Study on porosity of ceramic SiC using small angle neutron scattering*

Li Ji-Zhou (李际周), Yang Ji-Lian (杨继廉), Kang Jian (康 健),
Ye Chun-Tang (叶春堂)
(*China Institute of Atomic Energy, Beijing 102413*)
Y. Ito** and S. Imai
(*Institute for Solid State Physics, The University of Tokyo*)

Abstract The mechanical properties of functional heat-resistant ceramics SiC are significantly influenced by the concentration and dimensions of pores. Small angle neutron scattering measurements for 3 SiC samples with different densities are performed on C1-2 SANS instrument of the University of Tokyo. Two groups of the neutron data are obtained using 8 and 16 m of secondary flight path, 1 and 0.7 nm of neutron wave lengths, respectively. After deduction of background measurement and transmission correction, both neutron data are linked up with each other. The patterns of neutron data of 3 samples with Q range from 0.028 $\sim$ 0.5 nm^{-1} are almost with axial symmetry, showing that the shape of pores is almost spherical. Using Mellin transform, size distributions of pores in 3 samples are obtained. The average size ($\sim$ 19 nm) of pores for hot-pressed SiC sample with higher density is smaller than the others ($\sim$ 21 nm). It seems to be the reason why the density of hot-pressed SiC sample is higher than not hot-pressed sample.

Keywords Ceramic SiC, Porosity, Small angle neutron scattering

1 Introduction

The functional heat-resistant ceramics silicon carbide SiC is a highly feasible material for high temperature engineering applications[1]. Nowadays, hot-pressure sintering SiC has been widely used as the parts material of heat engines. It can resist the temperature as high as its decomposition temperature (2300°C), but the high temperature strength decreases only a little, and the thermal expansion coefficient is very small.

For hot-pressure sintering SiC, the effects of additives (B_4C and C[2], as well as Al_2O_3[3]) and other processing parameters on the sintering behaviour as well as mechanical properties were studied. The results can be summarized as follows.

a. Boron carbide, carbon or aluminium oxide are jointly necessary as additives for obtaining hot-pressed SiC of high density. The lower limit mass fraction of B_4C or C or Al_2O_3 addition required to give high density is about 0.005.

b. The strength of hot-pressed SiC is about 500 MPa which keeps almost unchanged from room temperature up to 1400°C and is nearly irrelevant to mass fraction of carbon up to 0.03.

c. The sample of SiC containing 0.01 mass fraction B_4C and 0.03 mass fraction C hot-pressed at 2050°C for 45 min under 40 MPa possesses the following properties: density 3.17 g/cm^3, bending strength at room temperature 480 MPa, coefficient of thermal expansion $4.6 \times 10^{-6}°C^{-1}$, hardness HRA 93.5.

d. Comparing with the sample of 3.17 g/cm^3, there are a lot of pores inside the SiC crystallites and the crystal boundary for other samples (such as 3.00 g/cm^3, at 2000°C).

In this paper, the size, shape and distribution of pores in SiC samples sintered with different kinds and amounts of additives as well as different sintering conditions are studied using SANS (small angle neutron scattering) technique.

2 Experimental

2.1 Sample preparation

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**Present address: Department of Physics, Yamanashi University, Japan
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The silicon carbide SiC samples with different kinds and amounts of additives (Al_2O_3, B_4C and C) were prepared in the Department of Material Science and Engineering of University of Science and Technology (Beijing). The characteristics of the prepared samples for SANS experiments are listed in Table 1.

Table 1 Data and sintering condition of 3 SiC samples

Samples	Size/mm	Additives	Sintering condition	Density
No.1	ϕ11.5×2.6	Al_2O_3, B_4C, C	hot-pressed	2.97 g/cm^3
No.2	ϕ10.0×5.7	Al_2O_3, B_4C, C	no hot-pressed	2.63 g/cm^3
No.3	ϕ10.0×5.7	Al_2O_3, Boric acid, C	no hot-pressed	2.60 g/cm^3

All samples were sintered using pure alpha-SiC powder (~3μm) as main component, and Al_2O_3 powder (325-mesh) as one of the additives (mass fraction is 0.03). Boron carbide B_4C (325-mesh, mass fraction is 0.01~0.02) and carbon C (mass fraction is 0.01) were used as other additives for both samples No.1 and No.2. For sample No.3, the additive of boron was in the form of boric acid. At first, mixtures of SiC and additives were formed into sheets by cold-pressing. Then, the sheets were sintered at 1950~2000°C for 1 h and furnace-cold. Hot-pressing was conducted at 0.3 MPa only for sample No.1.

2.2 SANS measurement

SANS measurements for 3 SiC samples were carried out on C1-2 SANS instrument located at the end of C1 guide tube of cold neutrons in the JRR-3 reactor of Japan Atomic Energy Research Institute. The 2D position sensitive detector with multidetector of 128×128 elements of 5 mm×5 mm cross section can be moved automatically in a vaccum tube to change the secondary flight path from 1 m to 16 m. The Q range is $5\times10^{-3} \sim 25\,nm^{-1}$. The neutron wavelength λ can be changed from 0.4 to 1 nm according to the preset of Velocity Selector, and $\Delta\lambda/\lambda = 0.08 \sim 0.3$. The maximum beam size is 20(H) mm × 50(V) mm. One by one, 30 samples can be measured.

The neutron data for 3 SiC samples measured with 8 and 16 m of distances between sample and detector, 1.0 nm (preset of velocity selector 12500 r/m) and 0.7 nm (18000 r/m) of neutron wavelengths have been obtained.

According to the results of transmissivity in Table 2, one can know that the amount of boron in sample No.1 is more than those in samples No.2 and No.3.

Table 2 Neutron transmissivity measurement

Samples	for 1.0 nm(12500 r/m)	for 0.7 nm(18000 r/m)
No.1	0.422	0.558
No.2	0.965	0.978
No.3	0.962	0.974

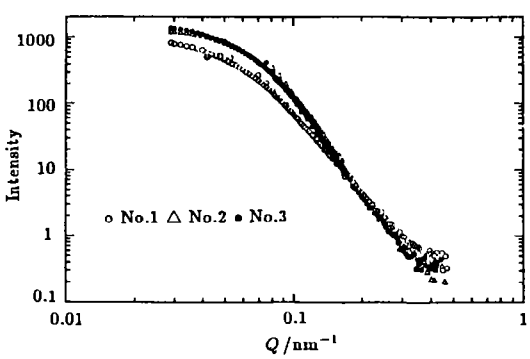

Fig.1 Comparison among SANS curves of $I(Q)$ for 3 samples

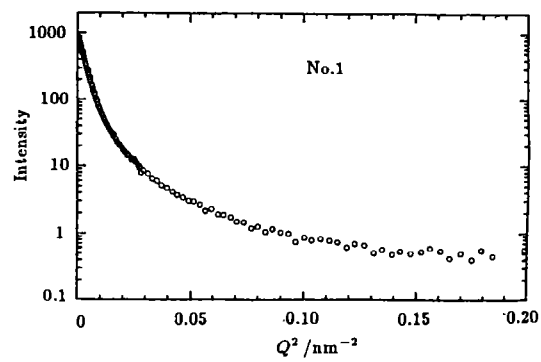

Fig.2 lg plot of $I(Q^2)$ for sample No.1

2.3 SANS curves

The scattered neutrons were collected by a position sensitive detector covering a relatively large range of the scattering angle Θ. The patterns of neutron data for 3 samples collected on a 2D position sensitive detector with 128×128 elements are almost with axial symmetry. It shows that the shape of pores, whose dimensions are relative to the Q range, is almost spherical.

Both neutron data of experiment 1 (with 8 m and 1 nm) and experiment 2 (with 16 m and 0.7 nm) were linked up with each other for 3 samples. The Q range is from 0.028 to 0.5 nm^{-1}. Fig.1 shows that the curves for samples No.2 and No.3 are similar, but different from the curve for sample No.1. Scattering curve for sample No.1 is presented in Fig.2.

3 Results and discussion

One of the most frequent applications of SANS is to treat the problem of scattering from polydispersions of particles (or pores) whose shape is known in principle. The tangent method and the Mellin transform both are available to treat this problem to give information on the radius-size distribution $D(R)$ of these particles (or pores)[4].

The tangent method assumes that the particle (or pore) distribution $D(R)$ can be divided into a number of groups with equal dimensions, in which R_{g_i} represents the radius of gyration of the particles in No.i group. The scattering curve, plotted as lg$I$ versus Q^2, can then be decomposed into single straight lines whose single slopes become $\frac{1}{3}\ R_{g_i}{}^2$. The relative group concentrations are easily obtained.

The Mellin transformation, where the measured scattering cross-section is due to scattering from spherical particles (or pores), allows to express the size distribution directly as[5]

$$D(R) = \frac{1}{3}\int_0^\infty Q^3 I(Q)\xi(QR)\mathrm{d}Q \qquad (1)$$

where

$$\xi(QR) = (QR)^{-1/2}[2-(QR)^2]J_{3/2}(2QR) - \tfrac{3}{2}(QR)J_{1/2}(2QR) \qquad (2)$$

in which $J_{3/2}$, $J_{1/2}$ are Bessell functions

$$J_{3/2}(x) = \sqrt{\frac{2}{\pi x}}\left(\frac{\sin x - x\cos x}{x}\right) \qquad (3)$$

$$J_{1/2}(x) = \sqrt{\frac{2}{\pi x}}\sin x \qquad (4)$$

To analyze the data easily, one can divide the integral of Eq.(1) into two parts:

$$D(R) = \tfrac{1}{3}\int_0^\eta Q^3 I(Q)\xi(QR)\mathrm{d}Q + \tfrac{1}{3}\int_\eta^\infty Q^3 I(Q)\xi(QR)\mathrm{d}Q \qquad (5)$$

SANS data can only be taken to a finite value of Q in any case, so that the integral must be cut off at some point η, which depends on the region of measured SANS data. If the η value is large enough, the second integral in Eq.(5) is negligible. The first integral may easily be evaluated on a computer for each R value of interest and $D(R)$ may then be obtained directly from the data.

Table 3 Comparison of average values of pore radius distributions for 3 SiC samples using tangent method and Mellin transformation

Samples	Tangent method	Mellin transform
No.1	19.3 nm	19.1 nm
No.2	22.2 nm	21.0 nm
No.3	22.6 nm	21.5 nm

The comparison of fitting results of pore radius distribution using the Mellin transformation among 3 SiC samples is shown in Fig.3. The comparison of the average value of pore radius distribution for 3 SiC samples using the tangent method and Mellin transformation respectively is listed in Table 3. The results of both methods are nearly similar.

4 Conclusions

The mechanical properties of ceramics are significantly influenced by the concentration and dimensions of pores or inclusions. In hot-pressed and reaction-bonded SiC the microvoid dimensions are usually in the range between 10^1 and 10^4 nm. This large extension of scattering center dimensions gives rise to the superposition of multiple neutron refraction from large voids and the usual diffraction phenomena for small voids.

For the sample No.1, hot-pressed the pressure was only 0.3 MPa, which was much less

than the pressure of 40 MPa, which is necessary for obtaining a sample of SiC with density 3.17 g/cm^3 (0.99 of theoretical density), so its density is only 2.97 g/cm^3. For the other 2 samples without hot-pressed, the densities are 2.63 and 2.60 g/cm^3, respectively. There are a lot of pores inside the SiC crystallites and the crystal boundary for these SiC samples. The results of pore radius distributions for 3 SiC samples are shown in Fig.3. It shows that the average value R_{av} of pore radius distributions for sample No.1 is smaller than the others ($\sim$ 10%).

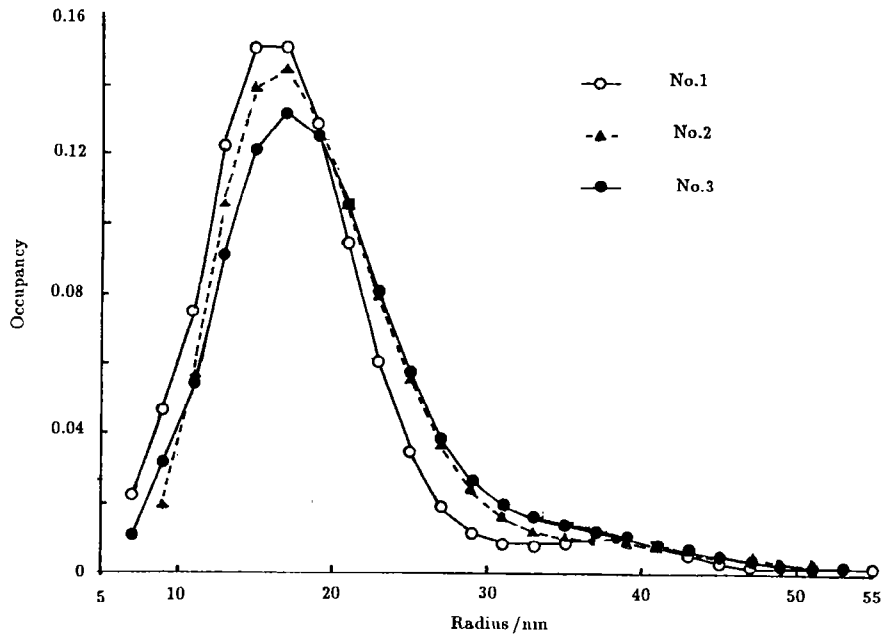

Fig.3 The comparison of fitting results of pore radius distributions using Mellin transformation among 3 samples

In addition, for samples No.1, No.2 and No.3 the dispersions of pore radius distribution are about 11.1, 11.9 and 12.6 nm, respectively (see the FWHM of peaks of pore radius distribution curves in Fig.3). From the curve of sample No.1 in Fig.3, besides the group of pores with $R_{av} \sim 19.0$ nm, there is another group of pores, whose R_{av} is about 37.0 nm.

Therefore, the smaller pore size and dispersion seem to be the reason why the density of hot-pressed SiC sample is higher than not hot-pressed samples; and the additive of boron in the form of boric acid is not advantageous to SiC sintering compared with B_4C.

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