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Strength and toughness of nanocrystalline SiO_2 stishovite toughened by fracture-induced amorphization

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ABSTRACT

The finding of “fracture-induced amorphization” in nanocrystalline SiO_2 stishovite lead to a proposal of a new type of transformation toughening by the direct transition from crystal to amorphous state, which is different from the classical martensitic transformation of zirconia. Here, we investigated strength and toughness of nanocrystalline stishovite by using micro-cantilever beam specimens of different sizes. The maximum strength of 6.3 GPa gave the estimate of the lower bound of critical stress for amorphization, which was much higher than the critical transformation stress of zirconia. The crack growth resistance curve (R-curve) rose steeply with crack extension of only a few μm, and reached to a plateau value of 10.9 MPa $m^{1/2}$. We discussed the effects of grain size, microstrain, and dislocation density on the critical stress, the transformation zone width, and thereby, the fracture toughness.

1. Introduction

Silica (silicon dioxide, SiO_2) is a common mineral found in many rocks and sands. More than 90% of the Earth's crust is composed of silicate minerals. Among them, quartz and silica glass are widely used because they are hard and transparent. However, they are brittle and easily broken. Stishovite is a high-pressure polymorph of silica stable at pressures above 9 GPa, and metastable at ambient conditions [1]. Stishovite has a denser structure than quartz, and has the highest hardness (33 GPa) of any stable/metastable oxide under ambient temperatures [2]. Hard materials with limited ability of plastic deformation tend to be brittle, then, the fracture toughness K_{IC} of a single crystal is 1.6 ± 0.3 MPa $m^{1/2}$ [3], which is not very high compared with that of silica glass (0.8 ± 0.3 MPa $m^{1/2}$) [4]. Recently, Nishiyama [5] found that a nanocrystalline SiO_2 stishovite with the grain size of ~100 nm had a fracture toughness of 13 ± 3 MPa $m^{1/2}$ by indentation fracture method (IF method [6]). This nanocrystalline material was synthesized by crystallization of silica glass at 15 GPa and 1473 K, in other words, the brittle glass is transformed to the novel advanced ceramics, which is tough and very hard, by the high-pressure synthesis.

At fixed synthesis pressure of 15 GPa, microstructures and mechanical properties of stishovite depend on the synthesis temperature. The average grain size increased with increasing the synthesis temperature. Williamson-Hall analysis revealed the microstrain was 0.4% in the sample synthesized at 1473 K, and decreased with increasing the synthesis temperature. TEM observation showed that dislocation density decreased with synthesis temperature. The fracture toughness also decreased with synthesis temperature, then, the fracture toughness of nanocrystalline stishovite increased with decreasing the grain size [5]. This effect of grain size on fracture toughness of stishovite is opposite to the behavior expected from the toughening mechanism by crack bridging [7], e.g., in alumina [8] and silicon nitride [7].

The fracture toughness of zirconia (ZrO_2)-based ceramics can be enhanced by martensitic transformation in the stress field of propagating cracks [9–11]. In analogy to the transformation toughening [12–14], Nishiyama [15] proposed a toughening mechanism by fracture-induced amorphization. Transformation of metastable stishovite with six-fold coordination to the stable phase with four-fold coordination often occurs through intermediate amorphous state, because the Gibbs free energy of stishovite is higher than that of amorphous SiO_2 at any temperature above 0 K at ambient pressure [16]. The direct transition of crystal to amorphous state, which is analogous to melting, is triggered by heating at 1 bar [17], or decompression at room temperature. Here, the term

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amorphization/vitrification is used below the glass transition temperature, and the term melting is used above it. The amorphization is induced by fracture since the tensile stress, which is equivalent to negative pressure, can be very large at the crack tip. The formation of amorphous phase with the thickness of a few tens of nanometers was observed on the fracture surface by X-ray absorption near edge structure (XANES) spectroscopy. Furthermore, fracture toughness increased with the amount of amorphous silica near the fracture surface [15].

Brittle ceramics can be toughened by crack-tip shielding which reduces the stress intensity factor experienced at crack tip. This effect depends on crack size, then, crack growth resistance increases with crack extension [18,19]. Yoshida et al. [20] developed a micro-mechanical test method using micro-cantilever beam specimens to determine the very early part of resistance curve (R-curve) of nanocrystalline stishovite, and showed that crack growth resistance increased from 4 MPa $m^{1/2}$ to 8 MPa $m^{1/2}$ with crack extension of only one micrometer. The effect of toughening mechanism is described by a stress intensity change ΔK between the applied stress intensity factor and the stress intensity factor at the crack tip, which is assumed to be equal to the intrinsic toughness K_0. In the transformation toughening, the extent of ΔK is given by Ref. [13].

$$\Delta K = 0.22 \frac{E}{1-\nu} V_f \varepsilon^T \sqrt{h} \tag{1}$$

where E is Young's modulus, ν is Poisson's ratio, V_f is the volume fraction of transformed phase in the transformation zone, ε^T is the dilatational strain accompanying transformation, and h is the transformation zone width. From Eq. (1), fracture resistance can be increased significantly by the amorphous layer with the thickness of 10–50 nm, because the volumetric strain associated with the amorphization of stishovite is from 60 to 90%, which is much larger than that in the tetragonal to monoclinic transformation of zirconia (4%). The effect of crack shielding ΔK increases with crack extention Δa, and saturates to Eq. (1) at a certain crack length $\Delta a^* \approx 10\,h$ [12]. The sharply rising R-curve is the result of very narrow transformation zone width of nanocrystalline stishovite. Materials with rising R-curve lead to an increase in the strength, in many cases, the steeper the initial R-curve, the higher the strength [21].

The objective of the present paper is to study strength and toughness of nanocrystalline stishovite, so as to clarify the effect of microstrain on R-curve behavior. We used a large micro-cantilever beam specimen to study how R-curve rises and attains to a steady-state (plateau) value. We show the crack growth resistance reaches to more than 10 MPa $m^{1/2}$ with crack extension around 8 μm. The lower bound of the critical stress for amorphization is also discussed from the fracture strength.

2. Experimental procedure

2.1. Materials

Nanocrystalline stishovite sample was synthesized by a Kawai-type multi anvil high pressure apparatus (LPR 1000-400/50, Max Voggenreiter GmbH, Germany). The starting material was pure bulk silica glass, whose dimension was 2.5 mm in diameter and 0.6 mm in height. All the impurities were less than 0.1 ppm except OH (about 800 ppm). The pure bulk silica glass was heated rapidly from 723 K to 1473 K under high pressure, 15 GPa. After holding at 1473 K either for 0.5 h or 5 h, temperature was decreased to 723 K, and decompression was started [5]. The average grain size of sample was determined by TEM observation, and microstrain was evaluated by X-ray diffraction pattern using Williamson-Hall method [22].

3 mol% Y_2O_3-stabilized tetragonal zirconia polycrystals (3Y-TZP) and alumina (Al_2O_3) samples were sintered using a spark plasma sintering machine (SPS-515S, Fuji Electronic Industrial). The temperature was measured by a radiation thermometers at surface of a graphite die. 3Y-TZP sample was sintered from commercial zirconia powders stabilized with 3 mol% Y_2O_3 (TZ3Y, Tosoh Co. Ltd., Japan). As-received powder was heated directly to 1673 K under a uniaxial pressure of 50 MPa. The heating rate was 50 K/min to sintering temperature, and holding 5 min at the temperature. Alumina sample was sintered from commercial α-alumina powder (TM-DAR, Taimei Chemicals Co. Ltd., Japan). As-received powder was heated under a uniaxial pressure of 80 MPa. The heating rate was 25 K/min from 873 K to 1273 K, and 8 K/min to 1423 K. After holding for 20 min at the sintering temperature, sample was annealed at 1273 K for 10 min in order to reduce the residual stress [23].

2.2. Fabrication of micro-cantilever beam specimens

The micro-cantilever beam specimens (Fig. 1(a)) was machined by a focused ion beam (FIB) machining (HITACHI-FB2100) using a high current Ga ion beam (40 keV, 32 nA), followed by fine machining at low currents (6 nA). A notch was introduced by using an even finer current beam (300 pA) in the direction perpendicular

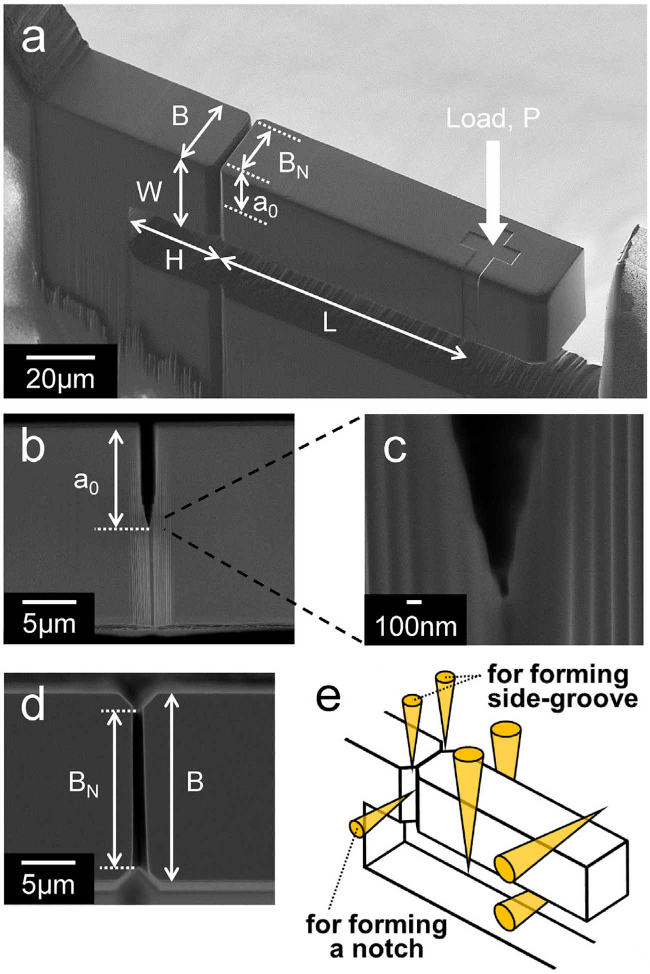

Fig. 1. R-curve testing by using a notched micro-cantilever specimen. (a) Geometry of the specimen, (b) side view of the notch, (c) notch tip, (d) top view of side-grooves, (e) ion beam directions during FIB machining.