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OXIDATION BEHAVIOUR OF A BORON CARBIDE BASED MATERIAL IN DRY AND WET OXYGEN

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Abstract

The oxidation behaviour of a B_4C based material was investigated in a dry atmosphere O_2 (20 vol.%)-CO_2 (5 vol.%)-He and also in the presence of moisture H_2O (2.3 vol%) as boron oxide is very sensitive to water vapour. The mass changes of samples consisting of a chemical vapour deposit of B_4C on silicon nitride substrates were continuously monitored in the range 500–1000°C during isothermal experiments of 20 h. The stability of boron oxide formed by oxidation of B_4C was also studied in dry and wet atmospheres to explain the kinetic curves. In both atmospheres, oxidation is diffusion controlled at 700 and 800°C and enhanced by water vapour. At 900°C and higher temperatures, boron oxide volatilisation and consumption by reaction with water vapour modifies the properties of the oxide film and the material is no more protected. At 600°C, B_4C oxidation is weak but the process remains diffusion controlled in dry conditions as boron oxide volatilisation is negligible. However, in the presence of water vapour, B_2O_3 consumption rate is significant and mass losses corresponding to this consumption and to the combustion of the excess carbon are observed.

Keywords: boron carbide, kinetic modelling, oxidation, water vapour

Introduction

Ceramic matrix composites (CMCs) reinforced by continuous SiC based ceramic fibres have been developed for thermostructural applications which require good mechanical properties and corrosion resistance [1]. The oxidation shortens the life of ceramic material by erosion when carbon is used as a fibre/matrix interphase [2, 3]. Their protection by coatings may be not efficient as cracks are formed as a result of thermal expansion mismatches or during loading. However, a self-healing behaviour can be observed if the cracks are sealed by an oxide, for example, silica resulting from silicon carbide oxidation [2]. In this case, the self-protection by silica formation occurs only above 1000°C because of the low kinetics of SiC oxidation. Another possibility is to incorporate boron containing phases which lead to the formation of bo-

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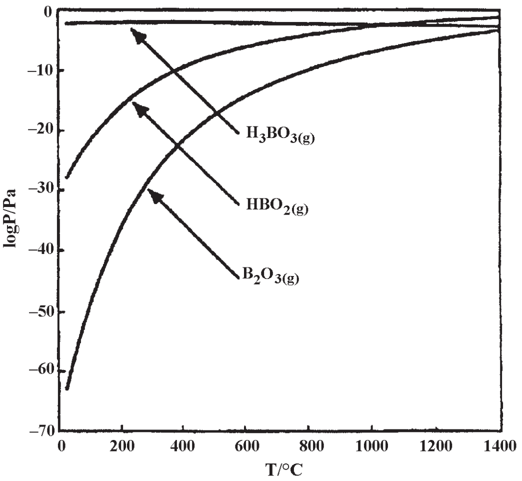

Fig. 1 Vapour pressure of B_2O_3, HBO_2 and H_3BO_3 with temperature in moist atmospheres obtained by thermodynamic calculation from Kobayashi [6]; $B_2O_{3(s,l)}=B_2O_{3(g)}$, $B_2O_{3(s,l)}+H_2O_{(g)}=2HBO_{2(g)}$, $B_2O_{3(s,l)}+3H_2O_{(g)}=2H_3BO_{3(g)}$

ron oxide (Eq. (1) which has a low melting point 450°C [4–10]. Nevertheless, the problem with borate is their volatility [11], which is dramatically enhanced by water vapour [4–6, 9]. At atmospheric pressure, volatilisation begins at around 900°C (Eq. (2)) and the reactions with water vapour give $HBO_{2(g)}$ (Eq. (3)) and $H_3BO_{3(g)}$ (Eq. (4)) (Fig. 1).

$$B_4C_{(s)}+4O_2=2B_2O_{3(s,l)}+CO_2 \quad (1)$$

$$B_2O_{3(s,l)}=B_2O_{3(g)} \quad (2)$$

$$B_2O_{3(s,l)}+H_2O_{(g)}=2HBO_{2(g)} \quad (3)$$

$$B_2O_{3(s,l)}+3H_2O_{(g)}=2H_3BO_{3(g)} \quad (4)$$

The kinetics of boron oxidation and of boron oxide consumption are thus important parameters for the oxidation resistance of boron containing composites. These parameters have been investigated [12] and the results are presented in this paper. The aim of the study is not to perform a complete kinetic study of boron carbide oxidation, but to understand the main phenomena occurring in dry and wet oxidising atmospheres in order to explain the results on the oxidation behaviour of composites [12–14].

Material and experimental

The starting material used in the experiments is boron carbide deposited by chemical vapour deposition on sintered silicon nitride coupons (10×10×8 mm^3). In our experimental conditions where the highest temperature is 1000°C applied for maximum duration of 20 h, the oxidation of Si_3N_4 is negligible and this substrate can be considered as inert [15].

The atomic elemental composition of the CVD deposit has been determined from microanalysis (CAMECA SX100). According to literature [16], a single phase domain in the system boron–carbon exists in the range from around 9 at.% C ($B_{10}C$) to around 20 at.% C (B_4C). The materials with higher carbon content are constituted of two phases, boron carbide and free carbon. An excess of carbon is thus present in the studied samples.

The oxidation of the material was followed by thermogravimetry using a thermobalance (Setaram B60). The mass changes were continuously monitored. A platinum wire and an alumina crucible were used to hold the sample in the furnace. The experiments were performed with a total flow rate of 1.8 $l\ h^{-1}$ either in a dry atmosphere consisting of oxygen (20 vol.%), carbon dioxide (5 vol.%) and helium or a wet atmosphere obtained by the bubbling of the previous gas mixture in a water bath maintained at a constant temperature (20°C). The resulting water vapour content was 2.3 vol.%. Isothermal kinetic curves have been obtained in the range 500–1000°C for duration of 20 h. The temperature ramp (10°C min^{-1}) was conducted under dry helium until the desired temperature was reached. Then the chosen atmosphere for the experiments was introduced and this corresponded to the starting time of the isotherm.

To study the rate of boron oxide consumption either by volatilisation (Eq. (2)) or by reaction with water vapour (Eqs (3) and (4)), previous samples have been oxidised in the dry atmosphere at 900°C until boron carbide was entirely transformed; this was achieved after 30 h of treatment. The obtained samples consisting of a boron oxide film on the silicon nitride substrates were then treated either in dry helium or in helium bubbled through water (2.3 vol.%). The thermogravimetric curves corresponding to boron oxide consumption were also continuously monitored.

Results and discussion

Boron carbide oxidation in a dry atmosphere He–O_2(20%)–CO_2(5%)

Isothermal kinetic curves obtained in the range 500–900°C are shown in Fig. 2. The ratio of the mass change (Δm in mg) to the geometrical area of the sample (S in cm^2) is represented.

At 500°C, a very weak mass loss is observed. At this temperature, the oxidation of boron carbide is negligible and the mass loss can be attributed to the combustion of superficial carbon. At higher temperatures, an overall mass gain corresponding to the combustion of carbon and to B_2O_3 formation is observed. Between 600 and 800°C, the mass gain follows a parabolic law ($(\Delta m/S)^2=kt$), which indicates a diffusion regime through the protective boron oxide layer. However, at 900°C, the mass gain becomes quite more important and the curve doesn't follow a parabolic law (Fig. 3). The volatilisation of boron oxide and a change in its viscosity may explain this behaviour. B_2O_3 layer becomes very fluid and spreads in the bottom of the crucible. The re-

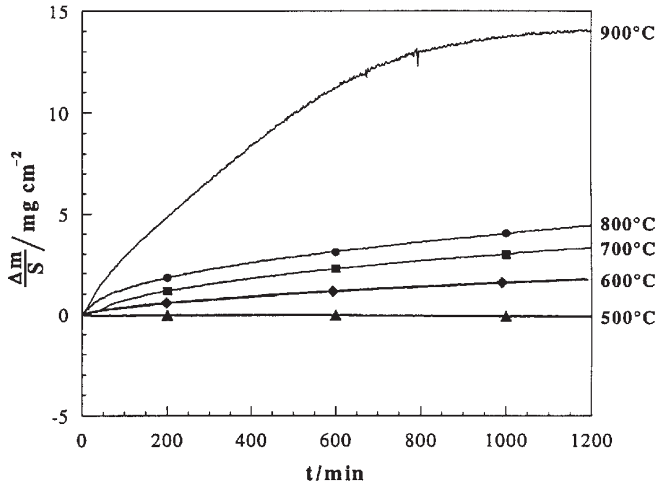

Fig. 2 Kinetic curves obtained during oxidation in dry atmosphere; He–O_2(20%)–CO_2(5%)

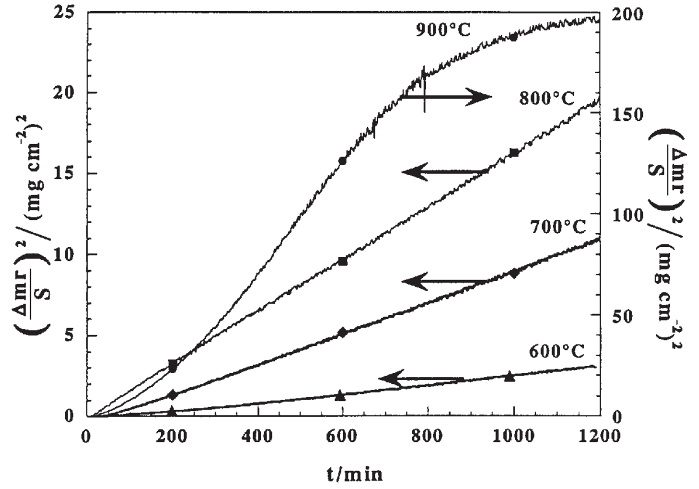

Fig. 3 Parabolic transformation of the kinetic curves obtained in dry atmosphere

sult is a non-homogeneous B_2O_3 thickness on the sample and the upper part may be completely uncovered. Thus, the kinetic modelling is too complex. The oxidation rate is consequently higher than that of experiments conducted in the range 600–800°C. The experiment performed at 900°C also indicates that the rate of mass loss due to B_2O_3 volatilisation remains weak compared to its rate of formation, otherwise a mass loss should be measured. We have verified that a mass loss effectively occurs if the experiment at 900°C goes on after 20 h because B_4C is entirely oxidised (no more mass gain).

Oxidation in a wet atmosphere He–O_2(20%)–CO_2(5%)–H_2O(2.3%)

The kinetic curves obtained in the presence of moisture are reported in Fig. 4. At 700 and 800°C, oxidation is enhanced by water vapour (Fig. 5) and the kinetic regime is parabolic ($(\Delta m/S)^2=k't$). This means that the oxidation remains limited by diffusion through boron oxide, but the diffusion is enhanced by water. Many parameters explain the kinetics enhancement, such as the thickness of the oxide scale related to the viscosity, and the nature of the diffusing species. This result also indicates that the

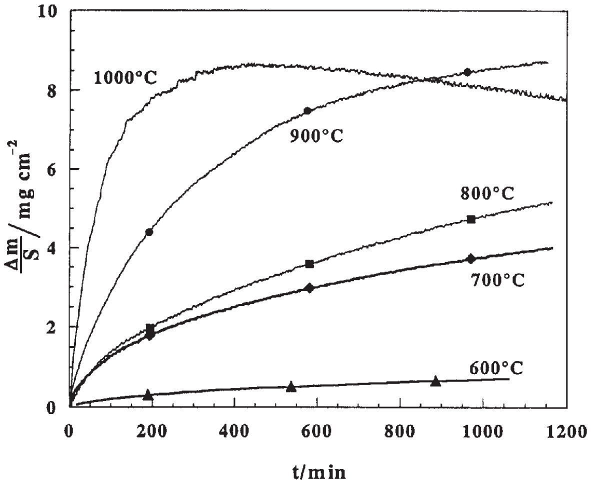

Fig. 4 Kinetic curves obtained during oxidation in wet atmosphere; He–O_2(20%)–CO_2(5%)–H_2O(2.3%)

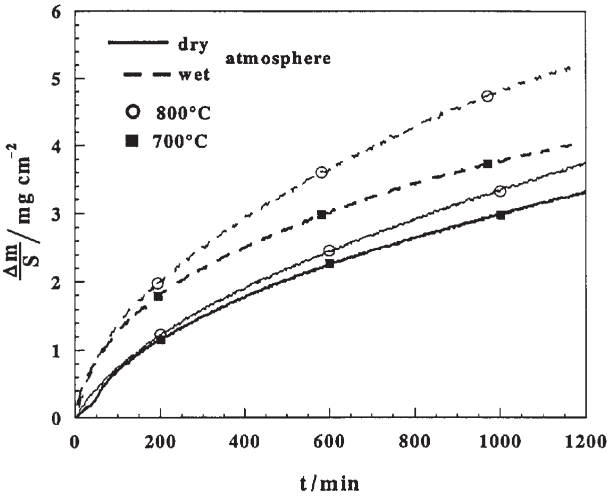

Fig. 5 Influence of water vapour on oxidation at 700 and 800°C

loss of B_2O_3 by volatilisation (Eq. (2)) or by reaction with water vapour (Eqs (3), (4)) is negligible compared to its formation from B_4C.

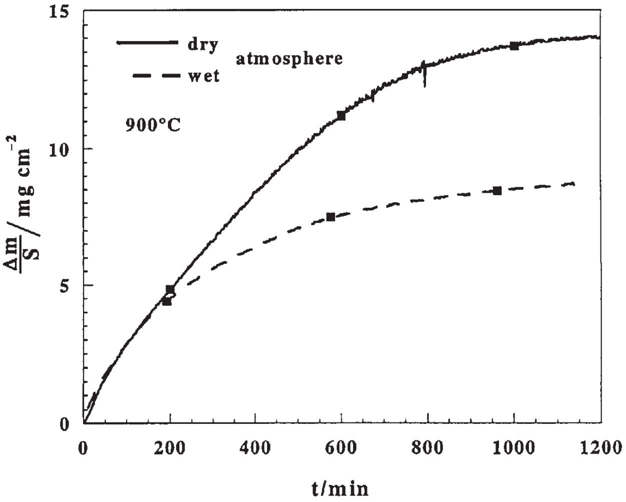

Fig. 6 Influence of water vapour on oxidation at 900°C

At 900°C, the global mass gain in wet atmosphere is lower than in the dry one (Fig. 6). As the experiments at 700 and 800°C reveal that water enhances diffusion through the oxide layer, the weaker mass gain measured at 900°C is explained by the loss of B_2O_3 (section 3.3). It occurs mainly by the reactions with water vapour (Eqs (3) and (4), Fig. 1) as this phenomenon is not observed in dry atmosphere.

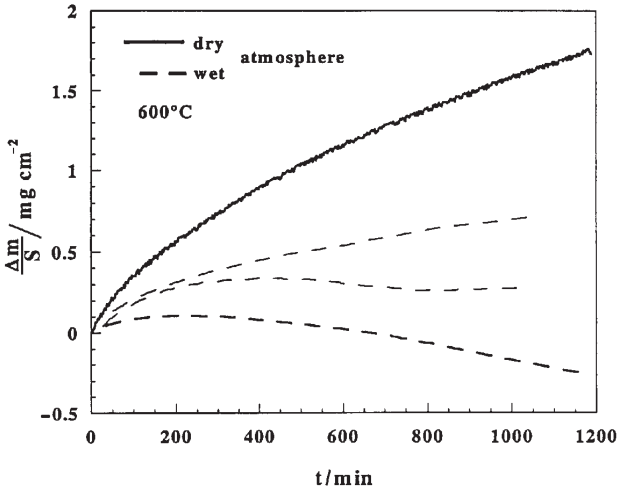

Fig. 7 Influence of water vapour on oxidation at 600°C

At 600°C, three experiments have been conducted under the same conditions He–O_2(20%)–CO_2(5%) with a controlled water vapour content (2.3 vol%) and Fig. 7 shows that the results are quite erratic: continuous mass loss, mass gain followed by a loss or continuous gain. This behaviour may be explained by considering the competition between the reactions and their kinetics. The reactions correspond to

– formation of boron oxide $\Delta m>0$ (Eq. (1))
– consumption of boron oxide $\Delta m<0$ (Eqs (2), (3) and (4))
– combustion of free carbon $\Delta m<0$ ($C+O_2=CO_2$).

If we consider the material composition, the global reaction results in a mass gain (Δm=+39.5 g/B_2O_3 mole). However, if the kinetics of B_2O_3 formation is very slow, the rate of B_2O_3 consumption by the reaction with water vapour becomes significant. A B_2O_3 layer cannot form and a preferential oxidation of carbon occurs, creating porosity inside the samples and leading to mass loss. Consequently, the behaviour of the samples at 600°C in the presence of water vapour is extremely dependent on the superficial microstructure of the sample (dispersion of carbon in boron carbide). This explains the scattering of the experiments at 600°C in a wet atmosphere. In a dry atmosphere, volatilisation is negligible and the experiments are reproducible.

Boron oxide consumption

The rate of B_2O_3 consumption in dry and wet helium has been followed with the preoxidised samples as indicated in section 2. The mass changes observed at various temperatures are shown in Fig. 8. In dry helium, no variation is detected until 800°C. At 900°C, a mass loss corresponding to B_2O_3 volatilisation is observed. In the presence of water, a mass loss is measured at 600 and 800°C. As volatilisation is negligi-

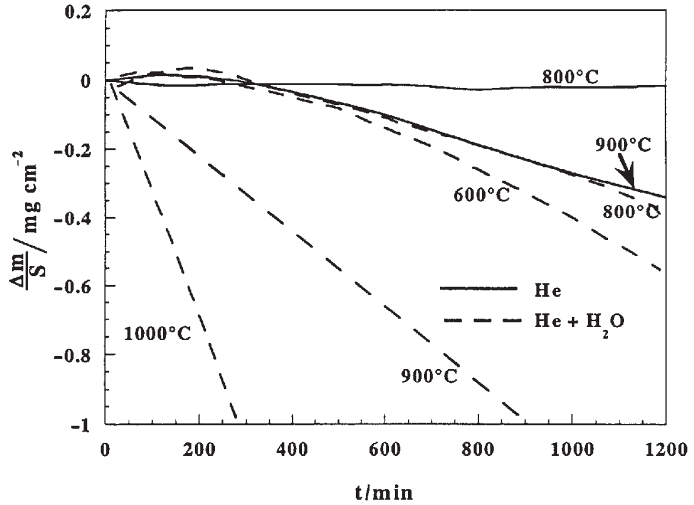

Fig. 8 Kinetics of boron oxide consumption in dry and wet atmosphere

ble at these temperatures, this mass loss is attributed to the formation of HBO_2 or H_3BO_3 (Eqs (3) and (4)). It can be seen (Fig. 8) that the loss is more important at 600°C than at 800°C. It may be explained by different rates for reactions (Eqs (3) and (4)). However, we cannot verify this point with thermogravimetric experiments. At 900°C, the mass loss is quite more important and corresponds to the removal of B_2O_3 by both volatilisation and reaction with water vapour. The rates of the global mass loss have been measured in the linear part of the curves (Fig. 8) and are reported in Table 1. The value calculated from the experiment in wet atmosphere at 1000°C is in good agreement with the one reported in the literature [9], measured in air containing 3% of moisture: 0.003–0.005 mg cm^{-2} min^{-1}.

Table 1 Boron oxide consumption rate in dry and wet helium

Temperature/°C	Rate of mass loss/mg cm^{-2} min^{-1}	
	He	He+H_2O (2.3 vol.%)
600	≅0	0.0007
800	≅0	0.0004
900	0.0004	0.0011
1000		0.0039

Conclusions

In a dry atmosphere, the oxidation of a boron carbide based material leads to the formation of a viscous boron oxide layer, which is protective until 800°C because its volatilisation is negligible. From 900°C, volatilisation occurs. It remains weak in term of mass loss but the oxide is no more protective.

In a wet atmosphere, boron oxide is consumed by reaction with water vapour. At 600°C, the consumption rate is close to the oxidation rate of B_4C and the behaviour mainly depends on the homogeneity of the sample and on the local pressure of water vapour. At 700 and 800°C, the oxidation rate of B_4C increases and is enhanced by water vapour; B_2O_3 consumption rate is negligible. At 900°C, this rate sharply increases and the resulting mass loss due to B_2O_3 removal is significant.

This study does not allow to quantify the kinetic parameters due to the viscosity changes of B_2O_3 at high temperature but it clearly points out that the incorporation of boron carbide in a composite may be efficient to provide a self-healing behaviour in the temperature range 700–800°. At lower temperature (600°C), the boron carbide oxidation rate is two low, or at least the composite has to be pre-oxidised at higher temperature to form a protective layer. At higher temperature (≥900°C), borate volatilisation seems to be an important problem to allow a good oxidation protection.

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