Transmission Electron Microscopy in Conjunction with Internal Friction Measurements

A Powerful Tool for Characterization of Ceramic Interfaces——

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Dedicated to Professor Dr. Kazuyori Urabe on the Occasion of his 60th Birthday

Three different non-oxide ceramics, Si₃N₄, SiAlON, and SiC were characterized with respect to their high-temperature micromechanical deformation behavior employing both transmission electron microscopy and the internal friction technique. The latter method was utilized to gain a direct measure of the high-temperature response of the respective material, i.e., the effect of the interfacial glass phase commonly observed in liquid-phase sintered ceramics on externally applied shear stress. Transmission electron microscopy provides complementary information about the structure and chemistry of internal grain boundaries, which are known to dominate the high-temperature mechanical behavior of the bulk ceramic polycrystal. In addition, the presence and distribution of amorphous or crystalline secondary phases were characterized by electron microscopy. It is shown that, apart from the overall microstructure, the interface structure and/or the local chemical composition is the main parameter affecting the internal friction behavior. As a consequence, this technique allows one to determine the effective interface viscosity of ceramic polycrystals and to reveal as to whether a bimodal grain-boundary structure has developed, e.g., if both wetted and non-wetted interfaces are present, as is shown for the SiC ceramic.

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1. Introduction

Structural ceramics have gained wide interest, in particular, due to their potential application at high service temperatures. Densification of Si₃N₄-based ceramics as well as special SiC grades is commonly performed by liquid-phase assisted sintering, in order to overcome the low self-diffusivities of such highly covalently bonded ceramics. Sintering additives used to achieve complete densification react with SiO₂ present on the powder-particle surface, due to the oxidation upon exposure to atmosphere, and form a silica-rich liquid above the eutectic temperature of the system. Upon cooling, remains of this liquid are present at triple-grain junctions and, in most cases, along grain boundaries as a secondary glass phase; one exception will be presented in this paper (SiAlON). High-temperature performance of non-oxide ceramics primarily depends on the volume fraction and composition of such glass residues, owing to the rather low glass-transition temperatures as compared to the deformation behavior of the matrix. Since ceramic polycrystals are comprised of refractory matrix grains surrounded by a less refractory vitreous phase, the modification and/or elimination of the low-melting secondary phases is required in order to overcome the aforementioned obstacle of residual glasses. A number of different approaches were reported on how to handle that particular problem, one of which was to simply reduce the glass-volume fraction by HIPping powder compacts without the addition of external sintering aids. Moreover, substitution of lanthanide oxides for commonly used metal oxides e.g., the addition of Y₂O₃ as a sintering aid has been explored to form more refractory intergranular phases. Post-densification heat treatment is also a widely accepted technique to minimize the amount of glass residue by creating refractory crystalline phases. In this case, crystallization reduces the volume fraction of residual glass at triple pockets, but can simultaneously lead to an enrichment of impurities within the amorphous intergranular films, in particular, when impurities are not incorporated into the crystal lattice of the secondary phase formed.

An elegant way of testing the efficiency of the different approaches followed during processing, in order to improve the high-temperature performance of the bulk ceramic, is the internal friction technique. If a shear stress well below the fracture stress of the materials is externally applied to a polycrystalline aggregate at temperatures where the intergranular glass film behaves like a viscous fluid film and the grains, however, still respond elastically, sliding of adjacent grains along a common interface can only occur within a limited displacement. The magnitude of this displacement is dictated by both the magnitude of the shear modulus, G, and the size of the matrix grains, d, forming the surrounding polycrystalline array. Once the applied stress is released, the grains are pushed back into their original position due to the constraint of the surrounding matrix and, under the assumption that no irreversible microscopic damage has occurred, the initial displacement will be fully recovered. This particular deformation process is the so-called anelastic relaxation, since the micromechanism of interface sliding is completely recoverable, however, with a specific time retardation. The relaxation mechanism described above is also known as the elastic aftereffect, first proposed by Zener.

The resistance of ceramic polycrystals against sliding
mainly depends on two intrinsic parameters: (i) the overall microstructure, i.e., the matrix grain morphology and/or the triple pocket size and (ii) the viscosity associated with the intergranular glass film. The latter parameter decreases with increasing temperature according to the activation energy which is related to the change of the intrinsic viscosity of the particular siliceous grain-boundary phase. Given the dual dependence of the grain-boundary sliding process on both the overall microstructure and the interfacial glass viscosity, the sliding process is of extrinsic nature, mainly because sliding occurs under the constraining action of the surrounding matrix. Assuming rather low stress levels, no significant dislocation motion occurs due to the highly covalent bonding nature. This in turn implies that the matrix grains maintain their elastic deformation even up to very high testing temperatures. It follows that the macroscopic relaxation process of such polycrystalline ceramics is in fact dominated by grain-boundary sliding when temperatures exceed the $T_g$ of the glass phase.

Internal friction studies on Si$_3$N$_4$ polycrystals, which focussed on the grain-boundary relaxation at elevated temperatures, were first conducted by Raj et al. followed by Mosher et al. and Tsai et al. Since liquid-phase sintering of Si$_3$N$_4$ requires the addition of metal oxides that form a low melting glass phase promoting densification, it was thought that the observed internal friction peak at relatively low temperatures was a consequence of the low viscosity of the eutectic glass phases present at triple pockets and along grain boundaries. However, the secondary phases in Si$_3$N$_4$ ceramics may be rather complex in composition and prone to crystallization as well as other diffusional processes, which can overlap with sliding processes along grain boundaries. Therefore, previous studies focussed on the internal friction and creep measurements of simple model systems like Si$_3$N$_4$ with pure SiO$_2$ addition as the only boundary phase. These internal friction data showed an exponential background, but no grain-boundary peak was observed up to 1350°C. On the other hand, it was shown that the background signal clearly shifted towards lower temperatures when trace amounts of impurities were present in the residual glass. In those earlier studies, the maximum possible temperature was obviously too low, in order to unequivocally detect sliding phenomena in Si$_3$N$_4$ doped with high purity SiO$_2$, which were expected to occur around 1700°C. Tanaka et al. reported on their basic systematic work on a model system of Si$_3$N$_4$ doped with a few hundred ppm of trace impurities (Ca-cations) localized at grain boundaries. They concluded that strength degradation at elevated temperatures in Si$_3$N$_4$ ceramics is caused by impurity enhanced cavity formation. A high impurity concentration was shown to have a two-fold effect: first, the promotion of slow crack growth and second, the formation of an internal friction peak which in turn was caused by impurity enhanced atomic diffusion dominating cavity nucleation. The maximum temperature applied in these studies was 1400°C. Pizzotti et al. were first to report on internal friction data obtained at temperatures exceeding the melting point of fused silica, which then revealed a distinct internal friction peak close to the SiO$_2$ melting temperature.

It is well established that transmission electron microscopy (TEM) is a helpful and powerful technique for the correlation between microstructural features and bulk material properties. One common driving force for the use of TEM is the aim to tailor materials properties in order to meet specific application-oriented requirements. Therefore, the relationship between processing, microstructure, and mechanical response has to be known in detail. It is beyond the scope of this paper to review the major contributions of TEM to material science, however, it should be emphasized that this technique allows one to gather a wide variety of different information with high spatial resolution like intrinsic defect structure such as grain boundaries and/or their local composition. The main TEM techniques are: (i) conventional bright- and dark-field imaging, (ii) diffractional information obtained by either selected area (SAD) or convergent beam electron diffraction (CBED), (iii) chemical microanalysis (EDX, EELS), and (iv) high-resolution imaging (HRTEM). One of the major contributions of TEM to the understanding of the performance of ceramic polycrystals was obtained by the characterization of grain-boundaries, in particular, the detailed investigations on intergranular films in liquid-phase sintered Si$_3$N$_4$. In general, different TEM techniques can be applied for the detection and evaluation of the film thickness. The measurement of the film width by diffusel dark-field imaging results in values 50-100% larger than those obtained by HREM imaging. Defocus Fresnel fringe imaging is an indirect method of obtaining intergranular film width. With this method the film thickness can be overestimated by about 20-35%, with the largest error stemming from the uncertainty in the exact location of the Fresnel fringe maxima within the image. Therefore, high-resolution lattice imaging is a method capable of the resolution required to obtain detailed information on the intergranular phase. It was shown to be applicable to quantitatively evaluate the intergranular film thickness in Si$_3$N$_4$ materials with an accuracy of $\pm 0.1$ nm. Moreover, it was reported that the interface structure, i.e., the intergranular film width in fact represents a fingerprint of the interface chemistry of the respective system. Segregation of cations to grain boundaries results in a change of the interphase thickness. Recent studies have shown that, apart from cation impurities, the incorporation of anions such as chlorine or fluorine can also cause a change in interface structure, as well as result in a significant decrease in subcritical crack-growth and creep resistance. Moreover, internal friction measurements performed at a maximum temperature of 1800°C revealed a distinct grain-boundary relaxation peak, which was attributed to the presence of anions at the interfaces. Thus, in addition to the volume fraction, the chemistry and respective atomic structure of the amorphous interphase is important with respect to high-temperature performance of the material. Therefore, further detailed information about structural and chemical characteristics of ceramic grain boundaries and their influence on the micromechanical response, monitored during internal friction experiments, which in turn dominates the macroscopic performance of the ceramic polycrystal, is required.

In this paper we report on the characterization of ceramic interfaces by transmission electron microscopy in conjunction with internal friction measurements up to very high temperatures. The aim of this contribution is to emphasize that this approach is an elegant and powerful tool to gain detailed insight into the atomic structure of internal interfaces and, most importantly, their effect on the high-temperature response of the bulk polycrystals. Six different ceramic materials are discussed here, two of each group (Si$_3$N$_4$, SiAlON, and SiC), which indicate how sensitive these materials respond to subtle changes of the internal interface structure and/or microstructure.

2. Experimental procedures

2.1 Specimen preparation

The Si$_3$N$_4$-model materials investigated were processed by hot-isostatic pressing (HIP) after encapsulation of the powder compacts in a borosilicate glass tube (Pyrex, Cor-
ning Glass Works, Corning, NY) evacuated to 0.1 Pa. High-purity α-Si3N4 powder E–10 from Ube (Ube Ind. Ltd., Ube, Japan) was used as the starting material. HIP cycles were conducted under Ar-gas pressure of 180 MPa for 2 h. For comparison, the undoped sample was HIPed to full density (>99.5% th.d.) by sintering at 2050°C, while the other Si3N4 model material was densified at 1900°C. Fluorine was added to the system by mechanical mixing with fine teflon powder (Tedioni E.I, du Pont de Nemeaux, Wilmington, DE). The powder blend was pre-heated in vacuum to 1200°C in order to depolymerize the teflon structure to tetrafluoroethylene, CF4, which was thought to be easily incorporated into the SiO2 glass structure at temperatures exceeding 1000°C.

The SiAlON materials were processed following the solid-solution approach proposed by Yabuta et al.56 The high-purity α-Si3N4 Ube E–10 powder was blended with 1.71 mass% AlN (Graco, Inc., Yamaguchi, Japan) and 6.4 mass% Al2O3 (TM–DR, Taisei Ind., Nagano, Japan) by ball milling for 5 h in ethanol. The composition of β’-SiAlON can be expressed by Si6–zAlzOzN8–z, with z ranging from 0 (β’-Si3N4) to 4.2. The amount of additives was chosen in order to achieve a homogeneous dilute β’-SiAlON with the composition of e.g., z = 0.5, Si6.5Al0.5O0.5N7.5, on solid state reaction with the intrinsic SiO2 (the oxygen content of the Si3N4 powder is about 1.32 mass%). The material denoted as z = 1 SiAlON was prepared similar to the dilute material, however, the amount of additives was changed accordingly. Upon spray drying, powder compacts were prepared by cold-isostatic pressing at 300 MPa. The powder compacts were gas-pressure sintered (GPS) at 1850°C for 10 h under 1 MPa of N2-gas pressure. Subsequently, the specimens were HIPed at the same maximum temperature used during GPS but held for 2 h under an Ar/N2-gas mixture at 185 MPa, which corresponds to a nitrogen partial pressure of 20 MPa suppressing the SiAlON decomposition at elevated temperatures.

The SiC materials were processed by HIPing of pure sub-micrometer sized α-SiC powder (Ibiden Co., Ltd., Gifu, Japan) with an average grain size of 0.3 μm and an oxygen content of about 0.2 mass% oxygen as a common impurity which arises from exposure to ambient air. The reference material was processed without further addition of silica while the other material was blended with 10 vol% of high-purity SiO2 powder (Hokko Chem., Osaka, Japan). HIP sintering was performed after encapsulating the BN-coated powder compacts in a borosilicate glass tube evacuated to 0.1 Pa. Prior to encapsulation the specimens were heated to 1200°C under a high vacuum of 10−5 Pa for 2 h. The HIP cycles were conducted, similar to the Si3N4 materials, under an Ar-overpressure of 180 MPa but with a maximum temperature of 2000°C for 2 h. The B+C-doped reference material was a commercial grade with concurrent addition of 0.15 mass% B and 0.15 mass% C (Ibiceram SC850, Ibiden Co., Ltd., Gifu, Japan) which was pressureless sintered at 2100°C for 1 h.

### 2.2 Microstructure characterization

The overall microstructure of all the materials studied was characterized by transmission electron microscopy (TEM) and additional analytical electron microscopy (AEM) employing both energy-dispersive X-ray spectroscopy (EDX, Voyager–II, Noran Instr., Middleton, WI) and electron energy-loss spectroscopy (EELS, Gatan, Model 666, Warrendale, PA, USA) with parallel detection. It should be mentioned that all the TEM images shown here were taken at the Ryukoku University in Seta at the laboratory of Prof. Dr. Kazuyori Urabe, to whom this paper is dedicated, using a 300 kV and a 400 kV microscope (Model 3000F and 4000EX, JEOL, Tokyo, Japan) with a point-to-point resolution of 0.15 and 0.18 nm, respectively. TEM foils were prepared by standard techniques involving cutting, mechanical grinding, ultrasound drilling, polishing and dimpling followed by Ar-ion thinning to perforation and light carbon coating to minimize charging under the electron beam, with the exception of the SiC samples which did not require any surface coating. It should be noted that the thickness of grain-boundary films was quantitatively measured using the HRTEM technique, as described in detail elsewhere.60

### 2.3 Internal friction measurements

The apparatus adopted for the simultaneous acquisition of the internal friction, Q−1, and the shear modulus, G, data was a torsional pendulum enclosed in a vacuum-tight system in which a controlled Ar- or N2-flow atmosphere was maintained throughout the experiment. Internal friction data were automatically recorded at intervals of 5°C employing the free-decay method.61 The measurements were conducted at the frequency range between 5 and 13 Hz on rectangular specimens with dimensions of $2 \times 3 \times 50$ mm. This special torsional pendulum allows one to apply very high temperatures (up to 2000°C) by enclosing the specimen with the carbon heater, while an infrared thermo-analyzer is used for temperature detection. The relatively high nitrogen pressure of 5 Pa throughout internal friction measurements of the Si3N4 and SiAlON materials was selected to minimize the decomposition process of Si3N4-based compounds that is likely to occur at temperatures exceeding 1600°C. The corresponding shear modulus, G, of the polycrystal was obtained according to the response vibration technique described by Nowick and Berry.62 Torsional creep was determined by applying a constant momentum through a magnetic force. Strains were detected by a high-sensitivity eddy-current type displacement meter after appropriate amplification. The precision of the strain measurements was better than $\pm4.0 \times 10^{-4}$ %. The constant shear stress applied during the experiment was 10 MPa, being identical to the outer-fiber maximum shear stress applied during internal friction data acquisition. The total time of the torsional creep experiment was only a few minutes. However, a transient stage of creep deformation due to microstructure relaxation occurs within a much shorter time, i.e., within a few seconds. Hence, an apparent steady-state creep rate is in fact determined within the total time of testing.

### 3. Results

#### 3.1 Silicon nitride ceramics

The salient features of the model Si3N4 material, processed without the addition of external sintering aids, were that a continuous intergranular glass film encompasses all the Si3N4 grains, which themselves showed an average grain size of about 1.0 μm, and that excess SiO2 typically segregated at triple pockets being 20–50 nm in size. The film thickness was quantitatively evaluated to be 1.0 ± 0.1 nm. This film thickness can be seen as a reference thickness since it represents the actual interphase width of a pure, undoped model system with no cation impurities present. Based on EELS data it was found that the intergranular film contained, however, a small amount of nitrogen which was estimated to about 6±2 at%. No crystalline secondary phases like cristobalite or tridymite were observed at triple pockets, which is consistent with the incorporation of nitrogen into the residual glass limiting the crystallization of such phases. A typical multi-grain region within this reference material in addition to a continuous intergranular film present at grain boundaries is given in Fig. 1.

In order to study, apart from the known effect of the ca-
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...concentration, the influence of anions on the intergranular film thickness, a small amount of fluorine was added to the pure system via powdered teflon. The incorporation of fluorine into the material was deliberately chosen in order to weaken the interfaces, which was expected to affect the internal friction signal. The overall microstructure of the F-doped Si₃N₄ was indistinguishable from the undoped Si₃N₄ (see Fig. 1). However, electron energy-loss spectroscopy (EELS) revealed the presence of fluorine both at triple-grain junctions and grain-boundary films. The determination of the F/O-ratio for the spectra obtained from triple pockets and interface regions revealed no major compositional changes, which suggests a homogeneous composition of the residual glass phase. Similar to the undoped system, no secondary phase crystallization was observed here. Based on the theoretical model of an equilibrium film thickness, first proposed by Clarke and coworkers, which will be discussed in more detail in Sec. 4.2, a constant film thickness is expected when a homogeneous interface chemistry is given. As compared to the pure undoped Si₃N₄, a slight increase in film thickness of Δh=0.1 nm was monitored upon fluorine addition, giving an interphase width of 1.1 nm as shown in Fig. 2. The F/O-ratio obtained by EELS data of triple pockets and grain-boundary regions, which did not show a major compositional change, was evaluated to be 25-30 at% fluorine within the residual glass, while neglecting the presence of nitrogen in this calculation. The observed widening is therefore due to the replacement of one oxygen by two fluorine ions, both of which have almost identical ionic radii with 132 pm and 133 pm for O²⁻ and F⁻, respectively, in order to allow for charge balance. The HRTEM observation is consistent with the EELS analysis and underlines that the grain-boundary structure is indeed affected by the incorporation of anions into the interfacial glass network, similar to the effect of cation incorporation.

The internal friction measurements of the undoped and F-doped Si₃N₄ are shown in Fig. 3 parallel to a schematic which illustrates the characteristic microstructural features affecting the internal friction response. The addition of fluorine produces a definite shift of the internal friction curve towards a lower temperature, which is well seen after subtracting the respective exponential background curves (Fig. 3(b)). The net contribution of the internal friction peak is responsible for the relaxation process operative at elevated temperature. The peak-top temperature, T_p, and the apparent activation energy, E, which were calculated from the peak shape and the peak width of Q⁻¹ as reported by Nowick and Berry, decrease from 410 kJ/mol for the...
pure system to about 210 kJ/mol with fluorine addition. The calculated values are similar to those reported by Ohashi et al. for viscous flow of vitreous silica containing chlorine. The E-value of the undoped sample is consistent with data obtained by Williams for the self-diffusion of oxygen in high purity SiO₂. The incorporation of fluorine into the glass structure obviously decreased the effective glass viscosity and hence influenced the internal friction data monitored.

3.2 SiAlON ceramics

The dilute SiAlON material with a z-value of 0.5, giving a nominal composition of Si₅.₅Al₀.₅O₀.₅N₇.₅, was mainly comprised of rather fine circular grains with an average diameter of 1–2 μm. Despite the attempt to produce a homogeneous monophase material, two different crystalline phases were observed, as shown in the low-magnification TEM micrograph of Fig. 4(a). Selected area diffraction (SAD) studies in addition to EDX analysis on both phases revealed that the matrix was composed of nitrogen-rich β-SiAlON, while the phase that showed anisotropic grain growth was identified as oxygen-rich O'-SiAlON. The latter phase typically revealed a high density of stacking faults, as can also be seen in Fig. 4(a). The oxygen content of this phase was estimated to be about 13 mol%. It is important to note that no amorphous residue such as large triple pockets filled with residual glass were observed in the dilute SiAlON. Hence, arrays of equiaxed β-SiAlON grains were directly attached to each other, forming a rather regular hexagonal array. The elongated O'-phase, however, seemed to interlock with the adjacent β-SiAlON grains, i.e., the crystal structure extended into former glass-filled regions, similar to microstructural features observed in Si₃N₄ materials after post-sintering annealing.

HRTEM imaging of two-grain junctions was consistent with the results obtained from low-magnification TEM: no residual glass could be observed. Figure 4(b) shows a characteristic clean grain-boundary between two β-SiAlON grains, as reported earlier for special low-angle grain boundaries. Direct bonding, as observed here, is thought to be the consequence of a stoichiometric reaction between Si₅N₅, AlN + Al₂O₃, and the intrinsic SiO₂. Apart from clean interfaces, the triple-grain pockets were also free of any residual glass. It should be noted that, when using the Fresnel fringe technique, i.e., imaging with a slightly

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defocused objective lens, the presence of paired dark or bright fringes, similar to characteristic interface fringes in Si₃N₄ materials, indicated interface wetting, however, no glass reservoir was detected at the adjacent multi-grain pockets. Based on HRTEM imaging it is concluded that this material is in fact composed of glass-free interfaces. The changes in inner mean potential, as indicated by the Fresnel imaging technique, are most likely attributed to subtle changes in interface chemistry, but not to the occurrence of a siliceous interphase.

When comparing the results obtained from the dilute SiAlON material (z=0.5) with the SiAlON of z=1, the overall microstructure is rather similar, i.e., composed of small equiaxed β-SiAlON grains. HRTEM imaging also did not reveal clear evidence for grain boundary wetting, as in the case of dilute SiAlON. However, two major differences were observed: (i) the O'-SiAlON phase did not occur here and (ii) some rather large triple pockets (up to 800 nm in diameter) filled with residual glass were found, as shown in Fig. 5. It should be noted that interfaces close to such large glass-filled pockets were as well non-wetted, similar to the dilute SiAlON material. Hence, the glass regions are not interconnected but represent isolated pockets. EDS analysis of the glass residue in such large pockets showed a distinct Al-peak apart from Si, O and a minor amount of N. An interesting observation is the precipitation of a small mullite crystal in one of these pockets, as reported earlier by Szabo et al. for epitaxial growth of mullite onto SiAlON. The formation of mullite (during cooling to room temperature) also indicates the dissolution of Al in the residual glass, which in turn lowers the effective glass viscosity.

The internal friction data of the two SiAlON materials with z=0.5 and z=1 are given in Fig. 6. The internal friction curve of the dilute SiAlON (z=0.5) simply follows a background curve with an exponential-like rise at 1740°C. The second SiAlON material (z=1), however, revealed a clear relaxation peak similar to those observed in the Si₃N₄ materials. The peak-top temperature in the latter SiAlON was shifted to lower temperatures as compared to the pure undoped Si₃N₄. The marked temperature downshift of 570°C is consistent with the dissolution of aluminum in the residual glass, as detected by both EDS and EELS analyses (see also EDX inset in Fig. 5(b)). Compared to the SiO₂-containing model system, the internal friction background component of the dilute SiAlON material shifted to lower temperatures. In addition, lower torsional creep rates were determined under constant shear stress. It is thought that, owing to the lack of residual glass in the dilute SiAlON material (z=0.5), a continuous pass for oxygen diffusion was inhibited, thus, despite the known softening effect caused by the formation of a solid solution between Al₂O₃ and Si₃N₄, a high deformation resistance was actually achieved by the change of the overall microstructure, i.e., by the interlocking of the matrix grains as well as the formation of clean interfaces.

3.3 Silicon carbide ceramics

The microstructural characterization of the two SiC materials investigated, (i) undoped and (ii) doped with 10 vol% SiO₂, revealed that the α-SiC phase transformation, which typically occurs around 1920°C, was strongly reduced here, although both materials were processed via HIPping at 2000°C. Hence, the major crystalline fraction in the undoped as well as SiO₂-doped sample was equiaxed cubic β-SiC with a average grain size of about 0.8 μm revealing only a minor volume fraction of hexagonal α-SiC. For comparison, a B+C-doped material was also included in this study, which showed an average grain size of about 1.0 μm and a much higher content of α-SiC. It should be noted that we do not place emphasis on this latter material, but mention the particular results obtained when appropriate. In the undoped SiC some small voids present at triple pockets were observed. In addition, graphite
precipitation was commonly found (see Fig. 7), which arises from the excess carbon (about 0.3 mass%) present in the starting β-SiC powder. In the silica-doped SiC, residual turbostratic carbon was also noticed, however, to a much lesser extent as compared to the undoped material. Apart from graphite observed at matrix-grain pockets, carbon precipitation was also depicted along grain boundaries in both samples. No isolated voids were observed in this highly doped SiC. Regions of similar size and shape were found to be filled with residual SiO2 glass. Although no external silica was added to the undoped SiC, the material showed a small fraction of residual SiO2 entrapped at triple-grain pockets. The presence of silica glass in this material is a consequence of the intrinsic oxygen content of the starting powder of about 0.2 mass%. With respect to the interface structure, the undoped material revealed a twofold characteristic: (i) clean interfaces, i.e., directly bonded SiC–SiC boundaries adjacent to rather small glass-containing pockets typically 10–20 nm in diameter and (ii) grain boundaries that were wetted by a continuous intergranular film with a thickness of 0.9 nm and 0.8 nm, as determined by the Fresnel-fringe technique and HRTEM imaging,

respectively. Figure 8 depicts the interface structure of the SiO2-doped material in (a) and a corresponding wetted boundary observed in the undoped SiC sample in (b). The internal friction behavior of the SiC materials studied are shown in Fig. 9 as a function of temperature. The sample HIPed without the addition of external silica showed a broad, rather intense relaxation peak, while the SiC doped with additional 10 vol% SiO2 also revealed an internal friction peak, however, with three distinctive differences: (i) a much lower peak intensity, (ii) a peak shift towards a higher temperature, and (iii) a remarkably reduced peak width (FWHM). Despite the peak shift to a higher temperature, the background of the SiO2-doped SiC rises faster than that of the undoped material. In comparison, it should be noted that the background curve of the B+C-doped SiC rises at a temperature of about 1800°C, the highest rise-temperature monitored for ceramic
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**Fig. 8.** HRTEM images of (a) one grain boundary observed in the SiO₂-doped SiC material revealing the presence of turbostratic graphite at the interface and (b) an interface found in the undoped SiC with a continuous intergranular glass film encompassing the grains. Note that such films were also detected in the SiO₂-doped SiC in addition to some turbostratic carbon which implies that both materials shows each type of interface depicted here, however, to a different extent. (c) HRTEM micrograph of a small glass pockets observed in the undoped SiC material.

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**Fig. 9.** (a) Schematic of a SiO₂-plus graphite-containing SiC microstructure giving the internal friction response monitored. (b) Internal friction data of undoped and 10 vol% silica-doped SiC. Note that the undoped sample revealed an intense and relatively broad relaxation peak while the SiO₂-doped SiC showed a less intense but sharper signal (see also Fig. 12). As compared to the undoped SiC, the peak top-temperature of the silica-containing SiC was shifted to a higher temperature, i.e., 1788°C being the highest relaxation temperature recorded for any ceramic polycrystal. The internal friction signal of a commercial B+C-doped SiC is also given for comparison.

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4. Discussion

4.1 Grain-boundary sliding

Since the pioneering work of Zener and Ke on metals, it is known that the damping–temperature curve of most ceramic polycrystals, monitored during internal friction data acquisition, first strongly increases followed by the detection of a characteristic peak and a further continuous rise of the signal up to rather high values of internal friction. The monitored peak and the successive rise of the signal is commonly denominated as the grain-boundary peak and the high-temperature background, respectively. The existence of a grain-boundary peak in addition to the rising background is based on the concept that the relaxation of the externally applied shear stress across incoherent interfaces, such as large-angle grain boundaries or phase boundaries, in fact constitutes a source of internal damping. This effect has been attributed to sliding processes at interface corners, where the stress concentration is highest upon polycrystals so far.

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relaxation.\(^{36,72}\) Most importantly, however, this effect is related to the viscosity of the secondary glass phase, which for example in case of Si\(_3\)N\(_4\) ceramics encompasses all the matrix grains. Therefore, the viscous sliding process along grain boundaries which occurs under an oscillating external stress can be rationalized as follows: with increasing temperature at a fixed frequency, the inherent viscosity of the grain boundary will gradually decrease until it reaches, at the peak-top temperature of the system, exactly the value for which the sliding rate of the interfaces equals the rate of the externally applied shear stress. Under this condition, sliding with the maximum dilatation, being allowed by the elastic deformation of the neighboring matrix grains, will produce a maximum energy-dissipation rate and thus determine the value of the peak-top temperature. Since the frequency of the measurement is inversely proportional to the time period in which the full anelastic displacement is experienced, an increase in damping frequency will involve a shorter time for the sliding to occur along the same elastic displacement. For this to happen, a lower glass viscosity will be required, as long as the externally applied stress is kept constant. The mechanism explains the shift of the internal friction peak towards higher temperatures when the damping frequency is increased while the viscosity is unchanged. Moreover, due to this interdependence, the obtained activation energy for the peak shift is directly associated with the temperature dependence of the intergranular glass viscosity; a value otherwise hard to be obtained. At the peak-top temperature, the intergranular glass viscosity, \(\eta\), depends on the microstructural parameters of a ceramic polycrystal and can be expressed as follows:

\[
\eta = \frac{G_d}{3 \pi d} (1 - \nu) d \tag{1}
\]

where \(d\), \(\nu\), and \(G_d\) are the average grain size, Poisson’s ratio, and the relaxed shear modulus of the polycrystal, respectively. The frequency of the internal friction experiments is given by \(f_0\) and \(\alpha\) stands for a numerical factor, which changes according to the morphology of the grain boundary. In order to calculate \(\alpha\), the relaxation shear modulus ratio, \(G_r/G_{\eta}\), can be used: \(^{39}\)

\[
\alpha = \left[\frac{G_r}{G_{\eta}}\right]^{-1} (1 - \nu) \tag{2}
\]

where \(G_r\) is the relaxed shear modulus, i.e., the shear modulus at the respective peak-top temperature. With a given \(\alpha\), \(\nu\), and \(G_{\eta}\) in addition to \(d\), the intergranular film thickness obtained by HRTFM imaging, the effective interfacial viscosity can be calculated. However, the deformation behavior of non-oxyde polycrystals in response to externally applied stresses at temperatures exceeding the eutectic temperature of the system is usually rather complex and difficult to generalize.\(^{71-79}\) On the one hand, the conspicuous lack of significant dislocation mobility in such highly covalently bonded materials may allow one to model the internal microstructural rearrangement of the matrix grains under stress conditions by simply considering the viscous nature of the intergranular glass phase, which implies that bulk deformation within the matrix grains is neglected. On the other hand, phenomena that are related to the formation of crystalline secondary phases or those that are distinctly related to diffusional processes may overlap. So-called dynamic microstructures are often observed in commercial Si\(_3\)N\(_4\) grades that contain a high volume fraction of secondary phase. These phases tend to undergo marked microstructural changes when exposed to higher stress/temperature levels, e.g., under cyclic fatigue testing conditions,\(^{76}\) which will interfere with the internal friction signal monitored. Therefore, the high-temperature deformation behavior of non-oxyde ceramics is commonly not characterized in detail. The complexity of commercial ceramic microstructures explains why the viscoelastic behavior of such grades hardly obeys a universal model of viscoelasticity. Therefore, the investigations of designed model systems, which allow for the exclusion of the microstructure complexity at least to some degree, become very important and in turn enable a distinction of specific operative mechanisms, as will be shown in the following.

### 4.2 Si\(_3\)N\(_4\) ceramics

Earlier experiments on high-purity Si\(_3\)N\(_4\) materials with and without a low amount of CaO addition performed by Tanaka et al.\(^{36,77}\) support the theoretical model first presented by Clarke and coworkers\(^{39,60}\) on the equilibrium thickness of amorphous intergranular films in liquid-phase sintered ceramics. Statistical analyses of a number of grain-boundary films in Si\(_3\)N\(_4\) provided further experimental verification of the theoretical considerations.\(^{30,50}\) The model involves the influence of two repulsive forces: (i) a steric force which is caused by the steric hindrance of SiO\(_4\) tetraedra present in the silicate films and (ii) a force produced by an electrical double layer along the interface owing to the segregation of cations at the boundary, which is thought to balance the attractive van der Waals dispersion force that acts across the interface. This force balance results in the observed formation of an equilibrium film thickness. Since the corresponding interface chemistry affects the local forces, a characteristic film thickness which depends on the individual composition is measured as for example 1.0 nm for the undoped system and 1.1 nm upon fluorine addition. Based on this model, it becomes obvious that the observed change in intergranular film thickness represents on the one hand a change in local chemistry, but on the other hand and more importantly, implies a structural change of the interface. As in the case of F-addition, the subtle change in film thickness is caused by the coupled incorporation of two fluorine ions, which repel each other, for one formerly bridging oxygen ion. The chemical shift creates a network structure composed of non-bridging sites (F–F sites), which affect both the interface viscosity and in turn the internal friction response.

The internal friction data obtained from the model system of Si\(_3\)N\(_4\) doped with pure SiO\(_2\), where neither transient phase changes, local crystallization phenomena, nor significant cavity nucleation were observed within the short period of high-temperature exposure, allowed us for the first time to unequivocally determine two anelastic mechanisms being operative: (i) grain-boundary sliding and (ii) diffusive flux of matter along interfaces. The sliding mechanism was revealed by the sharp internal-friction peak that appeared approximately at the \(T_g\) temperature of SiO\(_2\) glass of 1713°C (see also Fig. 3(b)). The exponential-like background of the internal friction curve seemingly reflects the same irreversible diffusion process that occurs at grain boundaries under creep conditions.

When investigating the Si\(_3\)N\(_4\) system that was processed with a grain-boundary phase having a markedly reduced inherent viscosity by deliberately adding trace amounts of anions to the starting powder blend, the internal friction grain-boundary peak shifted towards a lower temperature, i.e., towards the corresponding lowered melting temperature of the, in this case anion, containing residual glass. Apart from the temperature downshift of about 120°C, a decrease in activation energy due to the lowered grain-boundary viscosity was monitored. It should be noted that the grain-boundary viscosity obtained with the internal friction technique was consistent with the viscosity reported on macroscopic bulk glasses of similar composition.\(^{41}\) Moreover, preliminary results showed an enhanced intergranular fracture of the F-doped material, as compared to the undoped sample as well as a lower creep resistance.\(^{53,55}\) which is consistent with a weakening of the
interfacial glass structure and also explains why a lower HIPing temperature was sufficient for the F-doped system to achieve full densification and a similar grain size as compared to the undoped material. The variation in mechanical response of the F-doped samples is attributed to changes in the atomic glass structure (glass chemistry), owing to the incorporation of fluorine. This model experiment allowed, for the first time, to unequivocally relate grain-boundary sliding to the intrinsic intergranular glass viscosity and, more specifically, to the respective atomic structure evolved at the interface by incorporating coupled F-anions which create non-bridging sites in the glass network, as schematically shown in Fig. 10.

From the given results, i.e., the information obtained by HRTEM in combination with micromechanical data acquisition, it can be concluded that the atomic structure of the interface strongly affects the bulk material response at high temperatures. This also underlines the strong effect even small volume fractions of impurity cations/anions can have when high-temperature performance is of concern.

4.3 SiAlON ceramics

In addition to the clear evidence of the grain-boundary sliding mechanism, obtained by studying model Si3N4 systems, one basic open questions was whether it is possible to suppress such an internal friction peak, i.e., to eliminate the microscopic sliding process by simply changing the overall microstructure of the ceramic polycrystal. Since Si3N4 materials are a classical example of interface wetting strongly promoting grain-boundary sliding, SiAlON materials were included into the research activities, in order to be able to tailor the overall microstructure as well as the interface structure via the formation of solid solutions.65 In particular, it was intended to create glass-free interfaces as well as fully crystallized triple pockets with highly increased dihedral angles, which were both expected to hamper grain-boundary sliding. As could be shown by the combined effort of HRTEM and internal friction on the dilute SiAlON (z=0.5), the elimination of residual glass at multi-grain pockets and along grain-bounds led to the inhibition of reciprocal sliding of neighboring grains. Hence, the creation of clean interfaces and interlocking matrix grains effectively suppresses energy dissipation by viscous slip at elevated temperatures, as schematically shown in Fig. 11.

It is interesting to compare the exponential curve of the dilute SIAlON with the background component of e.g., the undoped Si3N4 reference material. In the SiO2-bonded material, the internal friction background is a consequence of an irrecoverable viscoelastic mechanism at the grain boundary and related to the torsional creep data acquired.76 Under the assumption that only rather small plastic strain is involved, the creep process can be expressed in terms of a strain rate:

\[ \gamma = (1/\eta) \cdot \tau \cdot \exp(-\Delta H_c/kT) \]  

where \( \tau \) is the applied shear stress, \( \eta \) stands for a constant with the dimension of a viscosity (viscosity parameter), \( k \) is the Boltzmann constant, and \( \Delta H_c \) the activation energy for the creep process. In case of a Maxwell-like behavior, the internal friction background, \( \tan \theta_u \), can be formulated as follows:

\[ \tan \theta_u = (G_u/2 \eta) \cdot (1/\eta) \cdot \exp(-\Delta H_c/kT) \]  

where \( G_u \) is the unrelaxed shear modulus of the polycrystal, which is assumed to be about 120 GPa for the materials studied here, \( \Delta H_c \) represents the activation energy for the viscoelastic process which actually generates the internal-friction background monitored, and \( \eta \) is the experimental frequency. If \( \Delta H_c \) equals \( \Delta H_B \), Eqs. (3) and (4) can be rearranged which allows to directly relate the recorded internal-friction background data to the torsional creep strain of the polycrystal:

\[ \gamma = (2 \pi \eta G_u \tan \theta_u) \]  

When plotting an Arrhenius diagram for the steady-state torsional creep rate, activation energies ranging between 150–200 kJ/mol where found (including the Si3N4 reference material), which are comparable to data reported by Williams for the diffusion of oxygen in fused silica.66 Hence, the calculated activation energies do not differ substantially, which leads to the conclusion that a common diffusion mechanism is operative. However, the activation energies obtained here are about a factor of 3 lower, as compared to data reported earlier by Raj and Morgan.27 Their activation energies are markedly higher, because in their case the activation energy reflects the sum of both atomic jump processes which control viscosity and the heat of solution of Si3N4 in the respective glass.80 However, since the materials studied here typically contain only a small volume fraction of residual glass and, more importantly, the materials experience only a short-term exposure to high temperatures, the heat of solution...
(estimated to be about 400 kJ/mol) does not contribute to the internal friction response and, hence, a much lower activation energy is determined with the given experimental setup.

When changing the z-value of the SiAlON system to about 1.0, the overall interface structure did not markedly change with the exception of the elimination of the O'-SiAlON phase, being consistent with crossing a tie-line within the phase diagram. The material typically revealed non-wetted interfaces, however, a number of multi-grain pockets were found to contain a high volume fraction of residual glass. Even the interfaces adjacent to these large glass pockets did not show any sign of an intergranular glass phase, but the internal friction data clearly showed the presence of a grain-boundary peak with a peak-top temperature about 570°C lower as compared to the undoped SiAlON system. Analysis of such glass pockets showed the incorporation of aluminum into the glass structure which explains, under the assumption of grain-boundary sliding, the pronounced shift to lower temperatures. The TEM observations in conjunction with the internal friction data led to the conclusion that this material is in fact an example for dynamic interface wetting at elevated temperatures. This implies that, when raising the testing temperature, the chemical composition of the glass phase changes due to enhanced dissolution of Al. This in turn changes the chemical potential in a way that it then acts as a driving force for dynamic grain-boundary wetting, which is responsible for the internal friction peak monitored. Therefore, the material is a very interesting example where HRTEM imaging of interfaces and internal friction data are at first glance contradictory. To yield direct proof for dynamic high-temperature wetting, quench experiments have to be performed, as in the case of Si3N4 materials, which allows to depict the interface structure present at elevated temperature.

4.4 SiC-ceramics

The internal friction data of the SiC materials studied in this paper were recorded up to temperatures as high as 2200°C. This is, to the best knowledge of the authors, the highest temperature ever applied during internal friction data acquisition. The occurrence of an internal friction peak strongly depend on the overall microstructure of the SiC samples, which is consistent with the results presented on the SiAlON and in particular on the SiAlON ceramic polycrystals. The damping curves as a function of temperature of the SiO2-containing SiC revealed a relaxation peak superimposed on an exponential-like background, the former arising from the energy dissipation process during grain-boundary sliding. However, in the B+C-doped SiC, only the typical background shape was found as internal friction signal, similar to the SiAlON material. The absence of a characteristic internal friction peak is a result of the non-wetted, glass-free interfaces observed in this commercial SiC grade. Again, the overall microstructure and the specific interface structure inhibited grain-boundary sliding.

The internal friction peak characteristics of the SiO2-containing SiC become more obvious, when deconvoluting the internal friction curve, which gives, in the case of the HIPed undoped SiC, two peak components positioned at 1594 and 1788°C, as shown in Fig. 12. The high-temperature component is consistent with the peak-top temperature obtained for the SiO2-doped SiC. The low-temperature component is attributed to sliding processes that are enabled by the precipitation of turbostratic carbon at both smaller triple pockets and along grain boundaries. Hence, in case of the undoped SiC, the unexpected situation of a bimodal interface structure/composition, i.e., boudaries wetted by a siliceous glass in addition to interfaces coated with turbostratic carbon, is responsible for both the higher internal friction peak intensity and the broadening of the peak. It should be noted that a similar bimodal distribution of the interface structure was also proposed for a model Si3N4 system doped with a small fraction of chlorine. The deconvolution of the internal friction peak also suggested the presence of pure SiO2 glass at interfaces in addition to a residual glass phase along grain boundaries, which incorporated some chlorine ions into the glass structure. HRTEM analysis of this material in fact revealed for the first time the occurrence of a bimodal distribution of the grain-boundary film thickness with boundaries showing 1.0 nm width (pure SiO2) and 1.3 nm thickness (chlorine incorporation).

The internal friction peak of both the undoped and SiO2-doped SiC were found to shift depending on the frequency of the measurement: the higher the frequency the higher the temperature. An Arrhenius plot of the damping frequency versus peak-top temperature allows to determine the activation energy of the viscous sliding process, i.e., the elastic aftereffect. The values obtained ranged between 415 and 422 kJ/mol and are consistent with the activation energy calculated for the SiO2-doped Si3N4 reference material of 410 kJ/mol and are therefore consistent with the HRTEM observation of the presence of a continuous intergranular film along grain boundaries.

5. Conclusions

The elastic aftereffect observed in ceramic polycrystals can be used to quantitatively measure the viscosity of the intergranular glass, a quantity which is otherwise difficult to determine. To allow for such a quantitative determination, however, two important experiments have to be performed in addition to the acquisition of the internal friction data: (i) high-resolution transmission electron microscopy studies of internal interfaces, in order to quantitatively measure the corresponding extension of the grain-boundary phase and (ii) a modulus relaxation test utilizing the same torsional geometry adopted for the internal friction experiment. The latter experiment enables one to distinguish between the effect of the intrinsic glass viscosity and the extrinsic interlocking effect of the matrix grains. Hence, internal fric-
tion data are an indirect mirror of processing and final microstructure evolution.

The respective microstructural characteristic of a ceramic polycrystal was shown to profoundly affect the macroscopic deformation response. The internal friction technique in conjunction with the modulus relaxation technique as well as quantitative HRTEM to obtain the intergranular film width is a unique and powerful tool for characterizing the short-term deformation characteristics of non-oxide ceramics up to temperatures as high as 2200°C. However, it should be noted that this approach is limited to predictions of the micromechanical response, which are related to short-term exposure at high temperatures and relatively low stress levels like the initial stage of creep deformation or cavity nucleation, but cannot be extrapolated to deformation mechanisms which apply when long-term exposure at both high temperature and high stress levels are discussed. Despite the given limitations, the development of the internal friction technique at very high temperatures opened the door for a new research field on the micromechanical response of interface related phenomena in non-oxide ceramic polycrystals, which was discussed by dwelling on three specific examples: (i) the anion effect in Si₃N₄ ceramics, (ii) dynamic wetting of interfaces at elevated temperatures in a SiAlON material, and (iii) a bimodal interface structure/chemistry in Sic polycrystals.

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