Internal Friction Analysis of CaO-Doped Silicon Carbides

Hitoshi Nishimura1, *, Yuichi Ikuhara2, Ken’ichi Ota1 and Giuseppe Pezzotti1

1Ceramic Physics Laboratory, Department of Materials, Kyoto Institute of Technology, Kyoto 606-8585, Japan
2Engineering Research Institute School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan

Internal friction originated from sliding and diffusional flow along grain boundaries was monitored (as a function of both temperature and damping frequency) in model SiC polycrystals with an intergranular SiO2 glassy film. Emphasis was placed on the change of the internal friction characteristics upon additional Ca cation. It is expected that Ca cation segregates to the intergranular glass phase and modifies its network structure. The presence of a relaxation peak of internal friction due to grain-boundary sliding enabled quantitative evaluation of the activation energy for viscous flow of the intergranular glass and the related viscosity magnitude. A peak-analysis procedure, according to the peak-shift method (i.e., monitoring peak shift upon damping frequency change), is proposed, which quantitatively revealed the activation energy for viscous flow in various impurity-doped intergranular glasses. The presence of chemical gradients at grain boundaries, namely the presence of families of boundaries within the SiC polycrystal with different chemical characteristics, has also been analyzed by taking into account the dependence of peak morphology on damping frequency.

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1. Introduction

It is of great interest to develop quantitative analytical methods to evaluate the intrinsic viscosity of grain-boundary glass phases, because softening of such a residual glass is one main factor deciding the high-temperature deformation behavior of ceramic materials. Recently, we have shown that the inherent rheological behavior of the grain-boundary glass phase in polycrystalline ceramics can be quantitatively evaluated by means of internal friction measurements.1–4) The use of internal friction to quantitatively evaluate the intrinsic viscosity of residual glasses segregated to ceramic grain boundaries has been first proposed by Mosher et al.5, 6) based on the anelastic relaxation mechanism discussed by Zener and Ke.7–9) In the internal friction behavior (as a function of temperature) of glassy bonded ceramic polycrystals, a relaxation peak systematically appears at relatively high temperature, which arises from the anelastic phenomenon of viscous slippage along grain boundaries.5, 10) When a glassy film continuously encompasses the grains as, for example, in Si3N4 or SiC ceramics, the peak is sufficiently intense to allow a quantitative analysis and, thus, the evaluation of the activation energy for viscous flow of the intergranular glass and the related viscosity magnitude. Reliable activation energy analyses can be performed by applying the peak-shift method1, 6, 10) that makes use of the peak shift occurring upon varying the damping frequency.

In this study, SiC/SiO2 materials are intentionally doped with two different amounts of Ca2+. Ca is a typical grain-boundary segregant in hot-pressed and sintered silicon nitride and silicon carbide ceramics. It is expected that Ca significantly modifies both structure and viscosity of the intergranular glass. As a matter of fact, the bulk structure of SiO2 glass can be changed by cation (example for Ca, Ba, Na, etc.) addition.11–13) In a similar way, the intergranular SiO2 glass network structure can be systematically varied and its viscosity lowered. Thus, the activation energy for viscous flow of intergranular glass and its inherent viscosity can be systematically evaluated by internal friction measurements in CaO-doped Si3N4/SiO2.21) Moreover, the presence of chemical gradients at grain boundaries, namely the presence of families of boundaries within the polycrystal with different chemical characteristics, are shown to influence the morphology of the internal friction peak.

2. Experimental Procedure

The starting powder was a high-purity submicron-sized β-SiC powder (Ibiden Co., Ltd., Gifu, Japan) which was added with 2.5 mass% high purity SiO2 (Hokko Chem., Osaka, Japan). Two additional SiO2-doped SiC samples were mixed with CaCO3 powder (Wako Pure Chemical Industries, Ltd., Osaka, Japan) whose amounts (mass%) corresponded to about 200 ppm and 1200 ppm CaO, respectively. Specimens were formed by cold isostatic pressing (CIPing) under 180 MPa and coated by BN. Before encapsulation into evacuated Pyrex glass tubes, a pre-heating cycle at 1473 K in high vacuum (i.e., about 10−5 Pa) was performed for two hours. During this cycle, CaCO3 thermally decomposed into CaO and volatile CO2, thus leaving in the specimen only residual Ca2+ cations. For comparision, a cation-free SiC/SiO2 sample was also prepared. A hot isostatic pressing (HIPing) cycle was conducted for all the specimens under an Ar-gas over-pressure of 180 MPa and a maximum temperature of 2273 K (for 2 h). After HIPing, all the samples achieved nearly full density (> 99.5%). The shear modulus of the present samples was measured by bending resonance method at room temperature. Powder X-ray diffraction of the HIPed samples revealed that the main crystalline phase in present samples was β-SiC, before and after internal friction measurements, namely, the same phase as the starting SiC powder. Polished surface were chemically etched in molten NaOH (10 s
at 653 K) and observed by field-emission scanning electron microscopy (FE-SEM). The grain size was measured using the method of interception by random circles, as proposed by Hilliard and Cahn.\textsuperscript{14}\textsuperscript{14}

A detailed microstructure observation was performed by transmission electron microscopy (TEM) using a Topcon EM-002BF transmission electron microscopes (operating at 200 kV with a point to point resolution of 0.18 nm) and an HITACHI H9000NAR (300 kV, 0.18 nm). TEM specimens were prepared by standard techniques, which involve mechanical grinding, dimpling to a thickness of about 20 μm and argon-ion-beam milling to electron transparency at about 4 kV. High-resolution electron microscopy (HREM) characterization for grain-boundary structures were performed by using H9000NAR. Energy-dispersive X-ray spectroscopy (EDS) was performed using Noran Voyager Energy-Dispersive X-ray Spectroscopy equipped with EM-002BF which probe size was less than 1 nm.

The apparatus used for measuring internal friction, \( Q^{-1} \), was a torsional pendulum that was enclosed into a vacuum-tight system.\textsuperscript{15} A controlled argon or nitrogen atmosphere was maintained throughout the experiments. The damping specimens were 2 mm \( \times \) 3 mm \( \times \) 50 mm in dimension. During heating, a maximum shear stress 50 MPa was applied, oscillating at a frequencies \( f = 0.5-3 \text{ Hz} \). The forced vibration method,\textsuperscript{10} which directly measures internal friction by detecting the phase shift \( \phi \) between externally applied shear stress and the strain response of the oscillating specimen (with an accuracy of \( \pm 0.01^\circ \)), was used. The internal friction value is calculated according to the relation

\[
Q^{-1} = \tan \phi = \tan[2\pi \Delta t/(1/f)]
\]

where \( \Delta t \) is the time-lag between the stress and strain damping wave in the specimen. By this method, applied frequencies can be continuously varied and internal friction could be precisely measured in various frequencies. The relaxed shear modulus was simultaneously measured as the ratio to that recorded at room temperature. A carbon heater, which directly circumvented the specimens was used for rising temperature. At relatively low temperatures (< 1873 K), a platinum thermocouple was employed for temperature measurements, while at higher temperatures the measurement was done by an infrared (IR) thermoanalyzer. Internal friction peaks, \( Q_\phi^{-1} \), were obtained by subtracting an exponential-like background from the experimental curves, according to a procedure shown in detail elsewhere.\textsuperscript{1,10}

3. Experimental Results

3.1 Materials

All the investigated samples achieved nearly full density (> 99.5%) after HIPping, therefore any effect of porosity on the internal friction assessment can be reasonably neglected. A room-temperature shear modulus of 145 GPa was measured, independent of composition. Calcium dopant of ppm order appears not to affect the room-temperature elastic properties of the SiC polycrystals. SEM observation showed that grain growth was slightly promoted by the addition of CaO, while the grain morphology remained predominantly equiaxed for any composition. An increase of the average grain size (from 0.8 to 1.2 μm) was found for the SiC containing the higher amount of CaO (1200 ppm). In the case of the low-doped CaO sample (200 ppm), the grain size only increased to 1 μm. This microstructural alteration is not considered here to hamper a direct comparison among the internal friction behavior of different polycrystals, however, it may support the hypothesis of an enhanced diffusion process (during densification) along the silicon oxide glass segregated to grain boundaries, due to an intergranular glass viscosity lowered by Ca cations.

A low resolution image of the 1200 ppm CaO-doped SiC polycrystal is shown in Fig. 1. Although an extensive phase transformation from the cubic \( \beta \)-SiC phase to the hexagonal \( \alpha \)-SiC structure was reported when SiC materials were annealed at temperature higher than 2193 K,\textsuperscript{16} the dominant crystal structure observed in the present materials after HIPping at 2273 K (and even after a successive internal friction run up to 2473 K, see next section) was the cubic \( \beta \)-SiC phase, as in the starting powder, with only a minor fraction of transformed \( \alpha \)-SiC grains. It was confirmed that triple-grain junctions were actually filled with a silica glass phase. HREM observation of the 1200 ppm CaO-doped material (Fig. 2) revealed that an intergranular glassy film of thickness about

![Fig. 1](image1.png) A conventional TEM image of 1200 ppm CaO-doped SiC/SiO\(_2\).

![Fig. 2](image2.png) HREM image of the SiO\(_2\) intergranular glass film with a thickness about 1 nm in 1200 ppm CaO-doped SiC/SiO\(_2\).
1 nm. According to previous reports, the grain-boundary film thickness is governed by interface chemistry, peculiar interface structures of residual silica being generally found in sintered silicon carbide. Typical EDS profiles collected (a) within a SiC matrix grain, (b) at a triple junction with glass phase, and (c) at a grain-boundary glass film in the 1200 ppm CaO-doped SiC/SiO₂ are shown in Fig. 3. The glass phase contained C anions, as quantitatively reported in a previous study. However, upon analysing many triple junctions, Ca was never detected. It was noted that Ca was only present at grain-boundary film. This result suggests that the calcium cations tend to preferentially segregate to the grain-boundary film, leaving the multiple-grain junctions non contaminated. This may be a general characteristic for segregation of cations with a large atomic radius at grain-boundaries in non-oxide ceramics, because a similar result was reported for a CaO-doped Si₃N₄/SiO₂ system. Moreover, it should be emphasized that the distribution of Ca cation at grain boundaries was inhomogeneous. An inhomogeneous distribution of Ca along the grain-boundary channel, which may arise from the preferential formation of a peculiar grain-boundary structure, is a phenomenon also observed in chlorine-doped Si₃N₄ polycrystals.

3.2 Internal friction measurements

Internal friction peaks as a function of temperature for a non-doped SiC polycrystal (with only SiO₂ at grain boundary) and two SiC polycrystals doped with different Ca fractions are shown in Fig. 4. These relaxation peak components were extracted by subtracting their respective exponential-like background components from the experimental curves (this procedure is shown in detail elsewhere). The peaks arose from a sliding process along glassy grain boundaries within the polycrystal. According to a lowered intergranular viscosity, additions of Ca-cation produced (i) shift of the peak-top temperature toward lower values, and (ii) a remarkable change in the peak morphology. The change of the intergranular SiO₂-glass network structure due to Ca dopant obviously led to both these trends. Similar trends for the internal friction behavior are found by doping the Si₃N₄/SiO₂ and SiC/SiO₂ system with different cations or anions.

In order to quantify the activation energy for the glass viscous flow, the peak-shift method was applied and the internal friction experiments were conducted at different frequencies of oscillation. It is generally found that the higher the oscillation frequency, the higher the shift towards higher temperature. The results of a peak shift characterization, namely, Arrhenius plots of the frequency of the measurement vs the inverse peak-top temperature are shown in Fig. 5. The respective slopes of these plots correspond to the activation energy for viscous flow of the intergranular glass phase and show that with increasing the Ca amounts, the activation energy becomes lower, as expected from understanding of bulk glass materials.
4. Discussion

A peak shift towards a lower temperature represents a lowering of the inherent viscosity of the intergranular glass phase. The viscosity value at the peak-top temperature, \( T_p \), can be quantitatively evaluated by the following equation. The details of this method are described in previous reports.\(^1\)\(^-\)\(^4\)

\[
\eta_l = \frac{G\delta}{2\pi f(1 - \nu)d}
\]

where \( G, \nu, \delta, \) and \( d \) are the shear modulus, the Poisson’s ratio of the SiC grains, the grain-boundary thickness, and the average grain-size, respectively. \( \alpha \) is a numerical factor (relaxation factor) that is dependent on the grain-boundary morphology and can be experimentally evaluated from the relaxation modulus ratio, \( G/G_R \), as follows:\(^1\)

\[
\alpha = \left[ (G/G_R) - 1 \right]/(1 - \nu)
\]

where \( G_R \) is the relaxed shear modulus of the polycrystal at \( T_p \) (as measured concurrently with internal friction in the torsion pendulum). \( G, \nu, \) and \( \delta \) were taken as 145 GPa, 0.25, and about 1 nm, respectively, for all the investigated specimens. \( d \) values for the undoped, 200 ppm, and 1200 ppm CaO-doped polycrystals were 0.8 \( \mu \)m, 1 \( \mu \)m, and 1.2 \( \mu \)m, respectively. Grain-boundary viscosity values can be calculated according to eqs. (2) and (3), however, before proceeding to this calculation, an interpretation of the peak morphology is needed for appropriately assessing the \( T_p \) values.

From the present experiments, it is clear that the dopant Ca segregated to grain boundaries remarkably altered the internal friction peak morphology. A standard shape for a thermally activated internal friction peak should obey the following equation:\(^10\),\(^24\)

\[
Q^{-1} = \frac{\Delta M \omega \tau}{(1 + \omega^2 \tau^2)}
\]

where \( \Delta M \) is twice the peak height, \( \omega \) is the angular frequency of vibration (\( \omega = 2\pi f \)), and \( \tau \) is the relaxation time for grain-boundary sliding. This standard peak is generally referred to as a single-relaxation (Debye) peak. A single-relaxation peak can be also expressed as a function of temperature, as follows:

\[
Q^{-1} = (\Delta M/2) \text{sech}[E/R(1/T - 1/T_p)]
\]

where \( E \) is the activation energy for the thermally activated phenomenon producing the peak, whose width is thus inversely proportional to \( E \). In the general case, however, it is recognized that the experimental peak of grain-boundary sliding arises from the overlapping of various single-relaxation peaks. Niblett has quantitatively shown how the morphology of an internal friction peak may depend on the presence of spectra of both relaxation times and activation energies.\(^25\) A spectrum of relaxation times arising from distributions of microstructural features, like as grain-boundary thickness, grain size, and grain boundary morphology, may broaden the grain-boundary sliding peak up to about a 30% in width.\(^23\),\(^24\)

However, due to the remarkable broadening here observed upon Ca doping, we shall rather suggest that the peak morphology is dictated by the presence of a spectrum of activation energies. Such a spectrum, in turn, arises from the inhomogeneous distribution of Ca-cation at grain boundaries or, in other words, from the presence, within the same polycrystal, of families of grain boundaries with different structures. A chemical gradient in the Ca-cation among different boundaries leads to the presence of classes of boundaries with different viscosities obeying different activation energies for the sliding process. The simplest interpretation is that each class of boundaries (i.e., with the same chemical composition) is represented by an individual peak component whose intensity is proportional to the fraction of grain boundaries having that particular chemical composition. A deconvolution of the experimental internal friction peaks of CaO-doped SiC polycrystals into two main components, as shown in Figs. 6(A) and (B), is suggested from (semi-empirical) morphological arguments. Independent of Ca content, the position on a temperature scale of the high-temperature component (with a maximum in \( T_{p2} \)) is found at around 1683 K (at 1 Hz). This component is broad and shifted by about 150 K with respect to that of the peak found in the undoped SiC material. On the other hand, a low-temperature peak component (centered at \( T_{p2} \)) is found in both doped materials, whose intensity increases with increasing the Ca fraction. However, despite the intensity change, the peak position in a temperature scale (i.e., shifted by about 400 K with respect to the peak of the undoped SiC) is independent of Ca fraction. According to these experimental evidences, we consider that, in both CaO-doped materials, the broad peak arises from a non-negligible fraction of grain boundaries which contain a lesser amount of Ca-dopant, but with a variable fraction of dopant. The low-temperature peak represents a class of heavily Ca-doped boundaries. It is noteworthy that the reciprocal intensities of the deconvoluted components change with increasing the nominal fraction of Ca-dopant added.

In other words, increasing the added Ca-fraction merely increases the fraction of heavily doped boundaries, which is represented by a higher intensity of the low-temperature peak component. An inter-

\[\text{Fig. 6 Deconvolution of the internal friction peak recorded in the 200 ppm (A) and 1200 ppm (B) CaO-doped SiC polycrystals.}\]
Fig. 7 Viscosities of grain-boundary glass phases as obtained from internal friction experiments are compared with bulk glass data. The symbols are the same as those used in Fig. 4. The cross symbol represents the peak 2 component in both 200 ppm and 1200 ppm CaO-doped SiC polycrystals.

The activation energy for viscous flow of the intergranular glass phases. The change in internal friction peak morphology upon changing damping frequency was also investigated. These characterization suggested that the structure of grain-boundary glass films change in a rather peculiar way upon addition of the Ca-cation. The grain-boundary glass viscosity lowered with increasing the amount of added Ca-cation. However, a highly inhomogeneous distribution of the Ca-cation produced a spectrum of activation energies, thus generating individual peak components representative of classes of boundaries with common chemical structure. This study confirms that the internal friction measurement is an effective method for the quantitative characterization of both grain-boundary structure and viscosity.

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