High-resolution stress mapping of Al₂O₃/monoclinic ZrO₂ and Al₂O₃/cubic ZrO₂(Y₂O₃) eutectics using scanning near-field optical microscopy

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Scanning near-field optical microscopy (SNOM) technique was applied to nanometer-scale residual stress mapping for directionally solidified Al₂O₃/monochromic ZrO₂ and Al₂O₃/cubic ZrO₂(Y₂O₃) eutectics, which are ranked as candidates for high-strength materials at high temperatures. These eutectic composites were grown using the micro pulling down (μ-PD) method with a radio frequency heating system. Topographic images and fluorescence spectra of those eutectic composites were measured simultaneously for each pixel on a sample. Its peak intensity, peak position, and peak width, which, respectively, correspond to the abundance of Al₂O₃, stress in the grain, and the anisotropy of that stress, were estimated for each fluorescence spectrum. The distribution of residual stress was observed on a sample surface with spatial resolution of 300 nm; the spatial resolution was constrained by the optical fiber aperture size. Tensile stress was observed in Al₂O₃ of Al₂O₃/mZrO₂ and compressive stress was observed in Al₂O₃ of Al₂O₃/cZrO₂. The stress distributions were visualized within a single Al₂O₃ grain. Considerable stress anisotropy was detected in the grain boundary between Al₂O₃ and ZrO₂ for both eutectics.

1. Introduction

Directionally solidified Al₂O₃/monoclinic ZrO₂ (hereinafter, Al₂O₃/mZrO₂) and Al₂O₃/cubic ZrO₂(Y₂O₃) (hereinafter, Al₂O₃/cZrO₂) eutectics are ranked as candidates for high-strength materials at high temperature [1–5]. Thermal and transformation-induced strains are well known to modify the mechanical behavior. Accommodation of such strains can be studied using the piezospectroscopic effect of the luminescence of Cr³⁺ in Al₂O₃. Chromium causes intense fluorescence when suitably excited. These characteristic lines correspond to the electronic transition of ions and are extremely sensitive to the local ionic environment in the host crystal, as described by the ligand field theory [2]. As a result, deformation that alters the interionic distances can shift the frequency of characteristic lines. Local stresses in solid materials and mineralogical samples can also be evaluated from the shift of the peak position of vibrational and fluorescence spectra [6–9]. The dissolution kinetics of ionic solid in aqueous solution has also been observed using confocal fluorescence spectroscopy [10]. However, conventional spectroscopic analysis using optical microscopy, which is constrained by the wavelength of probe light, is inadequate to provide sufficient spatial resolution for elucidating the relationship between the microstructure and the residual stress distribution at a scale of less than several hundreds of nanometers.

Recently, scanning near-field optical microscopy (SNOM) has been applied widely for observing nanometer-scale spectroscopic information. It is a unique method to obtain fluorescence and topographic images simultaneously with spatial resolution beyond the diffraction limit using near-field light [11,12]. Because of the difficulty in correcting weak signal intensity from the small area, its application has been limited. This paper reports an application of the SNOM technique to nanometer-scale residual stress mapping for directionally solidified Al₂O₃/mZrO₂ and Al₂O₃/cZrO₂ eutectics.

2. Experimental procedures

2.1. Sample preparations

For synthesizing eutectic fibers, we used commercially available reagents of 5 N purity Al₂O₃ (High Purity Chemicals Co.), 4 N purity ZrO₂ (Nippon Yttrium Co., Ltd.), 4 N purity Cr₂O₃ (Wako...
Pure Chemical Industries Ltd.), and 9N purity Y_2O_3 (Nippon Yttrium Co., Ltd.). Starting materials were prepared, respectively, according to the formula of 61 mol% Al_2O_3+38 mol% ZrO_2+1 mol% Cr_2O_3 and 61 mol%Al_2O_3+29 mol% ZrO_2+9 mol% Y_2O_3+1 mol% Cr_2O_3 for the Al_2O_3/mZrO_2 and Al_2O_3/cZrO_2 eutectics [13]. To increase the fluorescence efficiency of Al_2O_3, 1 mol% Cr_2O_3 was added to the parent samples.

For growing directionally solidified eutectics samples, the micro pulling down (µ-PD) method using a radio frequency heating system was applied with a pulling rate of 1 mm/min. The µ-PD apparatus used for this study was reported previously [14]. This apparatus was equipped in a tight SiO_2 glass tube; the air in this tube was controlled with N_2 gas flowing at ca. 1.5 L/min to avoid oxidation of the crucible. After the starting mixtures were melted in a conical iridium crucible using a 10-kW RF induction heating module, the melted sample was pulled through a capillary hole of ca. 300 μm diameter centered at the bottom of the crucible using the ⟨0 0 1⟩-oriented Al_2O_3 seed crystal positioned beyond that capillary hole. This seed crystal was pulled down at a rate of 1 mm/min. The melt meniscus and the growth process of the fiber samples were observed using a CCD camera through a quartz window.

For SNOM observations, the synthesized eutectic fibers were polished in two directions: perpendicular and horizontal to the ⟨0 0 1⟩ direction of the Al_2O_3 seed crystal. The microstructure of the grown Al_2O_3/mZrO_2 eutectics was examined using back-scattered electron (BSE) imaging and X-ray energy-dispersive spectral (EDS) analysis with a scanning electron microscope (SEM, JSM-5900LV; JEOL).

2.2. SNOM measurements

Laser-induced fluorescence spectra from the sample surface were collected using an SNOM system, which was built into a commercially available atomic force microscope (AFM,

![SNOM system alignment](image)

Fig. 1. Schematic showing the SNOM system alignment. Optical paths of laser input optics and transfer of the fluorescence signal to the polychromator and the photomultiplier are shown.

![Al_2O_3/ZrO_2 eutectics](image)

Fig. 2. Photograph of Al_2O_3/ZrO_2 eutectics, the lower left is a sectional slice perpendicular to the fiber direction, which corresponds to the c-axis of the Al_2O_3 seed crystal and the other two are horizontal to the fiber direction. SNOM measurements were conducted on the sections perpendicular to the c-axis.
SPM9500J2; Shimadzu Corp.). The technical features of the SNOM system used for this study were reported previously [15]. Fig. 1 shows the schematic alignment of this SNOM system. The SNOM head was mounted over the scanner of a commercially available AFM (SPM9500J2; Shimadzu Corp.). The maximum scanning range was 125 × 125 μm². Conventional shear-force control was applied for controlling the distance between the probe and the sample surface. A 780-nm beam of a laser diode (LD) illuminated a SNOM probe, and the resonance frequency of the probe was detected from the shadow of the probe using twin photodiodes. The present SNOM optical system was designed for the illumination-collection (I-C) mode for observing fluorescence signals from opaque or thick samples. An Ar-ion laser (488 nm, 5 mW) was used for sample excitation. The laser light was guided using a single-mode fiber, then collimated using an objective lens, and reflected by a dichroic mirror. It was then focused using a SNOM probe whose aperture size was 300 nm (NPS-300; Jasco Inc.). The aperture size constrains the spatial resolution at approximately 300 nm. Scattered light from the sample was introduced to the same fiber probe and passed through the same dichroic mirror, which cuts the excitation light. Furthermore, a signal light with wavelength longer than 505 nm was transmitted through an absorption filter, which cuts light with wavelength shorter than 505 nm. The signal intensity was detected using a photon-counting photomultiplier of a multi-channel spectrophotometer. For obtaining fluorescence spectra, a

Fig. 3. SEM–BSE images of the sectional slice of Al₂O₃/ZrO₂ eutectics: (a) perpendicular to the fiber direction and (b) horizontal to the fiber direction.

Fig. 4. Total fluorescence image and analyzed peak parameter mappings of Al₂O₃/mZrO₂ eutectics. The scanned area was 5.0 × 4.0 μm². (a) Total fluorescence intensity, (b) full-width at half-maximum (FWHM) of R₁, (c) pressure calculated from the peak position of R₁, (d) stress tensor perpendicular to the c-axis, (e) differences in wavelength between R₁ and R₂, (f) FWHM of R₂, (g) pressure calculated from the peak position of R₂ and (h) stress tensor parallel to the c-axis.
single polychromator (250 is; Chromex) equipped with an electrically cooled CCD camera (DU-104-BR-DD SH; Andor Technology) was used. This SNOM system was applied to observe photoluminescence and Raman spectra of natural polycrystalline diamonds, carbonado, with high spatial resolution [16].

Each ruby (Cr-doped Al₂O₃) fluorescence spectrum corresponding to a single pixel of the sample surface was obtained continuously for approximately 1 s on a eutectic sample. Ruby fluorescence spectra comprise two peak components: R₁ and R₂ peaks. For calculating peak parameters (peak height, full-width at half-maximum (FWHM), and peak position), each spectrum was fitted with two Lorentzian curves using the least-squares fitting method. The precision for determining the peak position using the fitting method is 0.001 nm [17,18], which corresponds to 2.75 MPa using the ruby pressure scale [19].

3. Results and discussion

Fig. 2 depicts an optical microscope photograph of the Al₂O₃/mZrO₂ eutectic composite synthesized in this study. The red color of the samples originated from Cr³⁺ doped in Al₂O₃. According to the EBSD analysis on the sample system studied here, the c-axes of the grown crystallite were perpendicular to the growth direction and parallel to the fiber direction [20,21]. The lower left one shows the sample sliced perpendicular to the c-axis of Al₂O₃; the other two cross sections are horizontal to the c-axis. SNOM measurements were conducted on sections that were perpendicular to the c-axis.

3.1. Microstructure of the eutectic fibers

BSE images of Al₂O₃/mZrO₂ eutectic fibers are depicted in Fig. 3. These images are perpendicular and horizontal cross sections to the rod axis of each eutectic fiber. All images show typical columnar colony microstructures because of cellular crystallization. The grain sizes of the microstructure of the perpendicular cross section of the eutectic fibers were as follows: inside the cellular structure, 100–300 nm, and at the area where each cellular structure contacts, from several micrometers to 10 μm. The grain size of the microstructure of the horizontal cross section of the eutectic fibers was from several micrometers to 10 μm. Therefore, our SNOM system, with a spatial resolution of 300 nm, can resolve each cellular structure contacting area of the perpendicular cross section of eutectic fibers and the entire microstructure of the horizontal cross section of eutectic fibers.

3.2. Fluorescence spectra of Cr-doped Al₂O₃ (ruby) and estimation of the stress tensor

The fluorescence spectrum of ruby includes two sharp peaks at 693 nm (R2) and 694 nm (R1). Each peak position shifts to higher wavelength with increased pressure. In addition, the pressure dependences of these two peaks are similar under isotropic stress. These peaks are useful as pressure scales [19]. In contrast, when anisotropic stress exists in the ruby, these two peaks act differently. For understanding the two-dimensional stress...
distribution in Al₂O₃/ZrO₂ eutectic composites, the following parameters were calculated from peak positions of ruby fluorescence spectra: hydrostatic stress, deviatoric stress, and stress tensor. Spectroscopic dependence on the stress tensor of ruby was determined [22]. Assuming that the piezospectroscopic effect is isotropic in the basal plane of alumina crystal, the relationship between peak shift and stress tensor is as follows:

\[ \Delta v_1 = 3.26(\sigma_{11} + \sigma_{22}) + 1.56\sigma_{33} \]

\[ \Delta v_2 = 2.73(\sigma_{11} + \sigma_{22}) + 2.16\sigma_{33} \]

In these equations, \( \Delta v_1 \) and \( \Delta v_2 \) are the shifts (cm⁻¹) of the R1 and R2 peak positions from the original positions; \( \sigma_{ij} \) (i=1,2,3) signifies stress components along the a-, m-, and c-axes of the hexagonal alumina lattice. In addition, \( \sigma_\perp \) is the transverse stress tensor in the alumina basal plane, defined as \( \sigma_\perp = 0.5(\sigma_{11}+\sigma_{22}) \); \( \sigma_\parallel \) is the stress component horizontal to the alumina c-axis, defined as \( \sigma_\parallel = \sigma_{33} \). Hydrostatic stress \( \sigma_h \) is also expressed using stress tensors as \( \sigma_h = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \).

3.3. SNOM images of the cross section of Al₂O₃/mZrO₂ eutectic fiber

Fig. 4 presents SNOM results on the cross section of Al₂O₃/mZrO₂ eutectic fiber perpendicular to the fiber axis. Fig. 4(a) portrays the total photon mapping measured using a photon counter for the cross section of the eutectic fiber. The red region corresponds to the high emitted-fluorescence intensity. The blue region corresponds to low fluorescence intensity. This map integrates light intensity over the region of the detectable wavelength. The fluorescence intensity of ZrO₂ is negligible relative to that of Cr-doped Al₂O₃. Furthermore, the fluorescent region corresponds to the Al₂O₃ grains. Raman spectra of ZrO₂ and Cr-doped Al₂O₃ are undetectable using the SNOM system because of the weak Raman intensity and high background induced by the intense fluorescence of the SNOM fiber. Therefore, the fluorescence spectra of Cr-doped Al₂O₃ were used for stress analysis of the eutectic fibers, as described previously. Fig. 4(b)–(h) depicts the following parameters: (b) FWHM of R1, (c) pressure calculated from the peak position of R1, (d) stress tensor perpendicular to the c-axis, (e) difference in wavelength between R1 and R2, (f) FWHM of R2, (g) pressure calculated from the peak position of R2 and (h) stress tensor parallel to the c-axis.

![Fig. 5](image_url)

Fig. 5. Total fluorescence image and analyzed peak parameter mappings of Al₂O₃/mZrO₂ eutectics. The scanned area was 5.0 x 5.0 µm². (a) Total fluorescence intensity, (b) full-width at half-maximum (FWHM) of R1, (c) pressure calculated from the peak position of R1, (d) stress tensor perpendicular to the c-axis, (e) difference in wavelength between R1 and R2, (f) FWHM of R2, (g) pressure calculated from the peak position of R2 and (h) stress tensor parallel to the c-axis.
between R1 and R2, (f) FWHM of R2, (g) pressure calculated from the peak position of R2, and (h) stress tensor parallel to the c-axis. A comparison of Fig. 4(a) and the pressure distributions shown in Fig. 3(c) and (f) shows that the tensile stress (negative pressure) was found in the Al2O3. This result is consistent with those of a previous report [3]. Furthermore, high spatial resolution of SNOM disclosed that the stress increased towards the center of the Al2O3 grains. In other words, the tensile stress was stronger at the center of the Al2O3 grain than at the grain boundary between Al2O3 and ZrO2. The FWHM distributions shown in Fig. 3(b) and (f) exhibit that the peak widths of ruby fluorescence spectra broaden around the grain boundaries of Al2O3, which implies that stress is more anisotropic around the grain boundaries. Melt-grown Al2O3–ZrO2 eutectics used for this study underwent a phase transition of ZrO2 from the cubic phase to the monoclinic phase during cooling with a volume increase of 4%. Our results suggest that the Al2O3 phase was tensed along with the expansion of ZrO2 grains. In addition, the boundary between Al2O3 and ZrO2 underwent anisotropic stress.

Stress ranges estimated from the two fluorescence peaks differ slightly from each other: −0.36 to 0.04 GPa for the R1 peaks and −0.5 to −0.06 GPa for the R2 peaks. The stress range calculated from R2 peaks was wider than the other because the anisotropic-stress dependences of the peak shifts are different between R1 and R2 peaks. The R2 peaks are insensitive to the deviatoric stress components. The stress range calculated from R2 peaks can be considered as nearly hydrostatic stress.

Two-dimensional mappings of stress tensors calculated using Eqs. (1) and (2) are displayed in Fig. 4(d) and (h). In fact, σ⊥ mapping (Fig. 4(h)) shows that the σ⊥ value took a larger negative value in the outer direction in an Al2O3 grain. The differences in the peak positions between R1 and R2 (Fig. 4(e)) and the σ⊥ value are inversely related. In contrast, σ∥ mapping shows that the σ∥ value took a larger positive value.

### 3.4. SNOM images of the cross section of an Al2O3/cZrO2 eutectic fiber

Fig. 5 portrays two-dimensional mappings of the total fluorescence intensity, along with each peak parameter and stress component of Al2O3/cZrO2 in a cross section perpendicular...
to the rod axis. The most marked difference in the stress distribution of Al2O3/cZrO2 from that of Al2O3/mZrO2 is that the stress value observed in the Al2O3 grain is positive corresponding to the compressive stress. This result is consistent with a report by Orera et al. (2002) [3] describing the ruby fluorescence in the macroscopic scale. Moreover, the difference between the maximum and minimum pressures of Al2O3/cZrO2 is considerably lower than that of Al2O3/mZrO2. The half width of the R1 peak increased substantially in the grain boundaries between Al2O3 and ZrO2 (see Fig. 5(b)). This observation suggests the anisotropic stress existing in the grain boundary. The widths of R1 and R2 peaks of Al2O3/cZrO2 were smaller than those of Al2O3/mZrO2, which indicates that the stress was more homogeneous in Al2O3/cZrO2 than that of Al2O3/mZrO2. The stress tensor (σc) parallel to the c-axis was higher at the outer part of Al2O3 grain (see Fig. 5(h)). In contrast, the stress tensor (σc) perpendicular to the c-axis decreased at the outer part of Al2O3 grain (see Fig. 5(d)). These behaviors of the stress tensor resemble those of Al2O3/mZrO2. Overall, the present experimental results suggest that the stress in the Al2O3/cZrO2 fiber is more isotropic and more homogeneous than that in the Al2O3/mZrO2 fiber. The contrast resulted from the difference in the phase transition during cooling between these two materials.

4. Conclusion

The SNOM measurements enabled high spatial resolution of the stress mapping within a single Al2O3 grain in Al2O3/mZrO2 and Al2O3/cZrO2 eutectics grown using the μ-PD method. In this study, the spatial resolution was as low as 300 nm, which can be improved using a fiber with a smaller aperture. Tenseile stress was observed in Al2O3 of Al2O3/mZrO2; a compressive stress was observed in Al2O3 of Al2O3/cZrO2. The tensile stress found in Al2O3/mZrO2 is attributable to the volume expansion in the tetragonal to monoclinic ZrO2. In contrast, compressive stress found in Al2O3/cZrO2 results from continuous thermal contraction during cooling. The stress distributions were visualized in a single Al2O3 grain. Considerable stress anisotropy was visualized in the grain boundary between Al2O3 and ZrO2 for both eutectics.

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