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Carbon reduction reaction in the Y_2O_3–SiO_2 glass system at high temperature

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Abstract

In order to assess the role of carbon with respect to the grain boundary chemistry of Si_3N_4-based ceramics model experiments were performed. Y_2O_3–SiO_2 glass systems with various amount of carbon (from 1 to 30 wt.%) were prepared by high-temperature treatment in a graphite furnace. High carbon activity of the furnace atmosphere was observed. EDX analysis proved the formation of SiC by the carbothermal reduction of SiO_2 either in the melt or in the solid state. The melting temperature of the Y_2O_3–SiO_2 system is strongly dependent on the amount of reduced SiO_2. XRD analysis of the products documented the presence of $Y_2Si_2O_7$, Y_2SiO_5 and Y_2O_3 crystalline phases in that order with an increasing amount of free C in the starting mixture. The reduction of Y_2O_3 was not confirmed.

Keywords: Carbothermal reduction; Glass; Grain boundary phase; Si_3N_4; Y_2O_3–SiO_2

1. Introduction

Y_2O_3–SiO_2 based glass is frequently detected as grain boundary (GB) films and triple points in Si_3N_4-based ceramics. The room temperature (RT) and high temperature (HT) properties of these materials depend on the properties of the GB phase. A slight change in the GB chemistry can cause significant changes in the mechanical behaviour.[1] The oxide GB system is also influenced by the carbon, which is always present in the atmosphere of furnaces furnished with graphite-heating elements and/or is introduced by the starting powder.[2] Possible chemical changes of the GB composition can then have a dramatic effect on the overall mechanical properties of the Si_3N_4-based ceramics.[3]

When the carbon activity is high, ($a_c \leqslant 1$), the reduction of SiO_2 within the Y_2O_3–SiO_2 glass system is possible according to the following reaction,[4]

$$\begin{aligned} &SiO_2(s,l) + 3C(s) \rightarrow SiC(s) + 2CO(g) \\ &K_1(1750^\circ C) = 96.4 \qquad \Delta G_1(1750^\circ C) = -76.8\,kJ/mol \\ &K_1(1900^\circ C) = 1.01 \times 10^3 \qquad \Delta G_1(1900^\circ C) = -124.8\,kJ/mol \end{aligned} \tag{1}$$

Based on the thermodynamic calculations, the reduction of the Y_2O_3 is not anticipated.

The effects of the carbon on the GB chemistry and thus on the properties of Si_3N_4-based composites are still not completely clear. For that reason, model experiments were performed in the Y_2O_3–SiO_2–C system under similar conditions to those under which real Si_3N_4-based composites are prepared. The present paper studies the possible reduction of SiO_2 by carbon and its influence on the phase composition, melting temperature and glass formation of the Y_2O_3–SiO_2 system at high temperatures ($T \geqslant 1750^\circ C$).

2. Experimental

Samples were prepared by mixing of powders of Y_2O_3 (PID, 99.99%, USA), amorphous SiO_2 (50 $m^2\ g^{-1}$, Aerosil OX-50, Degussa, Germany) and pigment grade carbon black ($S_{BET} = 1000\ m^2\ g^{-1}$). The ratio of SiO_2/Y_2O_3 is kept at a constant 2.57 in all the used compositions. The chemical compositions of the samples are given in Table 1.

The powder mixtures were ball-milled for 24 h in isopropyl alcohol. Dried mixtures were uniaxially cold pressed at a pressure of 100 MPa in a steel die to form

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green compacts with diameter of 10 mm, height of 5 mm. These pellets were heated at 1750 and 1940°C in a graphite crucible without/with a powder bed of Y_2O_3–SiO_2–BN composition. The powder bed consists of SiO_2 and Y_2O_3 in the same molar ratio as the sample, i.e. 2.57. The 20 wt.% of BN were added in order to prevent the densification of the powder bed during heating. The temperature of 1750°C and a slight over-pressure of nitrogen (0.15 MPa) were selected in order to have similar conditions to those during sintering of Si_3N_4/SiC composites. The chemical changes in the silicate melt, as a result of reactions with added carbon, were studied on the cooled samples. Samples SY1, SY2, SYC1, SYC5, SYC20A were heated with heating rates of 10°C/min to a temperature of 1750°C. Samples SYC20B and SYC30A, B were heated with heating rates 50°C/min and sample SYC30C was heated with rate 150°C/min to a temperature of 1940°C, Table 2. A slight over-pressure of nitrogen (0.15 MPa) was used as in the previous case.

The surfaces of completely melted specimens were polished to 1 μm finish and plasma etched with a gas mixture of CF_4 and O_2 to highlight the grain structures. The etched surfaces were examined by SEM (Jeol JSM-35), and the elemental analysis was conducted using energy disperse spectrometry (EDX, Cambridge, UK). The crystalline phases present in the ground samples were identified using X-ray diffraction (STOE powder diffraction system with CoK_α radiation).

Table 1
Composition of samples

Sample	Carbon content	Y_2O_3	SiO_2
	mol%/(wt.%)	mol%/(wt.%)	mol%/(wt.%)
SY1-2	–/–	28.0/59.3	72.0/40.6
SYC1	8.0/1	25.7/58.8	66.3/40.2
SYC5	32.1/5	19.1/56.4	48.8/38.5
SYC20A-B	69.0/20	8.7/47.5	22.3/32.5
SYC30A-C	79.4/30	5.7/41.7	14.9/28.5

3. Results and discussion

3.1. Carbon activity of the furnace atmosphere

Sample SY1 with the eutectic composition of the Y_2O_3–SiO_2 binary system (see Fig. 1 $T_E = 1660°C^5$) was heated in the graphite crucible at 1750°C for 2 h in a nitrogen atmosphere. This sample had not melted even though the temperature of the experiment was set 90°C above $T_E = 1660°C$. The carbon activity in the graphite crucible was high, nearly 1 and caused the partial reduction of SiO_2. This statement was proved also by XRD analysis. The presence of $Y_2Si_2O_7$ and Y_2SiO_5 phases was documented in the cooled sample, Table 2. This phase composition corresponds to the phase diagram shown in Fig. 1 since, by decreasing the SiO_2 content, the presence of $Y_2Si_2O_7$ and Y_2SiO_5 phases is produced. To verify the effect of the furnace atmosphere carbon activity, sample SY2 with the same eutectic composition as SY1, was heated in the graphite furnace under the same conditions (1750°C/N_2), but the sample was embedded in the Y_2O_3–SiO_2–BN powder bed. Sample SY2 was found to be completely melted. The XRD analysis showed the orthorhombic $Y_2Si_2O_7$ phase, and also the presence of SiO_2 and Si_2N_2O phases. The

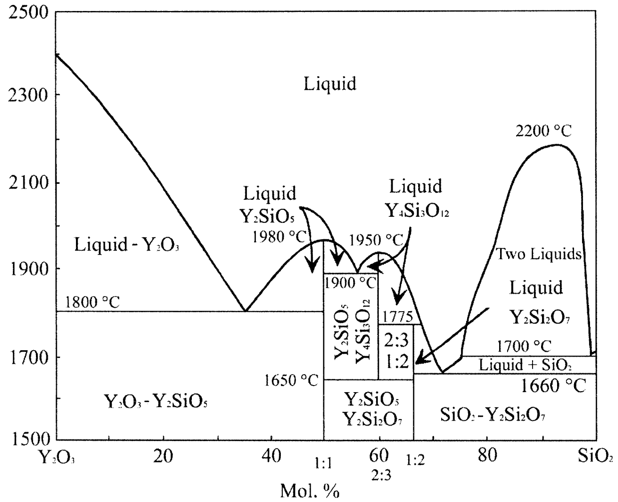

Fig. 1. Phase diagram Y_2O_3–SiO_2.[5]

Table 2
Results of the phase analysis of the samples fired at 1750 and 1940°C

Sample	Heating cycles	Heating rates	Molar ratio C_{free}/SiO_2	Phase detected by XRD
SY1	1750°C/2 h/N_2	10°C/min	–	$Y_2Si_2O_7$, Y_2SiO_5
SY2	1750°C/0.5 h/N_2	10°C/min	–	$Y_2Si_2O_7$-orthoromb., SiO_2, Si_2N_2O
SYC1	1750°C/2 h/N_2	10°C/min	0.14	$Y_2Si_2O_7$-monoclinic,
SYC5	1750°C/2 h/N_2	10°C/min	0.65	$Y_2Si_2O_7$, Y_2SiO_5
SYC20A	1750°C/2 h/N_2	10°C/min	3.09	Y_2SiO_5, Y_2O_3, SiC, $Y_4Si_2N_2O_7$
SYC20B	1940°C/0.5 h/N_2	50°C/min	3.09	Y_2O_3, SiC
SYC30A	1940°C/20 min/N_2	50°C/min	5.22	Y_2O_3, SiC
SYC30B	1940°C/2 min/N_2	50°C/min	5.22	Y_2O_3, SiC
SYC30C	1940°C/2 min/N_2	150°C/min	5.22	Y_2O_3, SiC

presence of the Si_2N_2O phase is most probably a consequence of the reaction:

$$\begin{gathered} 2SiO(g) + CO(g) + N_2(g) \rightarrow Si_2N_2O(s) + CO_2(g) \\ K_2(1727°C) = 1.05 \qquad \Delta G_2(1727°C) = -797.6 \text{ kJ/mol} \end{gathered} \tag{2}$$

which proceeds also at the low/negligible carbon activity.[6–8] Thus, the thickness of the powder bed between the wall of the crucible and the specimen is large enough to decrease the penetration and to slow-down the diffusion of CO/CO_2 from the furnace atmosphere towards the specimen. Carbon diffusion from the crucible/heating element to the sample is hindered not only mechanically but also by the reduction of the SiO_2 present in the powder bed.

These experiments show the pronounced activity of carbon in furnaces with carbon heating elements. Moreover, the use of carbon crucibles increases the value of a_c. In order to diminish the influence of the furnace/crucible carbon on the sample, and to achieve a better control of the reactions, the use of a powder bed containing SiO_2 is necessary. For this reason, all of the following experiments were performed with the powder bed to limit the effect of the carbon activity in the furnace/crucible atmosphere.

3.2. Activity of carbon introduced along with the starting powders

Samples with the addition of 1 and 5 wt.% of carbon (SYC1 and SYC5) were heated in the graphite crucible under the same conditions (1750°C /N_2) as above. These samples had completely melted and no carbon was visually detected after the heating cycles. The cooled drop-shaped samples were completely white. All heterogeneous reactions in the samples SYC1 and SYC5 proceeded in the Y_2O_3–SiO_2 melt. The resultant products contained a considerable quantity of pores, mainly in the centre of the samples as a result of evolving gases from the 2 steps of reaction (1):

$$SiO_2(l) + C(s) \rightarrow SiO(g) + CO(g) \tag{3}$$

$$SiO(g) + C(s) \rightarrow SiO(s) + CO(g) \tag{4}$$

Sample SYC1 contained predominantly $Y_2Si_2O_7$ phase. The surface of sample SYC5 was white after heating. On the other hand black grains of carbon were found in the bulk by SEM. EDX analysis of the SYC5 matrix showed the presence of the elements O, C, Y and Si (Fig. 2). XRD confirmed the presence of the $Y_2Si_2O_7$ and Y_2SiO_5 phases, while the carbon phases were below the detection limit of the XRD analysis. The results of

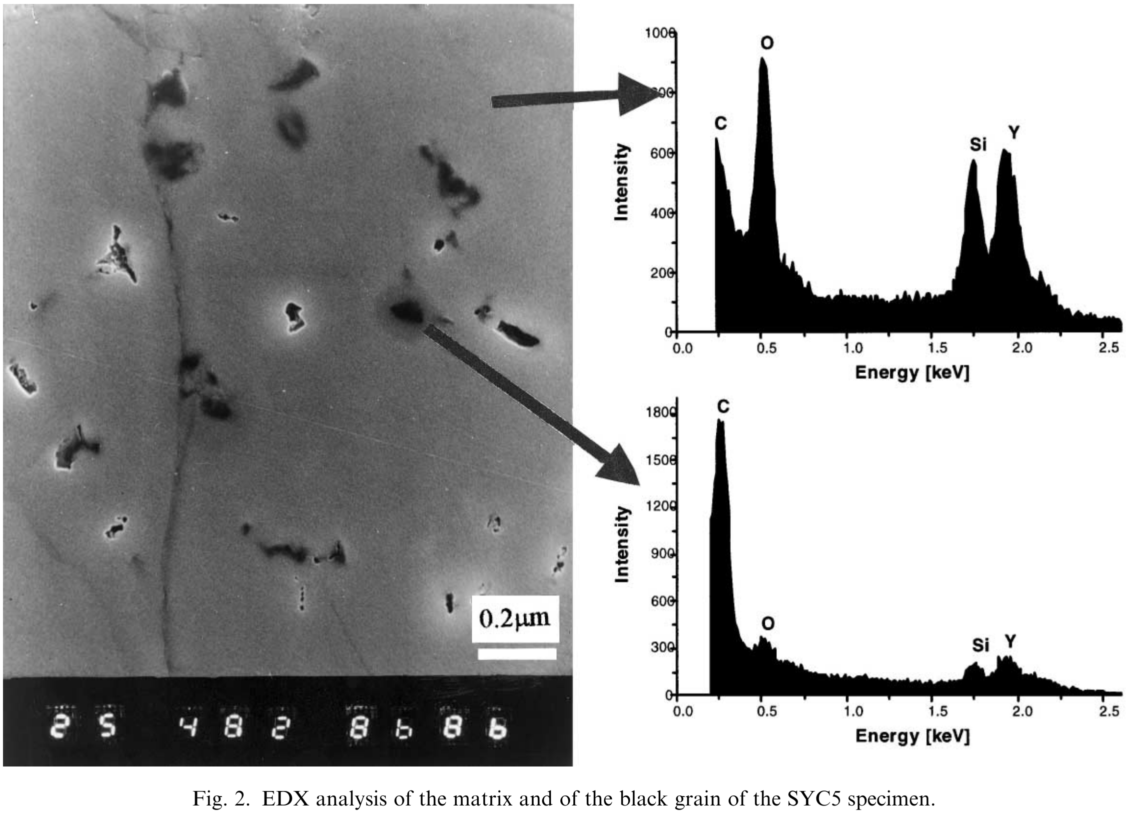

Fig. 2. EDX analysis of the matrix and of the black grain of the SYC5 specimen.

the phase analysis are summarised in Table 2 and are consistent with the phase diagram in Fig. 1, supposing the decrease of the SiO_2 content to occur by carbothermal reduction in the Y_2O_3–SiO_2 system.

The sample containing 20 wt.% of carbon, SYC20A had not melted at 1750°C/N_2 even though the powder bed was applied. The sample after heating was completely white, but its core was dark green. The XRD analysis confirmed that the green phase is SiC. Phases $Y_2Si_2O_7$ and Y_2SiO_5 were also detected. Addition of 20 wt.% of carbon into the sample SYC20A results in the molar ratio $C/SiO_2 = 3.09$, which was consistent with the reaction (1), where the stoichiometric C/SiO_2 ratio is 3. Decrease of the SiO_2 content in the Y_2O_3–SiO_2 system by reaction (1) caused a shift in the Y_2O_3–SiO_2 phase diagram (Fig. 1) to the region close to the higher eutectic temperature (T_E ($Y_2Si_2O_7$–$Y_4Si_3O_{12}$) = 1900°C). In order to prove the last statement, samples SYC20B and SYC30A-C were heated at 1940°C with increased heating rates. Formation of a melt was observed only in sample SYC20B. XRD analysis showed that the major phases in this specimen were Y_2O_3 and SiC (Table 2). EDX analysis of the matrix of the SYC20B specimen proved the presence of yttrium and oxygen in great amount and a small amount of silicon and carbon (Fig. 3). EDX analysis of the dark grains in the microstructure of this specimen showed the presence of silicon and carbon, and this observation supported the presence of SiC as indicated also by the XRD. This result confirms the formation of SiC with reaction between SiO_2 and C in the melt as proposed in previous paper of the authors.[9]

In specimens SYC30A-C, a considerable excess of carbon, molar ratio of $C/SiO_2 = 5.22$, was achieved by addition of 30 wt.% of carbon black to the starting mixture (Table 1). The formation of a melt was not observed in any of these samples, even though a high heating rate (150°C/min) was applied up to the temperature of 1940°C. The high heating rate was used to minimise the reaction time. XRD analysis of the SYC30A-C samples showed the presence of Y_2O_3 and SiC phases only (Fig. 4).

The highest amount of SiC was achieved at the lowest heating rate and the longest dwell time at the 1940°C. This observation is consistent with the assumption that the reduction kinetics is an important factor influencing the final composition of the Y_2O_3–SiO_2–C system and thus its physical properties. The reaction kinetics of SiC formation as a function of the heating rate and the holding time is seen on the diffraction records shown in Fig. 4. The sample SYC30C was heated at the elevated heating rate 150°C/min with dwell time 2 min and the area of the SiC peaks is smaller compared to sample SYC30B 50°C/min with the same holding time. Sample

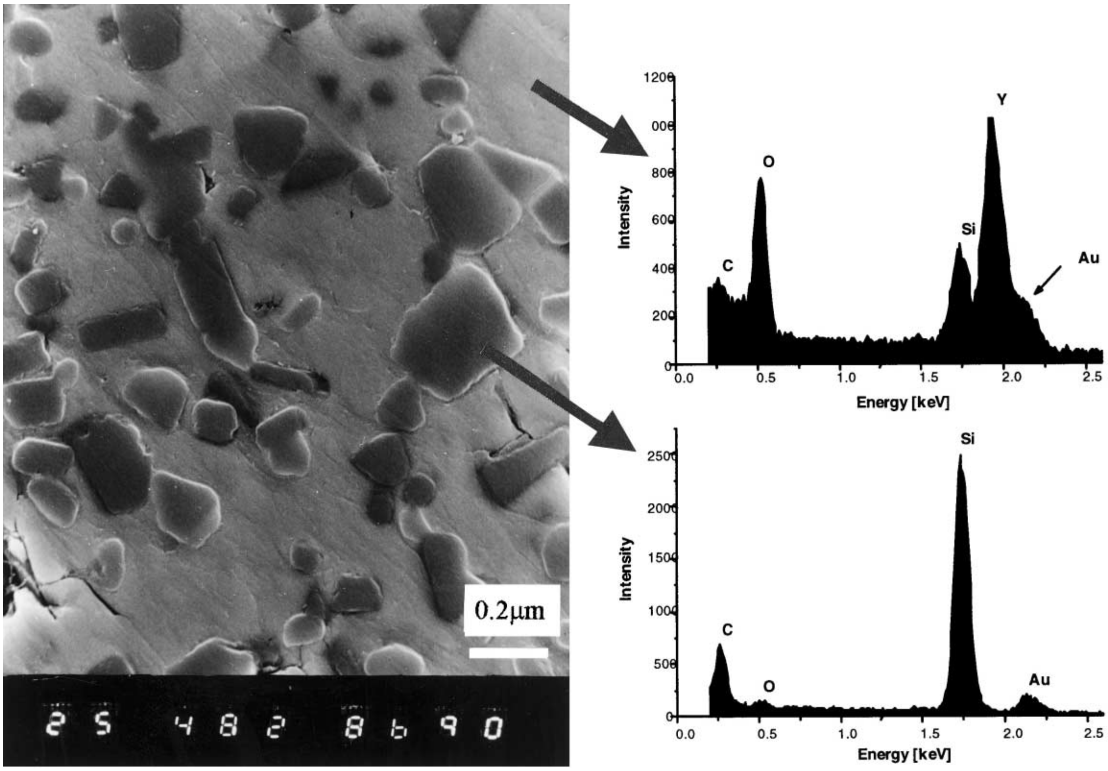

Fig. 3. EDX analysis of the matrix and of the dark grain of the SYC20B specimen.

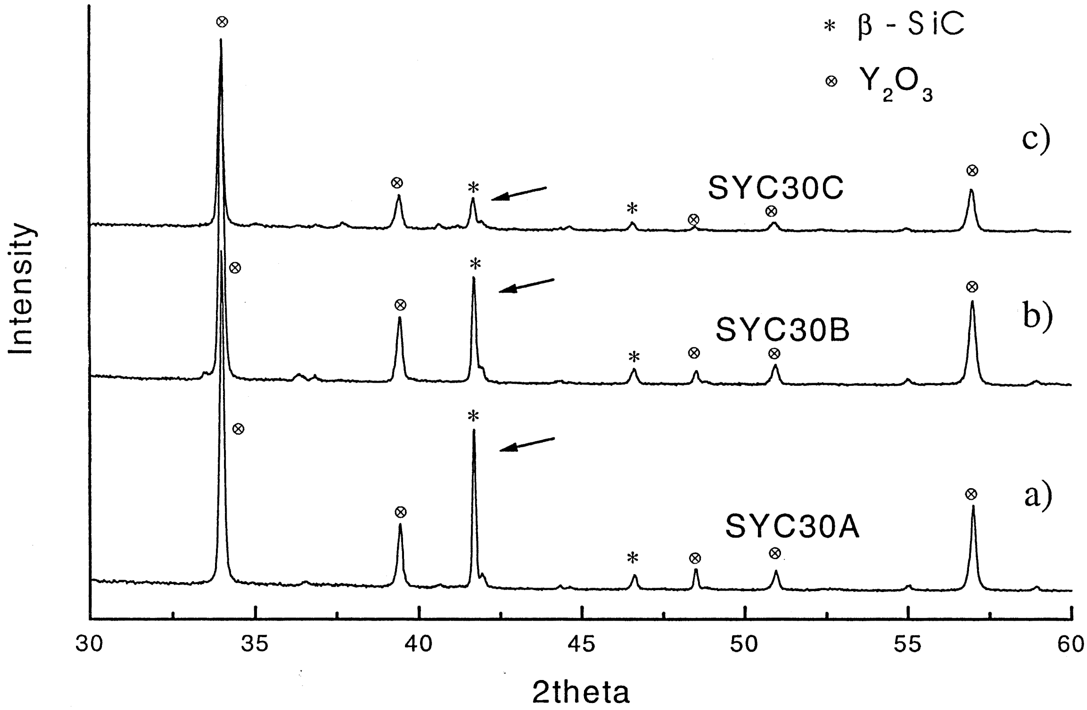

Fig. 4. XRD analysis of SYC30A-C samples. Heating rate, dwell time: (a) 50°C min^{-1}, 20 min; (b) 50°C min^{-1}, 2 min; (c) 150°C min^{-1}, 2 min.

SYC30A was heated at a heating rate of 50°C/min but with a holding time of 20 min. The area of SiC peaks is the highest in comparison to the SYC30B and SYC30C samples.

4. Conclusions

The carbon activity of a graphite furnace/graphite crucible system can be high, nearly 1 and can cause the reduction of SiO_2 in the system Y_2O_3–SiO_2. Reduction of Y_2O_3 was not observed.

The reduction of SiO_2 by carbon decreases the SiO_2 content in the system Y_2O_3–SiO_2 and causes a shift of composition and consequently of melting temperature towards a higher temperature, according to the Y_2O_3–SiO_2 phase diagram.

A powder bed of composition Y_2O_2–SiO_2–BN can decrease the penetration and diffusion of CO/CO_2 from the furnace atmosphere towards the specimen.

The XRD measurements confirmed the presence of SiC in the Y_2O_3–SiO_2–C system after heat treatment, when the C/SiO_2 molar ration was close to 3 or higher. The increased carbon content ($C/SiO_2 > 3$) in the starting mixture and the consequent carbothermal reactions caused an increase of melting temperature from 1660–1900°C.

The SiC content depends also on heating rate, dwell time and the heat-treatment temperature in the same samples SYC30A-C.

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