

Microstructural Characterization of C₆₀-Doped Zirconia Ceramics

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Microstructure of C₆₀-doped ZrO₂ ceramics sintered under ultra-high pressure was examined by SEM and HVTEM. The specimen sintered at 600°C was very soft and plastically deformed by forcing a micro indenter. HVTEM observations showed ZrO₂ grains covered with thin carbon films of several nanometers in thickness. A monolayer film with a plane spacing very close to that of a kind of carbyne was also observed on the surface of a ZrO₂ grain.

Key words: fullerene, C₆₀, sol-gel, lubricant, carbyne, zirconia

1. INTRODUCTION

C₆₀ is a well-known carbon cluster composed of 60 carbon atoms with a spherical shape of ~0.71nm diameter. C₆₀ is expected to be an excellent solid lubricant, because C₆₀ is reported to have a very high bulk modulus (~900Pa) exceeding that of diamond and to exhibit a low friction coefficient.^{1,2} On the other hand, since zirconia (ZrO₂) is a promising wear-resistant ceramic material which has been intensively studied in the field of tribology for its high-strength, toughness and chemically resistant properties, formation of ZrO₂-C₆₀ composites is of great interest from the view point of tribological application of C₆₀. C₆₀, however, is known to be stable only up to 900°C in an inert atmosphere,³ hence a low temperature processing is necessary in preparing the ceramics-C₆₀ composites. In our previous study to fabricate the powders of ZrO₂-C₆₀ using a toluene solution of C₆₀ and zirconium alkoxide, various forms of carbon allotropes such as graphite, carbyne, "n-diamond" and so on were observed by TEM.⁴ This report will show that C₆₀ can be uniformly incorporated into ZrO₂ bulk ceramics by using the powder which is prepared from an aqueous solution of C₆₀, C₁₆TMA(hexadecyl-trimethylammonium chloride) and zirconium oxynitrate dihydrate, and the unique structure of zirconia particles covered with thin carbon films.

2. EXPERIMENTAL PROCEDURES

Firstly, an aqueous solution of zirconium oxynitrate dihydrate (ZrO(NO₃)₂·2H₂O, ZOD) and C₁₆TMA were dissolved into a distilled water (100mL). Next, powder of C₆₀ was added to the solution and stirred strongly for 24h at room temperature. The molar ratio of C₁₆TMA and C₆₀ was fixed to be C₁₆TMA:C₆₀=150:1, and the concentration of ZOD was set to be 0.1molL⁻¹. An aqueous solution of NaOH was dropped into the above solution to obtain the precipitates of Zr(OH)₄ containing C₆₀ molecules. These precipitates were thoroughly

washed with water and dried at 100°C for 8h and then fired at 400°C for 3h in air with a heating rate of 10°Cmin⁻¹ in order to prepare the powder for hot-pressing. Our preliminary examination showed that C₆₀ is stable up to 400°C for this heating rate.⁵ The ZrO₂-3mass%C₆₀ powder was encapsulated into Au capsules and hot-pressed via a NaCl pressure transmitting medium in a cylinder of graphite heater by using an ultra-high pressure sintering apparatus under 5.5GPa at 600-900°C for 2h, quenched to room temperature, and pellets with a diameter of 5.3mm and a height of 2.2mm were obtained. Structural characterizations of the ZrO₂-C₆₀ ceramics were performed by FT-IR (Jasco Valor III), high-voltage electron microscope (HVTEM, JEM-ARM1250, 1250kV), SEM (Hitachi S-4200) and X-ray diffraction (XRD, MAC MXP-18, 40kV, 200mA, CuK_α). The mechanical testing of the ZrO₂-C₆₀ specimens were done by a micro indenter (Shimadzu HMV-2000).

3. RESULTS AND DISCUSSION

3.1 Surface morphology of the sintered ZrO₂-C₆₀ specimens

Change of the surface morphology caused by polishing is shown in Fig.1 for the ZrO₂-C₆₀ specimen sintered at 600°C. Fine needlelike structures are observed in the as-prepared specimen (photo (a)). Photo (b) shows the surface lightly polished with the diamond powder of 9μm. The needlelike structures are worn, and appear as if they were smoothed out with a spatula. Flattened scratch grooves formed by the diamond abrasive particles are found in the middle part of the image. These SEM observations indicate a ductile nature of the C₆₀-doped ZrO₂ bulk specimen. As shown in Fig.1(c), the surface became more flattened by the continuous polishing using the diamond powder of 1μm. The powder-like structure in the image is the wear debris formed through the abrasion of fine crystal grains.

The Vickers indentation testing showed 176±10 Hv in the ZrO₂-C₆₀ specimen sintered at 600°C, and 268±14

Hv in the ZrO_2-C_{60} specimen sintered at $900^\circ C$.

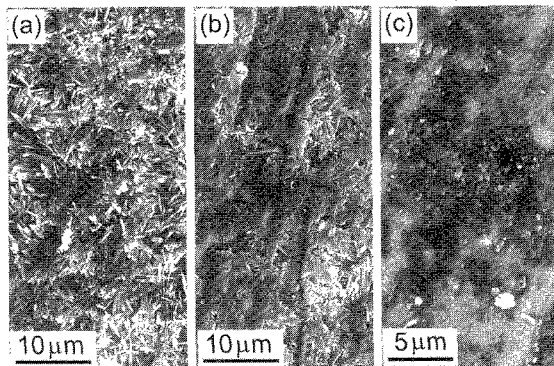


Fig.1 SEM images of the surfaces of as-sintered (a), and polished (b,c) ZrO_2-C_{60} specimens sintered at $600^\circ C$.

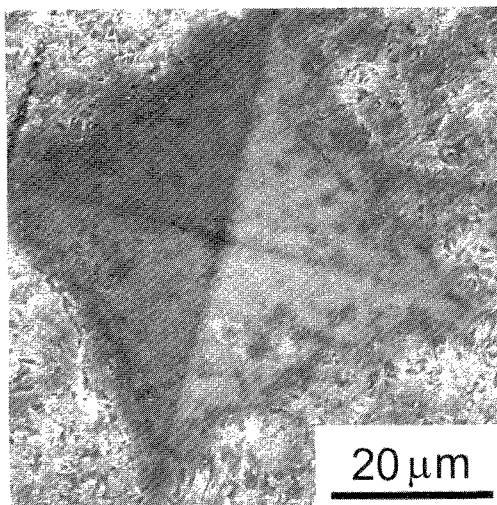


Fig.2 Indentation surface of the ZrO_2-C_{60} specimen sintered at $600^\circ C$.

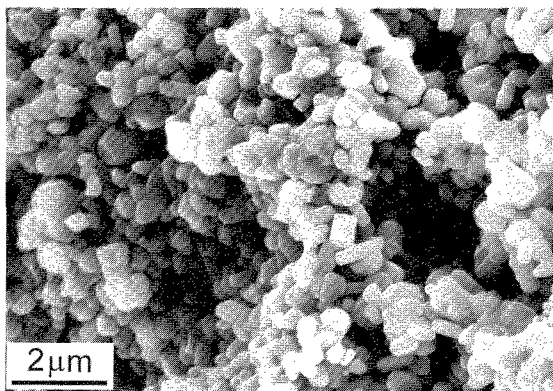


Fig.3 Fracture surface of the C_{60} -doped ZrO_2 specimen sintered at $900^\circ C$.

Although the hardness increased with increasing the sintering temperature, the present ZrO_2-C_{60} specimens are much softer than ordinal partially stabilized zirconia ceramics which exhibit ~ 1100 Hv.⁶ The indentation

surface of the specimen sintered at $600^\circ C$ (Fig.2) is found to be plastically deformed and flattened. The above ductile properties of the C_{60} -doped ZrO_2 specimens sintered at $600^\circ C$ may be explained by the fine ZrO_2 grain size of ~ 50 nm and the formation of thin carbon films covering the ZrO_2 grains, as shown in the following TEM observations. The specimen sintered at $900^\circ C$, however, was very brittle. Fig.3 shows a SEM image of the fractured surface of the specimen sintered at $900^\circ C$. The rugged image indicates that the sintered body is composed of strongly bonded parts and weakly bonded parts. The specimen sintered at $900^\circ C$ was shown to be composed of only monoclinic ZrO_2 ($m-ZrO_2$) by XRD.⁷ This fact may be a reason for the brittle nature of the specimen sintered at $900^\circ C$.

3.2 FT-IR analyses of the ZrO_2-C_{60} powders and the sintered ZrO_2-C_{60} specimens

Figs.4 and 5 show FT-IR spectra of the heat-treated ZrO_2-C_{60} powders and the sintered bulk specimens, respectively.

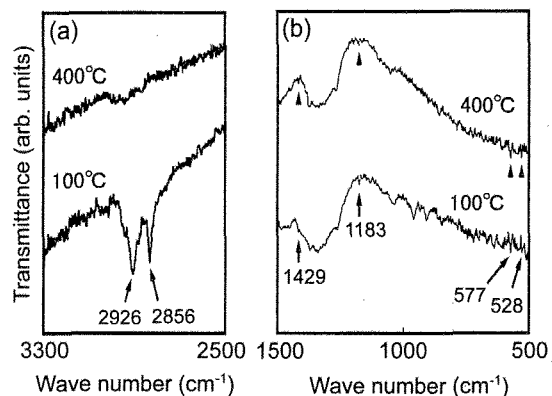


Fig.4 FT-IR spectra of the ZrO_2-C_{60} powders heat-treated at $100^\circ C$ and $400^\circ C$ in air. (a) shows the spectra for $C_{16}TMA$, and (b) shows those for C_{60} .

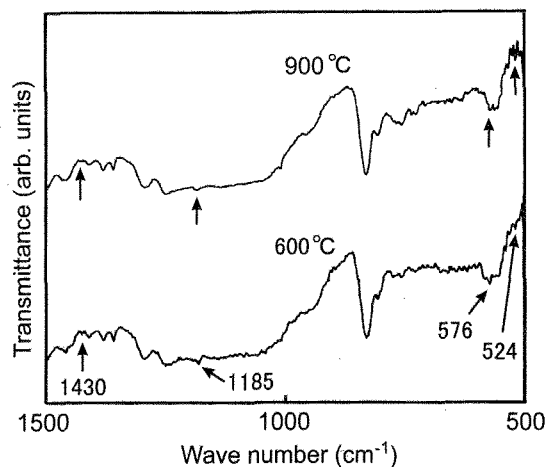


Fig.5 FT-IR spectra of the ZrO_2-C_{60} bulk specimens sintered at $600^\circ C$ and $900^\circ C$.

Both the figures show absorption peaks characteristic to C_{60} molecules at the places marked by arrows. The absorption peaks of C_{16} TMA become negligibly smaller in the powder heat-treated at 400°C as compared to the spectrum of the powder dried at 100°C (Fig.4(a)). This result shows that most of C_{16} TMA contained in the powder is decomposed by firing at 400°C . The absorption peaks of the sintered specimens also indicate the existence of C_{60} , although parts of the doped C_{60} transformed into different carbon allotropes as follows.

3.3 HVTEM observations of the sintered ZrO_2 - C_{60} bulk specimens

Fig.6 shows a direct evidence of remaining C_{60} in the specimen sintered at 600°C which was suggested in Fig.5. (220) planes of C_{60} (0.50 nm) are indicated there.

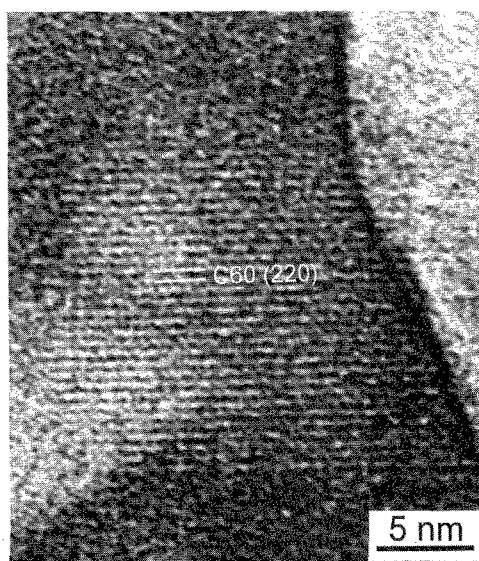


Fig.6 HVTEM image of a nanocrystalline precipitate of C_{60} observed in the specimen sintered at 600°C .

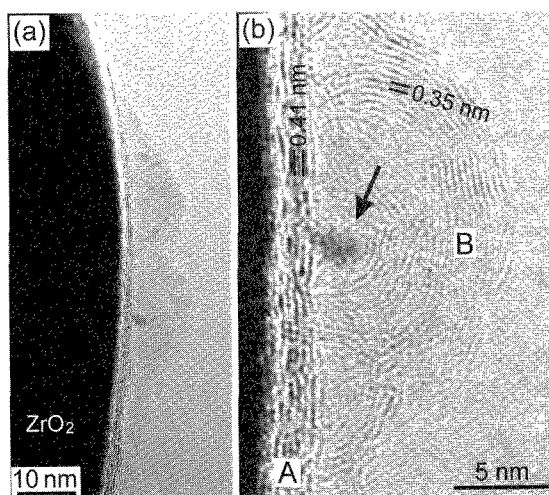


Fig.7 HVTEM images of a ZrO_2 grain surface covered with a thin graphitic film. (b) is a magnified image of (a).

Through a number of observations, however, no precipitates of C_{60} were found on the surface of ZrO_2 crystal grains. This result shows that the remaining C_{60} molecules are located apart from the surface of ZrO_2 grains.

Fig.7 shows a ZrO_2 grain covered with a thin film (A). The plane spacing of the onion shell structure of carbon (B) is 0.35 nm which is close to the basal plane spacing 0.3348 nm of graphite. The interlayer spacing of the graphitic film A, however, shows 0.41 nm which is much larger than that of B. The low-energy basal planes are formed to be in parallel with the round surface of the ZrO_2 grain. The graphitic film A must be the substance named "graphitizable carbon" which is graphitized at the temperature above $\sim 1800^\circ\text{C}$,⁸ because the wavy lattice planes with a plane spacing larger than that of graphite are observed. It is to be noted that a core is formed in the center of the onion shell structure (marked by arrow). The onion shell structure is very similar to a kind of carbon black which has a core in its center.⁹

The second type of carbon film covering the surface of ZrO_2 grain is shown as Fig.8 which exhibits an amorphous structure. This structure of carbon is classified as "non-graphitizable carbon". The non-graphitizable carbon is also called "glassy carbon" with a high hardness.

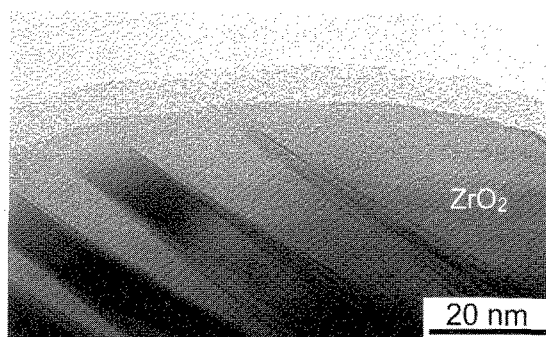


Fig.8 HVTEM image of a thin carbon film covering the surface of a ZrO_2 crystal grain.

The glassy carbon is reported to be suitable for wear-resistant applications when low contact stresses are imposed.¹⁰ The graphitic and amorphous carbon films are seen to wet the surface of ZrO_2 grains well. Since most of the added C_{16} TMA was shown to be decomposed in air by the heat treatment at 400°C , and the composition of the specimen sintered at 600°C was ZrO_2 -3.1mass%C which is very close to the initial nominal composition of ZrO_2 -3mass%C, the carbon films must have been formed by the transformation of C_{60} on the surface of ZrO_2 grains.

Fig.9 shows a film formed on a ZrO_2 crystal grain. The arrowed part is shown to peel off from the ZrO_2 grain surface, which confirms that the ZrO_2 grain surface is exactly covered with a monolayer film. The layer

spacing 0.60 nm is very close to the (11-0) plane spacing 0.5964 nm of a kind of carbyne "carbolite I" which was prepared by means of the arc discharge between carbon tips.¹¹ In the previous paper,¹² we reported the formation of carbyne in the C_{60} -doped ZrO_2 powder heat-treated at 500°C in air. Hence, it may be possible that the observed coating layer is composed of carbyne originating from the doped C_{60} molecules.

The above observations indicate that the surface of ZrO_2 grains acts as a catalyst that transforms C_{60} into various allotropes of carbon.

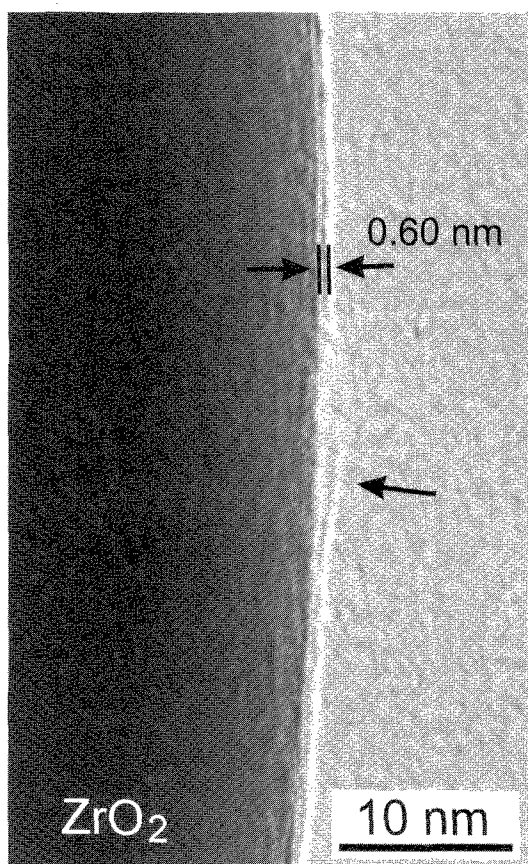


Fig.9 A monolayer film formed on a ZrO_2 grain in the specimen sintered at 600°C.

4. CONCLUSIONS

1. The ZrO_2 - C_{60} specimen sintered at 600°C was soft and deformed plastically, while the specimen sintered at 900°C was very brittle.
2. Remaining of C_{60} in the ZrO_2 - C_{60} specimen sintered at 600°C was confirmed by FT-IR and TEM.
3. ZrO_2 crystal grains covered with thin graphitic and amorphous carbon films were observed in the sintered specimens.
4. A monolayer film with a plane spacing which is very close to that of a kind of carbyne (Carbolite I) was found to be formed on the surface of a ZrO_2 crystal grain.

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