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Atomic-resolution observations of semi-crystalline intergranular thin films in silicon nitride

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Nanoscale intergranular films in doped silicon-nitride ceramics are known to markedly affect toughness and creep resistance. They are regarded as being fully amorphous, but are shown here to have a semi-crystalline structure in a Ce-doped Si_3N_4. Using two different but complementary high-resolution electron-microscopy methods, the intergranular atomic structure, imaged with sub-Ångström resolution, reveals that segregated cerium ions take very periodic positions, along the intergranular-phase/matrix-grain interface and as a semi-crystalline structure spanning the width of the intergranular phase. This result has broad implications for the understanding of the structure and role of the intergranular phase in enhancing the mechanical properties of ceramics.

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Silicon nitride has long been considered for numerous high-temperature structural components in gas turbines for electric-power generation and aerospace propulsion and in automotive engines. However, its widespread use has been severely limited by its brittleness, which invariably leads to structural unreliability; specifically, its fracture toughness is too low and sensitivity to flaws and cracks too high, resulting in poor damage tolerance. Such properties can be improved by careful microstructural and compositional design, in particular by controlling the presence and nature of the thin intergranular phases that form in the grain boundaries, invariably due to the presence of rare-earth atoms which are added to aid sintering.[1,2]

Silicon nitrides generally consist of elongated matrix grains that are randomly oriented, interlocked and separated by such nanometer-scale intergranular (IG) films. Their chemical composition and atomic structure are critical to mechanical properties because they control whether the ceramic fractures intergranularly or transgranularly. Transgranular fracture invariably results in poor toughness, whereas with intergranular fracture where the crack propagates along the IG film, the interlocking nature of the matrix grains leads them to remain intact and to bridge the crack, thereby significantly raising the toughness by resisting crack opening and sustaining part of the applied load that would otherwise contribute to crack advance.

For the past three decades, ceramic research has focused on these IG films. Their morphology in Si_3N_4 has always assumed to be amorphous, based on several transmission electron microscopy (TEM) studies[3-5] and thermodynamic calculations.[6,7] Further computational approaches have attempted to model the atomic bonding characteristics by using a variety of interface atom-coordinations, resulting in predictions for approximate atom positions along the interface between the matrix grain and the intergranular phase.[8-13] However, calculations describing an atomic structure model that encompasses the entire width of the IG film have been less successful, as essential experimental data about atom positions within the intergranular phase have not been available. Recent studies, however, of the grain-boundary/matrix interface have provided insight into how these IG films are affected by the presence of segregated rare-earth atoms.[14-16] Specifically, each rare-earth element attaches to the interface differently, depending on atomic-size, electronic configuration, and the presence of oxygen atoms in the boundary.[15] Calculations indicate that oxygen along grain boundaries in Si_3N_4 has a destabilizing effect on the bonding characteristics and serves as a trap for sintering atoms to migrate towards the boundaries.[9] However, due to the preferential attachment to certain interface sites, a partial ordering of the segregated atoms occurs. This is a critical observation as it implies that the IG films in Si_3N_4 ceramics are not entirely amorphous, as had been previously thought.[3-13]

In this work, we analyze the interface between the grain boundary and crystalline matrix in a high-purity Si_3N_4 ceramic, doped with 5wt% CeO_2 (and 1wt% Al_2O_3), using high-resolution scanning transmission electron microscopy (STEM) and sub-Ångström imaging with phase-contrast, high-resolution transmission electron microscopy (HRTEM). Our objective is to determine how this particular doping element attaches to the interface, and to determine the extent to which any partial atomic ordering of Ce atoms reaches into the grain-boundary phase.

The Ce-doped Si_3N_4 was fabricated via two-step gas-pressure HIP-sintering and had a microstructure comprising elongated Si_3N_4 matrix grains, with diameters of 0.2-1μm (aspect ratio ~ 15).[17] Phase-contrast microscopy was performed on ground, dimpled and ion-beam milled samples on a 300kV Philips CM300/FEG/UT microscope, with a field-emission electron source and an ultra-twin objective lens of low spherical aberrations (0.60mm) and chromatic aberrations (1.3mm). Partial aberration correction reduces image distortion to about its information limit of 0.8Å. Images were recorded through a Gatan Image Filter on a CCD camera permitting magnifications up to 38 million. Electron exit waves were reconstructed from series of 20 lattice images using the Philips/Brite-Euram software;[27,28] sub-Ångström resolution was achieved via phase retrieval and image reconstruction.[29,30] STEM imaging was performed with a 200kV monochromated FEI Tecnai F20 microscope, with a probe size of 0.14nm. The inner semi angle of the annular dark-field detector was 74 and 110mrad, with an objective semi-angle of 13.5mrad, conditions that are sufficient to minimize strain-field effects on the Z-contrast image.

HRTEM and STEM images, shown respectively in Figs. 1 and 2, depict the thin intergranular phase between two adjacent β-Si_3N_4 matrix grains, one of which is oriented along the low-index zone axis [0001]. The HRTEM image displays a resolution of at least 0.93Å (0.093nm) such that the position of individual atom columns, including the light nitrogen atom, can be readily discerned in the Si_3N_4 crystal structure. With such high resolution, the lattice planes of the opposing matrix grain can be imaged, the crystal orientation was identified as $[31\bar{4}1]$, and the thickness of the IG film determined to be ~7-8Å. The spatial resolution in the STEM image in Fig. 2 is 1.4Å; as this is not sufficient to allow imaging and identification of the opposing matrix grain lattice and its orientation, this matrix grain appears dark. However, the Z-contrast in the STEM image allows direct identification of the Ce atoms within the thin IG phase. Cerium is a relatively heavy element (Z=58) and thus it scatters the incoming electron beam in the microscope more strongly than silicon or nitrogen. Therefore the atomic positions of Ce become visible in the STEM image as bright spots in the IG phase. Note that the positions of these bright spots do not coincide with any atomic position of the Si_3N_4 crystal structure. Ce atoms do not substitute for Si_3N_4 host atoms in their atomic positions nor do they reside on interstitial sites in the Si_3N_4 crystal structure. Ce atoms, as well as other elements, segregate to the IG phase where they can be identified chemically by electron-energy loss-spectroscopy.[14,16] As a result, the bright spots in the STEM image represent a distinctly different atomic structure with a periodic arrangement of Ce atoms.

The other sintering aid element Al and the omnipresent Si, N and O atoms are not resolved in the grain boundary, as there their scattering power is less than for Ce and they are most likely not arranged periodically like Si and N in the Si_3N_4 crystal structure. A rather random, amorphous-like positioning of any atom in the boundary cannot be imaged due to the random electron scattering processes in the sample, which is another strong indication that the observed Ce atoms are indeed arranged as a crystalline-like structure in the thin grain-boundary films in this material. The entirely new information gathered with these high-resolution images is that the IG films are not completely amorphous and that Ce atoms order across the entire width of the film, essentially connecting both grains. This is contrary to most previous investigations.[17-21] Indeed, a previous study of this same material, using microdiffraction and diffuse dark-field imaging, concluded that the intergranular phase did not show signs of crystalline or semi-crystalline structure;[17] however, no direct imaging at the atomic level was possible at that time. We believe that the present results, which are only possible through recent advances to permit sub-Ångström STEM/TEM imaging,[22-30] represent a crucial new input for atomic structure calculations to assess the strength and the atomic bonding characteristics of the intergranular phase.

It is of note that a recent study[15] on the matrix-grain/IG-film interface has shown how rare-earth atoms attach and bond to the matrix grains depending on atom size and electronic configuration. Sm atoms, for example, arrange in single-atom periodic configuration at two distinct positions along the interface, whereas the larger La atoms do not attach in any periodic form to the interface. The present results on Ce fit well the parameters established in this prior work. Cerium, with atomic number N=58 and a valence shell radius of r=2.169Å, is slightly heavier and smaller than La (N=57, r=2.201Å), but it is lighter and larger than Sm (N=62, r=2.164Å). According to the atom-size dependence, the distance between the matrix grains and the Ce atoms becomes larger than established for Sm atoms. The arrangement of the Ce atoms, shown in Fig. 2, involves three distinct atomic positions, A, B and C, which form a triangle. The positions A and B are relatively close together and can be regarded as atom-pairs with an average separation of 1.81±0.2Å. The A-B atom pair axis is oriented perpendicular to the interface and attaches to the Si_3N_4 prism plane in periodic intervals of 7.08±0.1Å. Position C has a single-atom character, and is located between the periodic A-B atom pairs and opposite the open hexagonal rings of the Si_3N_4 prism plane. The average distance A-C and B-C is 3.39±0.15 and 3.54±0.18Å, respectively. These values compare well with crystallographic data for Ce nitride and oxide structures,[31-33] although the measured A-B separation is significantly smaller than in any of these structures. As the STEM images are a 2D projection of a 3D structure, atom positions A and B are likely shifted relative to each other along <0001>, such that the A-B connecting line is inclined and not perpendicular to the interface.

Although the opposing matrix grain is not visible in the STEM due to insufficient spatial resolution, by determining the IG-film thickness from the concomitant HRTEM image, the interface between the film and the opposing matrix grain can be located in the STEM image. This indicates an extended Ce-atom arrangement spanning the entire width of the IG film, with an invariable connection to the opposing matrix grain.

Finally, we note that for a direct overlay to the STEM image of any Ce-based structure, or single unit cell of it, the simple geometric constraints imposed by the film thickness (~7-8Å) must be considered. There are a variety of structural options depending on what the Ce atoms are bonded to N, O, Si or a combination thereof. Additionally, the different positions A, B, and C could possibly be associated with the different valence states that Ce atoms can take, i.e., +3 and +4. However, since known Ce-based unit cells vary between 3.89Å (CeN_2, Ce_2O_3) in their shortest and 13.056Å ($Ce_2Si_2O_7$) in the longest dimension, making them difficult to fit as set unit cells in the boundary space, a probable way of constructing the boundary Ce-based crystalline structure is by using only the basic building blocks of these unit cells, e.g., the common tetrahedral structure, specifically Si-O_4 tetrahedra and (in Ce_2O_3, $Ce_2(SiO_4)O$ and $Ce_2Si_2O_7$) O-Ce_4 tetrahedra. One possible design is that Ce-based tetrahedra are ordered along the IG film following the periodicity of the observed Ce-atom arrangements. Indeed, the Ce-Ce separations measured in the STEM agree well with the values of many Ce-nitride and oxide structures. One might think though that the restricted grain-boundary space and required high Ce-O coordination number (6-9) would limit the structural possibilities, as too many O and/or N atoms would need to fit in the limited space around/between the visualized Ce ions. The distance between a Ce ion and the surrounding O (N) ions is of the order of 1Å. Specifically, the effective ionic radius increases for a Ce^{3+} ion from 1.034 to 1.14Å when the coordination number increases from 6 to 8; on the other hand, the effective ionic radius decreases considerably from 1.034 to 0.8Å when the electronic configuration changes from Ce^{+3} to Ce^{+4} for a 6-fold coordinated Ce ion.[33,34] Additionally, between the simple CeO, CeN and the rather complex $Ce_2Si_2O_7$ structures are many other structural variations with a range of Ce-O(N) separations and tetrahedral-type sub-structures, such that forming a Ce-based crystalline structure that fits the structural data obtained in the STEM images should be feasible.

The experimental fact is that the Ce ions are located at very specific atomic positions along the grain boundary, as seen in the current STEM images, and since this is observed on a real material, there is no doubt that a Ce-based periodic structure exists along the thin grain boundaries in Si_3N_4. The precise grain-boundary structure is as yet unknown and will require further experimental and particularly computational studies, although ordering of the intergranular phase has been predicted in MD calculations.[35-37]

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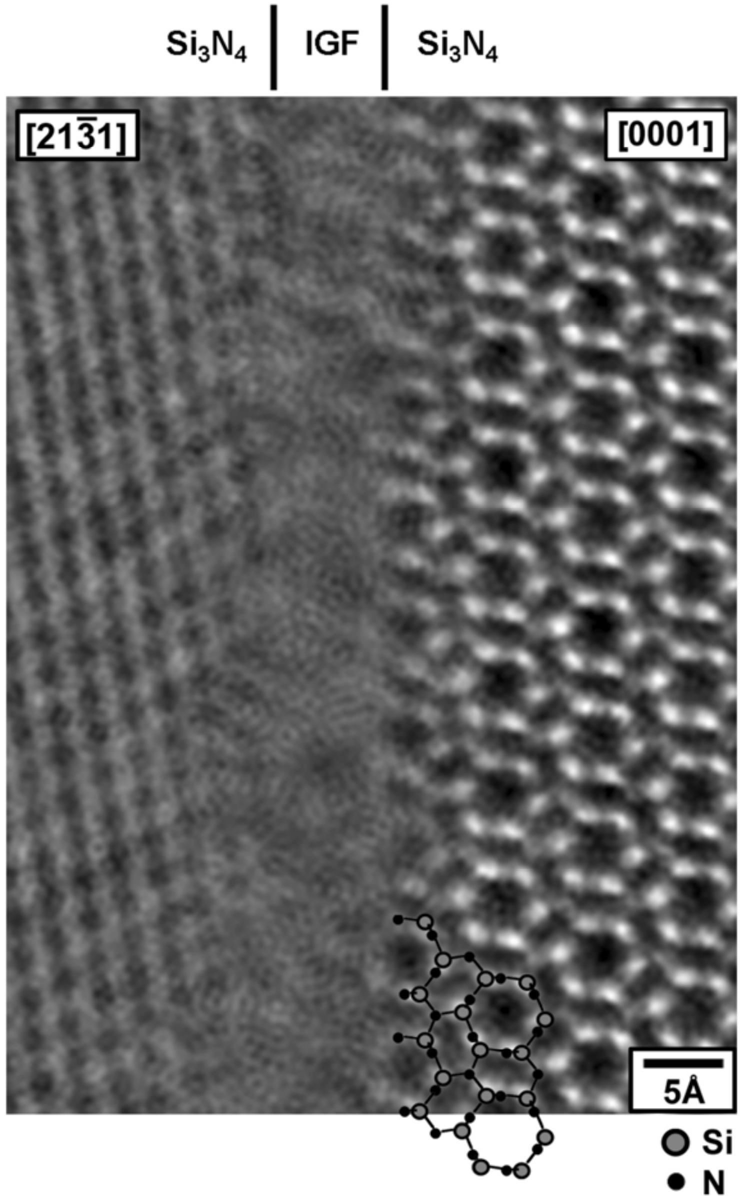

Figure 1: Phase-reconstructed HRTEM image showing the thin intergranular film (IGF) between two adjacent Si_3N_4 grains. The right grain is oriented along the [0001] crystallographic axis such that individual Si and N atom columns can be discerned in the crystal structure of Si_3N_4. The left grain is misoriented relative to the right grain along [31$\bar{4}$1]. The thickness of the intergranular film can be determined from this image to be ~7-8Å.

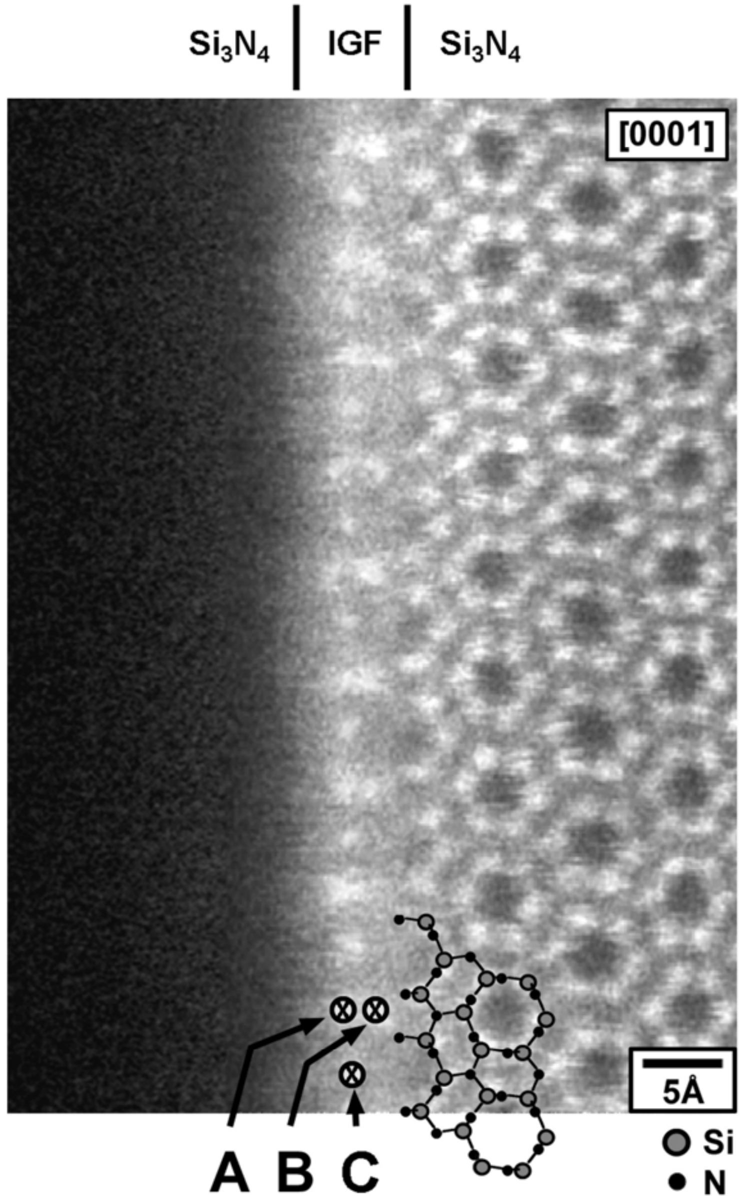

Figure 2: The corresponding STEM image shows the thin intergranular film (IGF) between the same two adjacent Si_3N_4 grains with the same orientations as in the HRTEM image. The spatial resolution obtained with this technique is not as high such that the lattice of the left grain cannot be depicted and it appears dark in the image. However, the Z-contrast obtained with this technique reveals the exact positions of the Ce-atoms within the intergranular film as bright spots, showing their atomic arrangement and structure, which spans the entire width of the thin intergranular film, connecting both Si_3N_4 matrix grains.