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In situ TEM observation of domain switch in $LaNbO_4$ added to $NiO–Y_2O_3$ stabilized ZrO_2 ceramic composite

Ben Ma,[a,b] Bo Chi,[a] Jian Pu[a] and Jian Li[a,*]

[a] *Center for Fuel Cell Innovation, State Key Lab for Material Processing and Tooling Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, 1037 Luo Yu Road, Wuhan, Hubei 430074, People's Republic of China*

[b] *College of Sciences, Wuhan University of Science and Technology, 947 He Ping Avenue, Wuhan, Hubei 430080, People's Republic of China*

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The morphology of domain structure in $LaNbO_4$ added to YSZ–NiO composite was examined using a focused ion beam prepared specimen in a transmission electron microscope with a straining stage. It is confirmed for the first time that the morphology is changed under load through domain boundary movement. The driving force for this domain switch is the difference in Gibbs free energy between domains with different crystallographic orientations. This domain switch improves toughness by dissipating stress build-up at the crack tips.

Keywords: Ceramic composite; $LaNbO_4$; Domain switch; In situ observation; Transmission electron microscopy

The conventional approach to toughening ceramic materials is to introduce a secondary phase in various shapes, such as particles, whiskers or fibers [1–3], into the ceramic matrix to make use of the toughening mechanism of phase transformation, micro-cracking, residual stress, fiber/whisker reinforcement or grain bridging. Recently, domain switch has been considered as another toughening mechanism in ceramic composites containing ferroics as the secondary phase [4–11]. The microstructure of ferroics contains domains in different orientations. The domain preferably oriented will grow at the expense of the other via domain boundary switch, while it is stressed by an external force. Thus it is expected that the domain switch can serve the purpose of toughening ceramic composite by dissipating the stress build-up at the tip of a propagating crack. $BaTiO_3$ [8,10,11], $LiTaO_3$ [6] and $LaNbO_4$ [4,12] have been proved to be effective in enhancing the toughness of ceramic materials, even if the domain switch has not been experimentally observed so far.

The purpose of this study is to confirm the stress-induced domain switch in $LaNbO_4$ by in situ observation using transmission electron microscopy (TEM). The $LaNbO_4$ was added to toughen $NiO–Y_2O_3$ stabilized ZrO_2 (YSZ) composite, which is a state-of-the-art substrate material for anode-supported solid oxide fuel cells.

$LaNbO_4$ powder was prepared by solid state reaction using La_2O_3 (99.9% purity, Sino-Pharm Chemical Reagent) and Nb_2O_5 (99.99% purity, Aladdin Chemistry) as the raw materials. The detailed procedure was reported previously in Ref. [13]: 30 wt.% of $LaNbO_4$ was added to 47 wt.% NiO (Type standard, Inco)–53 wt.% YSZ (TZ-8YS, Tosoh) powder mixture. The $LaNbO_4$–YSZ–NiO powder mixture was ball-milled, dry-pressed using hardened steel die and sintered at 1500 °C in air for 6 h to obtain a densified bar specimen (99% [13]) in a rectangular shape.

The preparation of the specimen for TEM in situ observation was performed inside a dual-beam focused ion beam (FIB) system (FEI Helios Nanolab 600i), equipped with a Schottky field emission gun column, a Ga ion beam column, Pt gas injection system and micromanipulator (Omniprobe). The procedure was as follows: (1) a Pt protective strip, $\sim 10 \times 3 \times 1$ μm, was deposited on the surface of the sintered bar specimen; (2) both sides of the strip were trenched by ion beam at 30 kV and 20 nA (Fig. 1a) to shape a thin "wall" between the two trenches; (3) the thin specimen was cut off from the bulk specimen by ion beam at a tilted (7°) position and placed on a Cu specimen holder by the micromanipulator (Fig. 1b); and (4) the thin specimen was further thinned sidewise to an appropriate thickness by ion beam for TEM observation (Fig. 1c). The bonding between the thin specimen and the specimen holder was established by deposited Pt. Figure 1d is the top view of Figure 3c, showing the final thickness of the

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[*] Corresponding author. Tel.: +86 27 87557496; fax: +86 27 87558142; e-mail: lijian@hust.edu.cn

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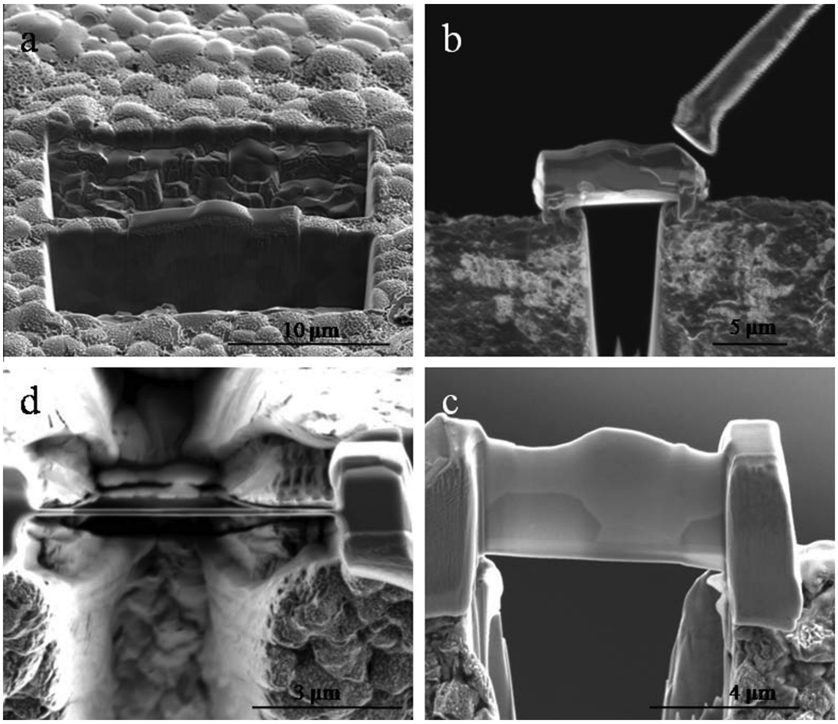

Figure 1. FIB preparation of specimen used for in situ TEM observation under tensile load.

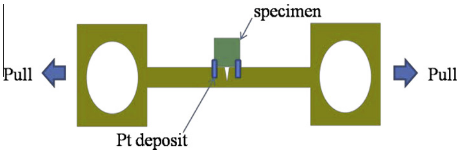

Figure 2. Schematic illustration showing the configuration of specimen used for in situ TEM observation under tensile load.

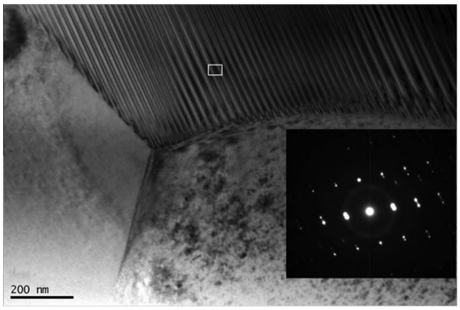

Figure 3. TEM microstructure of $LaNbO_4$ added NiO–YSZ ceramic composite and selected area diffraction pattern obtained from the grain of monoclinic $LaNbO_4$.

TEM specimen. As shown schematically in Figure 2, the Cu specimen holder was 2.4 mm wide, 8 mm long and 0.1 mm thick with two 1.5 mm holes at both ends to fit the straining stage; and the thin specimen was seated right on a preformed V-shape slot that facilitates the tensile experiment. In situ observation of the tensile load was performed by TEM, using a Jeol 2010 instrument at 200 kV with a Gatan single-tilt straining holder under a slowly increased tensile load.

Figure 3 demonstrates the microstructure of 30 wt.% $LaNbO_4$–NiO–YSZ composite, in which the monoclinic $LaNbO_4$ is featured by two domains with widths varying from 20 to 50 nm. Two sets of diffraction spots shown by the inset in Figure 3 indicates that the two domains are oriented in different crystallographic orientations, with a domain boundary located at a lattice plane in the $\{20\bar{4}\}_{\mathrm{I}}/\{402\}_{\mathrm{II}}$ family [14,15]. Figure 4 compares the domain structure in a $LaNbO_4$ grain before and after tensile load. It is noticed that the overall morphology of the domain structure was obviously changed (Fig. 4a and b) as a result of the tensile load, and more specifically the width of domain in the circled area was narrowed (Fig. 4c and d). These phenomena confirm for the first time that the domain boundary was indeed moved by the applied tensile load.

Tsunekawa [16] postulated a model for this domain switch. It suggests a sharp domain boundary and that all the atoms are moved from the positions in one domain to the positions in the other by a shearing on the domain boundary plane, followed by atomic shuffles to reach the final positions. This model may be crystallographically correct and may not be thermodynamically realistic, since high energy is needed to move all the atoms simultaneously through a large displacement. It is observed that there is a fine diffraction line connecting two corresponding diffraction spots from each domain, which implies that a diffuse domain boundary separating the two domains [15] and the atoms located in the boundary zone are progressively changing their positions from one domain to the other. In other words, a very short distance atom movement at the edge of the boundary zone can move the boundary as a whole, which makes the domain boundary easily moveable under a small load. With an external uniaxial stress σ_{ij}, the