

Investigation on pore structure and small-scale agglomeration behaviour in liquid phase sintered SiC using small angle neutron scattering

D SEN^{1,*}, J BAHADUR¹, S MAZUMDER¹, T MAHATA², M SYAMBABU² and P K SINHA²

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

²Energy Conversion Materials Section, Bhabha Atomic Research Centre, Vashi Complex, Navi Mumbai 400 705, India

*Corresponding author. E-mail: debasis@barc.gov.in

Abstract. Mesoscopic density fluctuations in liquid phase sintered silicon carbide have been investigated using small angle neutron scattering (SANS). The increase in the additives results in the modification in the pore size distribution and to some extent the total porosity. SANS revealed a mass fractal nature of the agglomerated matrix microstructure. The fractal dimension of the matrix does not change appreciably with the additives although the upper cut-off value of the fractal decreases significantly with the increase in the additives. The liquid phase sintering due to the presence of additives helps to achieve higher level of densification. However, the agglomeration hinders achievement of the fully dense pellets.

Keywords. Small angle neutron scattering; liquid phase sintering; pore structure; agglomeration.

PACS Nos 61.05.fg; 81.20.Ev

1. Introduction

Silicon carbide (SiC) is one of the potential candidates for high temperature structural components. However, the most crucial aspect that limits the applications of the SiC-based ceramics is their brittleness. Further, SiC is difficult to densify because of the covalent nature of Si–C bonding and also due to the low self-diffusion coefficient [1]. In addition to the solid state sintering process recently there has been much interest in liquid phase sintering [2] with the aid of metal oxide additives like Al₂O₃ and Y₂O₃ for enhanced properties of SiC. The additives form a liquid phase at temperatures beyond 1750°C. Subsequently, the liquid promotes better densification. However, in most of the situations the sintered product is not free from pores even after the densification with the proper addition of the sintering additives. The agglomeration behaviour of the primary particles also affects the microstructure and the density of the sintered product [3]. In many cases the agglomerated matrix

can be quantified in terms of fractal geometry. The origin of the term ‘fractal’ is due to the fact that some objects show a self-similarity over a wide length scale and is associated with some fractional dimension. Many properties of the fractal systems can often be described by functions that are proportional to a power of another parameter. This relation is frequently called a power law. Here it is interesting to note that most of the fractal objects encountered in nature are self-affined and are generally random, i.e., they are not created by the deterministic mathematical rules e.g. the Sierpinski gasket. It is noteworthy that self-similar fractals re-scale the same way along any spatial direction but self-affine fractals require different re-scaling factors for different directions.

SANS is an important non-destructive technique to probe the pore structure in ceramics [4] and other porous materials [5–7]. This technique is also effective in probing fractal morphology in materials. The present manuscript deals with the SANS investigations on the pore structure and small-scale agglomeration behaviour in liquid phase sintered SiC.

2. Experimental

SiC powders used in these experiments show a median particle size of $6.25 \mu\text{m}$ as obtained by particle size analyser (Horiba, LA-500). Yttria (Y_2O_3) and alumina (Al_2O_3) powders in the molar ratio 3:5 (weight ratio 4:3) were used as sintering aid. Powder mixtures were ball-milled in ethanol with silicon nitride balls for 8 h and was subsequently dried. Circular blocks of 32 mm diameter and thickness ~ 3 mm were prepared by hot pressing in graphite die under vacuum at 1850°C at 30 Mpa pressure for ~ 1 h. Samples with 100 (SiC-A), 96.5 (SiC-B), 93.0 (SiC-C) and 89.3 (SiC-C) wt% of SiC have been taken for SANS investigation. Density of the pellets was found to be 2.12, 2.46, 2.73 and 2.90 g/cm^3 , respectively. SANS experiments have been performed using a double crystal-based medium resolution SANS facility at the Guide Tube Laboratory of Dhruva reactor at Trombay, India [8]. The instrument consists of a non-dispersive (1, -1) setting of (1 1 1) reflections from silicon single crystals with the specimen between the two crystals. Measured SANS profiles have been corrected for background, transmission and instrument resolution.

Figure 1 depicts the corrected SANS profiles for the specimens in double logarithmic scale. The same profiles are plotted in Porod plot ($I(q)q^4$ vs. q) in figure 2 in a log-log scale.

3. Data analysis and discussions

From the preliminary analysis of the SANS data, at the two extreme regions of the accessible wave vector transfer, the following two features have been observed. Firstly, the tail of the profiles follows power-law behaviour over a wide q range from ~ 0.01 to 0.15 nm^{-1} . The exponents of the negative power law for all the specimens have been found to be less than 3 but greater than 2. Secondly, the lower q region data follow a double Guinier-type behaviour (inset of figure 1). From the scanning

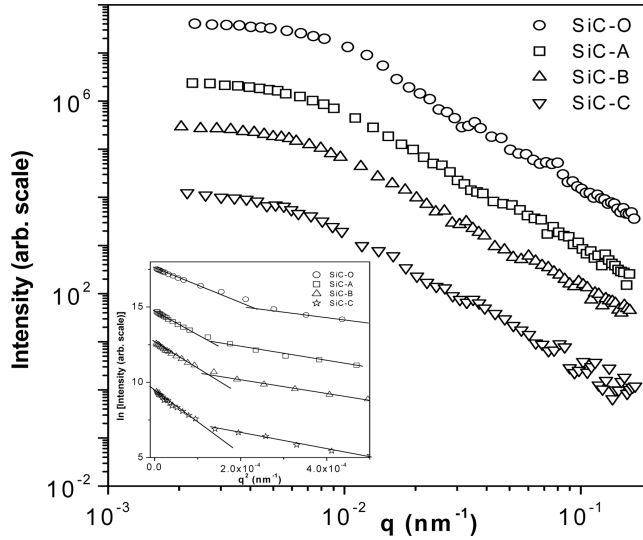


Figure 1. SANS data (log–log plot). Guinier plot (inset).

electron micrograph no inhomogeneity with high enough aspect ratio is observed and hence the pore morphology is approximated as spherical. It is noteworthy that the tail of the scattering profile from a polydisperse ensemble of spherical pores follows q^{-4} behaviour, which is in contrast to the first observation in the present case. However, it is important to mention that in many situations the agglomeration of the powder particles is unavoidable. Although ball milling breaks the agglomerates in larger length scale, the probability remains for existence of agglomerates in lower length scales. As mentioned earlier, often these agglomerated structures can be fractals in nature and can be represented by a mass fractal dimension d_m generally different from their Euclidean dimension. The scattering intensity from the mass fractals is given by

$$I_{\text{frac}}(q) = c_f P_f(q, r_0) S_{\text{frac}}(q, r_0) \quad (1)$$

where $S_{\text{frac}}(q, r_0)$ represents the structure factor for mass fractal [9]. $P_f(q, r_0)$ is the form factor of the basic units of the fractal with a radius r_0 . As the initial powder particles show significant polydispersity, the pores will also show a distribution in size. It is important to mention that the SANS profiles, over the whole experimental range (particularly higher q range) could not be explained solely on the basis of the spherical pores with any realistic distribution of the pores. This suggests the presence of scattering contributions from two different types of density fluctuations, namely, the pores and the agglomeration with fractal self-affine structure originating from the matrix. So considering both the contributions (i.e. from matrix-pore density fluctuation and also from fractal agglomerates) into account, the total scattering intensity can be written as

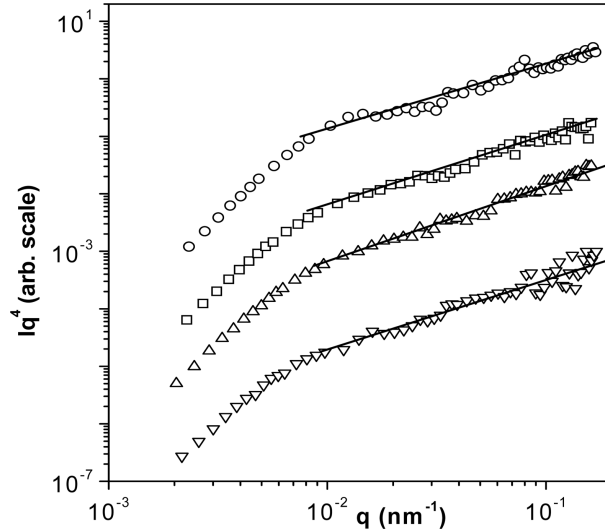


Figure 2. Porod plot showing the non q^{-4} behaviour.

Table 1. Parameters from the SANS analysis. $\langle \rangle$ represents the average value.

Sample	$\langle R \rangle$ (nm)	$[\langle R^2 \rangle - \langle R \rangle^2]^{0.5}$ (nm)	r_0 (nm)	d_m	ξ (nm)
SiC-0	132	43	25	2.41 ± 0.06	140
SiC-A	134	52	25	2.52 ± 0.06	120
SiC-B	135	56	25	2.52 ± 0.05	100
SiC-C	139	69	25	2.53 ± 0.05	80

$$I_{\text{total}}(q) = I_{\text{frac}}(q) + I_{\text{pore}}(q) = C_1 P(q, r_0) S_{\text{frac}}(q, r_0) + C_2 \int D(R) P(q, r) R^6 dr. \quad (2)$$

The fit of eq. (2) with the data are shown in figure 3 by a solid line. It is evident that the model explains well the present SANS data as is evident from the fit. The estimated parameters from the fit of the model to the data are tabulated in table 1. The estimated pore size distributions are depicted in figure 4.

The second observation as mentioned earlier i.e., the double Guinier-type behaviour for very low q region is also valid for the present model because of the presence of two different scattering contributions to the intensity profile.

The density of the samples increases with the increase in the additives because of the onset of better densification. From figure 4, it is seen that the pore size distribution is somewhat modified by the increase in additives. Firstly, the distribution becomes somewhat broader and the peak of the distribution shifts slightly towards the lower size region. The increase in the broadening in the distribution is manifested at both the ends of the distribution.

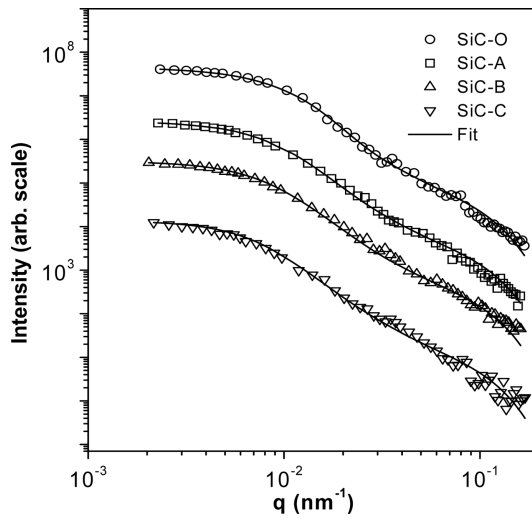


Figure 3. Fit of eq. (2) to the SANS data.

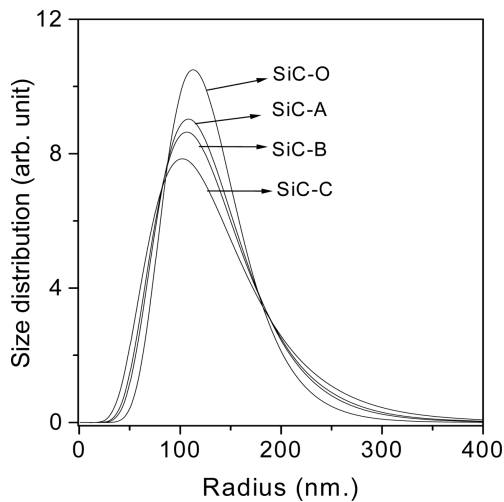


Figure 4. Estimated pore size distribution.

With the increased concentration of the additives *vis-à-vis* with the enhanced diffusion process, the shrinkage in pore size occurs. This modifies the lower end-tail of the distribution in one hand and the growth in pore size due to the coalescence of the smaller pores in the initial and the intermediate stages of sintering affects the higher end tail of the distribution on the other hand. The fractal dimension of the specimens is not much affected by the additives. The upper cut-off of the self-affinity decreased significantly with increase in the amount of the additive. This is due to the fact that the liquid phase alters and smoothens out the fractal structure in relatively larger length scales.

4. Conclusions

Agglomerated SiC matrix hinders the densification process. Increase in the amount of additives (Al_2O_3 and Y_2O_3) helps in improving the density of the sintered products via liquid phase sintering. The fractal dimension and the lower limit of the fractals remain unaffected by the increase in the additives but the upper cut-off of the fractal reduces. This is due to the fact that the liquid phases get attached at the pore–matrix interface channels and smoothen out the matrix structure at relatively higher length scales but the arrangements in the agglomerates in lower length scale structures are not affected significantly by the liquid phase. The enhancement in the amount of additives results in a slight increase in the average pore size and also the width of the pore size distribution via pore coalescence but the total porosity decreases.

References

- [1] K Motzfeld, Silicon carbide: synthesis, structure and properties, in: *Proceedings of the International Conference on Engineering Ceramics '92* edited by M Haviar, Reprint (Bratislava, 1993) pp. 7–42
- [2] F K van Dijen and E Mayer, *J. Eur. Ceram Soc.* **16**, 413 (1996)
- [3] H Ferkel and R J Hellmig, *Nanostructured Materials* **11(5)**, 617 (1999)
- [4] D Sen, T Mahata, A K Patra, S Mazumder and B P Sharma, *J. Phys.: Condens. Matter* **16**, 6229 (2004)
- [5] D Sen, S Mazumder and S Tarafdar, *J. Mater. Sci.* **37**, 941 (2002)
- [6] S Mazumder, D Sen, A K Patra, S A Khadilker, R M Cursetji, R Loidl, M Baron and H Rauch, *Phys. Rev. Lett.* **93**, 255704 (2004)
- [7] D Sen, T Mahata, A K Patra, S Mazumder and B P Sharma, *J. Alloys and Compounds* **364**, 304 (2004)
- [8] S Mazumder, D Sen, T Saravanan and P R Vijayaraghavan, *J. Neutron. Res.* **9**, 39 (2001)
- [9] J Texeira, *J. Appl. Crystallogr.* **21**, 781 (1988)