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A Model for the Formation of Nanosized SiC Powders by Laser-Induced Gas-Phase Reaction

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Abstract

Powder refinement is one approach to reducing the frequency of microstructural inhomogeneities in ceramic parts. Laser-induced pyrolysis of gaseous precursors is a reproducible and reliable process to fabricate nanosized particles. In the thermal decomposition of SiH_4 *and* C_2H_2 *by a continuous wave* CO_2 *laser, the size of the silicon carbide particles is adjusted according to their residence time in the reaction zone. The collision and coalescence model provides a satisfactory agreement with experimental results, whereas the nucleation theory is inappropriate, due to the small dimensions of the critical nuclei.*

Durch die Verwendung von Feinstpulvern kann die Defektgröße im Mikrogefüge keramischer Werkstoffe reduziert werden. Die mittels Laser durchgeführte Pyrolyse gasförmiger Verbindungen ist ein reproduzierbares und zuverlässiges Verfahren, um Pulver im Nanometerbereich herzustellen. Bei der thermischen Zersetzung von SiH_4 *und* C_2H_2 *mit einem* CO_2 *Laser ist die SiC-Teilchengröße nur von der Aufenthaltszeit in der Reaktionszone abhängig. Die Versuchsergebnisse können gut mittels der Kollisionstheorie erklärt werden, während ein Keimbildungsmodell wegen der zu geringen Größen der kritischen Keime nicht geeignet ist.*

L'utilisation de poudres de plus en plus fines permet de réduire l'importance des défauts microstructuraux d'une céramique. La pyrolyse de précurseurs gazeux induite par laser est un procédé fiable et reproductible de fabrication de particules nanométriques. Dans la décomposition thermique de SiH_4 *et* C_2H_2 *par un laser continu* CO_2*, le diamètre des particules de carbure de silicium ne dépend que de leur temps de séjour dans la zone réactionnelle. Le modèle des collisions est en bon accord avec les résultats expérimentaux, alors que la théorie de nucléation homogène ne convient pas en raison des dimensions trop réduites des noyaux critiques.*

1 Introduction

Vapour-phase synthesis of silicon carbide powders, whether classical,[1,2] plasma-[3] or laser-[4,5] induced, most often utilizes silane-derived precursors such as CH_3SiCl_3, or silane itself (SiH_4) with an additional carbon source which may be C_2H_4,[4,5] C_2H_2[5] or CH_4.[6] In experiments conducted by Haggerty *et al.* since 1977,[7] the laser process is based on the high absorption of SiH_4 at the 10·6-μm radiation of a continuous wave CO_2 laser. When the laser fluence is larger than $2{\cdot}5\,J\,cm^{-2}$, SiH_4 is decomposed into H_2 and a submicron silicon powder, the shaping and nitriding of which yield a high-quality reaction-bonded silicon nitride.[7,8] In general, hydrocarbons containing no $CH_2{=}$ group undergo no transformation when they are irradiated by a CO_2 laser beam, but decompose when they are associated with a sensitizer such as SiH_4. The recent identification of intermediate vapour-phase species Si, C_2 and SiC_2, observed after irradiating a SiH_4–C_2H_2 mixture with a continuous wave CO_2 laser,[9] permits in the present paper the development of a particle formation model for silicon carbide, in good agreement with experimental results and illustrating how particle size is adjusted to the reaction parameters.

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Table 1. List of synthesis conditions

Cell pressure	1 atm
Reactants' flow rates ($cm^3\,min^{-1}$) at 298 K and 1 atm	SiH_4: $540 > \Phi > 120$ C_2H_2: $300 > \Phi > 120$
Diameter of capillary inlet (mm)	1 or 2
Flow rate of carrier gas ($cm^3\,min^{-1}$)	2 200
Power of unfocused laser beam (*W*)	620
Diameter of unfocused laser beam (mm)	12
BET diameter of SiC particles (nm)	$15 < d < 50$
Residence time in the flame (s)	$1 < t < 10$
Temperature of the flame (K)	$1\,573 < T < 2\,073$

Table 2. Residence time and BET equivalent spherical diameter of SiC particles for three reactants' flow rates

	Run		
	1	*2*	*3*
SiH_4 flow rate ($cm^3\,min^{-1}$)	120	200	540
C_2H_2 flow rate ($cm^3\,min^{-1}$)	67·4	110	300
C/Si ratio	1·12	1·10	1·11
Residence time, *t* (s)	$8\text{–}10 \times 10^{-3}$	$2\text{–}4 \times 10^{-3}$	1×10^{-3}
BET diameter (nm)	51·8	30·6	15·9

2 Experimental

The experimental apparatus consists of a cross-flow reactor, where the horizontal laser beam intersects the gaseous reactants.[4,10,11] Crossing of both beams creates a flame, the temperature of which is measured by optical pyrometry; an inert gas (He or Ar) carries the powder to a collection chamber containing a porous metallic filter.

Typical values and ranges of experimental parameters are listed in Table 1; residence time, flame temperature and particle size all increase with decreasing flow rates (Table 2). As-formed powders (Fig. 1(a)) present the infrared spectrum of silicon carbide, and the X-ray diffraction patterns of crystalline β-SiC (Fig. 1(b)); their BET equivalent

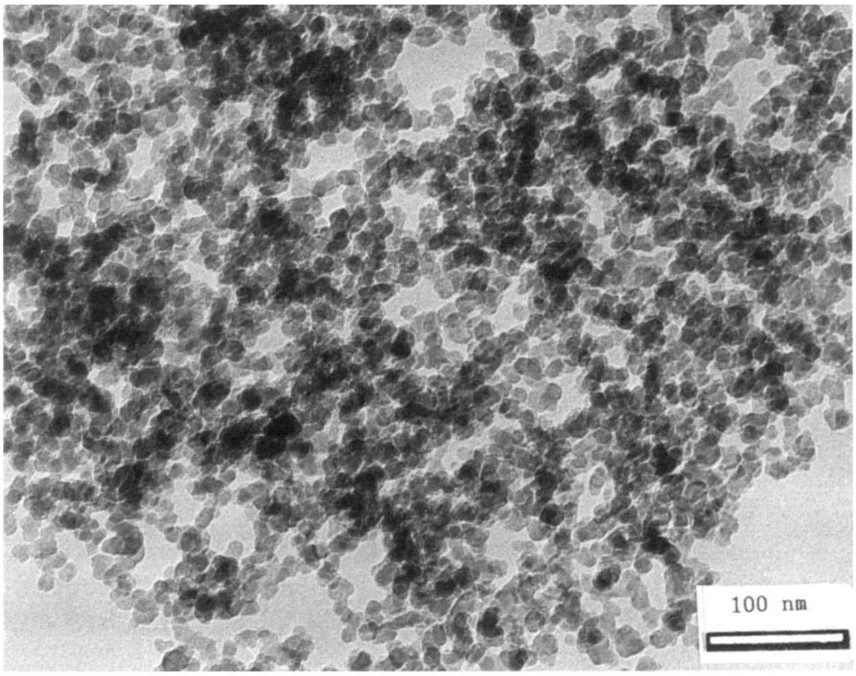

Fig. 1a. TEM photomicrograph of laser-synthesized SiC powder.

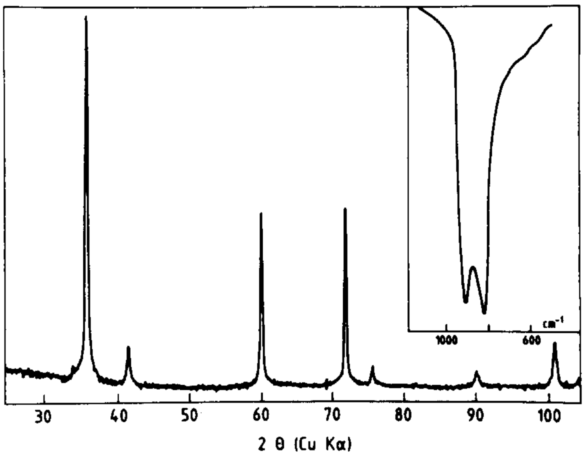

Fig. 1b. X-ray diffraction pattern and IR spectrum of laser-synthesized SiC powder.

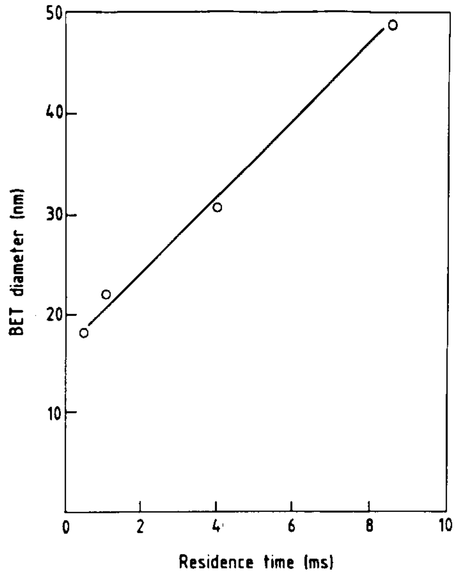

Fig. 2. As-measured BET equivalent spherical diameter (nm) of laser-synthesized SiC particles as a function of their residence time (10^{-3} s) in the flame.

spherical diameter varies with the residence time in the flame, as illustrated in Fig. 2.

Laser-induced pyrolysis of SiH_4 and C_2H_2 can result in a nearly complete reaction. For example, for SiH_4 and C_2H_2 flow rates of 300 and 165 $cm^3.min^{-1}$, the overall amount of reacted SiH_4 and C_2H_2 is in excess of 99 mol%, while the amount of SiC recovered per hour is 30 g, compared to the theoretical value of 32·2 g. The discrepancy is due to losses occurring in the powder collection and to the formation of minor by-products identified as C_2H_4, C_3H_6, $H_2C{=}C{=}CH_2$, $H_2C{=}CH{-}SiH_3$, $H_2C{=}CH{-}C{\equiv}CH$, $HC{\equiv}C{-}C{\equiv}CH$ and C_6H_6.

Two models have been considered to explain the vapour-phase formation of SiC particles: classical nucleation, and collision–coalescence. The results are presented in Section 3.

3 Results

The completeness of the reactants' pyrolysis and the experimental evidence[9] for intermediate species Si, C_2 and SiC_2 support the sequence:

$$SiH_4 \rightarrow Si + 2H_2 \qquad (1)$$

$$C_2H_2 \rightarrow C_2 + H_2 \qquad (1')$$

$$Si + C_2 \rightarrow SiC_2 \qquad (2)$$

$$SiC_2 + Si \rightarrow 2SiC \qquad (3)$$

for which the following assumptions are made: (i) all species are perfect gases, (ii) the flame's volume in the reactor is negligible and expandable, thus all reactions are at constant pressure and limited to the flame's volume, (iii) the thermal expansion coefficient of SiH_4 and C_2H_2 at constant pressure is $3{\cdot}6 \times 10^{-3}\,K^{-1}$, independent of temperature.[12]

3.1 Effect of temperature

The partial pressure of SiC and the concentrations of Si and SiC_2 in the flame are listed in Table 3 as functions of temperature, for initial flow rates of 300 $cm^3.min^{-1}$ SiH_4 and 165 $cm^3.min^{-1}$ C_2H_2 (values at 1 atm and 298 K).

3.1.1 Homogeneous nucleation model[13,14]

Considering the nucleation process as a sequence of additions of single molecules to the developing embryo, the following expression has been derived for the nucleation rate *J*:[15,16]

$$J(m^{-3}\,s^{-1}) = \gamma \frac{4\pi r^{*2}}{\sqrt{2\pi m k T}} p c_1 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

where ΔG^* is the Gibbs enthalpy of formation of a critical nucleus of radius r^*, $c_1 = p/kT$ is the monomer concentration and the so-called Zeldovich factor γ accounts for the departure of steady-state from equilibrium concentration of critical nuclei (about 10^{-2} in the usual case).

The free energy of formation of the critical nucleus, ΔG^*, is described by assigning macroscopic thermodynamic properties to the critical nucleus:[17]

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2}$$

where σ is the surface tension and ΔG_v is the free energy change per unit volume produced in the condensation process. In terms of the supersaturation ratio.

$$\Delta G_v = -\left(\frac{kT}{\Omega}\right) \cdot \ln\left(\frac{p}{p_0}\right)$$

where Ω is the molecular volume in the solid, and p_0 is the equilibrium vapour pressure of the solid at the temperature *T*. Eventually, the critical nucleus radius is expressed by

$$r^* = -\frac{2\sigma}{\Delta G_v}$$

Using[18] $\sigma = 1{\cdot}5\,J\,m^{-2}$, $\Omega = 2{\cdot}0696 \times 10^{-29}\,m^3$ and

Table 3. Evolution of SiC partial pressure (bar), Si and SiC_2 concentrations (mol m^{-3}) with temperature

T (K)	1 573·15	1 673·15	1 773·15	1 873·15	1 973·15	2 073·15
p (SiC)	0·2425	0·2423	0·2422	0·2420	0·2419	0·2418
n_{Si}	0·9271	0·8709	0·8214	0·7770	0·7373	0·7014
n_{SiC_2}	1·1325	1·0640	1·0033	0·9491	0·9005	0·8568

$p_0(\text{Pa}) = 1{\cdot}013 \times 10^5 \exp(-40\,184{\cdot}09/T + 12{\cdot}1365)$ for solid SiC leads to the variations of r^* and J versus temperature, indicated on Figs 3 and 4.

3.1.2 Collision and coalescence

According to the kinetic theory of gases,[19] the mean velocity C of Si atoms in the flame and their mean free path λ_{Si} are expressed by

$$C = \sqrt{\frac{8kT}{\pi m_{Si}}}$$

and

$$\lambda_{Si} = \frac{1}{\pi\left(n_{Si}\cdot d_{Si}^2\cdot\sqrt{2} + n_{SiC_2}\cdot d_{Si-SiC_2}^2\cdot\sqrt{1+\dfrac{m_{Si}}{m_{SiC_2}}}\right)}$$

in which k is the Boltzmann constant, m_{Si}, m_{SiC_2}, n_{Si} and n_{SiC_2} are masses and concentrations of Si and SiC_2 in the flame respectively, and $d_{Si-SiC_2} = \frac{1}{2}(d_{Si} + d_{SiC_2}) = \frac{1}{2}(2{\cdot}34 + 1{\cdot}812) = 2{\cdot}076$ A; values of d_{Si} and d_{SiC_2} are from Refs 20 and 21.

The collision rate per silicon atom is then $\Lambda(T) = C/\lambda$. Assuming successive collisions Si–SiC_2–Si–SiC_2–Si..., where each Si–SiC_2 collision forms 2 SiC molecules, the mass m (kg) of SiC aggregate formed after time t is $m = \Lambda \times 6{\cdot}6578 \times 10^{-26}t$, which corresponds to the radius $r(m) = (4{\cdot}9407 \times 10^{-30} \times \Lambda t)^{1/3}$.

Figure 5 shows the particle diameter as a function of time in the temperature range 1573–2073 K.

3.2 Effect of the reactants' flow rates

The computation detailed in the previous section for SiH_4 and C_2H_2 flow rates of 300 and 165 $cm^3 . min^{-1}$, has been repeated at one temperature (1773.15 K) for the three sets of reactants' flow rates listed in Table 2, whence by the three curves shown in Fig. 6. As can be seen on this figure, the three curves are almost superimposed and would start to separate from one another only at longer residence times in the flame.

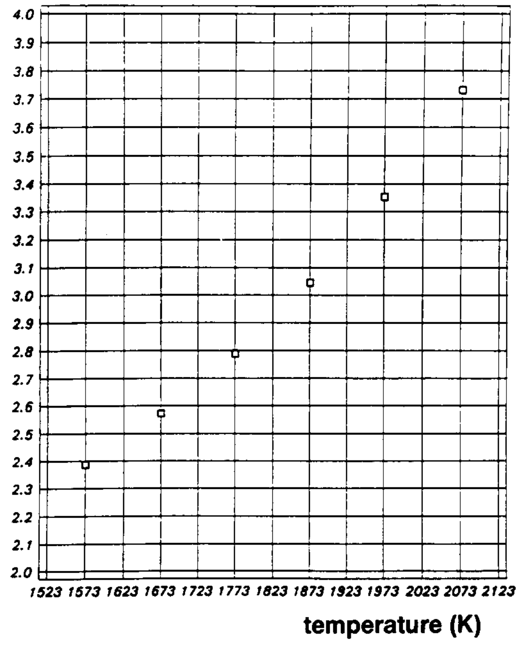

Fig. 3. Variation of the calculated radius of critical nuclei (A) with temperature (K).

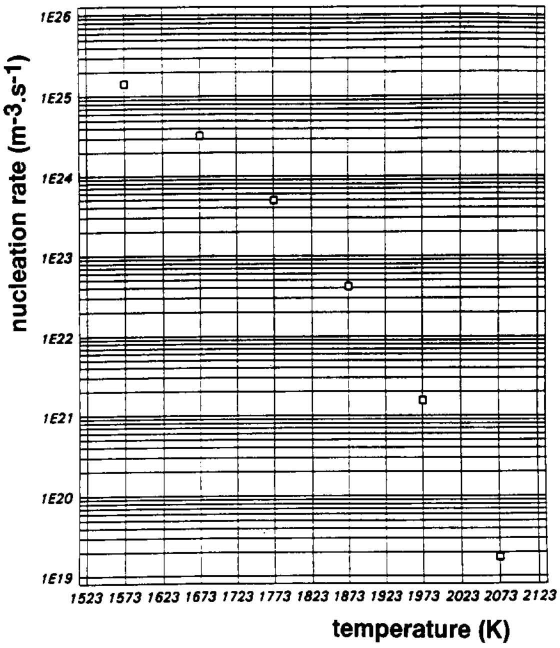

Fig. 4. Variation of the calculated nucleation rate ($m^{-3}s^{-1}$) with temperature (K).

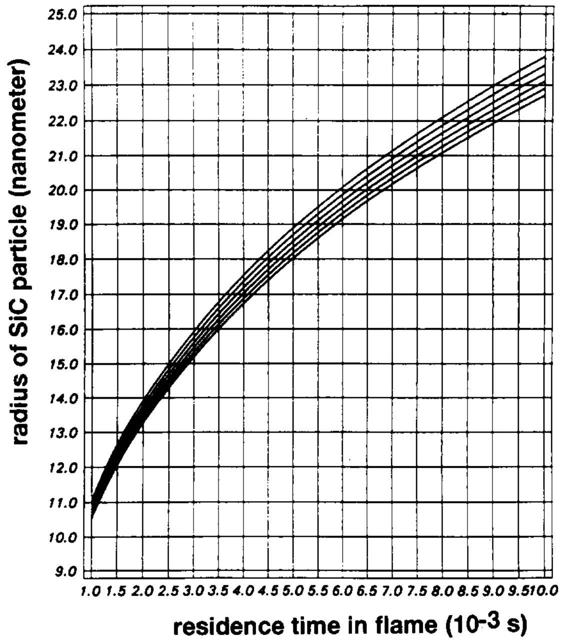

Fig. 5. Variation of the calculated radius (nm) of SiC particles with time (10^{-3} s) at temperature T = 1573·15 K + 100n; n = 0 (top) through 5 (bottom).

4 Discussion

In the conditions of Table 1 the laser-induced pyrolysis of silane bypasses the formation of disilane and higher polysilanes which would occur at low to moderate temperatures or low laser fluences,[22–24] and leads directly to the formation of silicon and H_2 as implied by reaction (1).[25] As to C_2H_2, its

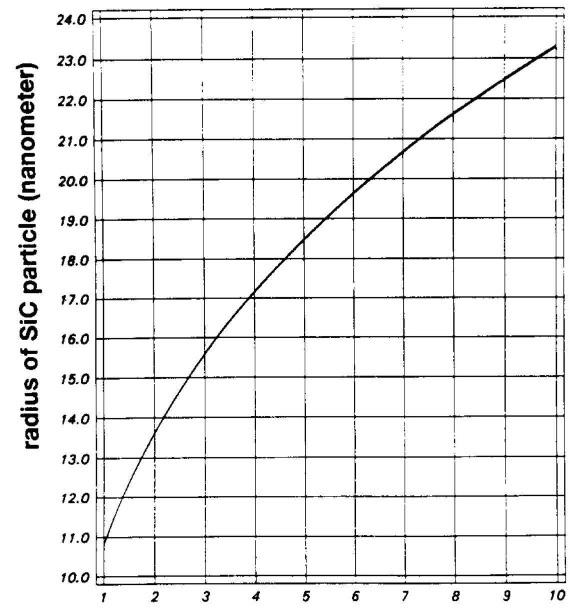

Fig. 6. Variation of the calculated radius (nm) of SiC particles with time (10^{-3} s) for the three reactants' flow rates of Table 2 (curves almost superimposed).

decomposition by the laser beam only occurs in the presence of a sensitizer such as SF_6 or SiH_4. The experimental detection[9] of C_2 atoms supports reaction (1′), for which a kinetic order of 2 relative to C_2H_2 has been found consistent with the fast SiC particle formation.[26] With the kinetic constant[27] $k = 2{\cdot}49 \times 10^{13} \exp(-(4402/T))\,\mathrm{mol}^{-1}\,\mathrm{litres}^{-1}$, the complete thermal decomposition of C_2H_2 is shorter than 10^{-6} s at any temperature higher than 1573·15 K.[26] Conversely, a kinetic order of 3, as is observed when C_2H_2 is associated with a very dilute sensitizer,[28] would ensure too slow decomposition kinetics for the present case.[26]

The homogeneous nucleation is not thought to apply to the SiC particle formation. Indeed, the critical radii indicated in Fig. 3 corresponded to SiC clusters of ten molecules or less, to which it is no longer valid to assign macroscopic thermodynamic properties.[29] Furthermore, Fig. 4 indicates that the nucleation rate decreases by six orders of magnitude between 1523 and 2073 K. This variation corresponds to an increase in the particle size by two orders of magnitude, far in excess of the threefold increase observed experimentally and mentioned in Table 1.

On the other hand, the application of the collision and coalescence theory is quite valid, since the Knudsen number of the Si–SiC_2 gas, $Kn = \lambda/r$, is always larger than 10^4 (and therefore > 1). Also, the theoretical results of Fig. 5 are in good agreement with the experimental results of Fig. 2, and one notices the minor influence of temperature on the particle size.

The influence of the reactants' flow rates on the particle size is even less pronounced for a constant C/S ratio (1.1 in this case, Table 2), as illustrated by the superposition of the three curves (Fig. 6). The flow rate is therefore not a critical parameter of the reaction. Varying the flow rates of the reactants merely changes the velocity of the reacting species, and thus their residence time in the flame, but the supporting curve $r = r(t)$ is always the same for a constant C/Si ratio. In practice the velocity of the reacting species also depends on the diameter of the capillary inlet and the cell pressure.

Furthermore, this model does not preclude the formation of SiC particles containing α-, mixed α/β- or amorphous microdomains, as has been recently observed for laser-synthesized nanosized powders,[30] and it pertains to single crystals as well as polycrystalline particles.

It should be noticed that the direct carburization of Si particles into SiC within the experimental time frame of 1 to 10 ms is only consistent with carbon grain boundary diffusion in SiC (Lihrmann, J. M., unpublished), which thus cannot explain the obtention of SiC single crystals mentioned in Ref. 4. For the same reason the shrinking heart model, previously used to describe laser-induced SiC particle formation,[6] is also believed to be less satisfactory than the collision model, all the more because it requires in addition questionable assumptions such as a constant particle volume or equal densities for Si and SiC.

5 Summary and Conclusions

The formation of nanosized SiC powders by laser-induced pyrolysis of SiH_4 and C_2H_2 is satisfactorily modelled with the collision and coalescence theory assuming intermediate species Si, C_2 and SiC_2. The size of the particles is only governed by the residence time of the reacting species in the flame, which in practice depends on the reactants' flow rates, the diameter of the capillary inlet and the cell pressure. This model offers the advantage of being applicable to various types of particle crystallinity and avoids addressing the direct carburization of silicon. The latter is inconsistent with the obtention of single crystal particles, whereas the nucleation theory can not be applied due to the too small critical radii.

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