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TEM Investigation of the Substances Formed by Decomposition of C_{60}

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Abstract

Substances formed by decomposition of C_{60} in C_{60}-doped zirconia (ZrO_2) and copper (Cu) powders are examined by TEM. The C_{60}-doped ZrO_2 powders were prepared from toluene solutions of zirconium alkoxide and C_{60}. The C_{60}-doped Cu powders were prepared by mechanical mixing of C_{60} and Cu. Transformations of C_{60} into graphite and "n-diamond" were observed in both the C_{60}-doped ZrO_2 and Cu powders, while carbyne and an unknown form of carbon closely resembling a substance which was reported by Vora and Moravec[1] were observed only in the heat-treated C_{60}-doped ZrO_2 powders.

Key words : C_{60}, fullerene, zirconia, tribology, composite, ceramics, sol-gel

1. INTRODUCTION

C_{60} molecules have been recognized in general as a promising material for various mechanical and electrical applications. Since C_{60} molecules have a spherical shape and are expected to have a very high bulk modulus,[2] formation of composites of C_{60} and ceramics or metals will be an efficient method to fabricate new tribological materials. From this point of view, attempts to form composites of C_{60} and ceramics were performed for zirconia (ZrO_2) that were prepared from the solutions containing an alkoxide of Zr and C_{60}.[3] In this study, we found that part of the doped C_{60} molecules transformed into graphite by heating at high temperatures. Mechanical mixing of the powders of C_{60} and metals is also an efficient method to form composites of metals and C_{60}. However, it was found that the doped C_{60} partly transforms into graphite during the mechanical mixing with copper (Cu).[4] The purpose of this paper is to present various forms of carbon that were found in the C_{60}-doped ZrO_2 and Cu powders prepared by sol-gel processing or mechanical mixing.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of the C_{60}-doped ZrO_2 powders

Toluene solutions of C_{60} and zirconium tetra n-propoxide (ZNP, Soekawa Chemicals, Japan) were prepared, stirred for 24h and aged for 72h. at room temperature until their gelation occurred. The concentration of ZNP in the solutions was fixed to be 0.1M ZNP. The C_{60}-doped ZNP gels were heated at 110°C in a vacuum furnace in order to obtain dried gel powders. These gel powders were heat-treated at 400°C ~ 500°C for 30min in Ar or in air to decompose and eliminate the contained hydrocarbons, and then C_{60}-doped ZrO_2 powders were obtained.

2.2 Mechanical mixing of Cu and C_{60} powders

Powders of Cu (99.8%, 200 mesh) and C_{60} were taken into a yttria-toughned zirconia (YTZ) pot (inner diameter 44 mmϕ, depth 40 mmϕ) with ten YTZ balls (diameter of 10 mm) in a drying box of N_2 atmosphere. The powder composition was fixed to be Cu-4.5 mass% C_{60}. The YTZ pot was shaken by a mechanical mixer (SPEX 8000 Mixer/Mill) with a frequency of 20Hz for 1h ~ 128h in order to obtain the compounds of C_{60} and Cu.

2.3 Structural characterization of the C_{60}-doped ZrO_2 and Cu powders

Structure of the specimens was examined by TEM (Jeol 2000FX, Hitachi H800, H9000). As-received new micro (plastic) grids formed on Cu or Mo meshes for TEM observations were minutely examined before use in order to identify extraneous substances stuck to the microgrids.

3. RESULTS AND DISCUSSION

3.1 Extraneous substances observed in as-received empty new microgrids

Various extraneous substances were observed in as-received empty new microgrids prepared on Cu and Mo meshes. One example is shown in Fig.1. The substance is identified as graphite from the electron diffraction pattern (EDP). The extraneous substances like Fig.1 are presumed to have stuck to the supporting plastic grids in the time of coating of reinforcing carbon films.

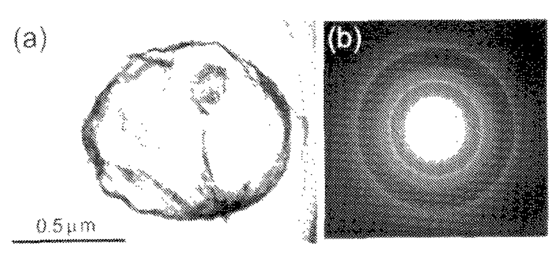

Fig.1 (a)TEM image and (b)EDP of an extraneous substance found in an as-received empty microgrid.

Fig.2(a) shows another e
is marked by arrow A. An EDX analysis (b) of this dark substance showed that it is composed of Cu. Tiny Cu particles marked by the smaller arrows with a size of 100nm order appeared on the microgrid when the Cu precipitate (A) was irradiated by a concentrated electron beam. This phenomenon is similar to that observed in the following mechanical mixing of C_{60} and Cu. The Cu particles are considered to have been formed by the deposition of Cu atoms sublimated from the precipitate A.

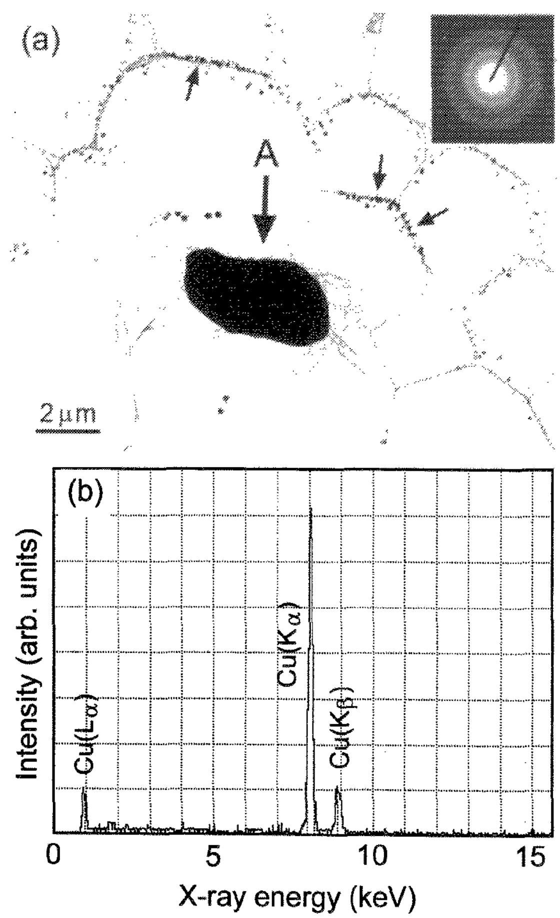

Fig.2 (a) TEM image of an extraneous substance (A) found in an as-received empty microgrid and the diffraction pattern of the tiny particles shown by the smaller arrows. (b) EDX spectrum of the substance A.

The above impurity substances like graphite and Cu precipitates were carefully eliminated in the following TEM observations.

3.2 TEM analyses of the C_{60}-doped ZrO_2 powders

Fig.3 shows a typical TEM image of a C_{60}-doped ZrO_2 powder, where C_{60} exists as a precipitate with a size of about 1μm.

In a C_{60}-doped ZrO_2 powder fired at 500°C in air, a precipitate of C_{60} with a mosaic structure was observed, and showed an EDP without 200 reflection spots (Fig.4). The absence of 200 reflection spots is characteristic to a pure C_{60} crystal.[5] Since C_{60} decomposes into CO and of C_{60} occurs at temperatures above 450°C, the appearance of the mosaic structure is considered to be due to a partial decomposition of C_{60}.[6]

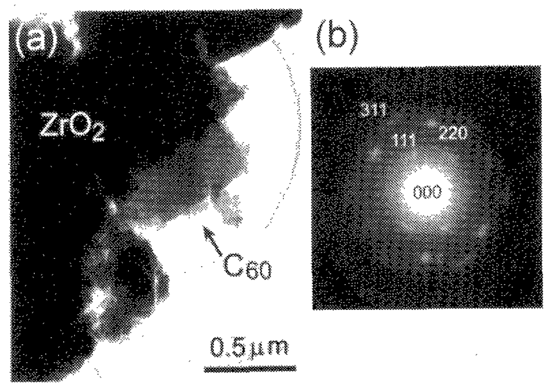

Fig.3 (a)TEM image and (b) EDP of a C_{60}-doped ZrO_2 (ZrO_2-2mass%C) powder fired at 400°C for 30min.

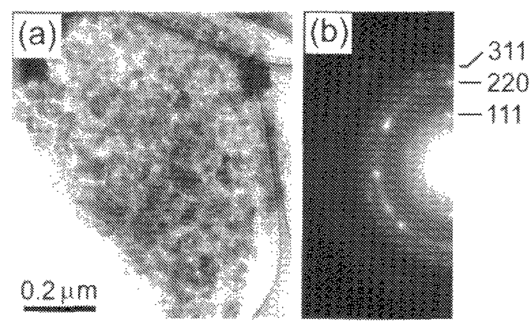

Fig.4 (a)TEM image and (b)EDP of a precipitate of C_{60} found in a C_{60}-doped ZrO_2 powder (ZrO_2 - 0.8mass% C) fired at 500°C for 30 min in air.

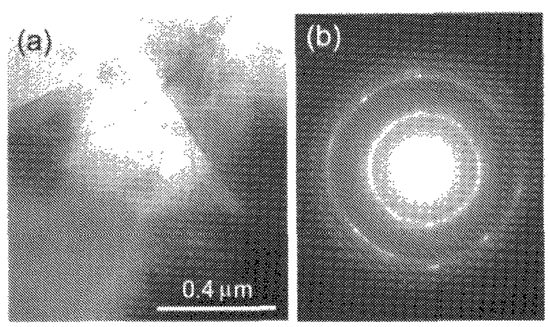

Fig.5 (a)TEM image and (b)EDP of graphite found in a C_{60}-doped ZrO_2 powder (ZrO_2 - 0.8mass% C) prepared by firing at 500°C for 30 min in air.

Although the C_{60} molecules doped into ZrO_2 were observed to remain after the heat treatment at 500°C in air, them were found to transform partly into the other forms of carbon. Fig.5 shows a formation of graphite which has the capsule-like graphite particles marked by the arrows.

A substance different from graphite was also observed as shown in Fig.6, where it can be indexed by a FCC structure with a lattice constant a = 0.357 ± 0.003 nm. Although this lattice constant is very close to that of diamond (a=0.357nm), the diffraction pattern shows an excitation of 200 reflections forbidden to diamond. This diffraction pattern can be explained by "n-diamond" which was reported by Hirai and Kondo in the study of shock-compressed graphite sheets.[7]

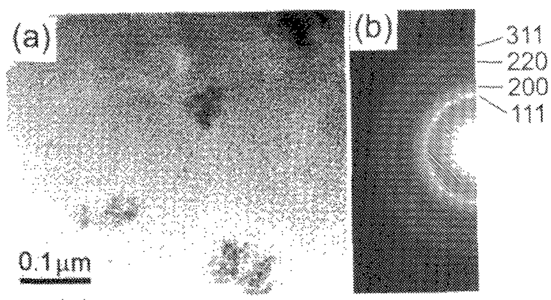

Fig.6 (a)TEM image and (b) EDP of a substance found in a C_{60}-doped ZrO_2(ZrO_2-0.8mass%C) powder fired at 500°C for 30 min in air.

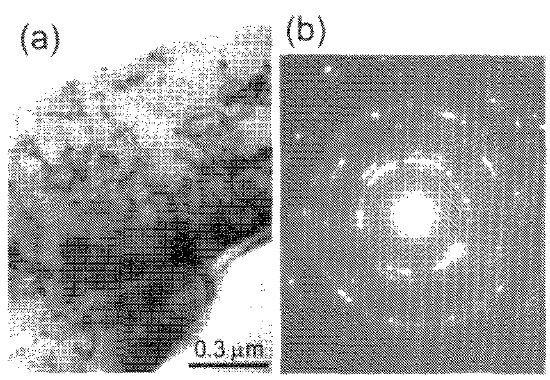

Fig.7 (a)TEM image and (b) EDP of an unknown form of carbon observed in a C_{60}-doped ZrO_2 powder (ZrO_2-2mass%C) prepared by firing at 500°C for 30 min in air.

The third form of carbon different from C_{60} is shown in Fig.7. The EDP of Fig.7(b) closely resembles the EDP shown in an experiment of rf plasma decomposition of butane by Vora and Moravec.[1]

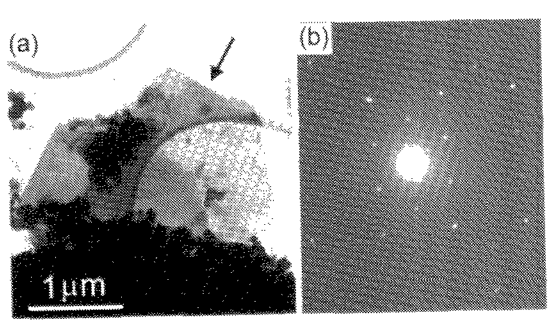

Fig.8 (a)TEM image and (b)EDP of carbyne found in a C_{60}-doped ZrO_2 powder (ZrO_2-2mass%C) fired at 500°C for 30 min in air.

The final form of carbon found in a C_{60}-doped ZrO_2 powder is presented in Fig.8 which shows a planar shape with a diffraction pattern of hexagonal symmetry. The habit planes are appearing to have a hexagonal symmetry, too. The substance is considered to be a kind of carbyne, because the plane spacing $d_{11\bar{2}0}$ indexed according to the paper by Kudryavtsev and Evsyukov[8] is 0.439 nm, and is consistent with the values $d_{11\bar{2}0}$ =0.435~0.446nm of carbyne.[8]

In our experiment, carbyne and the carbon shown in Fig.7 were found only in the C_{60}-doped ZrO_2 powders fired at 500°C in air, although graphite and "n-diamond" were observed in both the C_{60}-doped ZrO_2 powders and the mechanically mixed Cu-C_{60} powders as shown later. This result indicates that transformation of C_{60} into graphite and "n-diamond" easily occurs and does not need a strong thermal activation process.

3.3 TEM observations of C_{60}-doped Cu powders prepared by mechanical mixing

Dark particles as shown in Fig.9 were often observed in the mechanically mixed C_{60}-doped Cu powders. When the particles marked by A and B were irradiated by a concentrated electron beam, tiny particles (marked by the arrows in photo(a)) with a size of 10nm order appeared in the area around the irradiated particles. Continuing the electron beam irradiation, the dark particles changed their shape(photo (b)), and round particles (for example, marked by C) appeared, as if they were melt by the electron beam irradiation. In the part marked by D, a fibrous structure like cotton appeared.

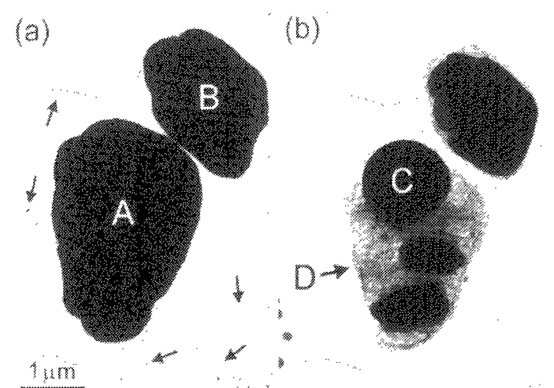

Fig.9 TEM images of compound particles in a C_{60}-doped Cu powder mechanically mixed for 128h.

Fig.10 shows an EDX analysis of a compound of the same kind as Fig.9. The peak of Mo is from the microgrid mesh. The EDX spectrum shows that the marked parts A and B are composed of Cu. It is clear that these Cu particles originated from the wear debris produced by the mechanical mixing.

The arrowed tiny Cu particles in Fig.9(a) must have been formed by an evaporation of Cu atoms during the electron beam irradiation and their deposition on to the microgrid.

Fig.11 shows magnified images of the cotton-like structure. The EDPs show that the fibrous parts are composed of graphite. The fibrous graphite structure formed at the early stage of mixing and turned to a granular structure with increasing mixing time.

The appearance of fibrous structure in the beginning of mechanical mixing suggests a formation of polymerized C_{60} molecules. This conjecture may be supported by the paper that C_{60} dimers are suggested to form in the mechanical alloying of C_{60}.[9]

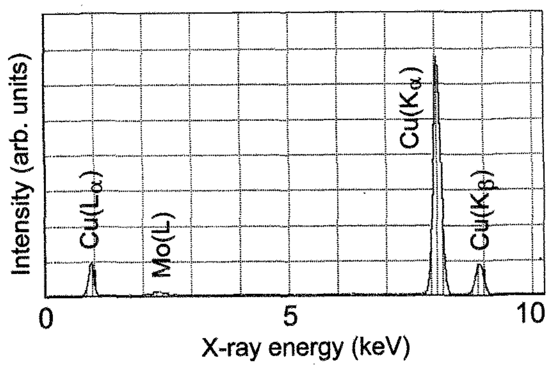

Fig.10 EDX analysis of a compound in a mechanically mixed C_{60}-doped Cu powder.

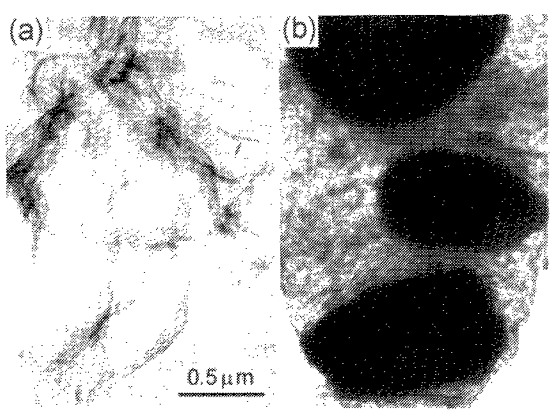

Fig.11 TEM images of compound particles in the C_{60}-doped Cu powders which were mechanically mixed for (a)2h and (b)128h, respectively.

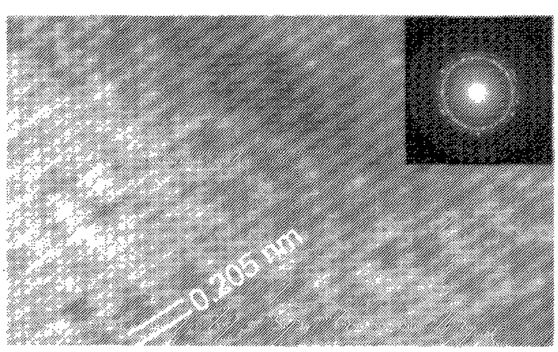

Fig.12 HRTEM image of a powder of C_{60}-doped Cu which was mechanically mixed for 32h.

Fig.12 shows a HRTEM image of a particle mechanically mixed for 32h. The diffraction pattern of the particle shows a FCC structure with a lattice constant a=0.355±0.002 nm. The straight lattice image clearly shows that a substance different from graphite, which is judged to be "n-diamond" here, was formed.

4. CONCLUSIONS

1. In the powders of C_{60}-doped ZrO_2 heat-treated at 500°C for 30 min in air, part of the doped C_{60} transforms into graphite, "n-diamond", carbyne and an unknown form of carbon with the same lattice constant as that reported by Vora and Moravec.[1]

2. In the Cu powders mechanically mixed with C_{60}, "n-diamond" and graphite are formed. The graphite shows a fibrous structure in the beginning of mechanical mixing, while the fibrous structure turns to a granular structure with increasing mixing time.

3. The wear debris of Cu produced by the mechanical mixing with C_{60} is melted by an irradiation of concentrated electron beam.

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