

# Carbothermal Synthesis of Submicrometer $\beta$ -SiC Powder Using Double Precursor Reaction Mixture

## Pridobivanje submikronskega $\beta$ -SiC prahu s karbotermično sintezo reakcijske mešanice dvojnega prekursorja

Keyorkijan V.,<sup>1</sup> Fakulteta za strojništvo Maribor

*The low temperature carbothermal reduction of colloidal silica has been applied for the synthesis of submicrometer  $\beta$ -SiC powder. The intrinsic kinetics of the overall reaction was studied over the temperature range ( $1473 < T < 1673$  K) and is of special interest for the low temperature, high yield synthesis of submicron  $\beta$ -SiC powder.*

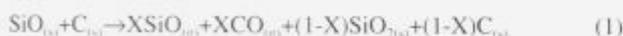
*Key words: carbothermal reduction, submicrometer  $\beta$ -SiC powder, non-milling, double  $\text{SiO}_2$ -C precursor, internal kinetics*

*Submikronski  $\beta$ -SiC prah smo pridobili z nizkotemperaturno karbotermično redukcijo koloidnega  $\text{SiO}_2$ . Kinetiko procesa smo proučevali v temperaturnem območju ( $1473 < T < 1673$  K), ki omogoča nizkotemperaturno sintezo submikronskega  $\beta$ -SiC prahu z visokim izkoristkom.*

*Ključne besede: karbotermična redukcija, submikronski  $\beta$ -SiC prah, postopek brez mletja, dvojni  $\text{SiO}_2$ -C prekursor, študij kinetike*

### 1. Analysis of the carbothermal reduction by weight loss data

The conversion of  $\text{SiO}_{2(s)}$  into  $\text{SiO}_{(g)}$  (X), the loss of  $\text{SiO}_{(g)}$  (Y) and the yield of SiC (Z) can be calculated using the stoichiometry of the overall reaction:



Note that loss of  $\text{SiO}_{(g)}$  caused by pumping (y) is not determined from the stoichiometry of the overall reaction (4).

In order to determine the fraction of  $\text{SiO}_{(g)}$  removed by pumping it is necessary to measure the conversion of  $\text{SiO}_{(g)}$  into  $\text{SiC}_{(s)}$  ( $W'$ ) at special experimental conditions (see experimental procedure) when all Si containing species remain in the system. Then  $y=0$  and  $W'=Z/X$ .

The actual conversion of  $\text{SiO}_{(g)}$  into  $\text{SiC}_{(s)}$  ( $W$ ) (at  $y \neq 0$ ) and  $W'$  (when  $y=0$ ) are than equal:  $Z'/X=Z/(X-y)$ ,  $Z' > Z$ ;  $Z'$  is the yield of SiC when  $y=0$ .

According to this, the loss of  $\text{SiO}_{(g)}$  caused by pumping could be expressed as  $y=X(Z'-Z)/Z'$ .

### 2. Experimental procedure

The synthesis of submicron  $\beta$ -SiC powder by the carbothermal reduction of colloidal silica has been investigated in vacuum ( $\approx 1.5$  Pa) for 0.5 h at temperatures between 1125-1400°C. The double precursor mixture (Reaction mixture I) consists of  $\text{SiO}_2$  particles (Cab - O - SiC, M5, Cabot) covered with carbon layer (one - to - one molar ratio) and fine carbon black particles (Carbon black, Monarch 1300, Cabot) doped with 0.6 wt % of amorphous boron (Ventron, 00438 - 325 mesh), **Fig. 1**. An intimately mixed carbon black - colloidal silica precursor (one - to - one molar ratio) and carbon black particles doped with 0.6 wt % of amorphous boron has been used as the comparative reaction mixture (Reaction mixture II). In order to analyse the kinetics of both steps of carbothermal reduction the weight of the reaction mixture, the weight of the specimens after carbothermal reduction and the weight of the specimens after removal of the free carbon were determined, respectively.

The loss of  $\text{SiO}_{(g)}$  component caused by pumping was determined using the following procedure. The mixture of colloidal  $\text{SiO}_2$  and phenolic resin (Viaphen, PR 881/60) was homogenised in acetone. After drying, the thick paste was pressed to form a solid composite. Samples were then heated in argon to 450°C for 4 h. Pyrolysed  $\text{SiO}_2/\text{C}$  specimen (one - to - one molar ratio) was placed into the crucible.  $\text{SiO}_2/\text{C}$  core in the form of pallet was completely covered with carbon black powder (doped with 0.6 wt% of boron). The crucible was then heated to temperatures between 1150°C - 1400°C for 0.5 h in vacuum. After the heat treatment, the pallet was very carefully mechanically separated from the carbon black powder. In order to remove free carbon, the protective powder was heated in air at 750°C for 24 h. The residual powder is pure SiC. Finally, the weigh of synthesised SiC measured by accuracy  $\pm 1\%$ .

<sup>1</sup> dr. Varujan KEVORKIJAN, dipl. inž. kem.  
Fakulteta za strojništvo  
Smetanova 17, 62000 Maribor

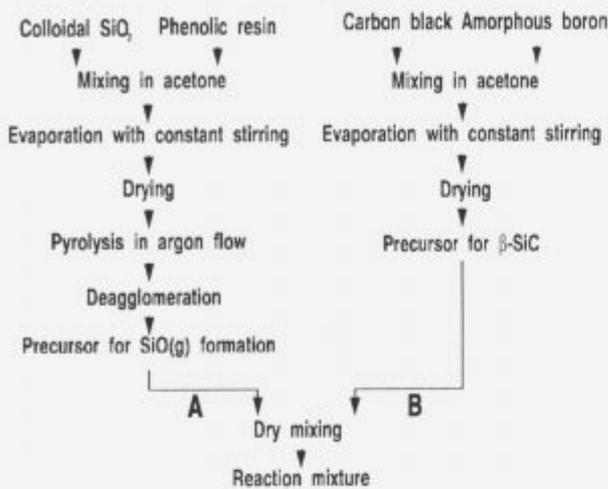


Figure 1: Flow sheet of reaction mixture synthesis process  
Slika 1: Shema priprave reakcijske mešanice

### 3. Kinetic studies

#### 3.1. $\text{SiO}_{(g)}$ formation

Assuming that the solid state reaction (2) is of zero order and its rate constant is defined as:  $k = dX/dt = k_0 \exp(-E_a/RT)$ . The activation energy,  $E_a$ , for Reaction 2 is determined by the slope of  $\ln k$  against  $1/T$ , Fig. 2-3. The experimental values for both types of reaction mixtures are almost the same:  $\approx 300 \pm 30$  KJ/mol which is in good agreement with literature data<sup>2</sup>:  $\approx 377$  KJ/mol.

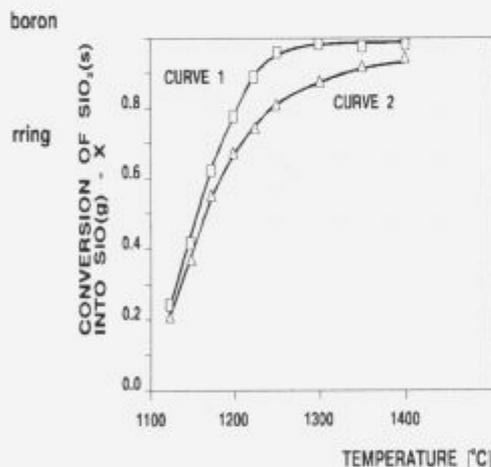


Figure 2: The conversion of  $\text{SiO}_2$  into  $\text{SiO}_{(g)}$  at different temperatures after the same holding time - 0.5 h

Slika 2: Konverzija  $\text{SiO}_2$  v  $\text{SiO}_{(g)}$  pri različnih temperaturah. Čas sinteze - 0,5 h

#### 3.2. $\text{SiC}_{(s)}$ formation

Using weight loss data, the conversion of  $\text{SiO}_{(g)}$  into  $\text{SiC}_{(s)}$  ( $W$ ) defined as:  $W = Z/(1-Y+y)$  is calculated and plotted in Fig. 4. On the basis of a shrinking core model, the rate constant,  $k$ , is:  $k = 1 - (1 - W)^{1/3} = k_0 \exp(-E_a/RT)$  if the chemical reaction is the rate-limiting step or:  $k = 1 - 3(1 - W)^{2/3} + 2(1 - W) = k_0 \exp(-E_a/RT)$  if the diffusion through  $\text{SiC}$  layer is rate-controlling. The activation energies for both scenarios are determined from the slope of the plots  $\ln k$  against  $1/T$ . The values obtained by the assumption that the chemical reaction is the rate-controlling step are 391 KJ/mol (for the reaction mixture I) and 220 KJ/mol (for

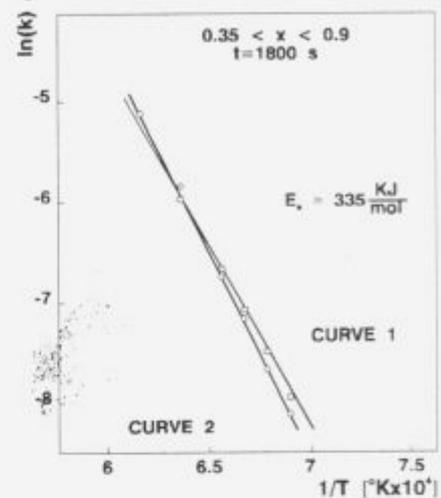


Figure 3: The activation energy for reaction 2 (Curve 1- $\text{SiO}_2$  particles cover with carbon layer; Curve 2- $\text{SiO}_2$  particles in contact with carbon black particles). Holding time 0.5 h

Slika 3: Aktivacijska energija za reakcijo 2 (Krivulja 1- $\text{SiO}_2$  delci prevlečeni s slojem ogljika; Krivulja 2- $\text{SiO}_2$  delci v stiku z delci ogljikovih saj). Čas sinteze - 0,5 h

the reaction mixture II), Fig. 5. However, the values of the rate constant calculated for a diffusion controlled process can be also fitted well by linear plots, Fig. 6. The activation energies calculated on this way are much higher: 577 KJ/mol for the reaction mixture I and 483 KJ/mol for the reaction mixture II.

### 4. Conclusions

The transformation of carbon black particles into  $\text{SiC}_{(s)}$  is modelled by a shrinking core model. On the basis of a detailed investigation of the reaction kinetics at different temperatures, it is postulated that the chemical reaction is the rate - controlling step at lower temperatures ( $T < 1473$  K) while diffusion of carbon through  $\text{SiC}_{(s)}$  layer being rate controlling at  $T > 1673$  K. However, over the temperature range of special interest ( $1473 < T < 1673$  K) in the low temperature, high yield synthesis of submicron  $\beta$  -  $\text{SiC}$  powder, it seems, that both rate steps proceed by almost the same rate masking on this way each other as the real rate limiting step. For the overall carbothermal reduction, collected experimental data strongly suggest that the  $\text{SiO}_{(g)}$  generation is the rate controlling step.

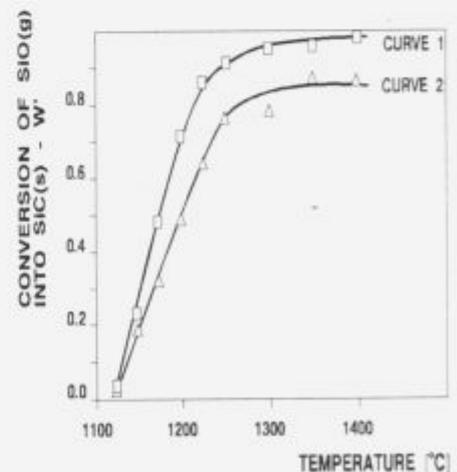


Figure 4: The conversion of  $\text{SiO}_{(g)}$  into  $\text{SiC}_{(s)}$   
Slika 4: Konverzija  $\text{SiO}_{(g)}$  v  $\text{SiC}_{(s)}$

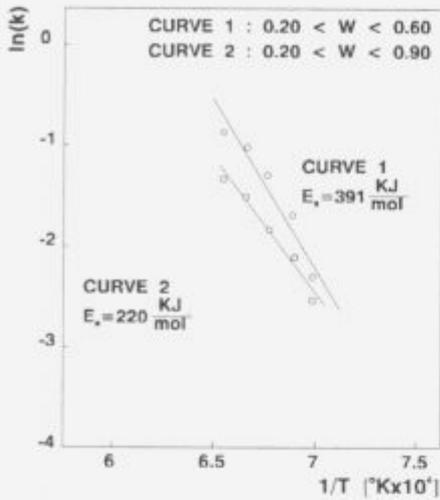


Figure 5: The activation energy for Reaction (3) based on the assumption that the chemical reaction is the rate - controlling step  
 Slika 5: Aktivacijska energija za Reakcijo (3) ob predpostavki, da kemijska reakcija določa hitrost karbotermične sinteze

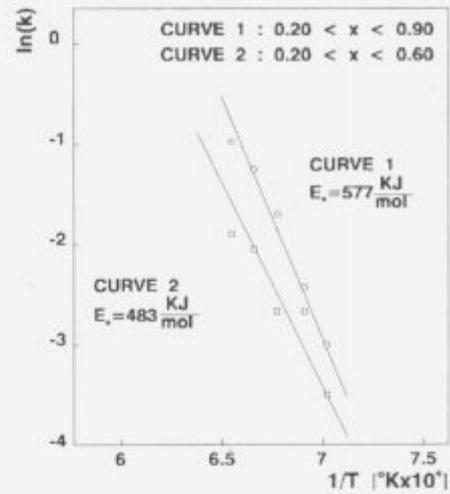


Figure 6: The activation energy for Reaction (3) based on the assumption that the diffusion is the rate - controlling step  
 Slika 6: Aktivacijska energija za Reakcijo (3) ob predpostavki, da kemijska reakcija določa hitrost karbotermične sinteze

### 5. References

<sup>1</sup> V. M. Kevorkijan, M. Komac, D. Kolar, Low - temperature synthesis of sinterable SiC powders by carbothermic reduction of colloidal SiO<sub>2</sub>, *J. Mat. Sci.*, 27, 1992, 10, 2705

<sup>2</sup> J. J. Biernacki, Formation of Silicon Monoxide and Application to the Growth of Vapor - Liquid - Solid Silicon Carbide Whiskers; Doctoral Dissertation, Fenn College of Engineering, Cleveland State University, Cleveland, OH, 1987