

KINETICS AND MECHANISM OF OXIDATION OF SILICON NITRIDE BONDED SILICON CARBIDE CERAMIC

M. Thorley and R. Banks

British Gas plc, Research & Technology, Gas Research Centre, Ashby Road, Loughborough, Leicestershire LE11 3QU, UK

Abstract

Thermogravimetry (TG) has been used to study the oxidation of a commercial silicon nitride bonded silicon carbide (SNBSC) ceramic. The oxidation was studied in air and carbon dioxide atmospheres between 800 and 1300°C. TG/mass spectrometry (MS) shows that the silicon nitride bonding phase oxidises first. The kinetics follow a multi-stage mechanism with diffusion control. Carbon dioxide was found to be a more powerful oxidant than air at temperatures above 1050°C.

Keywords: ceramics, kinetics, MS, silicon nitride bonded silicon carbide ceramic, TG

Introduction

Gas-fired furnaces provide economical systems for industrial heating, but in some applications the material that is being heated should not be exposed to combustion products. In such cases indirectly-fired furnaces must be used and gas-fired radiant tubes provide an efficient way to achieve this. In low temperature applications metallic tubes are used, but at higher temperatures and in more aggressive environments ceramic tubes are required.

British Gas has developed ceramic radiant tube systems for use in furnaces operating at 700–1250°C; the preferred ceramic is currently silicon nitride bonded silicon carbide (SNBSC). SNBSC forms the basis of an important range of industrial ceramics which combine mechanical strength with high thermal conductivity and stability at high temperatures. The microstructure of a typical SNBSC is shown in Fig. 1: silicon carbide grains (pale grey) are embedded in a silicon nitride bonding phase (dark grey), porosity appearing as black areas on the micrograph.

Several commercial ceramics manufacturers have made radiant tubes and these have been successfully used in industrial furnaces. However, at high temperatures, SNBSC can oxidise, leading to a volume expansion and loss of

strength of the tube. Tube oxidation and deterioration has been found in some commercial field trials [1].

In industrial use, the tubes are exposed to air and also to combustion products which contain water vapour and carbon dioxide: either of these gases can act as an oxidant. The previous paper [1] has described the overall effects of long term oxidation in air and in combustion products at temperatures between 800 and 1200°C.

The present paper describes a detailed investigation of the kinetics of the oxidation, and was part of a larger programme on advanced ceramics. The study used thermogravimetry (TG) and TG/MS to establish the kinetics of oxidation of SNBSC in air and carbon dioxide atmospheres between 800 and 1300°C.

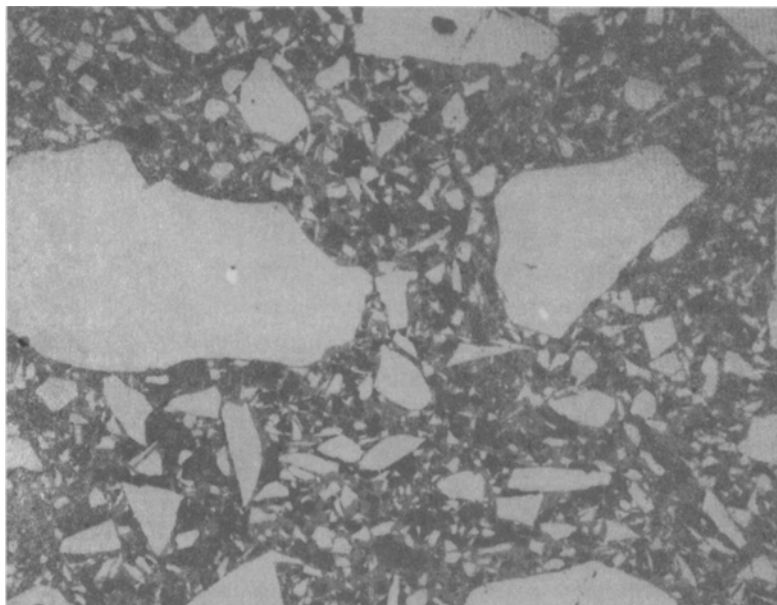


Fig. 1 Microstructure of a typical SNBSC ceramic

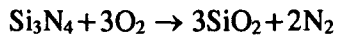
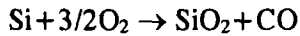
Background

There is an extensive literature on the oxidation of pure silicon carbide and nitride, but it is mostly concerned with the oxidation of single crystals or pure films [2]. There are few papers describing studies of commercial ceramics. The only paper in the literature on the oxidation of SNBSC is that by Völker [3]. He

found that the porosity of the material was important to the rate of oxidation, and that the oxidation involved mainly the nitride bonding phase. At high temperatures he found that oxidation was inhibited by the formation of an oxide glaze.

Similar effects are seen in radiant tubes where SNBSC oxidation is also inhibited by the formation of a protective oxide layer. This layer protects the substrate because of its low diffusivity to oxidising species such as oxygen.

The conversion of both SiC and Si₃N₄ to SiO₂ results in net mass increases:



Therefore, although thermogravimetry (TG) can be used to monitor the oxidation, TG alone cannot distinguish whether it is the silicon carbide grains or the silicon nitride matrix that oxidise initially.

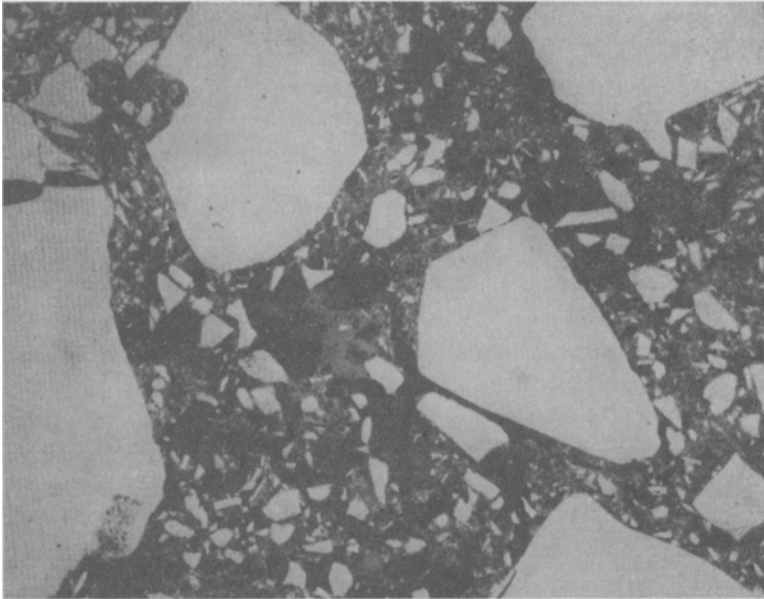


Fig. 2 Internal oxidation of an SNBSC ceramic

A previous study [1] used SEM/optical microscopy and showed that the silicon nitride oxidises first. This is illustrated by the micrograph in Fig. 2: the

phases are similar to those described for Fig. 1 with oxidation appearing as the darkest grey areas, concentrated around pores.

Experimental

The SNBSC used in this study was a commercial material which contained about 75% w/w silicon carbide, 23% w/w silicon nitride and 2% w/w additives. This material had a porosity of ca. 15%. Thermogravimetric studies were carried out in a Netzsch STA 409 Thermal Analyser, and used samples in the form of 1 cm cubes, each weighing typically 2.65 g.

TG experiments were carried out under isothermal conditions. A weighed cube was heated to the oxidation temperature in a flow of oxygen-free argon and was allowed to stabilise before the argon was replaced by the oxidising gas. Experiments were carried out in air and carbon dioxide at 50°C intervals between 800 and 1300°C: oxidation times were generally between 20 and 68 h. Gas flow rates in all cases were 50 cc/min.

Two combined thermogravimetry/mass spectrometry/evolved gas analysis (TG/MS/EGA) experiments were done by Netzsch Gerätebau in Germany using an STA 409 TG system coupled via a heated capillary to a Balzers quadrupole mass spectrometer. In the first experiment the sample was heated in oxygen at 5 deg·min⁻¹, to 1300°C, while in the second the sample was heated to 1000°C in argon then exposed to oxygen at this temperature for 14 h.

Results and discussion

Kinetics

The theoretical models used to explain oxidation in ceramics were originally developed for the oxidation of metals. Kofstad's review summarises many of the commonly encountered rate equations [4]. In these oxidation processes the rate determining step is the diffusion of reactants and/or products through the oxide layer. Reaction rates and equations depend on many factors including temperature, oxidant partial pressure, elapsed time of reaction, surface preparation and pretreatment, and the nature of the oxide layer.

Figure 3 shows typical TG curves for the oxidation of SNBSC; they are plots of the mass increase during oxidation in air at 800, 900 and 1000°C. At these temperatures the oxidation of pure silicon carbide and silicon nitride has been described by the Parabolic rate equation:

$$\Delta w^2 = k_p \cdot t + C$$

where Δw is mass gain at time t , k_p is the parabolic rate constant, and C is a constant.

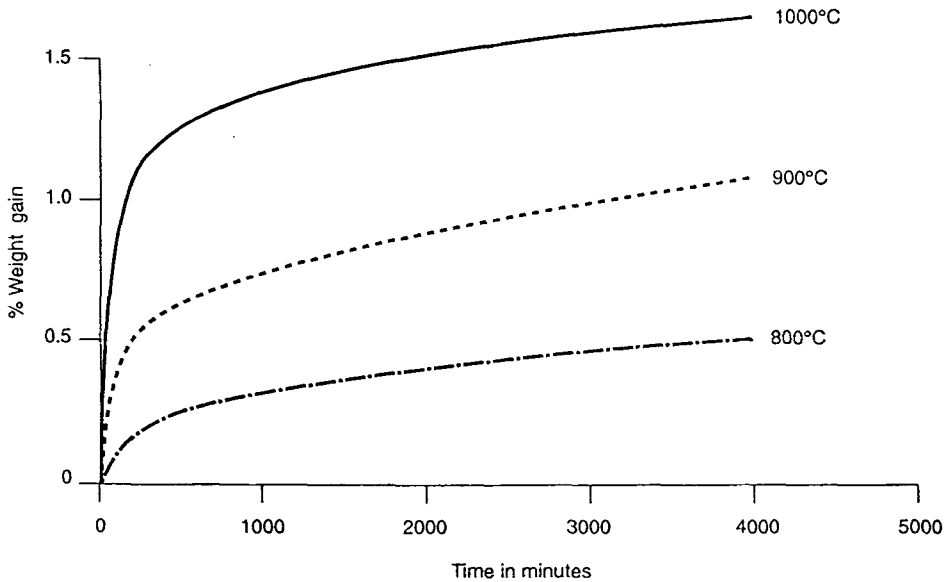


Fig. 3 Typical TG curves for the oxidation of SNBSC ceramic

Figure 4 shows a plot of Δw^2 vs. t for SNBSC oxidation in air at 800°C. In the initial stages the oxidation follows parabolic kinetics, but after about 100 min the plot deviates from this behaviour. To model the kinetics after the parabolic stage, the data were tested against a number of different rate laws, all of which describe diffusion-controlled kinetics: these included General Parabolic, Logarithmic, Asymptotic and Generalised Power equations.

In many previous studies of the oxidation of ceramic materials the reaction rate was initially quite rapid and then dropped off to a low or negligible rate; this was explained by the oxidation products blocking pores and preventing internal oxidation. In some cases the oxidation followed the Logarithmic rate equation, but many oxidation reactions follow a combination of rate laws.

Reactions intermediate between logarithmic and parabolic may often be approximated by the Generalised Power rate equation:

$$\Delta w^n = k_n t + C'$$

where ' n ' is the exponent, k_n is the General Power rate constant and C' is a constant. The Parabolic rate equation is a particular instance of this equation, where ' n ' = 2.

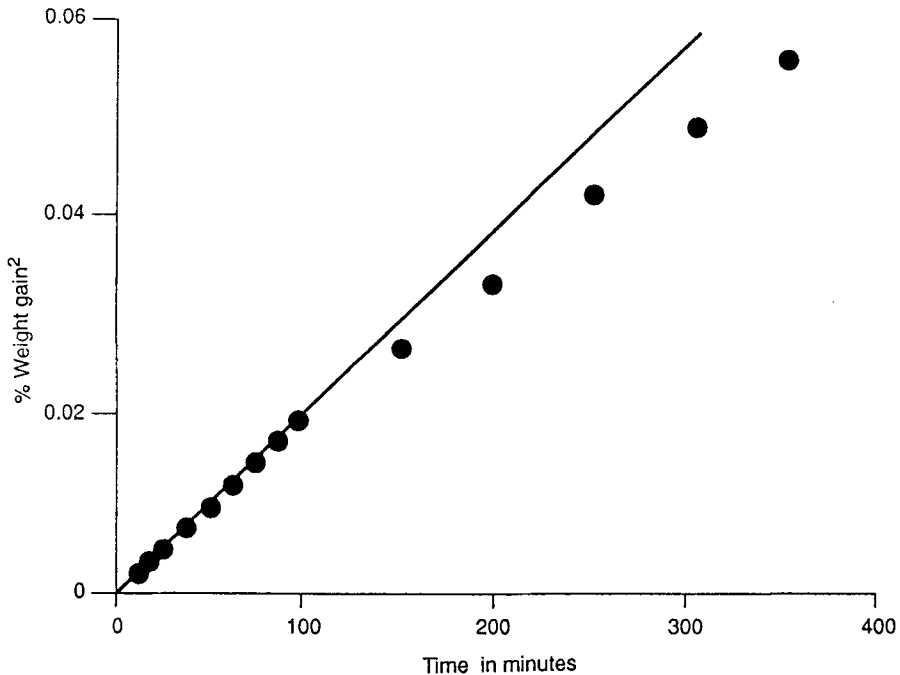


Fig. 4 Deviation of SNBSC oxidation from parabolic rate law kinetics

Air oxidation

The kinetic data for air oxidation can be modelled as a complex multi-stage process based on General Power rate equations, with successive stages having different values of ' n '. The powers of the various stages are listed in Table 1 and the duration of each stage is listed in Table 2. It can be seen from the tables that between 800 and 950°C, the kinetics can be fitted to a two-stage model with ' n ' = 2 (Parabolic) and ' n ' = 4 (Quartic). At temperatures above 1000°C, more stages are involved, each obeying the General Power equation, but with different values of ' n '.

The extent of oxidation increases up to 1050°C, goes through a maximum, and then increases again more slowly. This is shown in Fig. 5, in which the extent of oxidation, expressed as the % mass gain after 1000 min, is plotted against temperature.

Rate constant data for the first two oxidation stages (' n ' = 2 and ' n ' = 4 respectively) give linear Arrhenius plots for temperatures up to 1050°C. Activation energies for the first and second stages are 197 and 337 kJ/mol. Above 1050°C the kinetics do not follow the Arrhenius equation.

Table 1 Optimised values of generalised power law exponents for oxidation of SNBSC in air

$T / ^\circ\text{C}$	Oxidation stage number			
	I	II	III	IV
800	2.0	4.0	–	–
850	2.0	4.0	–	–
900	2.0	4.0	–	–
950	2.0	4.0	–	–
1000	2.0	4.0	8.5	
1050	2.0	4.0	9.0	15.5
1100	2.0	4.0	8.0	17.5
1150	2.0	3.5	7.0	11.0
1200	2.0	3.5	4.5	5.5
1300	2.5	3.5	4.5	9.5

Table 2 Time ranges for various stages of oxidation of SNBSC in air (times in min)

$T / ^\circ\text{C}$	Oxidation stage number			
	I	II	III	IV
800	20–150	200–4000	–	–
850	20–100	150–4000	–	–
900	10–90	100–4000	–	–
950	10–50	60–4000	–	–
1000	10–50	60–200	250–4000	–
1050	10–50	60–150	200–450	500–3500
1100	5–30	40–100	150–500	600–4000
1150	10–30	40–100	150–450	500–1150
1200	5–25	30–90	100–250	300–4000
1300	5–25	30–60	70–450	500–4000

The observed behaviour is almost certainly a consequence of the formation of a protective glaze, which restricts access both to the external surface of the ceramic and into pores in the bulk of the material. The micrograph in Fig. 6 illustrates a typical protective glaze on the surface of an oxidised SNBSC sample. The glaze is a complex mixture of silica and silicates containing aluminium, iron, alkali and alkaline earth metals.

The oxidation involves two distinct processes: one which takes place in internal pores, and one which takes place on the external surface of the ceramic [5]. At lower temperatures when the oxidation reaction proceeds slowly, oxygen

diffuses through the internal pore channels but these are progressively narrowed and blocked by the silica layer formed on their walls. At higher temperatures, the outer surface of the sample is oxidised rapidly, so that pore mouths are closed by glaze. This external pore closure takes place sooner at higher temperatures, resulting in improved oxidation resistance: the onset of glaze formation corresponds to the maximum observed in Fig. 5.

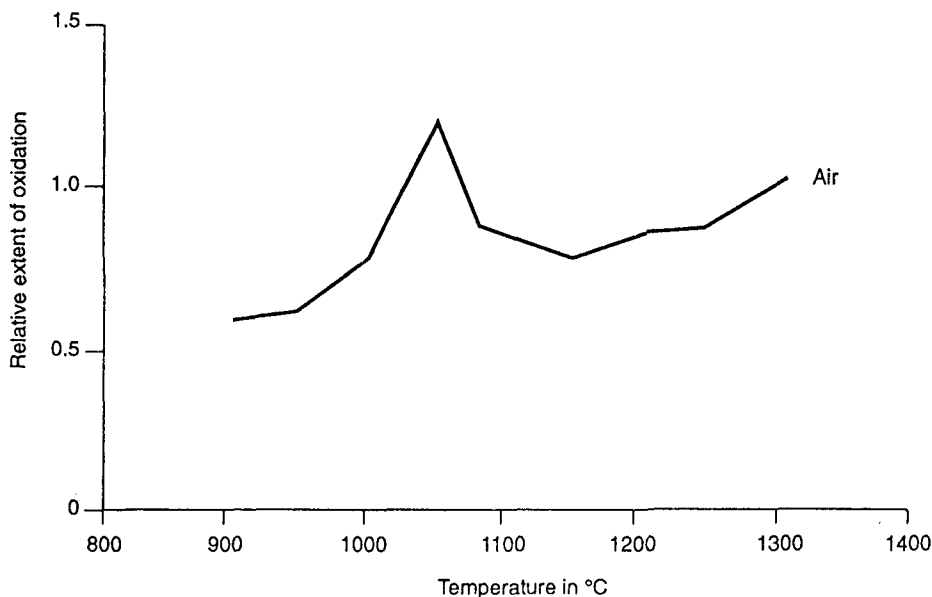


Fig. 5 Air oxidation of SNBSC ceramic

The effects above have been reported by Völker [3] for SNBSC brick and by Porz and Thümmeler [6] for reaction bonded silicon nitride (RBSN), at temperatures similar to those we have observed for our SNBSC material.

Previous studies have not reported the detailed kinetics established in this study. The exact mechanism is not yet fully understood, but microscopy studies have shown that the phase composition of the oxide layer changes with time: this would account for the observed changes in kinetics.

In the TG/MS/EGA studies carried out by Netzsch Gerätebau in Germany, nitrogen predominated in the evolved gases, showing that the silicon nitride oxidises first, rather than the silicon carbide. This confirms the results of the combined SEM/optical microscopy studies carried out by British Gas.

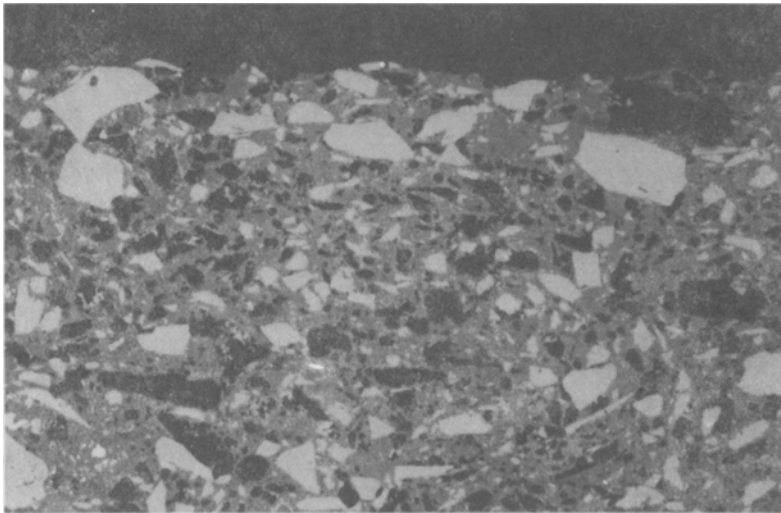


Fig. 6 Protective glaze on the surface of SNBSC ceramic

Carbon dioxide oxidation

The kinetics of oxidation in carbon dioxide are more complicated than in air. The oxidation again follows the General Power rate equation but requires more kinetic stages than in air. This can be seen from Table 3 which lists the powers of the various stages and Table 4 which lists the duration of each stage.

In carbon dioxide the extent of oxidation increases progressively between 800 and 1300°C, in contrast with air where a maximum is seen at 1050°C. This is shown in Fig. 7, which compares extents of oxidation in carbon dioxide and air as a function of temperature.

The most surprising observation is the high extent of oxidation produced by carbon dioxide. Carbon dioxide is not normally thought of as a powerful oxidant, but in this system, at higher temperatures, it is more effective than oxygen.

Table 3 Optimised values of generalised power law exponents for oxidation of SNBSC in carbon dioxide

$T / ^\circ\text{C}$	Oxidation stage number				
	I	II	III	IV	V
900	1.0	2.0	3.0	11.0	3.0
950	1.0	1.5	2.0	3.0	8.0
1000	1.0	1.5	2.0	5.0	15.0
1050	1.5	2.0	7.0	10.0	1.0
1100	1.0	2.0	7.0	17.0	–
1150	1.0	2.0	6.0	16.0	16.0
1200	2.0	3.5	6.0	10.0	10.0
1250	1.0	2.0	5.0	16.0	20.0
1300	2.0	6.0	20.0	24.0	–

Table 4 Time ranges for various stages of oxidation of SNBSC in carbon dioxide (times in min)

$T / ^\circ\text{C}$	Oxidation stage number				
	I	II	III	IV	V
900	0–15	20– 60	70–300	350–1000	1100–4000
950	0–10	15– 30	35–150	200–1300	1400–4000
1000	0–10	15– 50	55–150	200– 500	600–2250
1050	0–45	50–100	110–200	250– 600	700–2250
1100	0–25	30– 70	80–150	300–1100	–
1150	0–10	15– 35	40–110	120– 400	450–1100
1200	0–15	20– 30	35– 45	50– 150	200– 900
1250	0– 4	6– 15	20– 50	55– 400	450–4000
1300	0–10	15– 45	50–100	500–1100	–

The maximum seen for air oxidation (Figs 5 and 7) is attributed to the formation of a protective glaze. This is not found with carbon dioxide until a higher temperature. In air the glaze starts to form at 1050°C, and by 1200°C almost all the surface is covered in a thick glaze. In carbon dioxide the glaze does not start to form until 1200°C. The reason for the different behaviour in carbon dioxide is not clear: it might be that the alkali and alkaline earth oxides in the SNBSC react with the carbon dioxide rather than forming the silicate glaze.

The mechanism for carbon dioxide oxidation is not clearly understood from the present study. However, since we have observed similar behaviour for other silicon-based ceramics, further detailed studies to elucidate the mechanism using complementary techniques would be worthwhile.

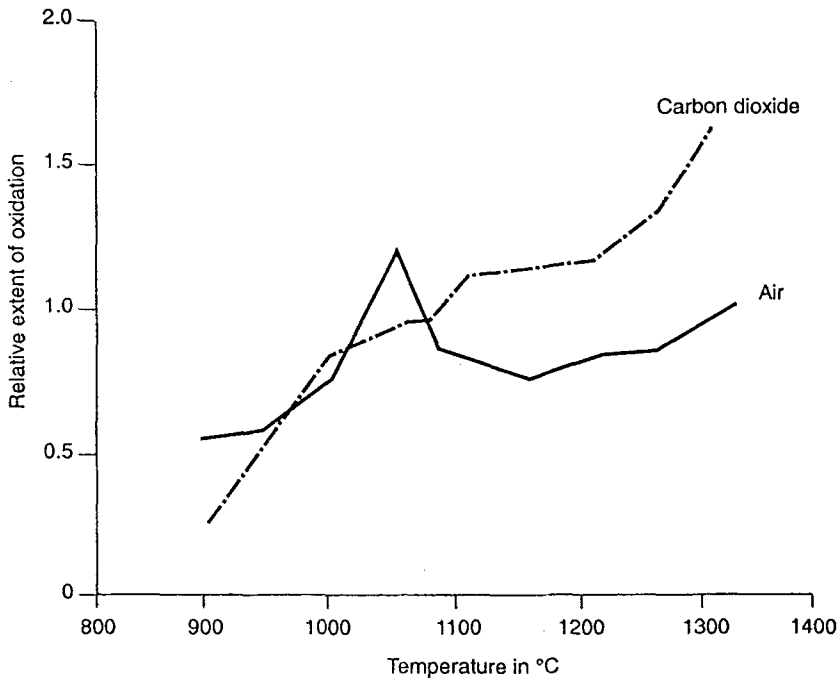


Fig. 7 Comparison of oxidation of SNBSC ceramic in air and carbon dioxide

Techniques such as TG/MS/EGA, FTIR microscopy and electron microscopy might provide the information necessary to understand the mechanism for carbon dioxide oxidation, and the marked differences from that for air oxidation.

Conclusions

The main conclusions from the present studies are:

1. The oxidation kinetics in both air and carbon dioxide can be modelled as a multi-stage, diffusion controlled process using simple mathematical equations.
2. The extent of oxidation in air goes through a maximum at around 1050°C; this is not the case for oxidation in carbon dioxide.
3. Carbon dioxide produces more extensive oxidation than air at temperatures above 1050°C: this is explained by the inhibition of glaze formation in carbon dioxide.

As well as the work described in this paper, the effects of water vapour, and of oxygen and carbon dioxide partial pressures on the oxidation have been studied in detail and will be reported elsewhere.

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Zusammenfassung — Mittels Thermogravimetrie wurde die Oxidation einer handelsüblichen, siliziumnitridgebundenen Siliziumcarbidkeramik (SNBSC) untersucht. Die Oxidation wurde sowohl in Luft als auch in einer Kohlendioxidatmosphäre zwischen 800 und 1300°C untersucht. TG/MS zeigt, daß die Siliziumnitridphase als erste oxidiert wird. Die Reaktionskinetik folgt einem diffusionsbestimmten Mehrstufenmechanismus. Oberhalb 1050°C erwies sich Kohlendioxid als stärkeres Oxidationsmittel als Luft.