The evolution of amorphous grain boundaries during in-situ heating experiments in Lu–Mg doped Si₃N₄

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Abstract
The presence of 1–2 nm wide intergranular glassy films (IGFs) found in ceramics such as Si₃N₄ and SiC strongly influences the properties of the material, including its fracture and creep behaviour. It is therefore important to know the evolution of the film as a function of temperature. Experiments, wherein liquid phase sintered Si₃N₄ samples were quenched from high temperatures, have been carried out before and shown intriguing results. In the current investigation, in-situ heating experiments have been conducted in 120 kV and 400 kV microscopes, in order to separate beam irradiation from temperature effects. Based on the literature, it was expected that no changes would occur to the IGF below 1000 °C. However, it was surprising to note that the thickness measured at 950 °C was higher than that at room temperature. The correlation in trends observed in both microscopes shows that electron radiation has a minimal contribution to the change in IGF width at 950 °C. No change to the thickness was observed when heating up to 650 °C. After cooling back to room temperature there is a reduction in the thickness and thus a tendency to regain the original value of the thickness before heating. We conclude from these observations that certain material transport processes could be active at rather low temperatures (for Si₃N₄). Possible mechanisms and sources of artifacts are also discussed.

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1. Introduction
It was an important realization that in ceramic systems like Si₃N₄, SiC, SrTiO₃, etc., equilibrium-thickness intergranular glassy films (IGFs) are present at grain boundaries [1]. These films are found to be resistant to crystallization and cannot be removed by usual post sintering heat treatments [2]. IGFs play an important role in determining the mechanical properties of the ceramic, such as fracture [3] and creep [4,5].

Important theoretical advances which have led to a better understanding of IGFs include: the force balance model of Clarke [6], the diffuse interface description of Bobeth et al. [7], the phase field model [8] and the wetting/adsorption approach [9,10].

Experiments have been carried out which have enhanced our understanding of the effect of various stimuli and treatments like pressure [11], heating [4], oxidation [12], creep [13,4], etc., on the evolution of the IGFs. It is seen that pressure can lead to desegregation (dry boundaries) in the Bi₂O₃ doped ZnO ceramic [11]. The important point in the experiment by Wang and Chang [11] is that: annealing at ambient pressure (650 °C, 24 h), restored the 1–1.5 nm thick IGF, thus showing the reversibility of the process (of loss of IGF) and establishing that IGF is an equilibrium configuration. Prolonged annealing [4] and oxidation [12] can lead to thinning of the IGF. Creep led to a bimodal distribution of the IGF thicknesses [4] and has provided evidence to settle the long-standing discussion regarding squeezing out of intergranular amorphous material [14].

Understanding the evolution of these films as a function of temperature has important consequences, as these films have profound influence on the properties of the ceramic, at elevated service temperatures. The high-temperature quenching experiments of Clarke [15] and Cinibulk et al. [16,17] have provided detailed information on the thickness of these films at high temperatures in the region 1350–1650 °C. The results of Cinibulk et al. [16,17], wherein quenching from 1420 °C to 1500 °C led
to anomalous thickness values, are surprising on one hand and somewhat confusing on the other.

In-situ heating experiments have proved to be an invaluable tool for the study of material behaviour with temperature [18]. In the case of IGFs, these types of experiments are expected to provide a direct access to the behaviour of these films as a function of temperature. The limitation in the case of in-situ heating experiments, applied to the study of IGFs, is that the maximum temperature obtainable, which is around 1000 °C, is far below the sintering temperature of ceramics like Si₃N₄ (~1800 °C).

It is conventionally thought that the kinetic processes are frozen below 1000 °C in Si₃N₄ [15,17] and hence little changes are expected to occur to IGFs. The observations of Clarke [15] and Cimbulk and Kleebe [17] correlate with this expectation. In the current work, in-situ heating experiments performed from room temperature (RT) to 950 °C, on Lu-Mg doped Si₃N₄ in 400 kV and 120 kV transmission electron microscopes. The choice of two different accelerating voltages is to study the effect of electron radiation at different incident energy on the evolution of the IGF (if any). Lattice-fringe imaging [19] is used in the 400 kV microscope to measure the thickness of the IGF and in 120 kV microscope, Fresnel fringes are used. The Fresnel fringe techniques include: the method of extrapolation of the Fresnel fringe spacing [19,20], Fourier filtered zero-defocus images [21] and reconstruction of the imaginary part of the potential profile from zero-defocus images. Multi-ple Fresnel techniques have been used for the determination of the thickness of the IGF to confirm the trends from the results obtained. This is essential due to errors inherent in the standard Fresnel extrapolation technique [21].

2. Procedures

2.1. Experimental

Dense silicon nitride samples have been prepared from milled and sieved α-Si₃N₄ (88.07 wt.%), SiO₂ (2.16 wt.%), MgO (1.07 wt.% and Lu₂O₃ (8.7 wt.%) powders by first cold pressing, then sintering at 1750 °C for 15 min at 10 bar pressure and finally hot isostatic pressing at 1750 °C for 60 min at 100 bar as described by Satet and Hoffman [3].

Specimens for TEM experiments were prepared by the standard techniques of grinding, dimpling and ion-beam thinning (Precision Ion Polishing System, Gatan Inc.) with an angle of inclination of 8° of ion beam to the sample followed by coating with a thin layer of carbon to minimize charging under the electron beam.

In-situ heating was performed in two different transmission electron microscopes (equipped with heating stages) which are operated at two different accelerating voltages. For these experiments boundaries of interest were tilted to orient them parallel to the incident electron beam.

The JEOL 4000FX electron microscope, operated at 400 kV, has a point-to-point resolution of 0.2 nm. The sample was heated in about 80 min from room temperature to 950 °C (HT) and was kept at that temperature for 1 h. Then the heating stage was switched off and the sample cooled to RT in about 5 min. Images were taken at RT, 650 °C, HT (after 1 h) and after cooling back to RT on Kodak electron image film (50-163) at a magnification of 500,000.

The other microscope was the Zeiss-912 (LaB₆, Köhler illumination), operated at 120 kV and equipped with an in-column energy filter. Experiments were performed using an electron beam convergence semi-angle of 1 mrad.

For energy-filtered images, a 15 eV energy window centered on the zero-loss peak was selected. The images were captured onto a 1024 pixel × 1024 pixel CCD array at a sampling density relative to the specimen of 0.19 nm/pixel. A series of images (through focal series) were acquired in the defocus range of 1–2.2 µm with a step size of 0.2 µm in both over- and underfocus conditions including the in-focus (zero-defocus) image. The zero-defocus condition was calibrated as accurately as possible.

In this microscope the sample was heated in about 30 min from RT to HT and was kept at that temperature for about 75 min. Then the heating stage was switched off and the sample cooled down to RT in about 5 min. Images at a magnification of 80,000 were taken before heating (at RT), at HT (10 min after reaching 950 °C) and after cooling to RT.

Digital micrograph software (Gatan Inc., Pleasanton, CA, USA) was used for image processing. The software was used to obtain one-dimensional intensity profiles across the image of the interface, from each of the images recorded in the Zeiss-912 and JEOL 4000 FX microscopes (integrated over a width of 100 pixels) and also for Fourier filtering of the images acquired in the Zeiss-912 microscope.

2.2. Thickness measurement

 Thicknesses from high-resolution micrographs were measured using lattice-fringe imaging [19]. In the conventional Fresnel extrapolation method for measuring the thickness of IGFs, fringe spacing (s) values are plotted as a function of defocus (Δf) [20]. Jin et al. [22] used the following formula relating fringe spacing (W) to defocus (Δf):

\[ W = W₀ + cΔf^{1/2} \]  

where \( W₀ \) is the IGF thickness, and \( c \) is a microscope dependent constant.

This formula implies a linear plot of s versus root of Δf and extrapolation to zero-defocus would give the thickness of the IGF. Investigations on Lu-Mg doped Si₃N₄ have shown the limitations of this approach for the calculation of the thickness of the IGF [21]. An alternative for better utilization of the fringe spacing data is to plot the peak to peak distance in overfocus range and Fourier filtered zero to zero distance in underfocus range, as a function of Δf. This method is seen to yield a better estimate of the thickness of the IGF, from the same set of Fresnel data [21].

To obtain the thickness of an IGF from zero-defocus images, the image is first Fourier transformed and then a mask (diffuse mask with \( d_{FWHM} = 0.2496 \text{ Å}^{-1} \)) [21] is applied on the central spot. The unmasked area is inverse Fourier transformed to real space, where the distance between the points of zero intensity...
(zero to zero distance), is measured on the 1D intensity profile across the interface (integrated over a width of 100 pixels). This distance is seen to correspond to the thickness of the IGF [21].

The imaginary part of the scattering potential profile, obtained from zero-defocus and zero energy loss filtered images is additionally used for measuring the thickness of an IGF. The outline of the method is described next and details will be published elsewhere. In the electron microscope the intensity of an image is given as \( I(r) = |\psi(r) \otimes \text{MTF}(r)|^2 \), where \( |\psi(r)| \) is the complex-valued electron wave function at the bottom side (exit-face) of the sample. Within the phase object approximation the exit-face wave function is given by:

\[
\psi(\vec{r}) = \exp[i\gamma V(\vec{r})] = \exp[i(\sigma V(\vec{r}) + iV'(\vec{r}))]
\]

where \( \sigma \) is the electron-specimen interaction constant, \( \gamma \) the specimen thickness and MTF(\( \vec{r} \)) is the microscope transfer function. The real part of the scattering potential (\( V(\vec{r}) \)) is due to elastic interaction of the electron with the specimen and the imaginary part (\( V'(\vec{r}) \)) describes the loss of electrons from the elastic channel (and thus the zero energy filtered image), due to inelastic scattering events. \( I(r) \) is a one-dimensional intensity profile across an experimental image of the IGF. For zero-defocus imaging (and the assumed ideal aberration free imaging conditions expected to hold for the low-resolution conditions in the present work), the following can be set:

\[
\text{FT}[\text{MTF}(\vec{r})] = \text{ft}(\vec{q}) = \begin{cases} 1, & |\vec{q}| \leq \text{q_{aperture}} \\ 0, & |\vec{q}| > \text{q_{aperture}} \end{cases}
\]

Eq. (3) describes a circular top-hat aperture function with a reciprocal-space radius of \( \text{q_{aperture}} \). Ignoring coherent aberrations and envelope functions related to chromatic aberration, partial spatial coherence and microscope instabilities; the following equation is obtained under zero-defocus conditions:

\[
I(r) = \left| \exp[-\sigma V'(\vec{r})] \right|^2 - \ln \int_{|\vec{q}|=\text{q_{aperture}}} |\text{FT} [\exp[\sigma (V(\vec{r}) + iV'(\vec{r}))] ]| \text{d}^2 \vec{q}
\]

where

\[
\sigma V'(\vec{r}, q_{aperture}) = -\ln \int_{|\vec{q}|=\text{q_{aperture}}} |\text{FT} [\exp[\sigma (V(\vec{r}) + iV'(\vec{r}))] ]| \text{d}^2 \vec{q}
\]

is a specimen- and objective-aperture-dependent ‘pseudo-absorptive’ scattering potential. Both the inelastic scattering described by \( V'(\vec{r}) \) and the pseudo-absorptive by \( V''(\vec{r}) \) increase with the atomic number \( Z \) of the scattering element. In fact, the high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) technique, being mainly based on \( V''(\vec{r}) \), is also called Z-contrast STEM for this reason. Hence, the sum of both the terms will be referred to as the ‘absorptive potential’ \( V_{\text{abs}}(\vec{r}) = V'(\vec{r}) + V''(\vec{r}) \) from here on. The Fresnel contrast due to variations in the electrostatic potential \( V(r, q < \text{q_{aperture}}) \) across the IGF vanishes at zero-defocus so that:

\[
\sigma |V'(\vec{r}) + V''(\vec{r})| = -\ln \sqrt{I(r)} = -\frac{1}{2} \ln I(r)
\]

Taking \( t \) and \( \sigma \) to be constant, the LHS is representative of the inelastic and high-angle scattering and thus the concentration of heavy elements at position \( \vec{r} \). The full width at half maximum (FWHM) of a profile of absorptive potential across the IGF gives a measure of its chemical thickness. The resolution of this method is limited by the size of objective aperture which in the current study was 8 Å. MATLAB R12 software was used for implementing the algorithm to determine the imaginary part of the potential profile across the interface from zero-defocus images.

3. Results

The results of the heating experiment in the 400 kV JEOL microscope using lattice-fringe imaging is presented first, followed by the Fresnel analyses of the data from the 120 kV Zeiss-912 microscope.

Fig. 1 shows high-resolution micrographs from the sample at various stages of in-situ heating experiment. The thickness of the IGF follows the plot shown in Fig. 2. The times at which the measurements were taken are also shown in the figure. It is seen that there is no change in the thickness of the film up to 650 °C. The thickness of the film increases to 2.6–3.1 nm on heating to HT. On cooling back to room temperature the film thickness reduces to 2.2–2.4 nm. As seen in Fig. 1, the range of values of the thickness of the IGF at high temperature and in the cooled condition is due to the variation of the thickness along the IGF.

Fig. 3 shows the underfocus (−1 nm) and overfocus (1 nm) Fourier filtered Fresnel contrast images (FF-FCI), obtained from a grain boundary at room temperature at an accelerating voltage of 120 kV (Zeiss-912 TEM). Since heating changes the equilibrium thickness of the grain boundary (Fig. 1) we had to use a new TEM sample of the same material for the experiment in Zeiss-912. The insets in Fig. 3 show a plot of the intensity profile across the image of the GB, which is used for the measurement of fringe spacing. Fig. 4 shows the plot of the fringe spacing data obtained at RT, HT and from the sample cooled to RT, as a function of the root of the defocus. The plot is generated using the zero to zero distance from the FF-FCI in the underfocus condition and the peak to peak (PP) distance in the overfocus FCI. The thickness of the IGF is obtained by extrapolation of the Fresnel through focal series spacing data to a zero-defocus value. Usually, the extrapolations in the underfocus and overfocus lead to different thickness values and the average is taken to represent the thickness of the IGF. Difference between the average value and either of the extreme (thicknesses obtained for overfocus and underfocus regions) is taken as the error in
Fig. 1. High-resolution micrographs (HRM) showing a comparison of the thickness of the IGF, during the stages of the heating cycle: (a) room temperature (RT = 24°C), (b) 650°C, (c) HT = 950°C and (d) cooled to RT. Lattice fringes seen in both of the grains are \{100\} planes according to http://cimrsg1.epfl.ch/CIOIS/crystal4.pl.

The measured thickness. It is noted from Fig. 4 that disparity is especially pronounced for the data from the specimen cooled to RT. The thicknesses obtained are: 0.8 nm (RT), 1.0 nm (950°C) and 2.1 nm (cooled to RT).

The series of images in Fig. 5 show the FF-FCI taken at zero-defocus at various stages of the heating cycle. The zero to zero distance (ZZ), measured from the corresponding plot of profiles across the GB (shown as inset to the figures), gives the
Fig. 2. Schematic showing the changes in the thickness of the IGF during heating, as seen from HRM.

Fig. 3. Fourier filtered Fresnel contrast images (FF-FCI) of a grain boundary region at RT: (a) underfocus of 1 nm, (b) overfocus of 1 nm. Insets in (a) and (b) show the plot of the profile across the image of the GB (AA), integrated over a width of 18.8 nm, which is used for measurement of the fringe spacing.

Fig. 4. Extrapolation of the Fresnel through focal series fringe spacing data to obtain the thickness of the IGF: (▲) RT, (■) HT = 950 °C, (♦) cooled to RT (IGF thickness values and error bars are listed in Table 1).

thickness of the IGF at the different stages of the heating cycle. The thicknesses measured using this technique are: 2.3 nm (RT), 2.5 nm (HT) and 3.2 nm (cooled to RT).

The absorptive potential profile \( V''(r) + V'''(r) \) from a zero-defocus image, is shown in Fig. 6. The FWHM measured from the plots gives a measure of the thickness of the IGF. The thicknesses obtained by this method are: 1.8 nm (RT), 2.1 nm (HT) and 3.0 nm (cooled to RT).

A compilation of the thickness obtained by the Fresnel techniques and high-resolution microscopy is shown in Table 1. To make a meaningful comparison of the different thicknesses obtained, the following points must be kept in mind: (i) the resolution of the two microscopes used for the experiment are not the same, (ii) the resolution of the different Fresnel fringe techniques used for measuring the thickness are different, (iii) the high-resolution and Fresnel fringe techniques are expected to be sensitive to different aspect of the IGF structure and composition (e.g., the high-resolution method is expected to capture ‘crystallinity’ of the IGF, mainly being determined by the width of the core (of the possibly diffuse IGF structural profile), while the Fresnel techniques are expected to capture the FWHM of the scattering potential profile) and (iv) the dwell time at high temperature and heating/cooling rates are different for the experiments in the two microscopes.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>High-resolution (400 kV microscope)</th>
<th>Fresnel fringes (120 kV microscope)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HRt (nm)</td>
<td>Extrapolation Ft (nm)</td>
</tr>
<tr>
<td>Room temperature</td>
<td>±0.1</td>
<td>–</td>
</tr>
<tr>
<td>650 °C</td>
<td>1.3</td>
<td>0.8 ± 0.5</td>
</tr>
<tr>
<td>950 °C</td>
<td>1.3</td>
<td>–</td>
</tr>
<tr>
<td>Cooled to 24 °C</td>
<td>2.6–3.1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>2.2–2.4</td>
<td>2.1 ± 1.2</td>
</tr>
</tbody>
</table>

a Micrograph was taken 70 min after reaching 950 °C.
b Micrograph was taken 15 min after reaching 950 °C.
From the compilation of the results (Table 1) it is seen that the trend observed is similar amongst the different Fresnel fringe techniques. However, there is considerable disparity in the actual values measured. It is also observed that the trend in the thickness values obtained using Fresnel fringe techniques, correlates with the high-resolution measurements at RT and HT but not in the sample cooled to RT.

4. Discussion

The results obtained in the present investigations are rather surprising in the light of the conventional line of thinking seen in the literature. Changes to IGFs are expected to occur at temperatures above 1200 °C as observed in the quenching experiments of Cinibulk and Kleebe [17] (henceforth referred to as CK).

The answer to the question: “the equilibrium configuration of the IGF is representative of which temperature?” is still not clear yet. It is usually assumed that the equilibrium film forms at the sintering temperature, especially in the case of quenched samples. IGFs have often been regarded as films due to partial wetting or as prewetting films [23,9]. They have also been described as graded multilayer adsorbates [24,25]. In such a framework of description the thickness of the film should decrease with decreasing temperature. Increasing the temperature, on the other hand, may lead to complete wetting as well. It may therefore be concluded that heating to any temperature lower than the sintering temperature should lead to thinning of the IGF, in the light of wetting theories, if this is kinetically permissible. This thinning of IGF has been observed in prolonged annealing experiments [4]. However, in terms of the enhanced kinetics at the GB, the striking similarity to premelting/prewetting phenomena observed in segregation in metallic systems, is to be noted [26,27]. In systems like Cu–Bi, enhanced...
GB diffusivity is observed due to prewetting of GBs by a liquid like layer [28].

The results of the present annealing experiments are different from the quenching experiments of CK, wherein they observe an increase in thickness with increasing quenching temperature (except for samples quenched from 1420 °C to 1500 °C). Keeping in mind differences in sample composition and the heat treatments, we will try to compare the results of the current studies with the experiments of CK. The major differences between the current experiments and those of CK are: (i) samples used by CK did not include Lu₂O₃; (ii) the thickness of the samples that CK used for quenching was about 100 μm and (iii) temperature range sampled by CK was greater than in the present study.

Due to the inherent limitation in the precision of the Fresnel fringe extrapolation method [29], the thickness measured from the high-resolution micrographs (HRMs), can be compared with the thickness measured by the Fresnel extrapolation method (Ft) only approximately and trends during the heating cycle rather than absolute values need to be observed. An increase in thickness at high temperature is observed using both the methods. However, a significant difference is seen in the thickness measured on cooling to RT. On the other hand, the trends observed by the different Fresnel fringe techniques are similar. Hence, from now on the HRMs will be used for making quantitative comparison. One important difference between the experiments in two different microscopes is the dwell time before the HRM micrographs were recorded. In the high-resolution machine, the HRM was taken 70 min after reaching 950 °C (to allow for drift to stop), while in the Zeiss microscope the picture was taken after 15 min. Hence, it is conceivable that complete equilibrium may not have been attained at the HT in the Zeiss microscope, as reflected in the thicknesses measured by the Fresnel methods.

From the results obtained using the JEOL 4000 FX microscope, it is seen that there is a tendency to restore the film thickness to a lower value than that at HT, in spite of the fast cooling rate. The TEM heating stage temperature decreased from HT to room temperature in about 5 min and had reached 650 °C, the temperature below which thickness changes are expected to be negligibly slow, in about 2 min. This implies that material transport processes may be rather fast even at temperatures well below 1000 °C.

The observation of such dramatically fast processes occurring at temperatures less than half the sintering temperature, may on one hand question the exact value of the temperatures that CK’s quenched samples were representative of; but more importantly, suggests effects inherent to the particular experimental setup used in this study to be non-negligible.

For the interpretation of the experimental results of the present investigation, the following possible influences have to be kept in mind:

(i) Electron radiation damage.
(ii) Thin specimen effects (0.01 μm in our experiments versus 100 μm in CK’s experiment).
(a) short diffusion paths to the nearest surface;
(b) less mechanical constraints due to lack of interlocking grains.
(c) stress on the IGF may be large due to small cross-sectional area.
(iii) Stresses due to thermal gradients in the sample during heating.

The effect of electron radiation may be ruled out by the argument that the observed trends were independent of electron beam accelerating voltage. Additionally, in the Zeiss-912 instrument, operating at a comparatively low 120 kV, the sample was not exposed to the electron beam for most of the heating cycle (‘beam-blanker’ was used for this purpose). It was only directed on the sample for the very short time, during recording of the images. In fact, after recording the first set of images (15 min after reaching HT), the next image was taken after the sample had cooled back to RT, in-between which, most of the changes in film thickness have occurred.

The thin TEM specimen affects the experiment in different ways. The part of the specimen investigated by TEM is usually near the edge and is free to move not only in the direction normal to the plane of the specimen, but also along inward radial direction. The proximity of free surfaces can act like a source or a sink for the material from the IGF and hence, the kinetics of processes like alteration of IGF width, may be enhanced. Additionally, thin specimen implies that the load on the grains has to be borne by an IGF material having a small cross-sectional area and hence stress concentration might be high. This can even lead to stress enhanced transport of material.

The argument of very fast diffusion processes being possible in such extremely thin specimen implies the observed IGF widths at elevated temperature to be equilibrium values. In light of no experimental evidence in literature for comparatively wide films and dramatic changes with temperature in bulk specimen annealed for much longer times (including the CK experiments), this seems rather implausible. The fact that the IGF thickness is not constant along the grain boundary strongly questions whether the amorphous layer is in any equilibrium state at all.

The third source of experimental artifact (as compared to a bulk specimen) seems the most plausible one. TEM samples of Si₃N₄ material having undergone tensile stress experiments revealed anisotropy in the distribution of IGF widths in the sample [4]. Films normal to the direction of external (tensile) force had widened to about 3 nm, while those parallel to it remained at 1–1.5 nm. In the absence of any external force acting on the specimen, stress induced by thermal gradients present in the sample, maybe playing a major role in producing the effects observed.

The geometry of the TEM specimen is sketched in Fig. 7a. For simplicity of argument we assume a constant thickness gradient defined by the wedge angle $\theta_w = \alpha \sin(\theta/2r)$, where $r$ is the thickness and $\alpha$ is along the radial direction. The heat is transferred to the specimen by conduction along the outer rim of the disc. The heat flow to the center of the specimen is limited by the heat conductivity through the ceramic. The heat conductivity of Si₃N₄ is 40 W m$^{-1}$ K$^{-1}$ and given that the specimen is very thin (i.e. a very small cross-sectional area/surface area ratio), we expect significant temperature gradients to be necessary for...
radiation of the surfaces is described by the following equation:

\[ Q_{\text{out}} = \sigma A \Delta T \]

where \( A \) is the area, \( \Delta T \) is the temperature difference between the surface and the environment. 

The steady state at which heat supply by conduction equals the heat loss by radiation is assumed to increase linear with the radius. Heat is supplied to the specimen center by conduction from the perimeter and is lost predominantly by radiation. The steady state at which heat supply by conduction equals the heat loss by radiation is described by the following equation:

\[ Q_{\text{in}} = Q_{\text{out}} \]

\[ Q_{\text{in}} = \sigma A (T_0^4 - T_{\text{RT}}^4) \]

where \( T_0 \) is the temperature of the specimen chamber, \( T_{\text{RT}} \) is the temperature of the microscope specimen chamber, \( \sigma \) is the Stefan–Boltzmann constant, and \( A \) is the area.

The above mentioned effect of specimen geometry offsetting the temperature gradient may be evaluated using standard numerical methods. Eq. (7) implies that the amount of radial heat flow passing through a ring in the specimen of radius \( r \) needs to be equal to the total heat flow through the top and bottom surfaces of this ring by radiation. Plugging in the correct terms for describing the circular geometry of the sample, a wedge angle \( \theta_w \) and assuming the validity of the Stefan–Boltzmann law (\( Q_{\text{out}} = \sigma A (T_0^4 - T_{\text{RT}}^4) \)), the temperature gradient is large for small wedge angles and smaller for larger angles, as expected. Assuming a thermal expansion coefficient of \( 3.5 \times 10^{-6} \text{K}^{-1} \), the temperature gradient may be translated into thermally induced strain as shown on the right vertical axis in the plot (Fig. 7b). The unit of strain has been adjusted to correspond to the typical microstructure observed in these ceramics (TEM image in background of plot). Assuming that the Si$_3$N$_4$ grains have a thermal expansion coefficient much smaller than that of the glass and that all the thermally induced strain is to be compensated by redistribution of glassy material; a strain of 8 Å/Å would imply that the IGFs linking a chain of 1 µm wide grains would widen by 8 Å each.

Since the specimen thickness along the electron beam was below 100 nm a mechanism similar to the one depicted in Fig. 7c (stretching of IGF) may be able to explain the apparent mass flow within the IGF.

In reality, effects of the microstructure of the ceramic are much more complicated than the assumptions made in the above discussion. Some grains may therefore also be forced to rotate with respect to one another, potentially leading to IGF configurations of non-constant width, as seen in this work. The local stresses produced in this way are expected to compound with the dispersion and steric forces envisaged in Clarke’s model [6]. A ceramic sample having relaxed all tensile stresses produced during heating will be under compressive strain when cooling down again.

The new thickness could therefore be representative of a new equilibrium at the higher temperature or one of the twisted interface configurations shown schematically in Fig. 8. A combination of the three possibilities shown in Fig. 8 can also be envisaged. It should be noted that Fig. 8c is expected to be strongly influenced by the thin specimen used in a TEM. In the current experiment, soon after reaching 950 °C the configuration seemed to be a combination of that shown in Fig. 8a and c, with lattice fringes penetrating into the IGF. On waiting for half an hour (when the micrograph in Fig. 1c was taken), complete equilibrium still seemed not to have been attained; with variation in thickness along the length of the IGF. This kind of configuration, additionally gives a good explanation of the thicknesses measured by the Fresnel techniques on cooling to RT.

The above mentioned effect of specimen geometry offsetting intergranular forces makes a direct comparison of the present...
work with experiments on bulk specimen difficult. However, the obvious accessibility of the current experimental conditions to observe fast material transport processes in these materials opens up a whole range of new possible experiments to study diffusion kinetics, viscosity of the amorphous phase, chemical composition of the IGF at different film widths, etc.

To reiterate, it is difficult to comprehend the results of the current work using the conventional line of thinking. The fracture experiments of Satet and Hoffmann [3], wherein they observe intergranular fracture, leads one to postulate that there must be a weak plane in the IGF, which debonds during fracture. In the absence of the weak plane, given the comparable strength of the bulk glass and the Si$_3$N$_4$ ceramic, the crack would propagate in a transgranular mode. Motivated by these observations, it is conceivable that there is a ‘core’ region in the IGF, wherein material transport processes are vastly different from the bulk glass.

5. Summary and conclusions

Keeping the various points brought out in the discussion in mind, the TEM observations of this work can be summarized as in Fig. 9. The Fresnel methods seem to capture the FWHM of the potential profile, while the HRt is representative of the core potential. The following conclusions can be drawn from the present investigations:

(i) Fast changes to IGF thickness (in Lu–Mg doped Si$_3$N$_4$) can occur at comparatively low temperatures (<1000 °C) under low irradiation doses, with electron beam energies as low as 120 keV.

(ii) The tendency of the IGFs to regain the width they had before annealing has been observed. However, the relaxation times were not long enough to observe complete reversibility of the changes in IGF width.

(iii) A tensile-compressive straining cycle may be realized by heating and cooling the sample due to thermal gradients in the TEM sample, as a result of its special geometry.

(iv) Although local stress vectors, induced by thermal gradients in the sample, may offset the forces determining the IGF equilibrium width in the force balance model, dynamic observations (e.g. video recording) of the kinetics of the relaxation process may give insight into details of diffusion processes and the viscosity of the intergranular glassy phase.

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