Hardness of cubic silicon nitride

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We report that polycrystalline cubic-Si_3N_4 with a spinel structure and low oxygen concentration (<0.5 wt%) shows Vickers hardness of 43 GPa when measured with the indentation load of 10 mN. The hardness decreases with the increase of the indentation load, which can be ascribed to the presence of weak grain boundaries. The high hardness can be well explained by its large shear modulus as predicted by first-principles calculations.

The positions of the first- and second-hardest materials are established by diamond and cubic boron nitride (c-BN) or other hetero-diamonds such as c-BC_2N.[1] However, there has been a serious competition for the bronze-medal winner in hardness. Boron oxides have been thought to be good candidates.[2] In 1996, stishovite SiO_2 has been reported to be harder than they are.[3] Very recently, cotunnite-type TiO_2 has been found to be even harder, having the Vickers microhardness (H_V) of 38 GPa.[4] Many nonoxides have been thought to show higher hardness than oxides. Despite the "excitement" about the theoretical prediction of C_3N_4 as a material as hard as diamond,[5] no report has unequivocally confirmed the high hardness of this material. Both TiB_2 and BP were reported to have H_V of 33 GPa.[6] Silicon carbonitride with the α–Si_3N_4 structure modified by introduction of C atoms has shown maximum H_V of 33 GPa.[7] A new candidate for ultrahard material, spinel-Si_3N_4 was discovered in 1999.[8] The new phase has been synthesized by several other groups.[9–11] Estimation for the elastic constants of spinel-Si_3N_4 has been provided by first-principles calculation.[10,12,13] In the present study, we confirmed that the H_V of the spinel-Si_3N_4 exceeds 40 GPa. This should be included in the class of the third-hardest materials among the currently available monolithic compounds.

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Commercially available Si_3N_4 powder usually contains a high amount of oxygen, ranging from 1 to 3 wt%. Since the oxygen atoms form stable Si-oxynitrides on the surface of the powders, it is not possible to remove them simply by evacuation at room temperature. For the present study, we selected high-purity β–Si_3N_4 powder with a low amount of oxygen, i.e., 0.5 wt%. The powder was encapsulated in a sealed Pt container ($1.0 \times 0.9 \times 1.8$ mm). Then high pressure was applied using a multi-anvil apparatus[14] at 18 GPa and 1800 °C at Okayama University. The temperature was monitored with a W25%Re–W3%Re thermocouple, located close to the center of the sample. The heater was composed of inner rhenium foil and an outer $LaCrO_3$ sleeve. Under the compression, a large current was applied to heat the sample, held for 20 min, and finally cut suddenly to quench the sample. After release of pressure, the sample was taken out of the high-pressure cell. The sample was subjected to x-ray diffraction (XRD) to confirm single phase of cubic Si_3N_4. The microstructure is shown in Fig. 1. Pores were rarely found. The grain size ranged from 20 to 200 nm. Since the starting powder was tightly sealed in a Pt container, the oxygen content was expected to remain unchanged from that of the starting powder. As a matter of fact, the oxygen content was found to be less than the detection limit by electron energy loss spectrum (EELS) analysis; i.e., less than 0.5 wt%.

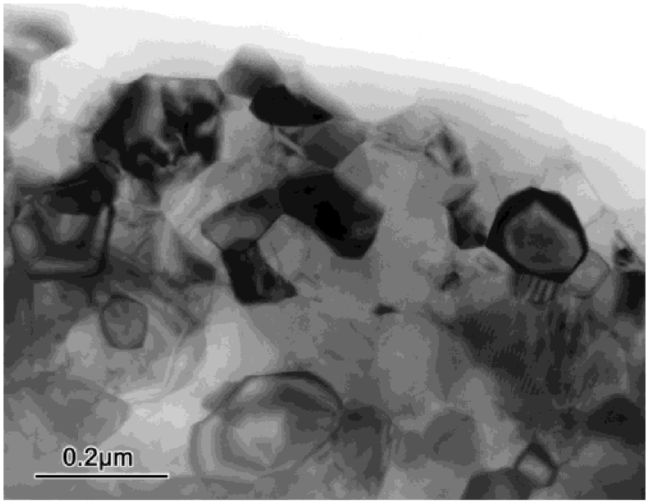

FIG. 1. Transmission electron micrograph of the spinel-Si_3N_4 sintered material.

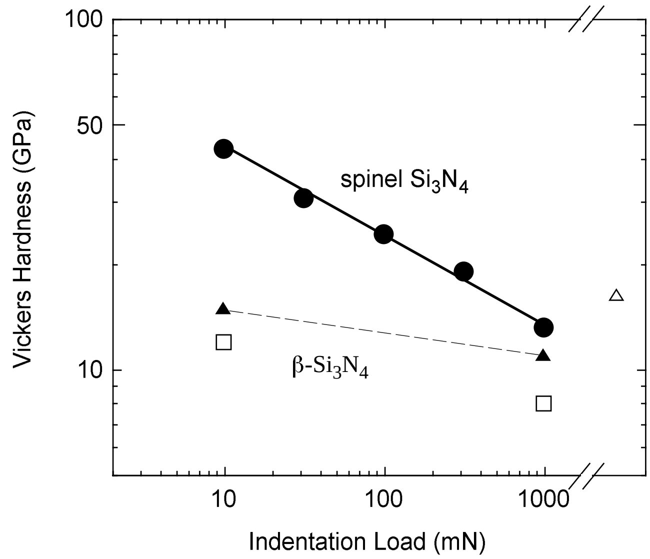

FIG. 2. Measured Vickers hardness of two materials as a function of indentation load. Open triangle denotes the reference value of β–Si_3N_4 in Ref. 17, measured with the indentation loads of 9.8 to 49 N.

Very recently two groups reported experimental H_V of spinel-Si_3N_4.[15,16] Jiang *et al.* synthesized a sample at 17 GPa and 1827 °C with a Pt container. They reported H_V of 35 GPa. However, the indentation load P_I was not shown in the report. Oxygen content in their sample was reported to be less than 1 at.%.[11] Zerr *et al.*[16] reported that the raw value of the "nanohardness" was 37 GPa, determined using an atomic force microscope with a cube-corner diamond tip as an indenter. Their maximum P_I was 5 mN. Their sample contained a high amount of oxygen. Nanoindentation was performed in sample areas with low (<4 wt%) and high oxygen contents up to 14 wt%. H_V at $P_I = 5$ N was estimated to be between 30 and 43 GPa for dense oxygen-free spinel-Si_3N_4. The large error was attributed to the high oxygen content of samples and the conversion between "nanohardness" and H_V at $P_I = 5$ N.

H_V of the present sample was measured by a microhardness tester (Shimadzu, DUH-W201S, Kyoto, Japan) with a Vickers indenter. Five P_I in the range of 9.8 to 980 mN were chosen, and H_V was measured at 10 locations. The standard deviation of H_V was smaller than 0.5 GPa for all conditions. H_V decreased with the increase of P_I as shown in Fig. 2. Microhardness in general shows some dependence on the indentation load. However, the dependence is not so significant as in this case. The result can be ascribed to the presence of grain boundaries which may be much weaker than the matrix. The indentation depth and diagonal increased from 100 to 1700 nm and from 700 nm to 12 μm, respectively, in the present experiments. Since the grain size ranges from 20 to 200 nm, the deformation zone induced by the indentation should include multiple grains. The presence of the weak grain boundaries can therefore be the reason for the significant dependence of H_V on P_I in the present study. To calibrate the microhardness with the hardness often used in engineering community, the microhardness of sintered β–Si_3N_4 sample was measured by the same technique. The β–Si_3N_4 sample was of high-purity, with a mean grain diameter of 1 μm, fabricated by hot-isostatic-pressing without additives.[17] H_V of the β–Si_3N_4 sample determined with P_I of 9.8 to 49 N was 15 GPa.[17] It is greater by 4 GPa than the present H_V with P_I of 0.98 N. It seems that the present method somewhat underestimates the hardness. We can expect a similar magnitude of underestimation also in the spinel-Si_3N_4 sample because both of the samples were measured in the same manner. The dependence of H_V on P_I is much smaller in the β–Si_3N_4 sample, since the average grain size of the β–Si_3N_4 sample is approximately one order of magnitude greater than that of the spinel-Si_3N_4 sample.

A comprehensive survey of superhard materials is given in Ref. 6. The experimental H_V values were assembled and plotted against bulk modulus and average shear modulus. The authors concluded that the shear modulus is a significantly better qualitative predictor of hardness than the bulk modulus is.[6] The idea is quite natural since hardness measures the ability to resist plastic flow. Theoretical shear modulus of the spinel-Si_3N_4 was predicted by two groups to be 258 and 261 GPa.[10,13] [In Ref. 16, experimental shear molulus of spinel-Si_3N_4 was reported to be 148 GPa by the nanoindentation method, which was approximately 57% of the theoretical value. The inconsistency may be ascribed to the high concentration of oxygen in the specimen.] It is plotted in Fig. 3, similar to the one in Ref. 6. The shear modulus of the spinel-Si_3N_4 can be located as the third position among hard materials, rivaling TiB_2. The high shear modulus of spinel-Si_3N_4 provides a good rationale why it

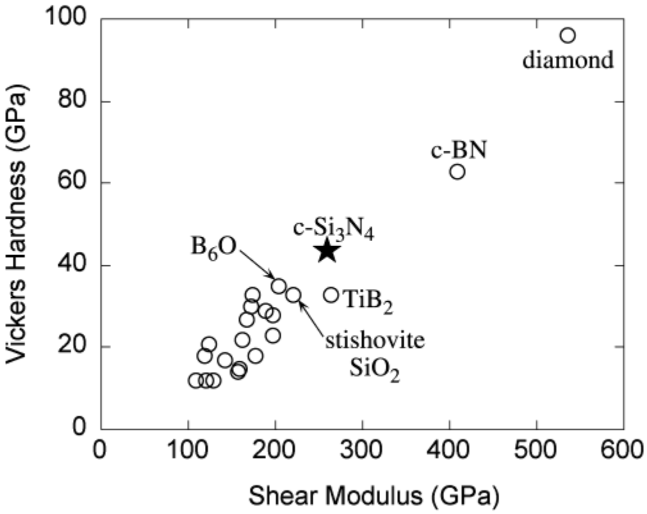

FIG. 3. A plot of Vickers hardness versus shear modulus. All data except for spinel-Si_3N_4 are taken from Ref. 6.

is very hard. Some transition metal compounds, such as HfN and WC, have been reported to show bulk modulus greater than 400 GPa.[6] It is also the case for the recently found cotunnite-TiO_2.[3] They are not necessarily harder than spinel-Si_3N_4 with a bulk modulus of approximately 300 GPa, since the hardness is not determined by purely volume-dependent reversible deformation.

In summary, we succeeded in fabricating dense polycrystalline cubic-Si_3N_4 with low oxygen concentration (<0.5 wt%). Vickers hardness was measured at five indentation loads. The degradation in the hardness with the increase in the indentation load can be ascribed to the presence of weak grain boundaries in the sample. The maximum H_V, 43 GPa, corresponds to the class of the third-hardest materials among the currently available monolithic compounds. The high hardness can be well explained by the large shear modulus predicted by theoretical calculations.

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