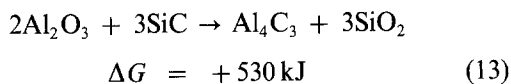
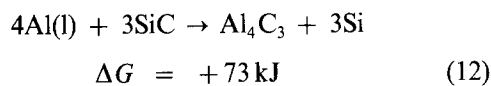
Figure 6 (a) Glassy layer of SiO₂. (b) Oxidation primarily in the Si₃N₄ phase.

After pre-oxidation for 48 h, the molten aluminium did wet the ceramic surface but no reaction appeared to have taken place (Fig. 8a). However, the coupon fractured while being removed from its holder. The fracture took place, through the nitride bonding phase, and cracks deflected around silicon carbide particles (Fig. 8b).

The coupon oxidized for 138 h suffered extensive damage in the molten aluminium and fractured extensively on removal from the melt. The fracture path was again mainly through the nitride phase.

There was a dark border around the coupon edges and the aluminium had wet the material surface, and penetrated into large pores in the nitride phase to a depth of ~ 1 mm in some cases. Both α and β forms of Si₃N₄ were visible within these pores. No aluminium attack on the carbide was observed (Fig. 9).

Some work has investigated the molten salt corrosion of silicon nitride [22, 23] but there is little reported literature on molten metal degradation. There are five reactions which might occur during liquid aluminium attack on silicon carbide/silicon nitride. These are shown with free energy values (for pure substances [19]) at 750° C.



It is evident that Reactions (13) and (15) will not occur. Also, attack on silicon carbide by aluminium is not favoured, and is one reason why this ceramic was chosen for use in immersion tubes. However, molten aluminium should attack silicon nitride, but as the aluminium does not wet the unoxidized ceramic there is no reaction. If the ceramic has been oxidized, it is vulnerable. The aluminium wets the material surface and Reaction (16) is strongly favoured.

The observed aluminium/ceramic interactions are in agreement with these points. Unoxidized ceramic is not wetted nor degraded by molten aluminium. Oxidized coupons are wetted and their mechanical properties adversely affected.

It has been found [17] that oxidized specimens of silicon nitride had higher yield strengths than unoxidized material. This effect was explained by treating the pores in the Si₃N₄ as flaws in the ceramic, and applying standard fracture theory. The silica formed by oxidation acted in two ways.

(i) Due to the volume increase during oxidation, silica partially filled the pores, reducing their size and blunting them;

(ii) increased the surface energy within the pore. Both effects increase the fracture yield strength, given by

$$\sigma_f = \frac{1}{A} \frac{(2E\gamma)^{1/2}}{(C)} \quad (17)$$

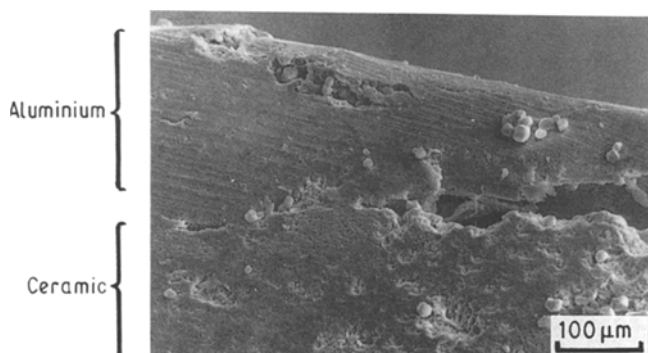


Figure 7 Layer of aluminium on the non-oxidized SiC-Si₃N₄ ceramic not wetting the substrate.

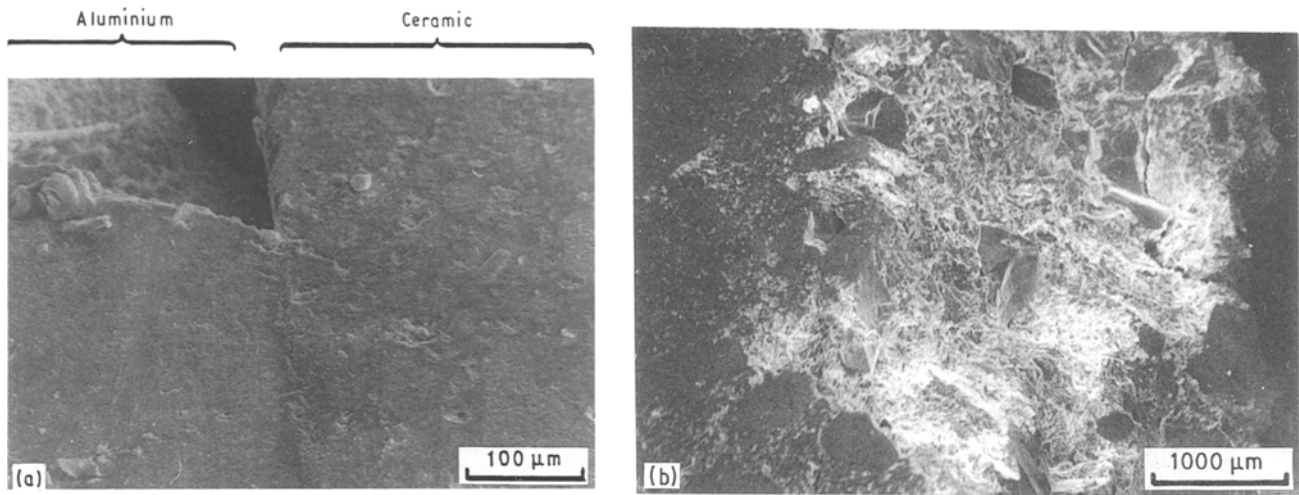


Figure 8 (a) No wetting by liquid aluminium after 48 h oxidation. (b) SiC particles standing proud on the ceramic surface after fracture.

where σ_f is the yield strength (N m^{-2}), A is a geometrical factor, E the Young's modulus (N m^{-2}), γ the surface energy (J m^{-2}) and C the flaw size (m).

The results obtained in this work suggest the following mechanism for liquid aluminium corrosion and embrittlement of the nitride-bonded ceramic. When molten aluminium contacts the oxidized ceramic, it wets it, penetrates the pores in the silicon nitride, and reduces the silica. Thus, the silica is removed from the edges of the pore and replaced locally by a mixture of silicon and alumina. The crystallographic form of this mixture has not been investigated in this work but it is unlikely that it will form as the normal structure of bulk alumina and silicon. Indeed, if these two crystalline materials replace the glossy silica the effect may be effectively to re-sharpen the crack tip thus leading to the observed decrease in fracture strength. Surface energy effects would not be expected to play a part as reported values of surface energy for SiO_2 , Si and Al_2O_3 are all in the range 1 to 10 J m^{-2} [24]. The silicon carbide is essentially unaffected by the liquid aluminium. The thin film of silica is removed from the grain surface, exposing the unreactive carbide. In service the degradation manifests itself as tube failure. Changes in crack characteristics mean that the tube yields under its own weight.

This principle can be applied to determine which

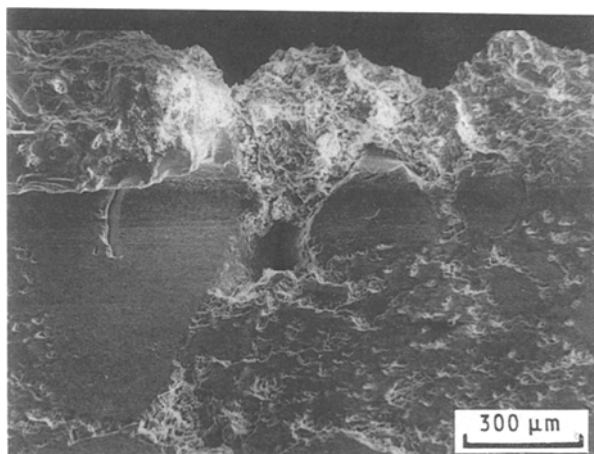


Figure 9 Aluminium layer wetting the ceramic surface pre-oxidized for 138 h at 1000°C .

liquid metals will degrade the oxidized ceramic. Any metal which will wet and react with silica will cause crack de-blunting and lead to failure. On the basis of thermodynamics, liquid aluminium, lithium and magnesium would be expected to give degradation. Melts containing these metals would attack the ceramic immersion tubes. Damage from melts of other technologically useful metals, such as zinc, results from normal thermal shock mechanisms, because reaction with silica would not be thermodynamically favoured.

5. Conclusions

Ceramic tubes are used in immersion heating systems for melting and holding non-ferrous casting alloys. The present work investigated the oxidation and liquid-aluminium corrosion of one currently used tube material, a silicon nitride/oxy-nitride-bonded silicon carbide ceramic.

Coupons of the ceramic were oxidized in air at 1000 and 1365°C for a range of times up to 138 h. Mass gain was recorded, composition was determined using XRD techniques and near-surface features were observed using optical and electron microscopy. The following conclusions were drawn.

1. The oxidation kinetics are approximately parabolic, as has been reported elsewhere.
2. Oxidation occurs principally in the porous silicon nitride phase. Reaction takes place internally at 1000°C and externally at 1365°C . The main oxidation product is cristobalite, a polymorph of silica.

Coupons, oxidized for 10, 48 and 138 h at 1000°C , were immersed in molten aluminium alloy at 750°C for 1 wk. The following points were determined.

4. Unoxidized material is not wetted by nor reacts with molten aluminium.
5. Oxidized ceramic is wetted by and reacts with molten aluminium. The result is serious degradation of the material, and mechanical failure at low stresses.

It is suggested that the mechanism for this attack involves crack de-blunting due to the removal of in-pore silica by reaction with liquid aluminium.

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