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Grain size and grain boundary effects on the mechanical behavior of fully stabilized zirconia investigated by nanoindentation

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Mechanical behavior of fully yttria stabilized zirconia (F-YSZ) was investigated by nanoindentation. The coarse- and fine-grained materials displayed similar reduced modulus and hardness. Clear pop-in was observed in coarse-grained F-YSZ, with the pop-in loads varying with grain orientation and distance from the grain boundary. Pop-in was not clear in nanocrystalline F-YSZ. The lower hardness of the grain boundary and the similar hardness of the two grain-sized materials indicate an intrinsic atomic structure difference in the coarse- and fine-grained F-YSZ.

Keywords: Grain size effect; Grain boundary effect; Pop-in; F-YSZ

Fully stabilized zirconia is widely used as thermal barrier coatings [1], oxygen sensors [2] and solid oxide fuel cell electrolytes [3] due to its high mechanical hardness, thermal shock resistance and high oxygen ion conductivity. Addition of some refractory oxides, such as CaO, MgO or Y_2O_3, into pure zirconia is needed to retain the phase at all temperatures and obtain fully stabilized zirconia. Recently, there has been increasing interest in producing bulk nanocrystalline fully stabilized zirconia. It has, however, proven difficult to densify the material without excessive grain growth. A method that has proven to be effective is the spark plasma sintering (SPS) technique [4], the processing technique used in the present study.

Interest in bulk nanoceramics has been sparked by the possibility that, compared with their coarse-grained counterparts, nanocrystalline materials may display attractive properties, such as high yield strength and toughness, and enhanced physical properties [5–7]. For metals and metal alloys, the yield strength increases with decreasing grain size according to Hall–Petch effect. For some ultrafine-grained metals, the yield strength does not follow the Hall–Petch relation: the yield strength remains constant or decreases with decreasing grain size [8]. For ceramics, the yield strength is not only dominated by the grain size, but also affected by the surface flaw size or the pores, and the testing temperature [9]. This has led to debate over whether or not a nanostructured grain size is beneficial.

Regardless of the benefits, it is obvious that a considerably larger amount of atoms reside along grain boundaries in nanocrystalline materials. Knowledge of the grain boundary effect on the overall mechanical properties is important to the development of bulk nanocrystalline materials. Several studies of grain boundary effect have been carried out on polycrystalline metals. Lilleodden et al. studied the grain boundary proximity effect on 1 μm grain-sized gold film and found that material near grain boundaries yields earlier than that in the center of the grains [10]. Soer et al. indented Fe–14% Si bicrystal and Mo crystals and found that the hardness at the yielding point increases with decreasing distance from the grain boundary [11]. For ceramics, although there have been studies on the nanoindentation properties of single crystal TiO_2, MgO and YSZ [12], and the pop-in phenomenon on single crystal MgO [13], little attention has been given to the mechanical properties and the role of the grain size and grain boundaries in polycrystalline ceramics.

In this work, the effect of grain size and grain boundary on the mechanical behavior of coarse- and fine-grained fully yttria stabilized zirconia (F-YSZ) were studied using nanoindentation. Two polycrystalline F-YSZ materials were prepared by the SPS technique

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using nano-sized powders of fully stabilized zirconia (ZrO_2–8 mol% Y_2O_3; Tosoh Co Tokyo, Japan) with an initial crystallite size of 50 nm. The SPS technique is similar to hot-pressing but uses high electric current densities that provide additional advantages to conventional sintering and hot-pressing. Our experimental set-up is similar to that used in Ref. [4]; the samples had a diameter of 20 mm and were ~2 mm in height. The two materials had very similar densities but dramatically different grain sizes, facilitating the study of the grain boundaries. Figure 1 shows the electron backscatter diffraction (EBSD) map (a) and scanning electron microscopy (SEM) image (b) of the two polycrystalline F-YSZ materials. Different processing conditions were used to produce materials with significantly different grain sizes. The material shown in Figure 1a was processed at 1500 °C, while that shown in Figure 1b was processed at 1300 °C. The holding time was 10 and 5 min, respectively, while the heating rate was 200 °C and applied pressure was 140 MPa in both cases. The pressure was applied at the beginning of the experiment (i.e., room temperature) and held constant for the length of the experiment. The average grain size of the two materials was measured by SEM to be 30 μm and 150 nm, respectively. For the coarse-grained material, the EBSD map was obtained on a metallographically polished sample surface tilted at 70°. The different contrasts in the map represent grains with different orientations. It should be noted that the dark color of the as-sintered samples indicates that they were non-stoichiometric (oxygen deficient). For the fine-grained material, the SEM image was taken from a naturally fractured surface.

Nanoindentation tests were carried out on the polished material surfaces by using a Ubi1 nanomechanical test instrument (Hysitron, Inc., MN). A three-sided diamond pyramidal Berkovich tip with a nominal radius of curvature around 150 nm was used as the indenter tip. The load and displacement were monitored continuously by a three-plate capacitive force/displacement transducer. Reduced modulus and hardness were determined from the load–displacement information following the procedure developed by Oliver and Pharr [14].

Multiple indentations with 1000–12 500 μN maximum load were applied to the coarse- and fine-grained F-YSZ and resulted in an effective contact radius of 0.3–1.3 μm. The roughness of the material surfaces was below 10 nm. From more than ten measurements on each material at different contact depths, the reduced modulus and hardness were measured to be 228.0 ± 9.9 and 19.5 ± 0.7 GPa for the coarse-grained F-YSZ, and 217.8 ± 10.9 and 18.9 ± 1.4 GPa for the fine-grained F-YSZ, respectively. Note that the reduced modulus for both materials are close to that measured by Kurosaki et al. on single crystal YSZ (10 mol.% Y_2O_3-doped ZrO_2) – 237 ± 12 GPa for (1 0 0) direction and 214 ± 9 GPa for (1 1 1) direction – while the hardness values are significantly higher than theirs – 12.4 ± 0.4 GPa for (1 0 0) and 14.8 ± 0.9 for (1 1 1) YSZ crystals [12].

Surprisingly, there is very little difference in the reduced modulus and hardness between the two materials, although their grain sizes are considerably different. However, there is a dramatic difference in the loading part of the load–displacement response between the two different grain-sized materials. Pop-in behavior was usually observed in the coarse-grained material. The pop-in was evidenced by a sudden displacement burst with load unchanged. Unloading before and after the pop-in indicated that the deformation before pop-in was completely elastic as the unloading completely overlapped with the loading path. Thus the pop-in phenomena can be considered as the transition from elastic to plastic deformation. However, in the fine-grained material, this transition was not clear. Figure 2 shows the load–displacement response of nanoindentation within the grains of the two different grain-sized F-YSZ materials.

In addition to grain size, grain orientation was also observed to affect the pop-in behavior. The nanoindentation results show little difference in the hardness and reduced modulus between the different grains. However, large variations for pop-in loads ranging from 300 to 900 μN were found between the different grains, while constant pop-in loads were found within the same grain. The variation in pop-in loads is likely due to the different grain orientations.

Comparisons of the load–displacement response were also made between the grain boundary and the grain interior. Figure 3 shows the scanning probe microscopy image of a group of indents on two grains and on the separating grain boundary. Figure 4 shows the typical load–displacement response of indents on the grain boundary and the two neighboring grain interiors. While no pop-in was observed for the indent on the grain boundary, a pop-in load of 668 ± 9 μN was observed for grain 1 and 550 ± 8 μN was observed for

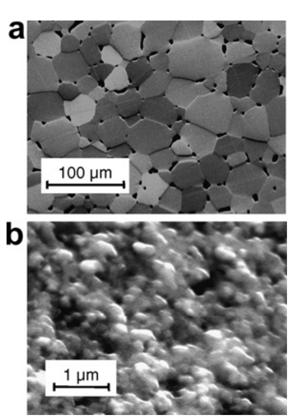

Figure 1. EBSD map of coarse-grained material with 30 μm grain size (a) and SEM image of fine-grained material with 150 nm grain size (b).

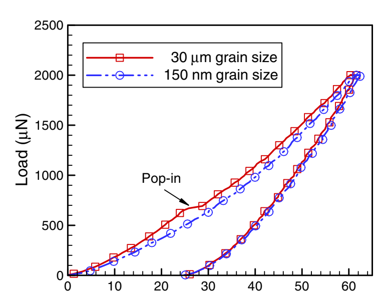

Figure 2. Load–displacement response of nanoindentation on 30 μm grain size and 150 nm grain size F-YSZ materials.