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Sodium-assisted oxidation of reaction-bonded silicon nitride

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The oxidation of reaction-bonded silicon nitride in air, and with small amounts of sodium carbonate applied to the sample surface, has been studied. The action of the alkali is to cause short-term enhanced oxidation,which is terminated when specific compositions of the product sodium silicate glass are attained. These correspond closely to liquidus compositions in the Na_2O–SiO_2 system, and it is postulated that the retardation in the oxidation rate at this stage is due to the formation of a stable tridymite film at the silicon nitride–glass interface. The implications for the high temperature stability of reaction-bonded silicon nitride components in alkali contaminated atmospheres are discussed.

1. Introduction

Because of the interest in silicon nitride as a high temperature turbine material, studies have been made of the oxidation resistance of both the hot-pressed [1, 2] and the reaction-bonded [3] forms. Attention has also been paid to the oxidation kinetics of silicon nitride powders [4–7] and pyrolytically deposited thin films [8]. Silicon nitride is thermodynamically unstable with respect to oxidation by air, and depends for its existence on a protective oxide film of low permeability to oxygen. Under certain operating conditions, such as in a marine environment, or with contaminated fuel, silicon nitride turbine components would also be exposed to potentially corrosive contaminants, such as sodium in the form of the chloride or sulphate. The influence of sodium and similar ions on the protective nature of the silica film in an air environment therefore needs to be established with certainty.

Studies of the corrosion of both hot-pressed and reaction-bonded silicon nitride, and of silicon carbide, in contact with molten sodium salts have been made [9–11]. It has been demonstrated that sodium sulphate alone can lead to accelerated corrosion in air environments, although even at 900° C under certain conditions, the corrosion rate over a limited period can also be very low. In this case a critical factor appears to be the O^{2-} ion activity, and markedly enhanced rates are observed in the presence of sodium carbonate, either as an additon in small percentages to the sulphate, or alone. The action of the alkali has been assumed to be that of removing by fluxing the passivating silica film. On the other hand, complete immersion of a test sample in a molten salt may not lead to the expected rapid corrosion, if oxygen access to the nitride or carbide surface is thereby hindered.

In the work reported here sodium, in the form of sodium carbonate, was applied in small quantities to reaction-bonded silicon nitride bars, and the subsequent kinetics of oxidation in air were measured in the temperature range 900 to 1300° C. In most cases the porous bars had previously been provided with an outer sealing film of silica by exposure to air at 1300° C. This was done in order to establish a reproducible basis for an examination of the action of other materials. Sodium carbonate was selected for initial studies because of its rapid reaction with silica at the temperatures of interest, and because of the relative stability of the resulting sodium silicate. Known amounts of sodium silicate could therefore be generated at the surfaces of the silicon nitride bars without the problems associated with the volatility, or relative lack of reactivity, of other sodium salts such as the halides, or sulphate.

2. Experimental

Small bars of reaction-bonded silicon nitride (Admiralty Marine Technology Establishment, Holton Heath, Dorset) of dimensions 35 mm x 5 mm x 1 mm, and of weights in the region of 440 mg were used. Each had a 0.5 mm diameter hole drilled in one end, and could be suspended by a platinum/20% rhodium wire in an alumina tube furnace heated by a spiral silicon carbide element. The amounts of major metallic contaminants present in the silicon nitride, as determined by X-ray fluorescence analysis, are shown in Table I.

TABLE I Major metallic contaminants present in the reaction-bonded silicon nitride

Element	Amount (wt%)
Aluminium	0.33
Iron	0.26
Calcium	0.15
Magnesium	0.07
Sodium	0.04
Titanium	0.04
Potassium	0.01

Provision was made for passing gases of controlled composition through the furnace tube, which could be isolated from the outside atmosphere for this purpose. A standard flow rate of 10 ml min^{-1} was adopted for all experiments. The water contents of the "dry" and "atmospheric" air used in this work were determined with an electrolytic hygrometer (Salford Instruments Ltd.). Continuous sample weight readings were obtained with a microbalance (C.I. Electronics Ltd.) in conjunction with a chart recorder to a precision of 20 μg. Corrections were applied to all readings to allow for the volatility of the platinum–rhodium suspension wire.

For the small number of experiments carried out in "dry" air, compressed cylinder air (B.O.C. Ltd.) was used, after passage through a drying train of silica gel, and dispersed phosphorus pentoxide. Laboratory air was otherwise pulled at a controlled rate through the apparatus with a water operated suction pump.

Sodium carbonate was normally applied to the silicon nitride bars by dipping in a 10 wt% solution, and the quantity of salt adhering was determined by weighing after suitable drying. For most experiments the silicon nitride bars were given a pre-oxidation treatment in air (4 h at 1300° C), to establish an outer silica film thick enough to seal access to internal porosity. This corresponded to the formation of approximately 20 mg of silica on each bar. A smaller number of experiments were made with the carbonate applied directly to the "as-received" bars.

In order to determine the evaporation rates of sodium oxide from the sodium silicate film under oxidation conditions, separate experiments were carried out using small silica bars. These were cut from vitreous silica tubing and had the same outer surface area as the silicon nitride bars (approximately 430 mm^2). Coatings of sodium carbonate were applied using the standard technique, and weight losses at temperatures in the region 1100 to 1300° C were recorded as a function of time. These were used subsequently to correct weight change data from oxidation experiments.

The furnace could be moved in a vertical direction independently of the samples and microbalance unit. Reactions were started by rapidly raising the preheated furnace so as to bring the sample into the hot zone. Temperature equilibration was complete within a matter of seconds. It was found advantageous to have the samples located in such a position during adjustment of the furnace temperature that they reached 150 to 200° C. Weight fluctuations caused by the desorption of surface moisture were thereby minimized.

3. Results

Typical weight gain data for the oxidation of reaction-bonded silicon nitride bars in atmospheric air (approximately 1.5% H_2O) are shown in Fig. 1. The oxidation rates in "dry" air (250 p.p.m. H_2O) at each temperature were the same within experimental error as those in wet air, as is shown by the Arrhenius treatment in Fig. 2. For this reason subsequent experiments using sodium carbonate were carried out in undried atmospheric air. The points in Fig. 2 appear to lie on two curves intersecting in the region of 1100° C. Because of the overall curvature of this plot precise enthalpy of activation values cannot be obtained, but they may be estimated as 130 kJ mol^{-1} for temperatures between 1100 and 1200 °C, and 320 kJ mol^{-1} for temperatures below 1100° C.

Although sodium carbonate is fairly stable towards decomposition in air at temperatures in the region of 1000° C, small quantities react rapidly with silica. The weight changes of sodium carbon-

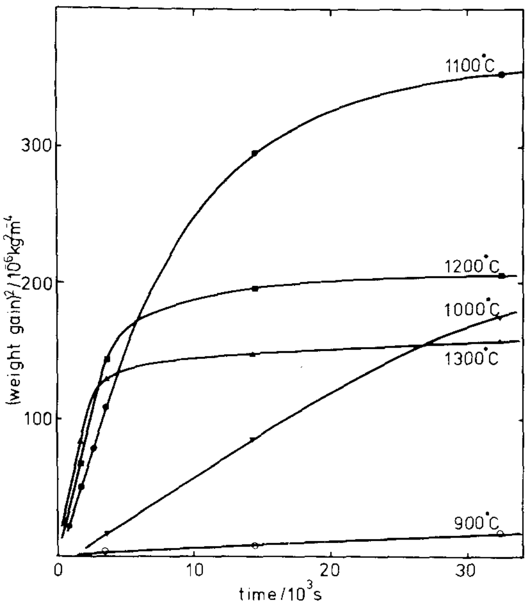

Figure 1 Typical weight gains due to the oxidation of reaction-bonded silicon nitride at temperatures between 900 and 1300° C in atmospheric air.

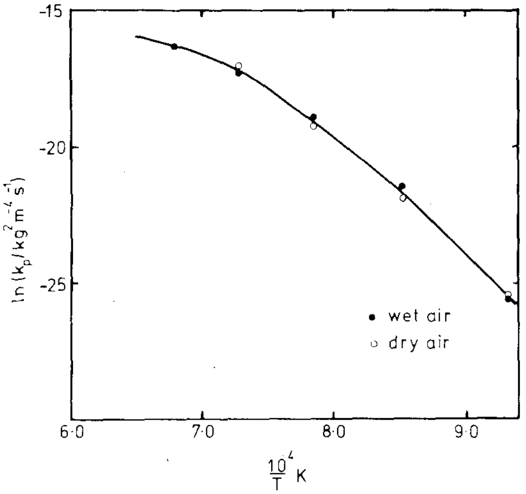

Figure 2 Arrhenius treatment of initial stage parabolic rate constants for oxidations in "wet" and "dry" air, at temperatures in the range 800 to 1200° C.

ate coated silica bars due to loss of carbon dioxide were found to be completed within two minutes at 850° C. It could be assumed therefore that the milligram quantities of sodium carbonate with which the silicon nitride bars were coated effectively behaved as sodium oxide, in rapidly generating sodium silicate. For this reason the quantities of sodium salt used are expressed in terms of (mg) sodium oxide. The sodium oxide in a sodium silicate glass is itself appreciably volatile at high temperature [12]. Corrections

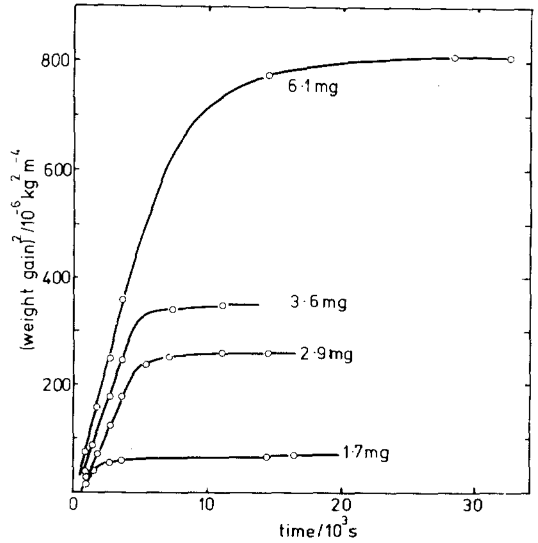

Figure 3 Weight gains due to oxidation in "wet" air at 1300° C of sodium carbonate-coated silicon nitride. Equivalent sodium oxide weights shown as mg per bar.

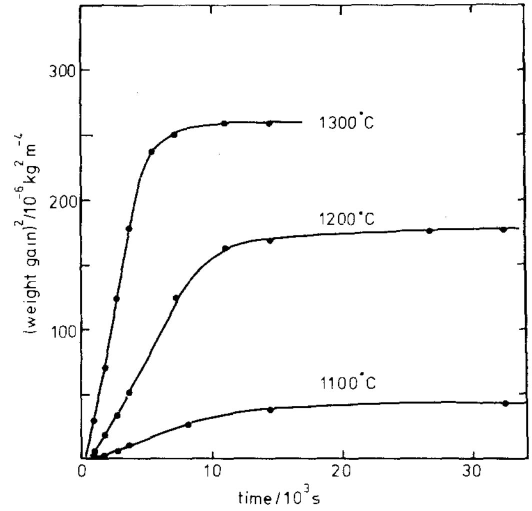

Figure 4 Weight gains due to oxidation in "wet" air of sodium carbonate-coated silicon nitride. Sodium oxide equivalent 6.1 mg in all cases.

were therefore applied to the microbalance readings for all experiments involving sodium oxide addition, on the basis of data obtained from the use of coated silica bars. These weight losses, which appeared to be essentially independent of the amount of sodium oxide initially present, were of the order of 10% of the weight gains later obtained during oxidations at 1300° C, and were by comparison negligible below 1100° C.

The effect of sodium oxide addition to a preoxidized silicon nitride bar was to cause short duration enhanced oxidation. The fast oxidation initially appeared to follow accurately a parabolic rate law, with an eventual termination which was fairly sharp at 1300° C (Fig. 3), and more gradual at lower temperatures (Fig. 4). It can also be seen from Fig. 3 that the value of the parabolic rate constant depends on the amount of sodium oxide added, as does the extent of reaction before termination of the fast oxidation stage. "As-received" silicon nitride bars showed a similar pattern of behaviour, and most points could be fitted to the smooth curves obtained from the pre-oxidized silicon nitride samples.

The extent of the initial fast oxidation stage, as expressed by the weight of silica generated, was approximately proportional to the weight of sodium oxide added. However a greater quantity of silica was generated at higher temperatures. This data is shown in Fig. 5, where it can be seen that points lie reasonably well on straight lines, with the exception of two experiments using "as-received" silicon nitride bars. An alternative way of presenting this information is in terms of the composition of the sodium silicate glass at the termination point of the fast reaction. These values are given in Table II. Corrections have been applied to allow for the loss by volatilization of sodium oxide during the period of the reaction to the termination point, and no account has been taken of silica formed in the pre-oxidation treatment.

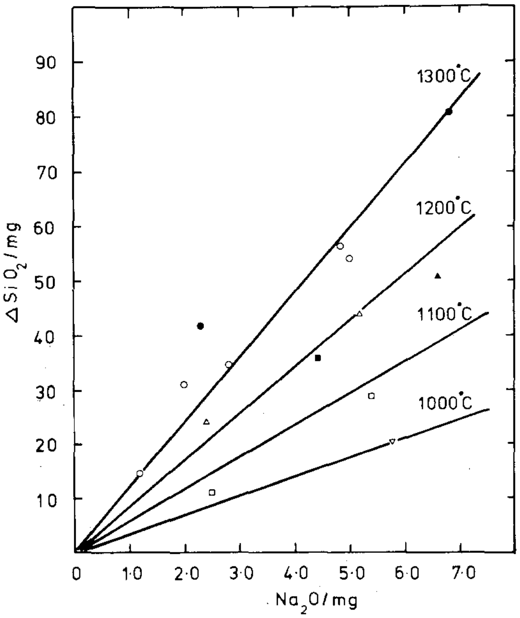

Figure 5 Weight gains due to silica formation during the fast stage oxidation in "wet" air of sodium carbonate-coated silicon nitride, as a function of sodium oxide weight. Solid points are for "as-received" bars.

TABLE II Product compositions at the fast reaction termination point

Temperature (°C)	Run	Final Na_2O content (mg)	SiO_2 yield (mg)	Product Composition (wt% Na_2O)
1000	83	5.8	20.3	22.2
1100	59	2.5	11.0	18.5
	70*	4.5	36.0	11.1
	60	5.4	28.7	15.8
				(Mean 15.1 ± 3.7)
1200	63	2.4	24.0	9.1
	62	5.2	43.9	10.6
	69*	6.6	50.6	11.5
				(Mean 10.4 ± 1.2)
1300	56	1.2	14.4	7.7
	57	2.0	31.0	6.1
	67*	2.3	41.9	5.2
	64	2.8	34.5	7.5
	88	4.9	56.4	8.0
	55	5.0	54.0	8.5
	68*	6.8	80.6	7.8
				Mean 7.2 ± 1.1)

*Denotes an "as-received" silicon nitride bar.

Although it had been expected that conversion of a protective silica layer to sodium silicate would lead to enhanced oxidation rates, the subsequent abrupt termination of the accelerated oxidation was unexpected. Additional experiments were therefore carried out to determine the reasons for this effect. The complete loss of sodium oxide from the product film appeared to be unlikely on the basis of the evaporation rates determined for sodium oxide from silica. That sodium oxide was still present in the samples at the end of the first stage of rapid oxidation was confirmed in one case by raising the oxidation temperature from 1000 to 1300° C, when immediate continuation of the fast oxidation was observed (Fig. 6). A second possible explanation was that oxidation ceased when microcracks, caused by sodium-induced devitrification of a largely amorphous silica film, had healed. This possibility was in part ruled out by the use of repeated additions of sodium oxide to the same sample. After each addition further enhance oxidation was observed (Fig. 7). Moreover, scanning electron, and optical, micrographs (Fig. 8) confirmed that the outer regions of the products of oxidation at reaction temperatures had considerable fluidity. Crack development was therefore most unlikely.

Accurate measurement of oxidation rate

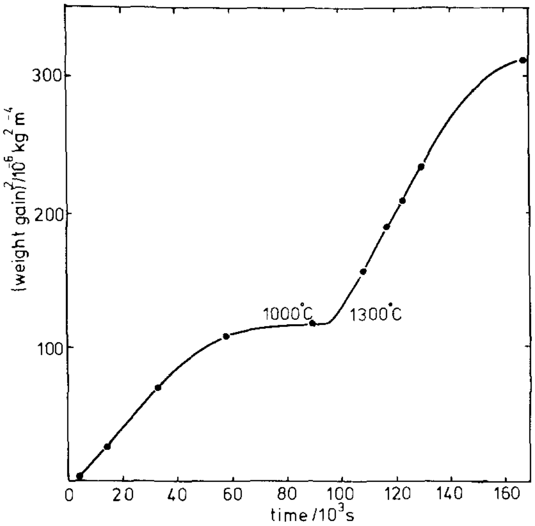

Figure 6 Weight gains due to oxidation in "wet" air of a silicon nitride bar coated with 6.1 mg sodium oxide equivalent, at 1000° C followed by 1300° C.

constants for the slower second stage in experiments involving sodium oxide additions was not attempted. They appeared to be closely similar to the values found for oxidations without the addition of alkali.

Qualitative X-ray examinations were made of randomly selected reacted silicon nitride bars. The crystalline oxidation product detected for samples heated in air was α-cristobalite. Tridymite (type S1) was also detected in bars oxidized in the presence of sodium oxide; in some of these samples tridymite was the only crystalline product found.

4. Discussion

4.1. Oxidation in air

The overall pattern of behaviour for the oxidation of reaction-bonded silicon nitride is now well known, and a satisfactory model has been provided by Evans and Davidge and colleagues [2]. The rapid initial stage corresponds to oxidation occurring throughout the porous material which may have a specific surface area as high as 12 000 $m^2\ kg^{-1}$. The much slower second stage is believed to develop when the thickening silica film on the outer surface of the sample seals access to internal porosity. The reaction interface area is then reduced by many orders of magnitude. Onset of the second stage occurs soonest at highest temperatures, an effect assumed to be due to the decreased viscosity of the silica glass. Faster oxidations of silicon nitride have been observed in wet oxygen and in wet air, compared with the dry gases [1, 4, 8]. However, the small quantity of water vapour in normal atmospheric air does not appear, from the present study, to have a signifi-

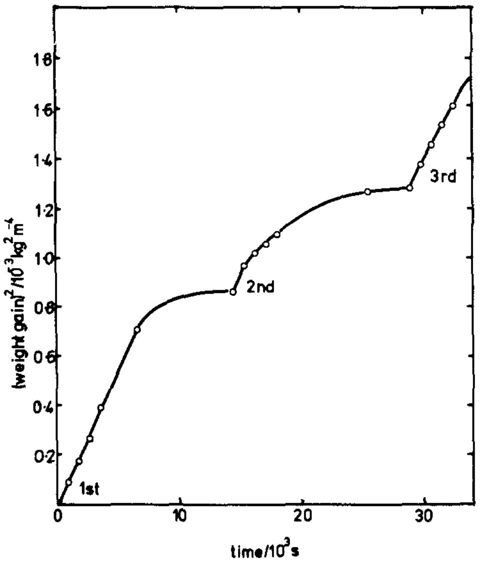

Figure 7 Weight gains due to oxidation in "wet" air of a silicon nitride bar coated repeatedly (5.9 mg sodium oxide equivalent).

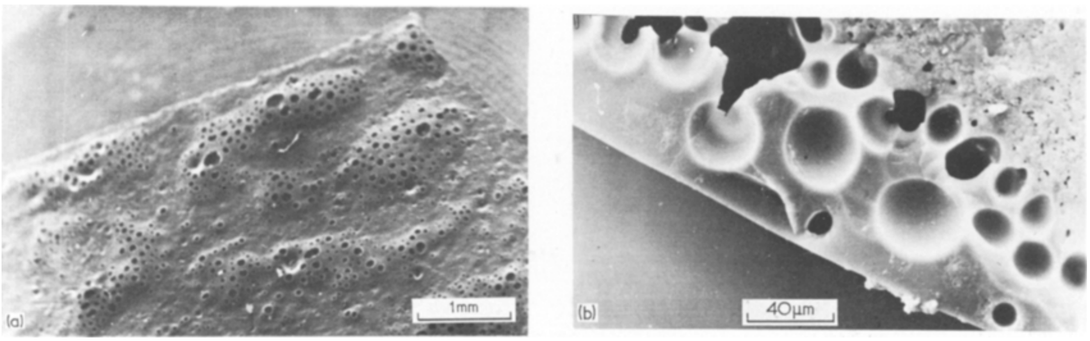

Figure 8 (a) Oxidation at 900° C of a pre-oxidized silicon nitride bar coated with 5.9 mg Na_2O. (b) Silicon nitride fracture face, after oxidation (900 sec) at 1300° C coated with 5.9 mg Na_2O.

cant effect on the reaction rates, and the slight irregular differences observed can be attributed to experimental error.

The curvature in the Arrhenius plot is qualitatively similar to that reported for both silicon nitride powder, and silicon carbide, by Fitzer and Ebi [5]. The change in slope occurs at approximately the same temperature (1100° C), but the enthalpy values in the present work are approximately twice the values reported (90 and 150 kJ mol^{-1}). These authors tentatively attributed the enthalpy variation to a change in the mechanism of the oxygen conduction process with increasing crystallinity of the silica film at higher temperatures. It was also suggested that outward nitrogen diffusion might become rate-controlling at temperatures above about 1200° C. The data of Horton [4] obtained with silicon nitride powder also contain the suggestion of a change of slope in the Arrhenius plot below 1100° C, with a high temperature activation enthalpy of 285 kJ mol^{-1}. The explanation offered in this case was that the form of the silica changed from amorphous to tridymite in the region of 1125° C.

The mechanism of diffusion of oxygen through silica films during the oxidation of materials such as silicon, silicon carbide, and silicon nitride, has been the subject of much discussion. Motzfeldt [13] has drawn attention to the remarkable similarity between the oxidation rates for these materials and the rate of permeation of oxygen through vitreous silica. Schaeffer [14, 15] has argued that molecular oxygen should be regarded as the mobile species in all these cases, and that the dissolved gas molecule represents an interstitial lattice defect. These defect sites in turn also might allow diffusion of lattice oxygen through an exchange, or interstitialcy, mechanism. Because the solubility of oxygen (and hence the defect concentration) is practically independent of temperature, identical enthalpies of activation for oxidation processes, oxygen self-diffusion, and gas permeation, should be observed. The range of values (84 to 297 kJ mol^{-1}) found experimentally [15–18] for the enthalpy of oxygen self-diffusion in silica glass is assumed to be the result of varying degrees of contamination, and the lower values, in the region of 90 kJ mol^{-1}, are considered to be the more reliable [14]. Little information is available about oxygen diffusion in crystalline silica. The self-diffusion coefficient for oxygen in quartz has however been found to be several orders of magnitude [16] smaller than that for silica glass.

The incorporation of network modifiers into the silica glass structure and the formation of non-bridging oxygens alters the pattern of diffusion behaviour. The general trend is for the enthalpies of activation to be larger than for pure silica, although diffusion rates may increase by several orders of magnitude because of compensation in the pre-exponential term [19]. Most of the data available for oxygen refer to lattice self-diffusion coefficients, but the diffusion mechanism has not been clearly established. Schaeffer [19] has suggested that increasing covalency of the Si–O bond caused by the less electronegative Na or Ca leads to a decreasing oxygen atomic radius, and hence increased mobility. Doremus [20] has calculated that the diffusivity of oxygen through a soda-lime glass composition is an order of magnitude faster than that through silica glass [21], with an activation enthalpy of 222 kJ mol^{-1} over the temperature range 1100 to 1300° C. This is to be compared with the value for silica of 113 kJ mol^{-1} in the region of 1000° C. There appears to be no information on possible relationships between the lattice diffusion of oxygen, and gas diffusivity, in the case of mixed glasses.

On the basis of published information about oxygen diffusion in silica, it seems unlikely that the high enthalpy values observed in the present study, and the similarly high values of Horton [4] and Franz and Langheinrich [8], relate to the simple diffusion of oxygen through a pure silica film. Changes in the film structure with increasing temperature have already been suggested as being responsible for the different sections in the Arrhenius plot, and could also provide exaggerated enthalpy values in the lower temperature regions while the structural changes were taking place. An alternative explanation which is likely to be valid for at least the present work, is that the protective oxide film is not pure silica, but a complex, partially crystalline, or inhomogeneous, silicate, containing the impurity metals which were originally present at the surface of the silicon nitride. This would help to explain the high enthalpy values found. The progressive melting of partially crystalline material would provide an explanation for the steeper curvature of the Arrhenius plot, with a decreased slope at temperatures above 1200° C when a more homogeneous phase had been established.

4.2. Oxidation in the presence of alkali

For the case of oxidations in the presence of sodium oxide, scanning electron micrographs show that the bulk of the reaction products is, at reaction temperature, a low viscosity glass. The accelerated oxidation rates are understandable in terms of an increased mobility of oxygen in a modified silica network. Three features regarding the overall oxidation kinetics have to be explained however:

(a) The apparent insensitivity of the reaction rate constant to the glass composition; this is shown (Fig. 3) by the accurate parabolic kinetics over a period of time during which the glass composition is changing because of silica formation and dissolution at the nitride–silicate interface;

(b) the sensitivity, on the other hand, of the parabolic rate constant to the absolute amount of alkali present (Fig. 3);

(c) the marked deceleration of the reaction when a certain value for the ratio (product $SiO_2:Na_2O$) is reached, the value of this ratio varying with temperature (Table II).

The first point implies that the oxygen diffusivity is not affected by changes in glass composition for the compositional ranges obtaining during the fast stage of the reaction. That this might be so is surprising but a similar feature has been reported by May and Wollast [22] for oxygen self-diffusion in the $K_2O–SiO_2$ system. In this system, which should provide a guide to behaviour in the $N_2O–SiO_2$ system, both silicon and oxygen self-diffusion coefficients were essentially independent of glass composition in the temperature range 800 to 1100° C. The same conclusion may be drawn from the data of May *et al.* [23].

For small additions of sodium oxide ($\leqslant 4$ mg) the parabolic rate constants appear to be a function of the square of the sodium oxide content (Fig. 9). Because the reaction interface area appears as a square term in the simple parabolic rate law for the diffusion of uncharged species, relating the square of the weight gain to time, the relationship shown by Fig. 9 suggests that the true reaction interface area is proportional to the mass of sodium oxide present. This is readily explicable if oxidation is taking place at the glass–nitride interfaces of glass-filled pores within the silicon nitride. The reaction interface area will then be proportional to the pore volume filled and in turn to the volume of sodium silicate glass generated in the first moments of reaction between the sodium carbonate and surface silica on the silicon nitride. This volume, it might be expected, would be approximately proportional to the mass of sodium oxide present. It would therefore appear that in the earliest stage of the reaction, the low viscosity glass is rapidly drawn by capillary attraction into porosity underlying the surface of the silicon nitride bar, to form the reaction zone. Scanning electron micrographs show the limited depth of penetration of the glass into the nitride (Fig. 8) and the existence of a "second phase rich" zone at the bar surface. For larger additions of alkali a "saturation" plateau is obtained, suggesting that the rate-controlling interface is now given by the outermost surface area of the silicon nitride bar, and hence is independent of the alkali content. This area was of course used, erroneously it now appears, as the effective reaction interface area in all calculations of reaction rate constants.

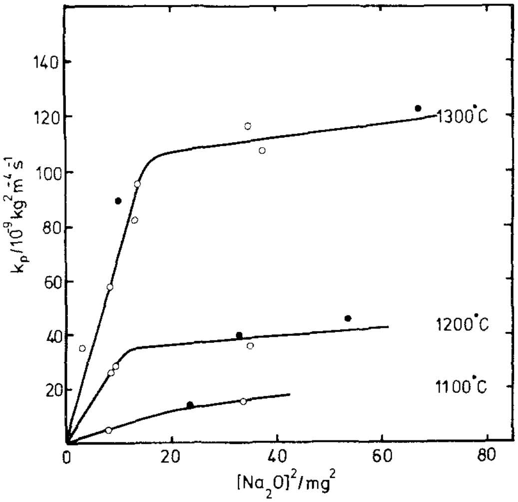

Figure 9 First stage parabolic rate constants for the oxidation of sodium carbonate-coated silicon nitride, as a function of the square of the weight of sodium oxide.

The eventual termination of the fast stage of oxidation can be explained in terms of the $Na_2O–SiO_2$ phase equilibrium diagram. It is assumed (following the discussion on the mechanisms of oxygen diffusion in Section 4. 1) that the reaction proceeds by the inwards diffusion of molecular oxygen through a sodium silicate glass. Oxidation of the silicon nitride takes place at the glass–nitride interfaces to generate silica. This silica will initially dissolve in the glass, and the development of a silica film on the nitride

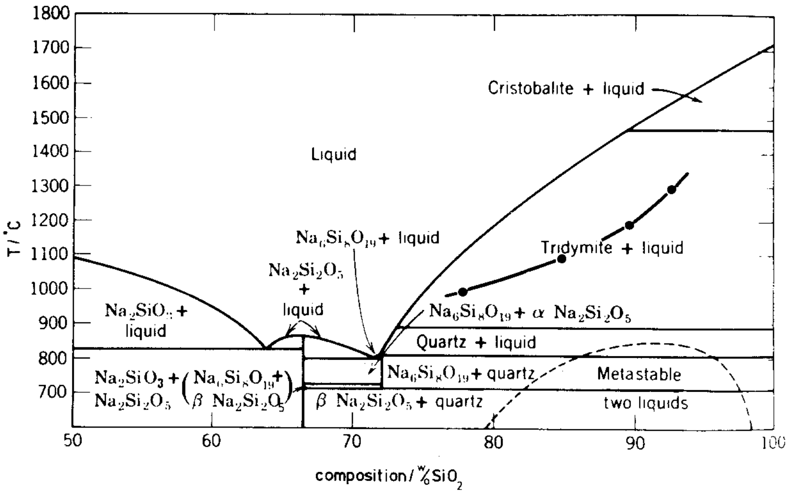

Figure 10 The phase equilibrium diagram for the system Na_2O–SiO_2, showing points for compositions at the fast stage oxidation termination point.

surface, through which oxygen diffusion would be relatively slow, is prevented. Measurements by Schwerdtfeger [24] show that the dissolution of silica in sodium silicate compositions is sufficiently fast to accommodate the observed silica formation rates. Solution of the silica will cease however when the glass composition attains the appropriate liquidus composition for the Na_2O–SiO_2 system. At this point silica (theoretically as tridymite) is stable in contact with the liquid, and further oxidation simply results in the thickening of the protective tridymite film. The slower diffusion of oxygen through the tridymite then becomes the rate controlling step. Reference to the Na_2O–SiO_2 phase diagram [25] shows that the points for the observed critical glass compositions for termination of the fast stage of oxidation lie in reasonable agreement with the liquidus curve (Fig. 10). The predominant crystalline phase observed in oxidation in the presence of alkali was, as required by the phase diagram, tridymite; in the absence of alkali, it was cristobalite. Slight displacements of the points to the silica-rich side of the liquidus may be explained in part by the existence of impurities in the silicon nitride, and in part by a slow attainment of equilibrium and the crystallization of tridymite from the silica-rich glass.

Many of the impurities originally at the surface of the silicon nitride crystallites in the reaction-bonded material would be concentrated in the silicate glass as oxidation proceeded, and the real system would therefore be at least a five component system, rather than the simple binary supposed. This would be likely to have liquidus compositions slightly displaced towards silica, compared with those of the binary system. A slow attainment of the equilibrium state might permit the initial formation of a silicate glass which was supersaturated with respect to silica, before nucleation and development of tridymite occurred. The end result, again, would be an overall SiO_2:Na_2O ratio larger than that expected.

The form of the Arrhenius curve for oxidation in the presence of alkali over the temperature range 900 to 1100° C (Fig. 11) is, within experimental error, identical with that for oxidation in air alone (Fig. 2). This suggests that the medium through which oxygen diffusion is occurring is essentially the same in both cases. Thus it seems that because of the existence of impurities in the silicon nitride, the protective "silica" film formed during normal oxidations in air, or in turbine gases, is in fact a complex silicate. It is also of

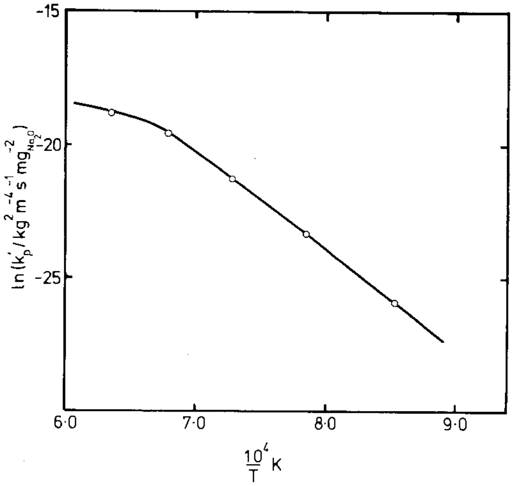

Figure 11 Arrhenius treatment of the initial slopes of plots of parabolic rate constant against square of sodium oxide addition (Fig. 9), for temperatures in the range 900 to 1300° C.

interest in this context that for the most part the oxidation behaviour of "pre-oxidized" and untreated silicon nitride bars in the presence of sodium oxide was the same, even though it might have been assumed that a certain amount of alkali would have been required to bring the "silica" surface film of the pre-oxidized bars to the liquidus composition before the fast oxidation could commence. Instead the plots of k'_p as a function of $(Na_2O)^2$ (Fig. 9) appear to extend to the origin. This suggests that this "silica" film, formed by short term oxidation at 1300° C, was already at a liquidus composition, so that any addition of alkali served to cause dissolution of the thin, true silica, film at the nitride–silicate interface. Ignoring the pre-formed silica in the semi-quantitative treatment of subsequent alkali-assisted oxidations appears retrospectively to have been justified, particularly so since most of the silica so formed is in the interior of the bar, and therefore not involved in further reactions.

5. Conclusions

This study shows the need for further detailed work on the oxidation kinetics of very high purity reaction-bonded silicon nitride. Only in this way can the true oxidation behaviour of the material be established, and the role of impurity elements and phases present in normal commercial materials be more clearly identified. Singhal [1] has drawn attention to the likely importance of secondary phases at the grain boundaries for the oxidation of hot-pressed silicon nitride. The action of alumina in causing accelerated localized oxidation of silicon carbide is also clear [26, 27]. It would be expected on the basis of this and previous evidence that the higher the purity of the silicon nitride, the slower would be its oxidation in air.

It appears that the occasional exposure of reaction-bonded silicon nitride to limited amounts of alkali would not result in serious corrosion, because of the eventual re-sealing action of the tridymite film. On the other hand it is clear that repeated, or continuous exposure to alkali or salts of alkali metals able to form the oxide, such as the chloride or sulphate, will in oxidizing environments lead to extensive corrosion, and eventually the complete degradation of the material.

In the case of the porous, reaction-bonded silicon nitride, the rate of the sodium assisted oxidation depends to a considerable extent on the degree of penetration of surface porosity by low viscosity liquid phases. Some measure of oxidation resistance might therefore be achieved by pre-impregnation with materials that are able either to increase the viscosity of the liquid phase, or to raise the liquidus and the solidus temperatures. On the basis of the $Na_2O–SiO_2$ phase diagram it can be predicted that the oxidation rate observed in the presence of alkali should fall markedly in the region of 800° C, the solidus temperature, because of reduced penetration of the pores of the material by the oxide phase.

Acknowledgements

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