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APPLICATION OF CONSTANT RATE THERMAL ANALYSIS (CRTA) TO THE SYNTHESIS OF SILICON NITRIDE BY CARBOTHERMAL REDUCTION OF SILICA

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The carbothermal reduction of silica under flowing nitrogen at a pressure of 1 atm has been followed by means of a CO IR detector attached to the gas output of a high temperature tubular furnace. The control of the reaction temperature is carried out by interfacing the analogical output of the IR detector to a controller that allows to monitor the sample temperature in such a way that the concentration of CO generated in the reaction is maintained constant at a value previously selected by the user. The reaction rate at a particular concentration of CO can be fixed by properly selecting the flow rate of the reactive gas.

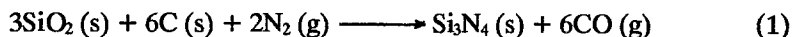
The influence of the reaction rate and the CO concentration on both the reaction temperature and the structure of the final product of the reaction are analysed.

Keywords: CRTA, synthesis of silicon nitride

Introduction

The increasing interest of silicon nitride ceramics has lead to a demand for high quality, low cost powders [1]. Three different methods [2] are used for manufacturing the silicon nitride actually available in the market :

1) direct nitridation of silicon; 2) thermal decomposition of silicon diimide and 3) carbothermal reduction of silica under nitrogen atmosphere. The last method has the advantage that silica and carbon are available and inexpensive raw materials. It takes place according to the following overall reaction:



It is well known [2-4] that the best mechanical properties of silicon nitride devices manufactured by sintering are achieved using α -Si₃N₄ pow-

ders as starting material. This fact explains that a number of authors have paid attention to study the influence of the experimental conditions on the structure of the final products of reaction (1). Durham *et al.* [1] have concluded that the yields of this reaction is depending on the partial pressure of CO that is very difficult to control, since it is a reaction product. The scope of the present work is to apply Constant Rate Thermal Analysis (CRTA) to control the CO concentration in order to determine its influence on the composition of the final products of the reaction of carbothermal nitridation of silica.

Experimental

Silica and carbon from Aldrich have been used. The textural and structural properties of these raw materials both at room temperature and after firing for one hour at a temperature closed to reaction one are included in Table 1.

Table 1 Characteristics of starting materials used

Sample	$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	
	$T_{\text{amb.}}$	1400°C
SiO ₂	280	1
Carbon	1500	800

The equipment used for synthesizing Si₃N₄ is shown in Fig. 1. The reactive gas used has been a mixture of 95% nitrogen + 5% hydrogen. The synthesis of Si₃N₄ has been carried out in a horizontal tubular furnace of high temperature (up to 1600 °C) and low thermal mass. A tube of mullite of 25 mm of inner diameter has been employed. The sample constituted by a mixture C/SiO₂ in a molar ratio 2/1 was located into a graphite boat. Both the flow rate of nitrogen and the concentration of hydrogen at the reactor feed have been regulated by means of two mass flow controllers. The flowing gas sweeps the CO generated in the reaction through a CO IR sensor ADC, model SB 300, with a single range 0–2% associated to a linear analogical output of 1 V f.s.d. This electrical signal has been interfaced to the furnace through a PID controlled that allows to monitor the temperature of the sample in such a way that the concentration of CO is maintained constant at the value previously selected by the user. Moreover, the reaction rate at

every particular concentration of CO can be chosen by properly selecting the nitrogen flow rate.

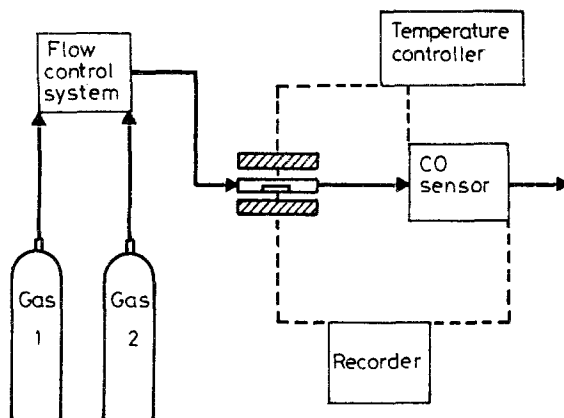


Fig. 1 A plot of the experimental system. The arrows shows the gas flow way

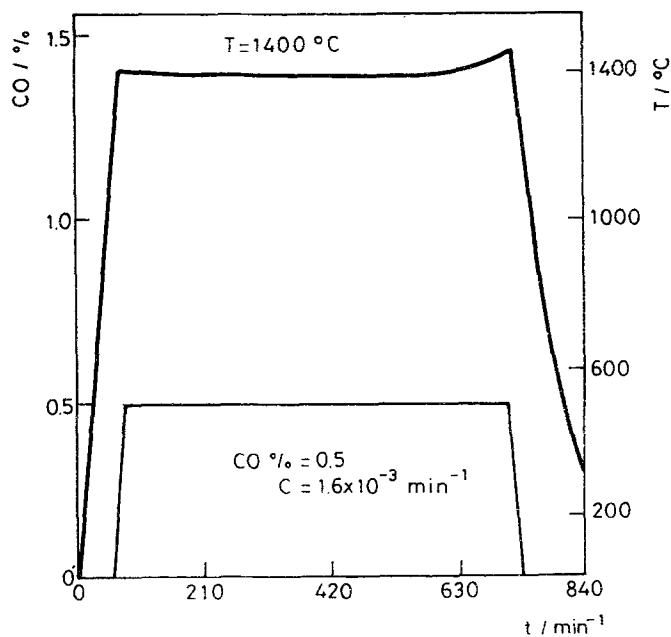


Fig. 2 CRTA plot obtained for the carbothermal reduction of silica at 0.53% CO and $C = 1.6 \cdot 10^{-3} \text{ min}^{-1}$.

The α/β phase ratio in the Si_3N_4 obtained has been estimated from the relative intensities of the (210) and (200) X-ray diffraction peaks of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$, respectively.

Results

Figure 2 shows the CRTA diagram for the carbothermal reduction of silica under a starting flow of 300 cc/min of the nitrogen-hydrogen mixture at a total pressure of 1 atmosphere. A CO concentration of 0.53% was maintained constant all over the experiment and the reaction rate was $C = 1.6 \cdot 10^{-3} \text{ min}^{-1}$ (i.e., the reaction was over after $1/C = 625 \text{ min}$). The reacted fraction α is given by the ratio between the area enclosed by the CO trace at the time t and the total area when the reaction is over. The values calculated from Fig. 2 are plotted as a function of the temperature in Fig. 3 together with the $\alpha\text{-}T$ plot obtained under similar experimental conditions but using a different reaction rate ($C = 5.2 \cdot 10^{-4} \text{ min}^{-1}$).

The above results point out that CRTA curves of the carbothermal reduction of silica moves at higher temperatures by increasing the constant reaction rate as expected from theoretical considerations [5].

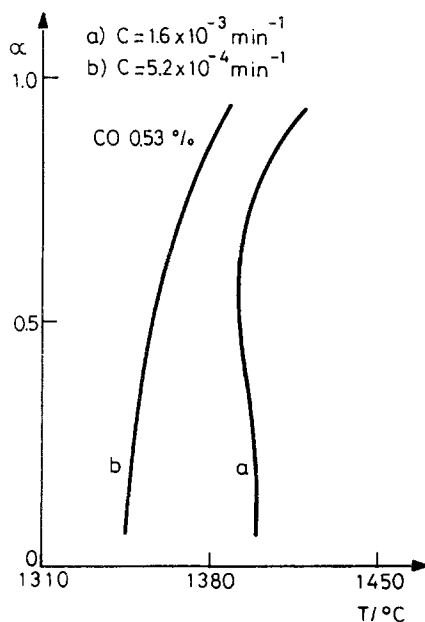


Fig. 3 $\alpha\text{-}T$ plots calculated from CRTA at different rates and 0.53% CO

Table 2 α -Si₃N₄/ β -Si₃N₄ ratios and temperatures for different reaction rates at constant CO concentration (0.53%)

C / min^{-1}	I_{α} / I_{β}	$T / ^{\circ}\text{C}$
$5.6 \cdot 10^{-3}$	5	1470
$4.5 \cdot 10^{-3}$	11	1440
$1.6 \cdot 10^{-3}$	16	1400
$9.0 \cdot 10^{-4}$	19	1400
$5.2 \cdot 10^{-4}$	30	1330

The ratios between the intensities of the (210) and (200) X-ray diffraction peaks of the α and β phases of a series of silicon nitride samples obtained at different constant reaction rate, C , but using the same value (0.5%) of the concentration of the CO generated in the reaction are shown in Table 2. It can be observed that the fraction of α -Si₃N₄ dramatically increases by decreasing the value of C . This fact would be explained taking into account that according to the literature [6] the percentage of α -Si₃N₄ increases by increasing the temperature used in the synthesis of Si₃N₄.

On the other hand, it has been considered of interest to study the influence of the CO partial pressure on the reaction of carbothermal reduction of silica. Table 3 summarizes the values of the ratio $I_{(210)}/I_{(200)}$ determined from the X-ray diffraction diagrams of the product obtained at $C = 9 \cdot 10^{-4} \text{ min}^{-1}$ as a function of the CO concentrations. These results point out that the concentration of α -Si₃N₄ dramatically increases by increasing the concentration of CO in spite that the reaction temperature moves from 1227 °C to 1400 °C by increasing the CO concentration from 200 ppm to 0.53%.

In summary, the results included in Tables 2 and 3 allow to conclude that the synthesis of α -Si₃N₄ from carbothermal reduction of silica is improved

Table 3 α -Si₃N₄/ β -Si₃N₄ ratios and temperatures for different CO concentrations at constant reaction rate ($9 \cdot 10^{-4} \text{ min}^{-1}$)

CO / %	I_{α} / I_{β}	$T / ^{\circ}\text{C}$
0.53	19.0	1400
0.25	11.0	1355
0.12	7.0	1340
0.08	4.5	1285
0.04	2.5	1240
0.02	2.4	1227

both decreasing the constant reaction rate, C , and increasing the partial pressure of CO gas in the vicinity of the sample.

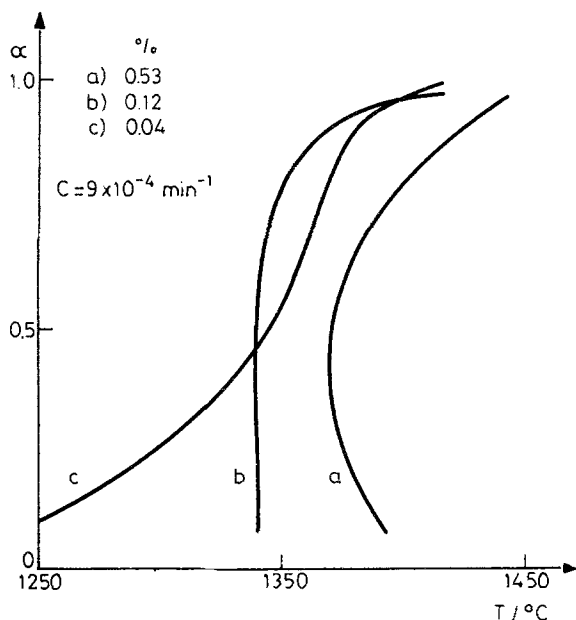


Fig. 4 $\alpha - T$ plots calculated from CRTA at different concentrations of CO and $C = 9 \cdot 10^{-4} \text{ min}^{-1}$

On the other hand, the $\alpha - T$ plots obtained at a constant reaction rate $C = 9 \cdot 10^{-4} \text{ min}^{-1}$ but at different residual concentrations of CO are included in Fig. 3. Taking into account the relationships shown in previous papers [5] between the shape of CRTA traces and the kinetics obeyed by a solid state reaction it can be concluded that, by increasing the CO concentration, the kinetics of the carbothermal nitridation of silica moves from being controlled either by a diffusion (0.04% CO) or phase-boundary process (0.12%) to be controlled by the formation and growth of nuclei, according to an Avrami-Erofeev mechanism when the concentration of CO selected has been increased until 0.53%. If we bear in mind that the ratio $\alpha\text{-Si}_3\text{N}_4/\beta\text{-Si}_3\text{N}_4$ increases by increasing the concentration of CO, the results included in Fig. 4 would be interpreted by considering that the α and β polymorphs are formed by separate and parallel reaction paths. A similar conclusion has been previously reached by Rossetti *et al.* [7] from the kinetic analysis of the reaction of nitridation of high purity oxide free silicon powder. However, further re-

search is necessary in order to clarify the mechanism of formation of α and β silicon nitride from carbothermal reduction of silica.

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Zusammenfassung — Bei 1 atm Druck wurde im Stickstofffluß die carbothermische Reduktion von Silika mittels eines CO IR Detektors verfolgt, der am Gas-Output eines Hochtemperaturröhrenofens angeschlossen wurde. Die Reaktionstemperatur wird kontrolliert, indem das Analogsignal des IR-Detektors über ein Interface an eine Kontrolleinheit geleitet wird, welche die Verfolgung der Proben temperatur auf die Art ermöglicht, daß die Konzentration des bei der Reaktion entstehenden CO auf einem konstanten Wert gehalten wird, den der Anwender zuvor einstellt. Die Reaktionsgeschwindigkeit kann bei einer ganz bestimmten CO-Konzentration durch entsprechende Wahl des Volumendurchsatzes des reaktiven Gases fixiert werden.

Es wurde der Einfluß von Reaktionsgeschwindigkeit und CO-Konzentration sowohl auf die Reaktionstemperatur als auch auf die Struktur der Reaktionsendprodukte untersucht.