

Preparation of monodispersed spherical silicon carbide by the sol–gel method

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Monodispersed spherical SiC gel powders were synthesized by hydrolysis and condensation of phenyltrimethoxysilane (PTMS) or a mixture of PTMS and tetraethylorthosilicate (TEOS) from a system of silane–H₂O–catalyst to which no co-solvent such as alcohol was added. The experiments were conducted through two routes; base catalysed and acid–base catalysed routes. In each process, excess water was used as a dispersing medium in addition to a hydrolysing agent. In the base-catalysed route, monodispersed spherical gel powders were obtained regardless of NH₄OH content used in this experiment when the concentration of silane and the molar ratio of TEOS to PTMS were less than 0.5 mol l⁻¹ and 0.5, respectively. In the acid–base catalysed route, polydispersed powders were produced when the concentration of silane exceeded 0.25 mol l⁻¹. When heated above 1400 °C, the initially monodispersed powders sustained their shape in the PTMS–TEOS system, but bulk and fibre phase were produced in the PTMS system.

1. Introduction

A sol–gel process using metal alkoxides has been widely applied for the synthesis of so-called ideal powders; homogeneous, controlled size and shape, and high purity. Powders synthesized from these precursors have been limited to oxides because of metal–oxygen–metal bonds formed by hydrolysis and condensation. However, many workers have shown that it is possible to synthesize non-oxide powders from organometallic compounds other than metal alkoxides.

Recently, White *et al.* [1, 2] manufactured SiC powders from a system of silane–H₂O–catalyst which had been suggested at first by Avnir and Kaufman [3] in manufacturing SiO₂ xerogel. According to the authors, the gel derived from phenyltrimethoxysilane (PTMS), where the molar ratio of H₂O to silane was from 2–6, was monolithic bulk and was decomposed on heating to a mixture of carbon and SiO₂ in which the molar ratio of carbon to SiO₂ was about 4. The reaction products obtained from this carbothermal reduction consisted of SiC and free carbon. Hatakeyama and Kanzaki [4] manufactured spherical SiC powders from a system of silane–alcohol–H₂O–catalyst which has been commonly used in the sol–gel process. Monodispersed powders were obtained from acid–base catalysed route of PTMS–TEOS system only when an excess amount of NH₄OH was added.

In the light of these results, we attempted to synthesize monodispersed spherical SiC powder from the system of silane–H₂O–catalyst. In this system, no co-solvent such as alcohol was added and an excess

amount of H₂O was used as a dispersing medium in addition to a hydrolysing agent.

2. Experimental procedure

The starting silanes were phenyltrimethoxysilane (Shin-Etsu Chemical Co. Ltd, Tokyo, Japan) and tetraethylorthosilicate (Fluka AG, Chemische Fabrik, Buchs, Switzerland). Two synthesis routes were investigated: (1) base-catalysed and (2) acid–base catalysed routes. In the base-catalysed route, PTMS or a mixture of PTMS and TEOS was directly poured into the solution of H₂O and NH₄OH with stirring, and the reaction was allowed to proceed for 10 min. In the acid–base synthesis, prehydrolysis was undertaken in the solution of H₂O and 0.05 mol HNO₃ to silane for 10 min, then NH₄OH was poured into this solution with stirring and the reaction allowed to proceed for 10 min. In all experiments, the volume of the total batch was 200 cm³ and the molar ratio of H₂O to silane was greater than 100. Thus, H₂O acted not only as a hydrolysing agent but also as a dispersing medium.

After reaction, all the samples were covered with polyethylene wrap and aged for 24 h without stirring. The reaction and ageing were carried out at 20 °C. The gel powders were separated by drying in a hood until no remaining liquid was seen, and then dried again under a vacuum at 60 °C for 6 h.

The gel powders were placed in a graphite crucible and heated to various temperatures for 2 h in a flowing argon atmosphere. The heating rate was 20 °C min⁻¹. X-ray diffraction (XRD; RTP-300RC, Rigaku,

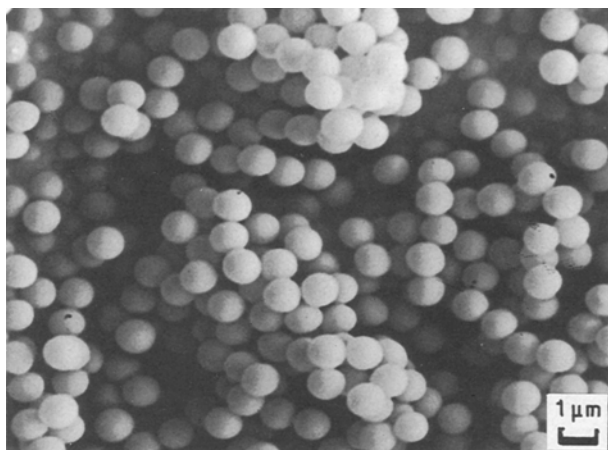


Figure 1 Scanning electron micrograph of powder derived from base-catalysed route of the PTMS system. The concentration of PTMS and the ratio of $\text{NH}_4\text{OH}/\text{PTMS}$ were 0.5 mol l^{-1} and 4, respectively.

Japan) analysis was conducted to identify the crystalline phase of the powders. The shape and the size of the powders were observed using scanning electron microscopy (SEM; JSM-840, Jeol, Japan). Thermal gravimetric and differential temperature analysis (TG-DTA; TG-DTA 92, Setaram, France) was also conducted in a flowing helium atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$. Zeta potential measurements (4700 PS/MW, Zetasizer 3, Malvern, UK) were carried out at 20°C . Samples were prepared by ultrasonification in 10^{-2} mol NaCl solution and the pH was adjusted to 10 in all cases.

3. Results and discussion

3.1. Base-catalysed route of the PTMS system

A scanning electron micrograph of typical monodispersed spherical gel powder derived from the base-catalysed route of PTMS system is shown in Fig. 1. Monodispersed spherical powders were obtained under conditions where the concentration of PTMS was from $0.125\text{--}0.5 \text{ mol l}^{-1}$ and the molar ratio of NH_4OH to PTMS was from 1–8. Powders produced under these conditions had diameters of about $1 \mu\text{m}$ and narrow size distribution regardless of the variations in PTMS and NH_4OH concentrations. These results are quite different from those of Hatakeyama and Kanzaki [4] or the general trends of the TEOS system [5–11] in which the particle size and distribution varies with silane and NH_4OH .

In the TEOS system, as the amount of H_2O used in the sol-gel process increased far above a critical point, the effects of NH_4OH and H_2O on the variation of particle size became negligible and the size decreased to about $0.2 \mu\text{m}$ [6, 11]. In the PTES-TEOS system developed by Hatakeyama and Kanzaki [4], an excess amount of NH_4OH (above 16 mol to silane) had to be added to obtain monosized spherical gel powders with diameters of about $1 \mu\text{m}$ which was the minimum size in that system. In these systems, the silane- H_2O -alcohol-catalyst system was used for powder production. However, in this work, no co-solvent, such as alcohol, was added and an excess

amount of H_2O was used as a dispersing medium in addition to a hydrolysing agent. Monosized spherical gel powders having diameters of about $1 \mu\text{m}$ could be obtained over a relatively broad composition range. This can be considered to occur as follows.

The manufacturing method of monosized spherical SiO_2 particles through the solution process can be classified into two groups: the first, developed by Iler [12] contains nucleation and growth through molecular addition in basic aqueous solution and results in dense particles; the other, developed by Stöber *et al.* [5] contains nucleation and agglomeration of primary particles in partially aqueous solution containing alcohol, the so-called sol-gel method, and results in porous particles. Growth of SiO_2 derived from Iler's method proceeds by Ostwald ripening and greatly depends on the solubility of the solute. Because the solubility of SiO_2 in water is low under normal temperature and pressure, large particles can only be obtained by ageing for a long time under high temperature and pressure. However, SiO_2 particles derived from the sol-gel process using silicon alkoxides grow easily to submicrometre size in a relatively short reaction time.

These phenomena can be explained by the DLVO theory [13, 14] which defines the relation between electrostatic repulsion force and van der Waals attraction force. Primary particles nucleated in a basic solution can be dispersed by a strong electrostatic repulsion force. The energy barrier, V_B , which inhibits agglomeration between two particles in this dispersion can be expressed as

$$V_B = -\frac{A\kappa a}{12} + 2\pi\epsilon a\Psi^2 \quad (1)$$

where A is the Hamaker constant, κ the Debye-Hückel parameter, a the particle diameter, ϵ the dielectric constant of the liquid medium, and Ψ the surface potential. The first term on the right-hand side, which is negative, is a contribution due to van der Waals attraction force, and the second, which is positive, is a contribution due to electrostatic repulsion force.

According to the equation, the energy barrier can be decreased by lowering the dielectric constant and/or the surface potential. Dielectric constants of alcohols are very low compared with that of water [15]. Therefore, as excess alcohol is mixed into water as in the sol-gel process, the energy barrier decreases and agglomeration of particles occurs above a particular point of addition, which leads to growth of particles with porous structure having high surface area [16].

This is considered to be the reason why particles derived from the sol-gel process differ in properties and grow so large compared with those derived from Iler process. However, because alcohol was not added at all in this work, the alcohol present in the solution was only caused by hydrolysis and condensation of silane. Because the amount of silane used was very small with respect to H_2O , the alcohol content existing in the solution was too small to affect the dielectric constant.

Fig. 2 shows the schematic surface state of SiO_2 and particles produced from PTMS. In contrast to SiO_2 ,

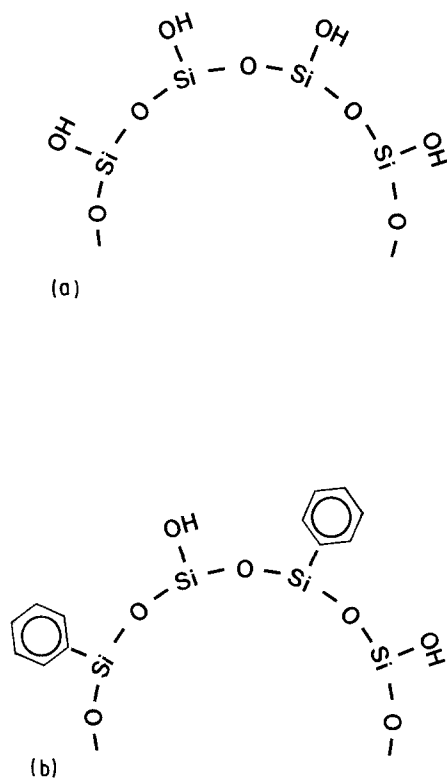


Figure 2 Schematic drawings of the surface structure of (a) SiO_2 and (b) gel powder derived from the PTMS system.

the surface state of particles derived from PTMS can be considered to be partially covered with phenyl groups. In general, the surface potential of particles in solution depends on the magnitude of surface charge influenced by the degree of hydration of the surface [17]. Thus the number of hydratable sites at the particle surface derived from PTMS seems to be smaller than that of SiO_2 . Therefore, the surface potential of particles produced from PTMS must be lower than that of SiO_2 under the same condition. So it can be deduced that particle growth in this work is induced by the decrease in surface potential due to the existence of surface phenyl groups.

Zeta-potentials of powders derived from PTMS exhibited similar values (~ 20 mV) over the entire composition range and were very low compared with that of SiO_2 (approximately -80 mV). This assists in the conclusion that the surface of particles derived from PTMS is partially covered with phenyl groups, causing aggregation and particle growth by decreasing the energy barrier due to a surface potential decrease.

3.2. Base-catalysed route of the PTMS-TEOS system

It has been reported that powders manufactured from

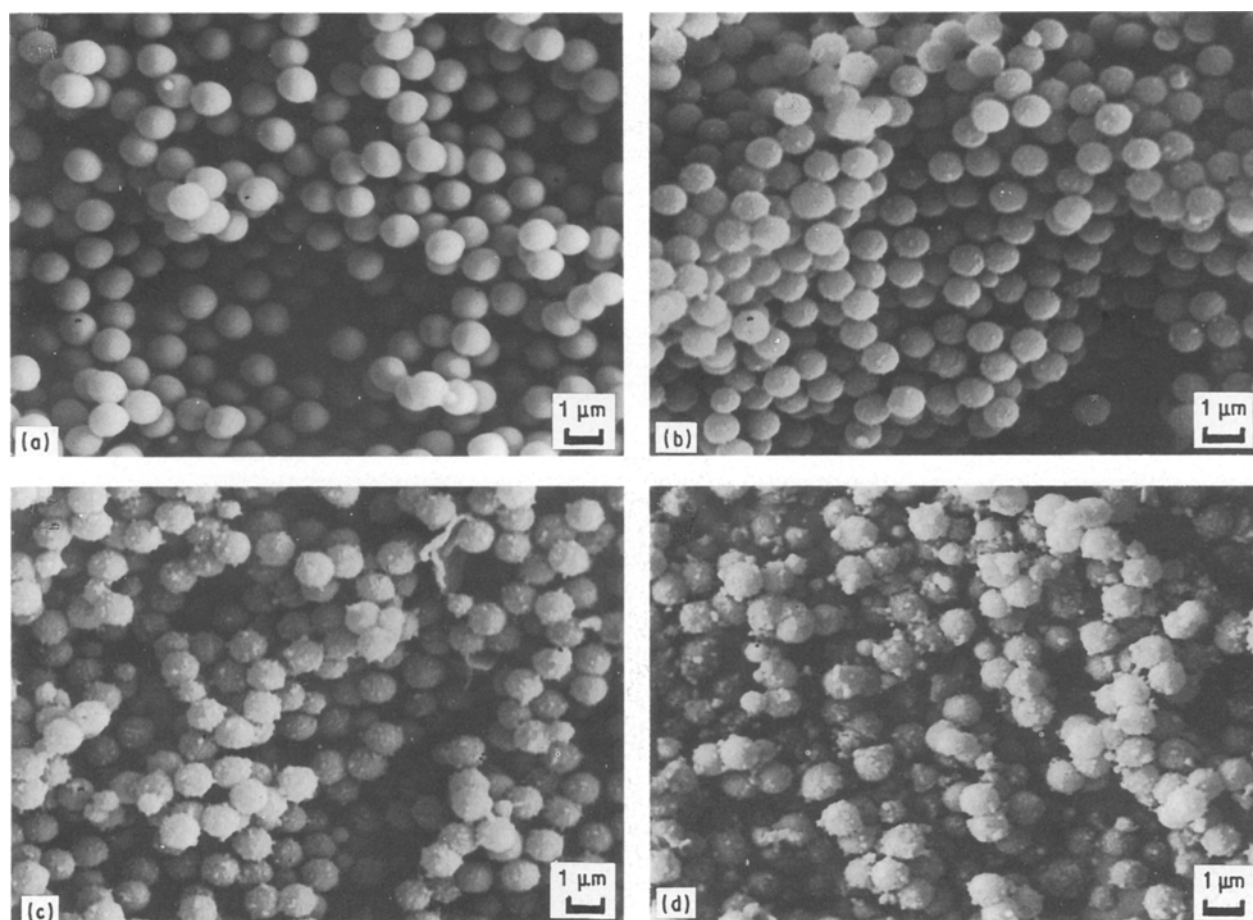


Figure 3 Scanning electron micrographs of powders derived from the base-catalysed route of the PTMS-TEOS system. The concentration of silanes was 0.25 mol l^{-1} and the ratios of TEOS/PTMS and that of NH_4OH /silane were (a) 0-2, (b) 0-4, (c) 0.5-4, and (d) 1-4, respectively.

the PTMS system have a carbon to silicon molar ratio of 4 when heat treated, and contain free carbon [1, 2]. Thus, it is necessary to control the molar ratio of carbon to silicon. Silicon alkoxide is normally used for this purpose. In this work, TEOS was used and the effects of NH_4OH and TEOS in the solution of PTMS-TEOS on particle size and size distribution were examined.

Fig. 3 shows scanning electron micrographs of powders exhibiting changes in particle size and shape with respect to NH_4OH and TEOS contents in the base-catalysed route of PTMS-TEOS system. The concentration of silanes was held to 0.25 mol.l^{-1} . In low TEOS (molar ratio TEOS to PTMS of < 0.5) and NH_4OH (molar ratio of NH_4OH to silanes < 4) content, the particle size was about $1 \mu\text{m}$ and the shape was spherical. These results are very similar with those of PTMS system. But as NH_4OH and TEOS contents increased, a number of fine particles with size of about $0.05 \mu\text{m}$ were precipitated on particle surfaces and monolithic bulk gels were increased. When the molar ratio of TEOS to PTMS was as large as 2, the products were no longer spherical particles but monolithic bulk.

This is considered to be due to the difference in hydrolysis rates between PTMS and TEOS in basic solution and results in two classes of primary particles; one has particles of composition close to SiO_2 and the other has a composition close to particles derived from PTMS. The latter grow first, as in the case of the base-catalysed route of the PTMS system, but the former is stable against agglomeration and remain stable in suspension [12]. On drying, these stable particles either precipitate on the surfaces of grown particles or form monolithic gel. As a result, the number of small particles covering the surfaces of grown particles and the probability of forming monolithic bulk gel were also increased as the TEOS and NH_4OH contents increased.

3.3. Acid-base catalysed route

Fig. 4 shows scanning electron micrographs of typical powders manufactured by the acid-base catalysed

route of the PTMS system. The experiments were conducted under the same conditions as the previous base-catalysed route of the PTMS system. The powders show two different aspects with respect to the concentration of PTMS regardless of the amount of NH_4OH used. When the concentration of PTMS was 0.5 mol.l^{-1} , the particle-size distribution was broad and a particle size larger than $5 \mu\text{m}$ was observed. However, when it was equal to or less than 0.25 mol.l^{-1} , the particle size fell to about $0.3 \mu\text{m}$ and the size distribution was very narrow.

In acidic solution, the rate of production of silanol groups is fast, by rapid hydrolysis reaction of PTMS [18, 19]. When this solution is changed to basic condition, the nucleation rate becomes rapid and the number density of nuclei produced increases rapidly in a short time through consumption of existing silanol groups [20].

When the silane concentration in the solution increases to 0.5 mol.l^{-1} , the number density of nuclei produced becomes high and the probability of interaction between two particles increases, and finally the stability ratio drops [21-26]. Because of this, rapid coagulation occurs in the case of high-silane-concentration solution and results in polydispersed particles, as is generally known. When equal to or lower than 0.25 mol.l^{-1} , however, although the nucleation rate is still rapid, the number density of nuclei produced is too low to affect the stability ratio and results in monodispersed particles.

Production of finer particles in this work compared with the base-catalysed route can be also explained as follows. In the base-catalysed route the supply of nuclei which agglomerate to existing particles continues for a long time because of the slow hydrolysis rate. In the acid-base catalysed route, the period of nuclei supply is short because of rapid hydrolysis in acid solution which exhausts unreacted silane and provides plenty of silanol. Therefore, the agglomerates in base solution cannot grow further, due to an excess of seed particles and a deficiency of nuclei.

In the PTMS-TEOS system, similar trends also resulted and fine particles which were seen in the base-catalysed route were not observed. In acidic solution,

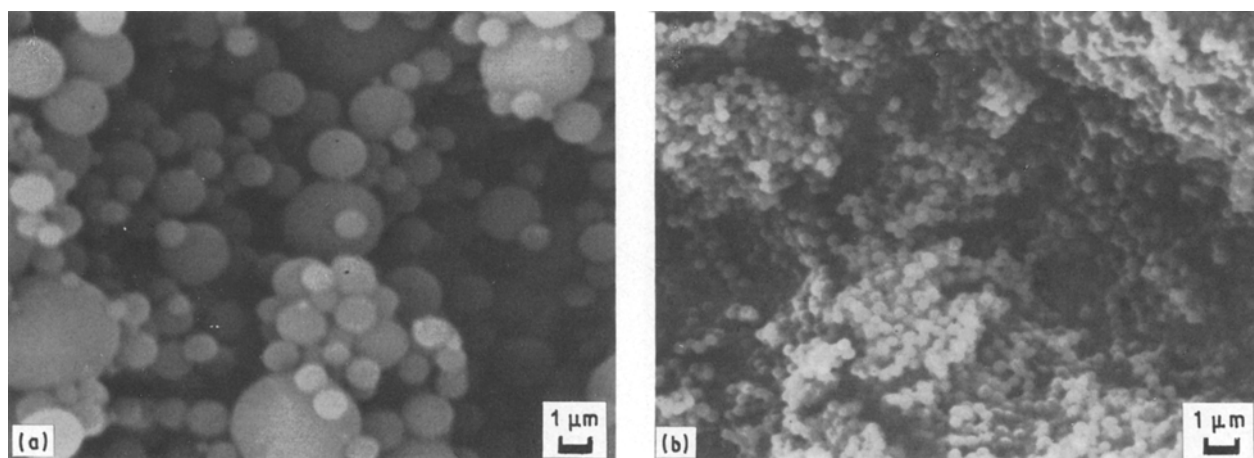


Figure 4 Scanning electron micrographs of powders derived from the acid-base catalysed route of the PTMS system. The concentrations of PTMS and the ratios of $\text{NH}_4\text{OH}/\text{PTMS}$ were (a) 0.5 mol.l^{-1} , 2, and (b) 0.25 mol.l^{-1} , 2, respectively.

a homogeneous solution was observed within 10 min, due to the rapid hydrolysis rate of PTMS and TEOS [18, 19] and this resulted in homogeneous mixing between PTMS and TEOS silanols and inhibited phase segregation when changed to a basic solution.

3.4. X-ray diffraction and thermal analysis

Fig. 5 shows TG–DTA curves of gel powders synthesized from the base-catalysed route of PTMS–TEOS system. A weak and broad endothermic peak in the DTA curve occurred near 200 °C. This peak resulted from dehydration. A sharp exothermic peak was observed at 530 °C and a broad peak appeared at 750 °C, probably due to the decomposition of phenyl

groups. Above 750 °C, no weight loss was found. The weight loss of the powders caused by dehydration and decomposition was about 40%.

Fig. 6 shows scanning electron micrographs of powders calcined at 1400 °C for 2 h. After calcination, the initial spherical shape was sustained in the powders derived from the PTMS–TEOS system and this phenomenon resembles that observed by Hatakeyama and Kanzaki [4], but the powders derived from the PTMS system changed to monolithic bulk and fibre phase, as reported by White *et al.* [1, 2]. Thus it can be considered that bonds due to TEOS on the PTMS play a critical role in sustaining particle structure.

Fig. 7 shows XRD patterns of the powders derived from the acid–base catalysed route of the

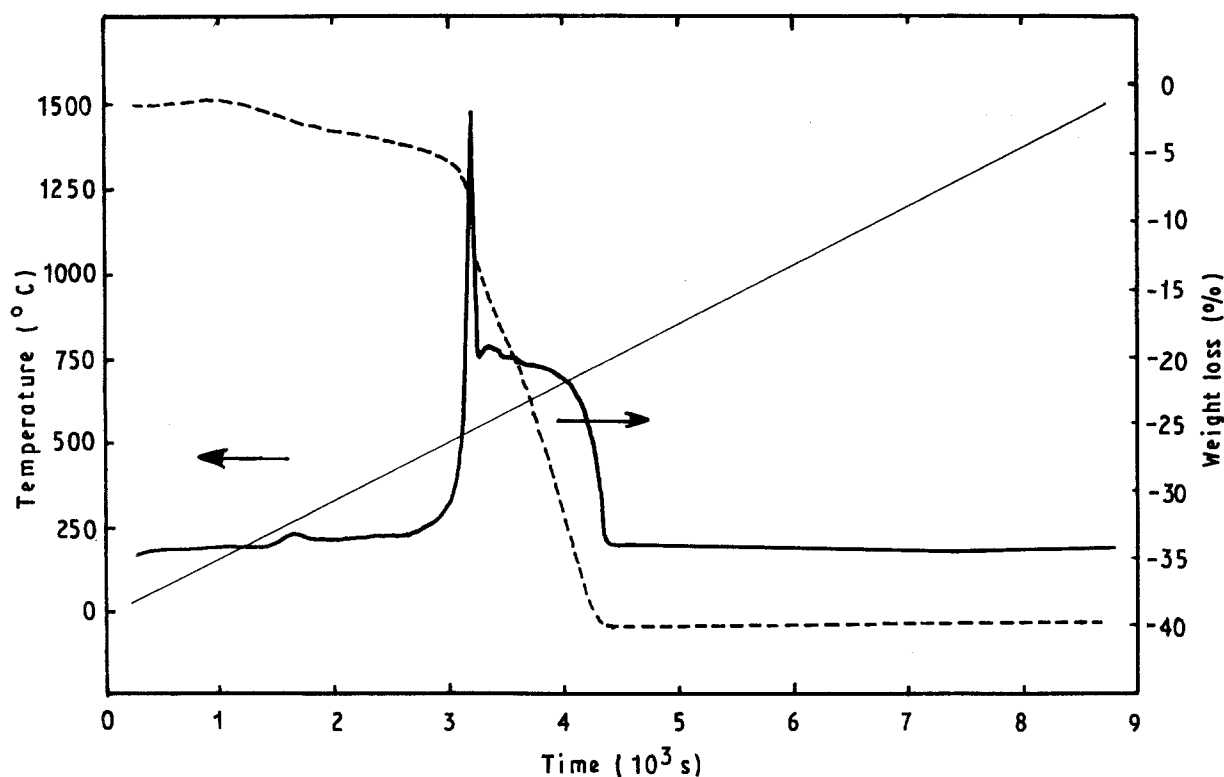


Figure 5 TG–DTA curve of the powder derived from the base-catalysed route of the PTMS–TEOS system. The concentration of silane and the ratio of $\text{NH}_4\text{OH}/\text{PTMS}$ were 0.25 mol l^{-1} and 4, respectively (—), DTA, (---) TG.

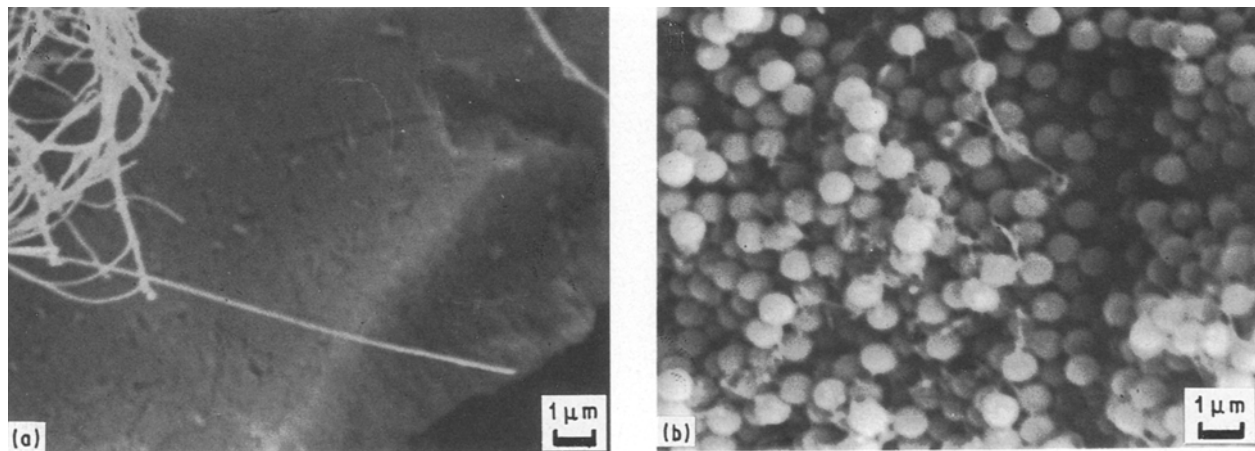


Figure 6 Scanning electron micrographs of powders derived from the base-catalysed route calcined at 1400 °C for 2 h. The concentration of silane and the ratio of $\text{NH}_4\text{OH}/\text{silane}$ were 0.25 mol l^{-1} and 4, respectively. (a) Powders derived from the PTMS system, (b) powders derived from the PTMS–TEOS system.

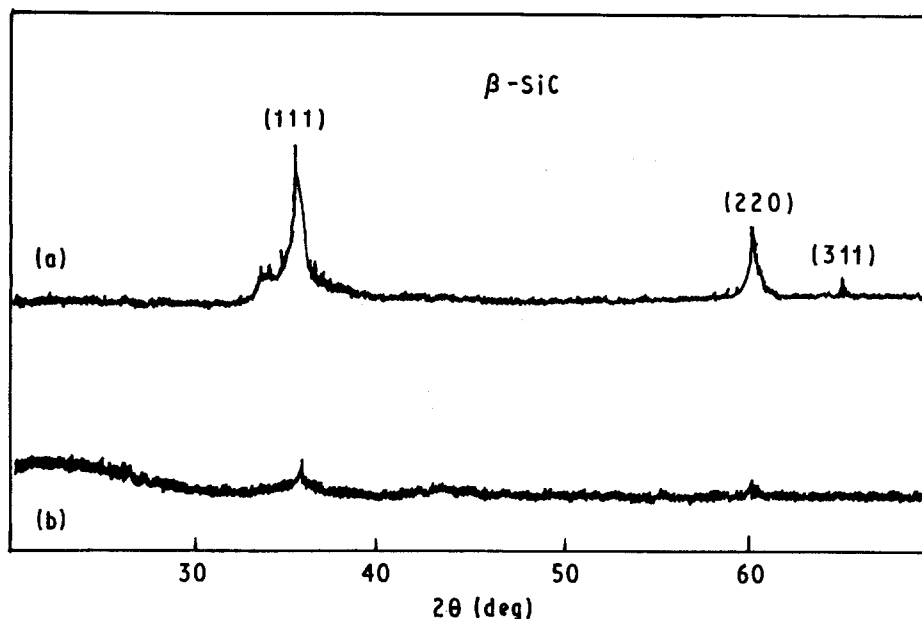


Figure 7 XRD patterns of calcined powders derived from the base-catalysed route of the PTMS-TEOS system. The concentration of silane and the ratio of $\text{NH}_4\text{OH}/\text{silane}$ were 0.25 mol l^{-1} and 4, respectively. (a) 1400°C , (b) 1500°C .

PTMS-TEOS system calcined at 1400 and 1500°C . Amorphous gel powders transformed to $\beta\text{-SiC}$ at 1500°C . Similar phenomena were observed regardless of manufacturing processes.

4. Conclusion

Monodispersed spherical gel SiC powders were prepared by the hydrolysis and condensation of PTMS or a mixture of TEOS-PTMS from the system of silane- H_2O -catalyst, in which no co-solvent such as alcohol was used, but excess H_2O was used in the role of dispersing medium. Monodispersed spherical gel powders could be obtained when the molar ratio of TEOS to PTMS was less than 0.5 and that of NH_4OH to silane less than 4. The mechanism of particle growth could be deduced as being due to the surface potential decrease caused by the existence of surface phenyl groups. When heated above 1400°C , the monodispersed spherical particle shape was sustained in the PTMS-TEOS system but the initially spherical shape changed to bulk and fibre phase in the PTMS system.

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