Recent Development of TEM for Advanced Ceramics

Yuichi Ikuhara
Institute of Engineering Innovation, The University of Tokyo

This paper reviews several recent improvements in new transmission electron microscopy (TEM) to characterize advanced ceramics. As theoretical calculations are getting popular, quantitative analyses for high resolution electron microscopy (HREM) and electron energy loss spectroscopy (EELS) are performed to determine the grain boundary atomic structures and chemical bonding state in ceramics. TEM in-situ straining technique has also been developed to directly characterize the atomic structures of crack walls in structural ceramics by using the crack induced tension (CIT) method which uses the micro-indenter driven by a piezo actuator. Ultra high resolution electron microscopy (UHREM) is a powerful technique to discriminate the species of atoms which are located closer to each other within 0.1 nm, and therefore light elements such as nitrogen and oxygen can be directly observed in the structure image. Low electron dose HREM can be applied to characterize soft ceramics such as zeolite and biomaterials by using a slow-scan CCD camera system. Scanning transmission electron microscopy (STEM) has been recently developed to directly obtain the atomic image by high angle annular dark field (HAADF) technique and also STEM-EELS-EDS combined technique to map the chemical composition and bonding state with a high spatial resolution. Ceramic sciences will be further developed by the newly developed TEM methods demonstrated here.

Introduction

Transmission electron microscopy (TEM) is a powerful technique to characterize the microstructures, and has been intensively applied for advanced ceramics [1]. High resolution electron microscopy (HREM), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) are the main techniques to characterize atomic structures, chemical composition and chemical bonding state in microstructures. These techniques have successfully provided many important information to understand the properties in advanced ceramics, i.e., grain boundary and interface phenomena are one of the key factors to understand the nature of the properties, and hence TEM has been widely used to elucidate the nature [2]. TEM has thus long been in an integral part of ceramic research. However, the capability of TEM analysis is not always perfect. We frequently need the microstructural information, which cannot be obtained by a conventional TEM, to further understand the properties and microstructures in advanced ceramics. In this article, some of recent improvements in TEM analyses are demonstrated.

One of the most striking development for TEM characterization is that theoretical calculations get popular and can be applied to quantitatively analyze the atomic and electronic structures. Combining with the theoretical calculations, complex and distorted atomic structures are possible to be determined by HREM [3,4], and the origin of chemical shifts that appeared in EELS can be quantitatively interpreted [5,6]. Quantitative analyses for grain boundary structures and energy loss near edge structures (ELNES) are shown as the examples. In-situ observation in a TEM has contributed to the development of materials science and also played an important role for the basic knowledge of material phenomena. However, most of results obtained by the in-situ observation are of metals. This is because the specimen treatment was difficult for brittle ceramics. Although ceramics are expected as the structural materials, the atomic structure of the cleavage plane has even not been clarified. In-situ HREM observation can reveal the atomic structure on the cleavage plane, and an example of Si$_3$N$_4$ observation will be demonstrated in this paper [7,8]. The resolution of conventional HREM is 0.17-0.20 nm at 200-300 kV, however, the resolution of about 0.1 nm can be achieved by using atomic resolution high voltage electron microscopy (ARHEM) [9]. It will be shown here that ARHEM can be applied to discriminate Ga and N in the GaN thin film. Electron irradiation damage is sometimes very serious in characterizing soft materials by TEM. In this case, low electron dose HREM is possible to reduce the density of electron dose by using a slow-scan CCD camera system. An example of direct observation of the channel structures in zeolite was demonstrated [10]. Scanning Transmission Electron Microscopy (STEM) has been recently paid much attention for direct atomic imaging and also STEM-EELS-EDS combined technique has emerged to characterize the chemical composition and bonding state at very narrow region such as grain boundaries and interfaces [11]. Several examples will be shown in this paper.

Quantitative Analysis

HREM for ceramic grain boundary

HREM has been intensively applied to investigate the atomic structures in ceramics, and it has successfully provided important information on microstructural factors such as grain boundary, interface, lattice defect and so on. The macroscopic properties of ceramic materials are strongly influenced by the presence of grain boundaries. Therefore, quantitative characterization of the grain boundaries is needed to obtain materials with better or novel properties. In order to quantitatively evaluate the grain boundary atomic structures, well-defined specimens and theoretical calculations are needed in addition to HREM observations [3]. We have characterized many kinds of ceramic grain boundaries so far [12-15], and a result for zirconia grain boundary will be introduced as an example of quantitative analysis [5]. In this study, Σ= 9 [110] symmetric tilt grain boundary was fabricated by the hot-joining technique as a model specimen.

In order to predict the grain boundary atomistic structures theoretically, the systematic lattice statics calculations were performed using the GULP program code [16]. It has been well demonstrated that the lattice statics calculations were effective method for predicting the stable grain boundary structures in many kinds of ceramic materials [17,18]. In the calculation, the atomistic interactions are described by a potential function which divides the interatomic forces into long-range interactions (described by Coulomb’s Law and summated by the Ewald method) and short-range interactions treated by a pairwise function of the
Fig. 1 The lowest energy structure of the $\Sigma = 9$, (221) grain boundary obtained by the lattice statics calculations. Note that high density of cation sites with seven-fold coordination are formed along the boundary, as indicated by the small solid arrows.

Buckingham. The potential parameters used in this study were taken from the literature reported by Lewis and Catlow [19]. The lattice energies were calculated summing all the potentials of constituent ions in the calculation cells. The grain boundary excess energies were estimated by subtracting the calculated lattice energy for the single crystal cell with the same number of ions from the calculated lattice energy for the cell including the grain boundary. The calculated energies were then evaluated as a function of the translation states, and the atomic configurations with local energy minima were subsequently selected as the equilibrium structures.

Figure 1 shows thus obtained the lowest energy grain boundary structure predicted by the lattice statics calculations [15]. The grain boundary excess energy was calculated to be 3.01 J/m$^2$, and the lowest energy grain boundary structure had a rather large boundary expansion of 1.00Å, resulting in the formation of slightly large free volumes at the core of the boundary. The open spaced structures at the boundary core in real material may arise as channeling contrast on the HRTEM image where there are no atomic columns. Such contrast would make the interpretation of experimental HRTEM image be complicated, and require extensive image simulation in various kinds of possible structure models to determine the real atomistic core structures. To avoid such ambiguity, the atomic-resolution high-voltage electron microscopy (ARHVEM) was applied to directly determine the atomic column of cation sublattice at the present grain boundary. Cross-sectional HRTEM observations were then mainly carried out by a JEOL JEM-ARM1250 (1250 kV) transmission electron microscope to directly image the atomic column structure of the boundary. In this case, the thickness of the sample specimen was controlled to be as thin as about 4nm, and the image was taken under near the Scherzer defocus of about -38nm, so that the atomic columns can be imaged as black dots reflecting their potentials.

Figure 2(a) shows the ARHVEM image of the $\Sigma = 9$, (221) grain boundary [15]. As can be seen in the image, the black dots were imaged slightly elongated in the [001] directions. This is because the anion sites are located very close to the cation sites in this direction. Since the open spaced cation sublattice structure can be directly observed in the micrograph, this boundary is confirmed to have a periodical array of asymmetrical structure units along the grain boundary, as indicated by the solid lines in Fig. 2(b). Fig. 2(c) shows the calculated HRTEM image based on the predicted model as shown in Fig.1. The simulated image approximately agrees with the experimental image, as for the periodical array of asymmetrical structure units. The cation sites with different coordination state are accumulated along the calculated $\Sigma = 9$ grain boundary structure, indicated by the solid arrows in Fig. 1. These sites have seven-fold coordination of oxygen ions, and almost keep the cubic polyhedra. The density of the coordination deficient sites is considered to be related to the grain boundary energy in zirconia ceramics.

**ELNES Interpretation**

Microscope approach is very useful for obtaining information about the projected atomic structure of the specimen, but EELS is also useful to analyze, not only structures but also chemical composition and bonding states from the electron illuminated area. Typically, the near edge fine structure of the EEL spectrum (ELNES) is used for the fine scale characterizations. Since ELNES arises from the electron transition from a core-orbital to the unoccupied bands, the spectral features of ELNES reflect the unoccupied partial density of states (PDOS) of the objective atom. ELNES therefore contains a wealth of information on the bonding and electronic structure around the target atom. In order to quantitatively interpret ELNES, theoretical calculations using a first principles method are needed. To obtain the wave function at the initial state and the final state, a first-principles band structure calculation using the orthogonalized linear combinations of atomic orbitals (OLCAO) method was employed. The OLCAO method is a density functional theory (DFT) based on the local density approximation (LDA) [20]. In the electron transition process, an electronic hole is generated at a core orbital, which is called core-hole. The attractive potential from the nucleus becomes intense and the wave-function is more localized at the nucleus by the presence of the core-hole. The core-hole effect has been shown to greatly affect the accuracy of which the EEL spectral features can be reproduced [21,22]. In this study, the core-hole effect was fully taken into account in the self-consistent iterations by removing an electron at the core orbital and putting it at the lowest band. In order to introduce the core-hole, only the core orbital of the core-hole atom is excluded from the orthogonalized process. A sufficiently large supercell is also necessary to minimize the interaction of neighboring core-hole atoms in the adjacent cells. Figure 3(a) shows the experimentally obtained O-K ELNES for SrTiO$_3$. Supercells of 135 atoms were constructed by the 3x3x3 of the unit cells for SrTiO$_3$. By employing such supercells, approximately 10Å distance can be made among the core-hole atoms. The four irreducible k-points were used for the self-consistent iteration for the SrTiO$_3$ electronic structure, respectively. Both the final and the ground states were separately calculated. The theoretical transition energy was evaluated by the subtraction of the total energy at the ground state from that of the final state. Each transition probability is broadened using the Gaussian function of $\Gamma = 1.0$ eV for comparison with the experimental spectrum. In order to calculate the high resolution spectrum, eight
k-points were employed.

To demonstrate the importance of a sufficiently large supercell while using the core-hole methodology, the size dependence of the supercell on the calculated O-K ELNES spectra of SrTiO$_3$ is shown in Fig. 3(b) [6]. All spectra were calculated using the above methodology. A small supercell results in the inaccuracy of both the peak positions and relative intensities of the peaks. Agreement is satisfactorily achieved at a size of 135 atoms. The calculated spectrum at the ground state is also shown in Fig. 3(c). The spectrum at the ground state is calculated from the transition probability between the core-orbital to the conduction band both at the ground state. It is found that the spectral features change by the introduction of the core-hole. A sufficiently large supercell and the introduction of core-hole are thus the key for the accurate reproduction of ELNES spectra through first principles calculations.

**TEM In-Situ Characterization**

It is important to clarify the internal structure of crack tips in ceramics for a fundamental understanding of fracture phenomena. A so-called process zone is considered to exist at the crack tip. However, the nature of the zone and also the atomic structure of the crack wall have not been clarified. It is quite possible that, using static methods to observe a pre-cracked tip by TEM, the structure of the crack tip changes during specimen preparation, for example by ion-beam thinning. In contrast, in-situ TEM methods for observing the fracture behavior are very effective in clarifying the microstructure of a crack wall, because the crack can be dynamically produced to form a fresh surface in a TEM. TEM in-situ straining experiments have already been accomplished to obtain very valuable information. There are, however, few reports on experimental TEM studies of the crack tip and wall in brittle ceramics.

In this study, a crack was introduced in silicon nitride ceramics by in-situ TEM straining experiments [7,8]. The method for the observations was the crack-induced tension (CIT) method [23]. This method employs the micro-indentation in a TEM, which means that the compressive force of the indenter makes a tensile force perpendicular to the crack. **Figure 4** shows the TEM holder with CIT method. A tensile force is applied to the specimen by the nano-indentation which is precisely controlled by a piezo actuator (CIT method).

**Figure 5 (a)** shows a bright field image of a typical transgranular crack in Si$_3$N$_4$ ceramics obtained by the present in-situ straining TEM experiment [7]. The corresponding selected area electron diffraction pattern (SADP) taken from this grain is shown in Fig. 5 (b), indicating that the Si$_3$N$_4$ grain was observed along the [0001] direction. It can be seen that no dislocations were observed around the crack and the fractured surfaces are sharp and straight, as can be expected from the brittle fracture. **Figure 5 (c)** shows the HREM micrograph of the crack walls shown in Fig. 5 (a). In the observed
In the transgranular fracture, several kinds of (1100) planes can be considered as the atomic planes. In order to consider the detailed structures of the crack walls at an atomic level, 6 kinds of fracture models along (1100) planes can be considered as shown in Fig. 6A (a) to (f) [7]. In the schematic illustration of Si$_3$N$_4$ crystal shown in Fig. 6A, large and small circles correspond to Si and N atoms, respectively. Fig. 6B show the most stable (1100) surface structures which were predicted by the first principles calculations, corresponding to the respective 6 kinds of fracture models. The atomic relaxation is thus taken into account in all models. The HREM simulated images obtained from these models are shown in Fig. 6C (a) to (f). The conditions of crystal thickness and defocus values for HREM simulation were 3 nm and –47 nm, respectively. As can be seen in Figs. 6C (a) to (f), the image contrasts near the cleaved surfaces were different between these possible cleavage planes. In addition, from close comparison between the experimental and simulated images, it is confirmed that the model “a” shown in Fig. 6A was in good agreement with the experimental image. That is, the cleavage fracture occurs along the double silicon layers on the (1100) plane. The terminated atomic structure can be thus evaluated by directly observing the crack wall just after crack is propagated.

Ultra HREM

As mentioned above, HREM is very useful to characterize the atomic structures in ceramics. However, the point-to-point resolution of a conventional HREM is usually 0.17-0.20 nm, and it is impossible to distinguish the species of atoms which are located closer within the resolution. In the recent nano-characterization, we sometimes need to directly observe light elements such as oxygen, carbon and nitrogen which are main constituent atoms in ceramics. The light elements are frequently bonded to neighboring cations at the interatomic distance less than 0.1 nm, and the ultra high resolution is, therefore, needed to discriminate the atoms. GaN films are the potential candidates to be applied to optical and electronic devices [24]. An epitaxial wurtzite GaN (0001) film grown on a sapphire (0001) substrate has a polar structure of which the axis is parallel to the growth direction. Recently, control of the lattice polarity in III-nitride films has become a topic of interest due to its significant influence on the optical and electrical properties of the films. The polarity in GaN films is one of the important keys to determine the properties, however, the polarity cannot be identified by conventional TEM technique. In order to determine the polarity, coaxial impact collision ion scattering spectra (CAICISS), reflection high-energy electron diffraction (RHEED) and convergent beam electron diffraction (CBED) have been applied, however, they provide only average information about the lattice polarity in the illuminated area. To discriminate
between Ga and N, and hence to determine the absolute polarity, a resolution of 0.113 nm is needed. We proposed the application of ARHVEM to characterize the GaN film [9, 25]. The point-to-point resolution of the electron microscope is about 0.1 nm. ARHVEM, therefore, can be used to directly observe the Ga atoms and N atoms on only one image and determine the absolute polarity without the complicated image analysis required in conventional HREM.

Fig. 7 shows HREM image of GaN sample observed by ARHVEM (JEOL JEM-ARM1250) at an accelerating voltage of 1250 kV. Spherical and chromatic aberration constants of the objective lens are designed to be Cs=1.4 mm and Cc=2.4 mm, respectively. The HREM image was observed along the [1120] zone axis. The smallest intercolumn distance between Ga and N in this orientation is 0.113 nm. Initially, the condition of GaN imaging was systematically checked, because there has been no report on the direct imaging of Ga and N atoms in GaN. In Fig. 7, the inset at the upper right in the micrograph is a simulated image obtained using an electron microscopy software. The simulated image with Scherzer defocus and 3.2 nm thickness suggests that Ga and N atomic columns can be imaged as darker and lighter spots, respectively. The experimental image in Fig. 7 was taken under the similar defocus and thickness conditions as the calculation. In the experiment, the focus series around the Scherzer condition was taken, and the thickness of the sample was systematically checked by comparing the experimental and calculated images depending on the amount of defocus. The experimental image is in good agreement with the calculated image and it was found to be possible to discriminate between Ga and N atoms by ARHVEM.

Low Electron Dose HREM

Recently, some soft ceramics such as zeolites, bioceramics and so on have been paid much attention because of their special functional properties for environmental assessment. The properties of such soft materials are also related to their atomic structures, and HREM is one of the most effective methods to characterize such materials. However, it has been hard to characterize the soft materials by HREM, because the soft materials are usually very sensitive to electron beam irradiation. They have metastable structures and weak chemical bonding and quite easily damaged by electron irradiation to form an amorphous structure. Then, it is usually impossible to record an image under ordinary conditions of HREM observations (beam current density>10A/cm²). Several researches have been performed on zeolites using ordinary HREM with a special technique [26]. However, this technique involves taking a picture with film very quickly before irradiation damage occurs and cannot be used for normal observation. A recording technique for TEM images with a slow-scan charge-coupled-device (CCD) camera (SSC camera) has been developed so far, which makes it possible to observe using HREM with a low electron beam dose [27]. An example of observation of the channel structures in zeolite Y is introduced here. HREM observations were performed on a con-
Scanning Transmission Electron Microscopy

STEM has been developed to obtain finely focused electron probe less than 0.2 nm, and has applied for characterizing materials. Particularly, a high-angle dark-field STEM (HAADF-STEM) has been used as a kind of atomic-resolution imaging [28-32]. The contrast obtained by HAADF-STEM reflects the atomic number (Z), and hence the contrast is called Z-contrast. In addition, recent development of Cs correction technique enables us to obtain further fine probe size less than 0.1 nm, and has been paid much attention for materials scientists [31,32]. Figure 9 shows an example of Z-contrast obtained by STEM with Cs-correction for SrTiO$_3$ projected along [001] direction, in which bright and gray contrasts correspond to Sr and Ti, respectively. Z-contrast is thus expected to be very powerful technique rather than HREM for characterizing ceramics, however, one of the weak points is in observing light elements such as oxygen, nitrogen and carbon because of the scattering factor of these elements are small. So far, ARHVEM has been superior to Z-contrast on this point, but very recently, the group of Pennycook experimentally showed that light elements also can be directly imaged by BF-STEM image using a Cs corrector [11]. In order to obtain a nano-probe smaller than 1 nm in a transmission electron microscope, the field emission gun is needed because the size of illumination is small and the brightness is high. Grain boundary composition and chemical bonding state for several ceramics have been successfully investigated by the nano-probe using the small Cs pole-piece. Fig.10 shows (a)STEM image and (b) Lu-Kα image obtained by STEM-EDS mapping with the probe size of 0.5 nm for the grain boundary in the Lu$_2$O$_3$ doped Al$_2$O$_3$ [33]. It can be clearly seen that the continuous segregation layer is formed along the grain boundary. The thickness of the segregation layer is about 1 nm. This kind of EDS mapping is also an advantage of STEM technique.

Summary

TEM is a very powerful technique to characterize microstructures in advanced ceramics. However, we frequently encounter difficulties which cannot be solved by conventional techniques. The difficulties are in quantitative analysis, resolution of in-situ TEM, limitation of atomic resolution, spatial resolution and so on. In this case, we need to overcome the difficulties by developing and contriving the method to procure essential information on microstructures at the necessary conditions. In this article, some attempts were demonstrated to show quantitative analysis for grain boundary atomic structures and ELNES, in-situ straining TEM, ultra HREM, low dose HREM, high spatial analytical STEM. Now, TEM has thus many functions, and will add another functions in the near future. Taking account of recent improvements, TEM is not only a microscope, but also plays a role as a nanolaboratory to process nano-materials and to characterize microstructures in dynamic environment. That is, the fields of TEM is gradually transferring from “Seeing is believing” to “Seeing is creating”. This approach will create a new field of TEM characterization, and contribute to the development for the nano-technology in the near future.

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