*Int. J. High Technology Ceramics* **2** (1986) 279–290

# Corrosion of SiC, $Si_3N_4$ and AlN in Molten $K_2SO_4$–$K_2CO_3$ Salts

Tsugio Sato, Yoshimi Kanno and Masahiko Shimada*

Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Sendai 980, Japan

## SUMMARY

*Silicon carbide, silicon nitride and aluminium nitride ceramics were immersed in potassium sulphate–potassium carbonate melts in air or in a nitrogen atmosphere at 1013–1200°C to examine their corrosion behaviour. Aluminium nitride ceramics exhibited great resistance to corrosive attack from potassium salts under these conditions, exhibiting only a slight weight loss. Silicon carbide ceramics dissolved slowly in molten potassium carbonate ($K_2CO_3$), but rapidly dissolved in both potassium sulphate ($K_2SO_4$) and 50 mol% $K_2SO_4$–50 mol% $K_2CO_3$ melts. The weight loss of silicon carbide in these potassium salt melts was larger in air than in nitrogen. Silicon carbide ceramics reacted with $K_2SO_4$ melt quantitatively and the stoichiometry of $K_2SO_4/SiC$ was 0·8. On the other hand, the weight loss of silicon nitride ceramics was appreciable in all potassium salt melts. The reaction between $Si_3N_4$ and $K_2SO_4$ or $K_2CO_3$ proceeded quantitatively and the stoichiometry of $K_2SO_4/Si_3N_4$ and $K_2CO_3/SI_3N_4$ was 1·6 and 3·5, respectively. The presence of oxygen accelerated the reaction between $Si_3N_4$ and $K_2CO_3$, but greatly retarded the reaction between $Si_3N_4$ and $K_2SO_4$, due to the formation of a protective film. The oxidation mechanisms of $Si_3N_4$ and SiC with $K_2SO_4$ and $K_2CO_3$ melts are discussed on the basis of the experimental results.*

## 1. INTRODUCTION

Considerable efforts have been made recently to develop new energy conversion systems with increased fuel efficiencies, such as magnetohydrodynamic (MHD) generation, high temperature gas turbines, etc., in which the operating temperatures are much higher than metal alloys would

---

* To whom correspondence should be addressed.

*Int. J. High Technology Ceramics* 0267-3762/86/$03·50

permit. Consequently, only certain ceramic materials are good candidates for use as structural materials. However, in an MHD generator, the electrodes and insulating walls are exposed to a high temperature potassium-seeded plasma. Since the plasma contains about 1 wt% of seed materials such as $K_2CO_3$ and $K_2SO_4$, potassium salts condense on the wall and cause severe corrosion. It is also well known that in a high temperature gas turbine system, condensed NaCl and $Na_2SO_4$ salts may cause corrosion. Therefore, the structural materials used for energy conversion systems should not only have excellent thermal and mechanical properties but must also be resistant to the oxidation–reduction reaction in the corrosive environment of elements such as K, Na, V, S, etc.

Since ceramics based on silicon carbide, silicon nitride and aluminium nitride can retain outstanding fracture strength to high temperatures and are remarkably resistant to thermal shock and oxidizing combustion environments, they are considered good candidates for structural applications at high temperatures. Many investigators have studied the physical and mechanical properties of these ceramics; however, only limited data on their corrosion mechanism in molten salts have been reported.[1–10] McKee and Chatterji,[1] Mayer and Riley,[2] Brooks *et al.*[3] and Erdoes and Altorfer[4] have investigated the behaviour of silicon carbide and silicon nitride in a variety of molten salt/gas environments. According to their reports, the oxygen potential at the surface of silicon carbide and silicon nitride was a critical parameter for the 'active' and 'passive' oxidation in gaseous and molten salt environments. Tressler *et al.*[5] reported that the degree of corrosion of silicon carbide and silicon nitride with molten $Na_2SO_4$–NaCl salts depended on the concentration of free oxide ions in the molten salts. Becher[8] studied the fracture strength degradation of silicon carbide and silicon nitride ceramics resulting from the exposure to coal slags at high temperatures, and he reported that the corrosion behaviour of silicon carbide and silicon nitride ceramics depended on the chemical constitution of the coal slags, and that silicon carbide ceramics generally exhibited greater resistance to corrosive attack than silicon nitride ceramics. In the previous investigations, however, only qualitative experimental results on chemical reaction have been reported, so that the details of the corrosion reactions are still not clear. In the present work, a series of corrosive reaction experiments was conducted to obtain more detailed information of the corrosion behaviour of silicon carbide, silicon nitride and aluminium nitride ceramics in $K_2SO_4$–$K_2CO_3$ melts.

## 2. EXPERIMENTAL

The materials selected were silicon carbide and silicon nitride, fabricated by pressureless sintering using additives of boron and carbon for silicon

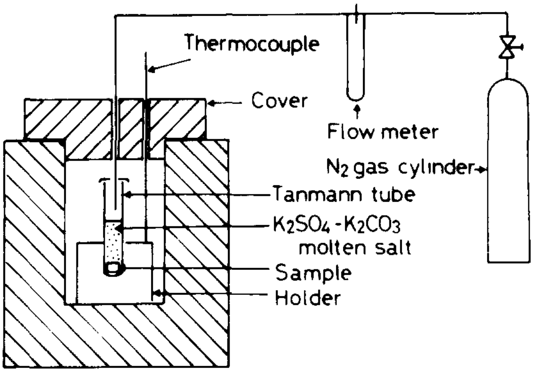

**Fig. 1.** Schematic diagram of the reaction apparatus.

carbide, and yttrium oxide and aluminium oxide for silicon nitride (made by the NGK Spark Plug Co. Ltd), and aluminium nitride without additives, fabricated by high pressure hot pressing at the Institute of Scientific and Industrial Research, Osaka University. These materials were cut into bars of rectangular cross-section (typically 5 mm × 4 mm × 8 mm). Figure 1 shows diagrammatically the apparatus for the corrosion tests. In each experiment a weighed sample and powdered reagent-grade $K_2SO_4$ and/or $K_2CO_3$ were put into a Tanmann tube of high purity alumina, 16 mm in diameter and 170 mm in length, which was then placed into an electric furnace controlled at a desired temperature. The reaction temperature, $T$, was set to the value of $T/T_m = 1{\cdot}1$ ($T_m$ = the melting point (K) of each salt). Nitrogen gas of higher than 99·99% purity was injected into the Tanmann tube at the rate of $20\,\mathrm{ml\,min^{-1}}$ when the corrosion test was carried out in a nitrogen gas atmosphere. After maintaining the desired temperature for a given time, the Tanmann tube was removed from the electric furnace and quickly cooled to room temperature. The samples were washed in hot water, dried and weighed. Crystalline phases and microstructures on the surface of the samples exposed to the molten potassium salts were examined by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

## 3. RESULTS AND DISCUSSION

### 3.1. Thermodynamic aspects of the stability of silicon carbide, silicon nitride and aluminium nitride ceramics in molten $K_2SO_4$–$K_2CO_3$ salts

The oxidation reactions of silicon carbide, silicon nitride and aluminium nitride and the reducing reactions of $K_2SO_4$ and $K_2CO_3$ can be expressed as eqns (1)–(10), when the reactions are expressed on the basis of the transfer of oxygen.

Oxidation reactions:

$$2/3\,SiC(s) + O_2(g) \longrightarrow 2/3\,SiO_2(s) + 2/3\,CO(g) \quad (1)$$

$$SiC(s) + O_2(g) \longrightarrow SiO(g) + CO(g) \quad (2)$$

$$1/3\,Si_3N_4(s) + O_2(g) \longrightarrow SiO_2(s) + 2/3\,N_2(g) \quad (3)$$

$$4/3\,Si_3N_4(s) + O_2(g) \longrightarrow 2Si_2N_2O(s) + 2/3\,N_2(g) \quad (4)$$

$$2/3\,Si_3N_4(s) + O_2(g) \longrightarrow 2SiO(g) + 4/3\,N_2(g) \quad (5)$$

$$4/3\,AlN(s) + O_2(g) \longrightarrow 2/3\,Al_2O_3(s) + 2/3\,N_2(g) \quad (6)$$

Reducing reactions:

$$1/2\,K_2SO_4(l) \longrightarrow 1/2\,K_2S(l) + O_2(g) \quad (7)$$

$$2K_2SO_4(l) \longrightarrow 2K_2SO_3(l) + O_2(g) \quad (8)$$

$$2K_2CO_3(l) \longrightarrow 2K_2O(l) + 2CO(g) + O_2(g) \quad (9)$$

$$K_2CO_3(l) \longrightarrow 2K(l) + CO(g) + O_2(g) \quad (10)$$

$$1/2K_2S(s) + O_2(g) \longrightarrow 1/2\,K_2SO_4(s) \quad (7')$$

$$2K_2SO_3(s) + O_2(g) \longrightarrow 2K_2SO_4(s) \quad (8')$$

$$2K_2O(s) + 2CO(g) + O_2(g) \longrightarrow 2K_2CO_3(s) \quad (9')$$

$$2K(s) + CO(g) + O_2(g) \longrightarrow K_2CO_3(s) \quad (10')$$

Chemical free energy change of the oxidation reactions written by eqns (1)–(6) and (7′)–(10′) are shown as a function of temperature in Fig. 2.

Although all the compounds, $K_2SO_4$, $K_2CO_3$, $K_2S$, $K_2SO_3$ and $K_2O$, melted at the experimental temperature, the free energy changes of these compounds were calculated on the basis of the solid–gas reactions expressed by eqns (7′)–(10′) because of the lack of thermodynamic data for the molten $K_2S$, $K_2SO_3$ and $K_2O$ salts. If the dashed lines in Fig. 2, which are derived from eqns (7′)–(10′), are above the full lines, which represent the reactions expressed by eqns (1)–(6), the oxidation of SiC, $Si_3N_4$ and AlN by $K_2SO_4$ and $K_2CO_3$ is thermodynamically favourable. Potassium sulphate possesses a strong oxidizing activity and might oxidize SiC, $Si_3N_4$ and AlN. Further, the reduction of $K_2SO_4$ to $K_2S$ is more advantageous than that to $K_2SO_3$, and the reduction of $K_2CO_3$ to K and CO is more advantageous than that to $K_2O$ and CO.

### 3.2. Weight loss of SiC, $Si_3N_4$ and AlN in molten $K_2SO_4$–$K_2CO_3$ salts

SiC, $Si_3N_4$ and AlN specimens were immersed into $K_2SO_4$, 50 mol% $K_2SO_4$–50 mol% $K_2CO_3$ and $K_2CO_3$ melts exposed to air at 1200, 1068 and 1013 °C, respectively. The weight losses of these specimens by corrosion with potassium melts are shown in Figs 3, 4 and 5.

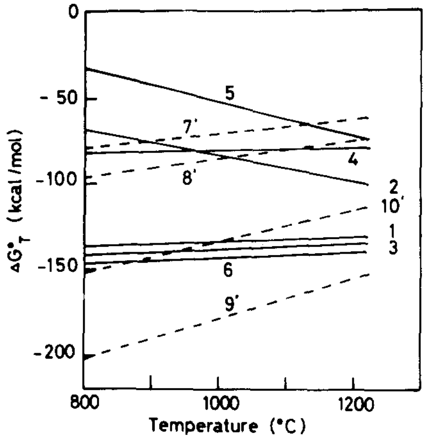

**Fig. 2.** Chemical free energy changes as a function of temperature for the possible oxidation reactions in the system of SiC, $Si_3N_4$ or AlN and $K_2CO_3$ or $K_2SO_4$. (Lines 1–6 and 7′–10′ refer to eqns (1)–(6) and (7′)–(10′) given in text.)

Silicon carbide dissolved very slowly in $K_2CO_3$ melts, but rapidly in $K_2SO_4$ and 50 mol% $K_2SO_4$–50 mol% $K_2CO_3$ melts. The rate of the weight loss of the silicon carbide specimen in 50 mol% $K_2SO_4$–50 mol% $K_2CO_3$ was much faster than that in the $K_2SO_4$ melt. It is expected that the rate of solution of silicon carbide in potassium salt melts depends not only on the oxidizing activity but also on the basicity of the melts.[1,2]

On the other hand, the weight loss of silicon nitride was appreciable in all potassium salts used. The rate of weight loss was the fastest in the $K_2CO_3$ melt, and decreased with increasing concentration of $K_2SO_4$ in the melts.

It is notable that aluminium nitride exhibited good resistance to

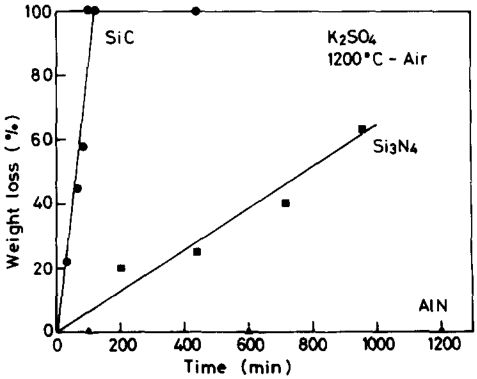

**Fig. 3.** Weight loss of SiC, $Si_3N_4$ and AlN specimens in molten $K_2SO_4$ exposed to air at 1200 °C.

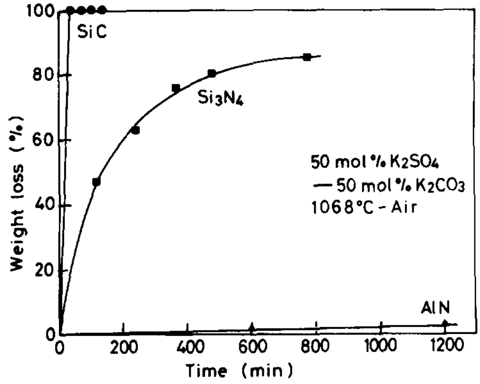

**Fig. 4.** Weight loss of SiC, $Si_3N_4$ and AlN specimens in molten 50 mol.% $K_2SO_4$–50 mol% $K_2CO_3$ exposed to air at 1068 °C.

potassium melts and little weight loss was observed in all potassium salts used. The present results are in good agreement with those reported by Sata and Kasukawa.[10]

### 3.3. Stoichiometry of the reaction of SiC and $Si_3N_4$ with $K_2SO_4$ and $K_2CO_3$ melts

A series of experiments was conducted in which silicon carbide and silicon nitride specimens were immersed into $K_2CO_3$ and $K_2SO_4$ melts, exposed to air or nitrogen atmospheres for 20 h; the initial molar ratio of $K_2CO_3$ or $K_2SO_4$ per SiC or $Si_3N_4$ was systematically changed from 0·5 to 5·0. The results of XRD from the surface of the reacted specimens showed only the diffraction peaks corresponding to SiC or $Si_3N_4$, but $K_2O.4SiO_2$

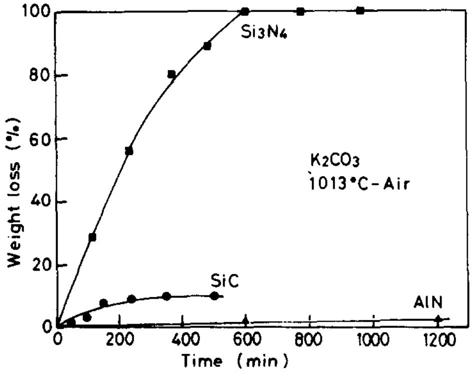

**Fig. 5.** Weight loss of SiC, $Si_3N_4$ and AlN specimens in molten $K_2CO_3$ exposed to air at 1013 °C.

was detected by XRD in the flux. Further, sulphide was detected by qualitative analysis using $AgNO_3$ solution in the flux of the $K_2SO_4$–SiC and $K_2SO_4$–$Si_3N_4$ systems. The SEM photographs of the SiC and $Si_3N_4$ specimens corroded in $K_2SO_4$ melts exposed to air and nitrogen are shown in Fig. 6. Extensive roughening of the surface and bubbles of evolved gas were observed for the SiC– and $Si_3N_4$–melt interfaces. As seen in Fig. 6(D), a film of about 50 μm was formed below the roughened surface of the specimen when silicon nitride was immersed in the $K_2SO_4$ melt exposed to air. This may be the protective film which is described later.

The amount of the weight loss of silicon carbide and silicon nitride specimens for each test is shown in Figs 7 and 8. As seen in Fig. 7(A), the weight loss of silicon carbide increased linearly with increasing initial molar ratio of $K_2SO_4$/SiC; the reaction of SiC and $K_2SO_4$ seemed to proceed quantitatively under the reaction conditions. The stoichiometry of $K_2SO_4$/SiC was determined to be 0·8 from the plots of weight loss versus initial molar ratio of $K_2SO_4$/SiC for the melt exposed to nitrogen

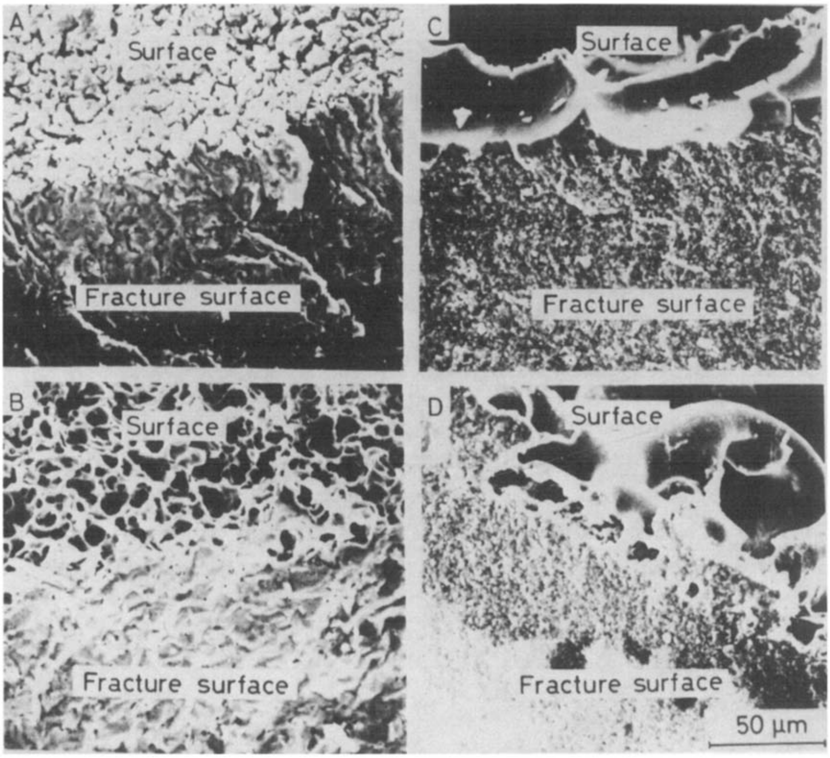

**Fig. 6.** Microstructural characteristics of SiC and $Si_3N_4$ specimens immersed in molten $K_2SO_4$ exposed to air or nitrogen: (A) SiC–$K_2SO_4$–$N_2$; (B) SiC–$K_2SO_4$–air; (C) $Si_3N_4$–$K_2SO_4$–$N_2$; (D) $Si_3N_4$–$K_2SO_4$–air.

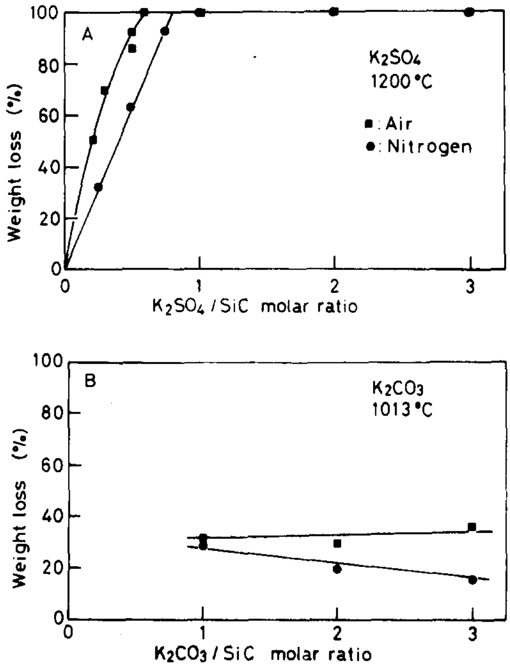

**Fig. 7.** Relations between weight loss of the SiC specimens and the initial molar ratios of (A) $K_2SO_4/SiC$ and (B) $K_2CO_3/SiC$.

gas. The stoichiometry value for the $K_2SO_4$ melt exposed to air was 0·6, which implied that SiC was partially oxidized by oxygen. The value of 0·8 for the stoichiometry of $K_2SO_4/SiC$ was quite close to the value of 0·75 corresponding to the simplified reaction expressed by eqn (11):

$$4SiC + 3K_2SO_4 \rightarrow 4SiO_2 + 4CO + 3K_2S \quad (K_2SO_4/SiC = 0{\cdot}75) \quad (11)$$

Equation (11) is the combination of the reactions shown by eqns (1) and (7). It is expected that $SiO_2$ dissolved in the salt melt as potassium silicate and no free $SiO_2$ could be observed on the surface of the remaining specimen by EPMA and XRD. Since potassium silicates, $K_2O \, . \, nSiO_2$ $(n < 5)$, and potassium polysulphides, $K_2S_x$ $(x < 6)$, could form liquid phases at 1200°C, the following reactions were considered:

$$5SiC + 4K_2SO_4 \rightarrow K_2O \, . \, 5SiO_2 + 5CO + K_2S + 2K_2S_2 \quad (K_2SO_4/SiC = 0{\cdot}8) \quad (12)$$

$$16SiC + 13K_2SO_4 \rightarrow 4(K_2O \, . \, 4SiO_2) + 16CO + 5K_2S + 4K_2S_2 \quad (K_2SO_4/SiC = 0{\cdot}81) \quad (13)$$

Although further studies should be carried out to confirm the species of

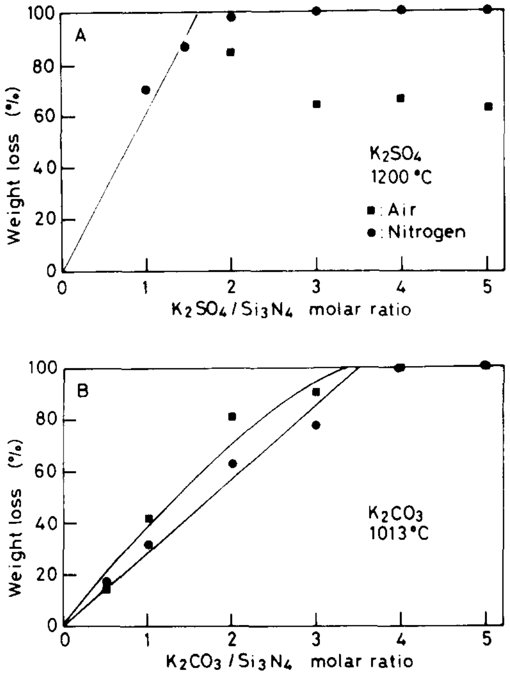

**Fig. 8.** Relations between weight loss of $Si_3N_4$ specimens and the initial molar ratios of (A) $K_2SO_4/Si_3N_4$ and (B) $K_2CO_3/Si_3N_4$.

polysulphide, the present results indicate that the first step of the reduction of sulphate was not the formation of sulphite but of sulphide.

McKee and Chatterji[1] and Tressler *et al.*[5] reported the formation of $SO_2$ by the reaction between SiC or $Si_3N_4$ and $Na_2SO_4$–NaCl melts. No reaction equation was given in their report. It is considered that the formation of $SO_2$ is possible, due to the reaction between the initial production of sulphides and residual sulphate in the SiC or $Si_3N_4$–$Na_2SO_4$ melt system:

$$3Na_2SO_4 + Na_2S \rightarrow 4Na_2O + 4SO_2 \qquad (14)$$

Reaction (14) is based on the results reported by Turkdogan and Vinters[11] in the excess $CaSO_4$–C system. In the present experiments no formation of $SO_2$ occurred in the system of SiC–$K_2SO_4$ melts when $K_2SO_4$/SiC was less than 0·8; however, above 1·0 the formation of $SO_2$ would have occurred.

As seen in Fig. 7(B), the reaction between SiC and $K_2CO_3$ was much less than in either $K_2SO_4$ or the mixed salts and no relation was found between the weight loss of the SiC specimen and the initial molar ratio of $K_2CO_3$/SiC. Silicon carbide might not react with $K_2CO_3$ directly and the weight loss of the SiC specimen in $K_2CO_3$ melt might be caused by the oxidation of SiC to $SiO_2$ owing to dissolved oxygen. The following dissolution of $SiO_2$ into $K_2CO_3$ was expected:

$$2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO \qquad (15)$$

$$4SiO_2 + K_2CO_3 \rightarrow K_2O\,.\,4SiO_2 + CO_2 \qquad (16)$$

The reaction between $Si_3N_4$ and $K_2SO_4$ exposed to nitrogen proceeded quantitatively as seen in Fig. 8(A). The stoichiometry of $K_2SO_4/Si_3N_4$ was 1·6, which was close to that of the simplified reaction expressed by eqn (17):

$$2Si_3N_4 + 3K_2SO_4 \rightarrow 6SiO_2 + 4N_2 + 3K_2S \qquad (17)$$
$$(K_2SO_4/Si_3N_4 = 1{\cdot}5)$$

Therefore, the reactions shown by eqns (18) and (19) are actually expected to proceed:

$$20Si_3N_4 + 33K_2SO_4 \rightarrow 12(K_2O\,.\,5SiO_2) + 40N_2 + 9K_2S + 12K_2S_2 \qquad (18)$$
$$(K_2SO_4/Si_3N_4 = 1{\cdot}65)$$

$$16Si_3N_4 + 27K_2SO_4 \rightarrow 12(K_2O\,.\,4SiO_2) + 32N_2 + 3K_2S + 12K_2S_2 \qquad (19)$$
$$(K_2SO_4/Si_3N_4 = 1{\cdot}68)$$

On the other hand, when a $Si_3N_4$ specimen was immersed into $K_2SO_4$ melt exposed to air, the reaction did not proceed quantitatively. In Fig. 6(D), an intermediate thin layer in the microstructure between the roughened surface and the unreacted inside body was observed; a protective layer of $SiO_2$ which did not react with the acidic melt of $K_2SO_4$ might be formed on the surface of $Si_3N_4$ grains in the presence of oxygen.

In contrast with the results of the reaction of SiC and $K_2CO_3$, $Si_3N_4$ reacted with $K_2CO_3$ melts quantitatively. The stoichiometry of $K_2CO_3/Si_3N_4$ was determined to be 3·5 by the reaction of the $Si_3N_4$ specimen with $K_2CO_3$ melt exposed to nitrogen gas, which was close to that of the simplified reaction of eqn (20):

$$3K_2CO_3 + Si_3N_4 \rightarrow 3SiO_2 + 2N_2 + 3CO + 6K \qquad (20)$$
$$(K_2CO_3/Si_3N_4 = 3{\cdot}0)$$

A similar reaction has been confirmed to proceed in carbonates–$SiO_2$–$Si_3N_4$ systems.[9] As mentioned before, since $SiO_2$ dissolves as potassium silicates in the $K_2CO_3$ melts, the following reactions could be postulated:

$$7K_2CO_3 + 2Si_3N_4 \rightarrow 2(K_2O\,.\,3SiO_2) + 4N_2 + 7CO + 10K \qquad (21)$$
$$(K_2CO_3/Si_3N_4 = 3{\cdot}5)$$

$$81K_2CO_3 + 24Si_3N_4 \rightarrow 18(K_2O\,.\,4SiO_2) + 48N_2 + 81CO + 126K \qquad (22)$$
$$(K_2CO_3/Si_3N_4 = 3{\cdot}4)$$

Since $K_2CO_3$ slowly evaporated under the present reaction conditions a further study is necessary to confirm the stoichiometry of $K_2CO_3/Si_3N_4$.

## 4. CONCLUSIONS

1. Aluminium nitride ceramics exhibited good resistance to molten potassium salts.
2. Silicon carbide dissolved rapidly in molten potassium salts in the presence of $K_2SO_4$.
3. Silicon carbide reacted with $K_2SO_4$ melt quantitatively and the stoichiometry of $K_2SO_4/SiC$ was 0·8.
4. Silicon nitride dissolved rapidly in all potassium melts.
5. The reactions of silicon nitride with $K_2SO_4$ melt were prevented by the formation of a protective film in the presence of oxygen.
6. Silicon nitride reacted with $K_2SO_4$ and $K_2CO_3$ quantitatively and the stoichiometries of $K_2SO_4/Si_3N_4$ and $K_2CO_3/Si_3N_4$ were 1·6 and 3·5, respectively.

## ACKNOWLEDGEMENTS

The authors are indebted to the management of NGK Spark Plug Co. Ltd for supplying the test pieces of SiC and $Si_3N_4$ used in this study. This work has been carried out partially with the support of the grant-in-aid for energy research of the Japanese Ministry of Education.

## REFERENCES

1. McKee, D. W. and Chatterji, D., Corrosion of silicon carbide in gases and alkaline melts, *J. Am. Ceram. Soc.*, **59** (1976) 441–4.
2. Mayer, M. I. and Riley, F. L., Sodium-assisted oxidation of reaction-bonded silicon nitride, *J. Mater. Sci.*, **13** (1978) 1319–28.
3. Brooks, S. M., Ferguson, J. M., Meadowcroft, D. B. and Stevens, C. G., Corrosion above 700 °C in oil-fired combustion, in *Materials and Coatings to Resist High Temperature Corrosion*, Eds D. R. Holmes and A. Rahmel, Elsevier Applied Science Publishers, London, 1977, 121–38.
4. Erdoes, E. and Altorfer, H., Corrosion behavior of hot-pressed and reaction-bonded silicon nitride in condensed phase, in *Materials and Coatings to Resist High Temperature Corrosion*, Eds D. R. Holmes and A. Rahmel, Elsevier Applied Science Publishers, London, 1977, 161–74.
5. Tressler, R. E., Meiser, M. D. and Yonushonis, T., Molten salt corrosion of SiC and $Si_3N_4$ ceramics, *J. Am. Ceram. Soc.*, **59** (1976) 278–9.

6. Bourne, W. C. and Tressler, R. E., Molten salt degradation of $Si_3N_4$ ceramics, *Am. Ceram. Soc. Bull.*, **59** (1980) 443–6, 452.
7. Ferber, M. K. and Tennery, V. J., Behavior of tubular ceramics heat exchanger materials in acidic coal ash from coal-oil-mixture combustion, *Am. Ceram. Soc. Bull.*, **62** (1983) 236–43.
8. Becher, P. F., Strength degradation in SiC and $Si_3N_4$ ceramics by exposure to coal slags at high temperatures, *J. Mater. Sci.*, **19** (1984) 2805–14.
9. Wusirika, R., Problems associated with the melting of oxynitride glasses, *J. Am. Ceram. Soc.*, **63** (1984) 232–3.
10. Sata, T. and Kasukawa, K., Alkali corrosion and vaporization of MHD materials, *Rev. Int. Hautes Tempér. Réfrect., Fr*, **17** (1980) 174–83.
11. Turkdogan, E. T. and Vinters, J. V., Reduction of calcium sulphate by carbon, *Trans. Inst. Min. Metal.*, **C85** (1976) 117–23.

*Received 22 April 1985; amended version received 21 October 1985; accepted 15 May 1986*