

CARBOTHERMAL REDUCTION OF A FREEZE GEL SILICA-CARBON ARTEFACT

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Introduction

The reaction of carbon with silica leading to silicon carbide is essentially an interfacial one. Hence, depending on the shape of the carbon - silica interface, various textures of SiC may be obtained. In a previous study, it was shown that carbon fibres covered with a silica layer may be a route for obtaining fine tubes of SiC after removal of the excess of carbon by gasification (1). In a more general way, SiC materials of desired design may be prepared by an appropriate selection of the silica - carbon artefact. This study reports on the conversion of porous freeze gel silica pellets infiltrated with carbon into porous SiC.

Experimental

Silica discs (30 mm in diameter, 3 mm in thickness) were prepared from a mixture of colloidal silica (mean particle size equal to 25 nm) and quartz powder (mean particle size equal to 1 μm) using the freeze gel procedure (2). The volume fraction of pores in the disc is close to 0.6. The silica samples were then impregnated with a phenolic resin and carbonized at 900°C. The average composition of the carbon-silica disc is equal to 27% carbon, 49% colloidal silica and 24 % quartz by weight. Silicon carbide (SiC) was produced by heat treatment of the silica - carbon artefact in argon at 1550°C. The weight change of the sample during heat treatment was measured gravimetrically using a microbalance (Mettler AE240). The alumina sample holder was previously carburized in order to avoid any reaction with the carbon contained in the disc. Two types of heat treatment were considered. The first one was carried out in a continuous flow of argon equal to 20 l/h (dynamic condition). In the second case, the carbothermal reaction was conducted in a closed system with a starting pressure of argon equal to 70 kPa (static condition). The weight losses of the silica - carbon artefact and of the carbon resin as a function of treatment time in dynamic condition are shown in Fig. 1 along with the corresponding temperature profile (heating and isothermal plateau). It is seen that the carbothermal

reaction starts at about 1200°C whereas the weight loss of the carbonized resin is almost completed at 850°C. Hence, the weight loss corresponding to the fraction of carbon in the disc being pyrolysed without reaction with silica can be determined. After cooling, the amounts of unreacted silica and carbon are determined gravimetrically by selective dissolution in HF solution and by gasification in air at 800°C respectively. The presence of β -SiC in the remaining sample was verified by X-ray diffraction.

Results and discussion

The amount of produced SiC can be determined from the weight loss of the silica - carbon artefact during heat treatment and by considering the following overall reaction :



It can also be estimated gravimetrically after removal of the remaining silica and carbon and the results obtained from both methods differ by less than 5%. Since the amount of carbon in the disc is far smaller than the amount of silica, the formation of SiC will be determined in respect from the consumption of carbon. The fraction of unreacted carbon, f , after heat treatment at 1550°C followed by an isothermal plateau of 1 hr is compared for static and dynamic operating conditions in Table 1. It is seen that in the dynamic condition, nearly all carbon has been consumed and only half of it has reacted in static operation of the furnace. The yield of SiC, τ , defined as the ratio of the amount of C converted into SiC according to Eq. [1] to the total amount of consumed carbon is also shown in Table 1. The results indicate that the conversion of carbon into SiC is also more effective in dynamic operation of the furnace than in static operation, in which some carbon is consumed without forming SiC. In fact two distinct reactions have to be considered for the formation of SiC:



The fact that in static condition only half of the carbon has reacted suggests that the accumulation of CO will hinder the formation of gaseous species in reaction [2]. In fact, one may estimate that in static operation of the furnace, the partial pressure of CO may reach 1kPa, whereas in dynamic conditions, this value will not exceed 0.1kPa. Moreover, the accumulation of CO in the reactor will also affect the yield of SiC by inhibiting the reaction of SiO with C (Eq. [3]). It may be concluded that in static operating condition about 20% of the carbon consumed according to reaction [2] does not react further with SiO to give SiC. This fraction is significantly smaller when operating in dynamic conditions (7%), indicating that almost all consumed carbon reacts according to the overall reaction [1].

Table 1. Carbon consumption and formation of SiC

Operating condition of furnace	Fraction of unreacted carbon (<i>f</i>)	Yield of SiC (τ)
Dynamic	< 0.1	0.93
Static	0.37	0.80

The amount of SiC obtained after different treatment time at 1550°C in dynamic conditions of 100 mg of carbon-silica disc is shown in Table 2. The highest amount of SiC is observed for treatment times between 1 to 3 hrs with an amount SiC close to the stoichiometric one (34 mg). It must be noted that a significant proportion of SiC (18 mg) is already obtained during heating to 1550°C. However, for longer treatment time at 1550°C, a slight decrease in carbide is found which is due to its reaction with the remaining oxide :



Hence the operating conditions exert quite a significant effect on the yield of silicon carbide.

Table 2. Amount of SiC obtained after different isothermal treatment in dynamic condition

Isothermal treatment time (hr)	SiC (mg)
0	18
1	29
3	34
6	29

After removal of the excess of silica by HF treatment, consolidated silicon carbide samples are obtained. Scanning electron micrographs of silicon carbide samples confirm that their texture originates from carbon located in the macropore voids of the silica disc. In the case of dynamic treatment, SiC has a spongy aspect, the cavities resulting from the removal of silica.

When the carbothermal reaction is conducted in static operating conditions, the surface of the disc is covered by SiC whiskers which are probably obtained by chemical vapour deposition with SiO and CO as primary reactants. The SiC texture underneath is however similar to the previous one. In particular, no whiskers were found in the inner part of the sample. The occurrence of whiskers at the disc surface confirms also the remove of SiO from the pellet which was evidenced by a lower yield of SiC in static conditions. The specific surface area of the resulting SiC as determined by krypton adsorption is close to 30 m²/g which is far superior to the starting macroporous silica sample (0.3 m²/g).

Conclusions

Infiltration of phenolic resin into the macroporous voids of a freeze gel silica disc followed by subsequent carbonization permits the manufacturing of carbon-silica artefact. Carbothermal reduction of the artefact may lead to a quantitative formation of silicon carbide provided there is a rather low partial pressure of carbon monoxide during the process. The as-obtained silicon carbide has a macroporous texture associated with a significant surface specific area. This process may be used for designing ceramic materials with specific properties.

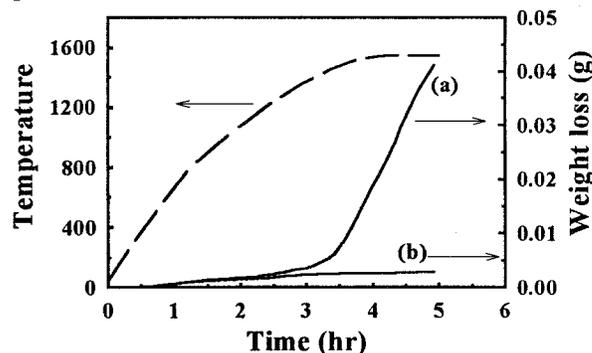


Figure 1: (—) weight losses as a function of treatment time of (a) silicon-carbon artefact, (b) carbon resin; (---) temperature profile of the reactor

References

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