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Effect of degradation on surface and mechanical properties of C_{60} and C_{60}/C_{70} single crystals

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Abstract

High purity C_{60} and C_{60}/C_{70} mixed crystals have been exposed to air at room temperature for about two years. The surface observations with optical microscope show that the mixed crystals degraded extensively due to photopolymerization than the pure C_{60} crystals. The mechanical properties of the crystals were investigated using the Vickers microhardness indentation technique.

Keywords: Fullerenes; Crystal growth; Surface degradation; Microhardness

1. Introduction

The discovery of fullerenes [1] and later developments in the preparation and isolation methods [2] have attracted considerable attention of the scientific community due to the technological and commercial significance of their counterparts graphite and diamond. The physical, chemical and electronic properties of C_{60} and C_{70} have been studied extensively. The most important among the physical properties are the stability and mechanical properties. Several studies have already been carried out on the air oxidation nature of C_{60} under different conditions and many controversial results have been reported [3–9]. Taylor et al. [3] illustrated that C_{60} in solution is affected by light and oxidation. Later it was shown that even the pure C_{60} powder kept in standard

conditions (room temperature and ambient pressure) absorb a few percentage of oxygen leading to non-sublimable residues [4]. Irradiation of C_{60} thin films to UV/visible light under ambient pressure produces an amorphous carbon (a-C) product insoluble in toluene [5].

The photosensitive nature of C_{60} leads to the instability of C_{60} single crystals when subjected to different conditions such as (i) crack lines develop on the surface of the C_{60} crystals when exposed to light [6–8], (ii) the exposition of C_{60} crystals to UV/visible light results in toluene insoluble residues and the polymerized crystal surfaces exhibit high resistant to thermal sublimation than the interior portion of the crystal [4], (iii) the laser irradiation of C_{60} single crystals yields an amorphous carbon in oxygen atmosphere while the crystal remains unaffected in an inert atmosphere [9].

In most of the above cases, C_{60} crystals have been subjected to the said conditions comparatively for a shorter duration and also there has been no

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mention about the role of impurities (especially higher fullerenes) on the surface degradation of fullerene crystals. Also there exists a limited number of reports on the hardness studies of C_{60} crystals which is known to be quite sensitive to the presence of impurities and the crystal structure of the material [10–12]. The requirement of high quality crystals of sufficiently large size restricts the systematic studies on the load dependence of hardness, especially, the role of degradation on the mechanical properties of the C_{60} crystal.

We have grown C_{60} and C_{60}/C_{70} single crystals by sublimation method using pure C_{60} and fullerene mixture as source materials [13]. Solvent and other hydrocarbon impurities have been removed during crystal growth adopting modified growth procedure [14]. The present work aims at the studies on the effect of degradation due to the prolonged exposition of C_{60} and mixed C_{60}/C_{70} crystals to air at room temperature (about two years). The surface features of the exposed crystals have been studied with optical microscope. Vickers microhardness studies have been carried out on the C_{60} and mixed crystals. Single crystal and powder X-ray diffraction analyses have been carried out to confirm the crystallinity of the samples. High Pressure Liquid Chromatographic (HPLC) studies have been carried out to find the purity and composition of the C_{60} and C_{60}/C_{70} crystals.

2. Experimental

The fullerene containing soot has been prepared by the conventional electric arc technique [2]. The pure C_{60} has been separated from the fullerene mixture by liquid chromatography. High purity C_{60} and mixed C_{60}/C_{70} crystals have been grown using fullerene mixture as the source material [13]. Large sized solvent free crystals have been grown by the physical vapor transport method using a two-segment quartz ampoule and two-zone furnace as described elsewhere [14]. The HPLC analysis on a Vydac C18 reverse-phase column using toluene/acetonitrile (1:1 v/v) as an eluent to confirm the purity of the C_{60} crystals and the composition of C_{60} and C_{70} in the case of mixed crystals. For HPLC studies samples have been prepared by

dissolving the grown crystals in toluene [14] and chromatogram was monitored by a UV detector ($\lambda = 310$ nm). The grown crystals were kept exposed in air at room temperature for about two years. The surface features of the exposed crystals were studied using Optical Microscope.

Powder X-ray diffraction studies were carried out using a Siemens D-500 powder diffractometer and low-background specimen holder made of Si(911) single-crystal wafer [15]. The sample for XRD was prepared by mechanically crushing a few tiny crystals of C_{60} into powder. Single crystal X-ray diffraction analysis was carried out on the C_{60}/C_{70} crystal with Philips PW1100 diffractometer using $MoK\alpha$ ($\lambda = 0.71069$ Å) radiation.

Hardness measurements were carried out on both the pure C_{60} and C_{60}/C_{70} crystals by subjecting them to the static indentation tests in air at room temperature (300 K) using Leitz Wetzler microhardness tester fitted with Vickers pyramidal indenter and attached to a Leitz incident light microscope. Crystals with well developed facets were selected for the hardness measurements and fixed on clay to keep the desired crystal face perpendicular to the diamond indenter. The indentations were made for different loads and the contact period of the indenter with the specimen was maintained as 10 seconds for all the cases. The microhardness value was taken as the average of the indentations made, with both diagonals being measured. Several trials of indentations at each load were carried out and the Vickers hardness number was estimated from the relation

$$H_v = 1.8544 p/d^2 \text{ kg mm}^{-2},$$

where H_v is the Vickers hardness number, p is the applied load and d is the diagonal length of the indentation impression.

3. Results and discussion

High purity C_{60} and C_{60}/C_{70} single crystals have been grown by sublimation method. Well faceted, defect free crystals with dimensions up to 2–3 mm were obtained. Powder X-ray diffractogram of pure C_{60} crystals reveals that the crystallites form in fcc structure with a lattice value of 14.16 Å which agrees well with the standardized powder data [16].

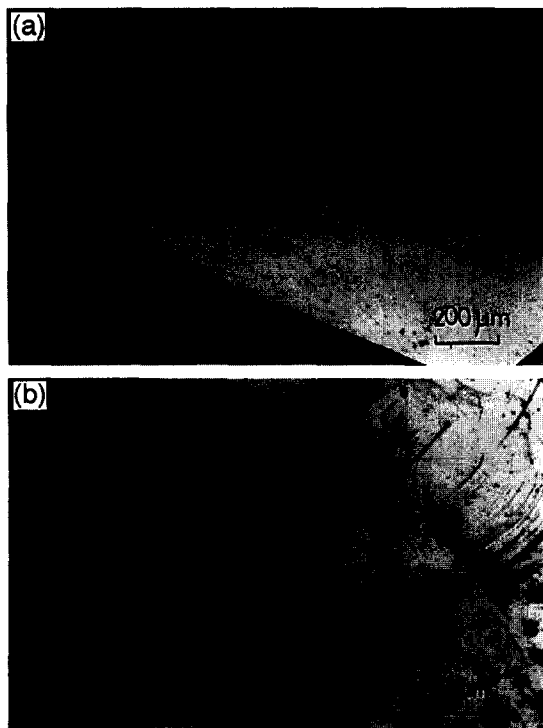


Fig. 1. Optical micrograph of (a) a typical C_{60}/C_{70} mixed crystal (98:2), (b) an instability pattern with macrosteps at one edge.

Fig. 1a shows the optical micrograph of the as grown C_{60}/C_{70} mixed crystal. Many rectangular bars of the similar kind have been obtained in a single run which indicates that the crystals grow faster in the lateral direction than in the vertical direction. This can be understood from the fact that the crystal habits and morphology varies with respect to the nature and quantity of the dopants incorporated into the crystals [17,18]. In the present work, morphology of the mixed C_{60}/C_{70} crystals were found to vary from rectangular bar shape to an elongated hexagonal prism shape depending upon the percentile of C_{70} incorporated in the crystal. HPLC studies show the presence of C_{60} and C_{70} in the ratio of 92:8 in the hexagonal shaped crystals. Single crystal X-ray analysis reveals that the crystal forms in an hexagonal close packed (hcp) structure with lattice values of $a = 10.042(2)$ Å and $c = 24.607(2)$ Å. When the content of the C_{70} exceeds 10%, an instability pattern appears on the grown crystal with different surface features. Fig. 1b shows one such feature with macrosteps on a crystal surface

with the step edges pointing towards the inner part of the crystal. The steps have not been distributed uniformly on the surface and they appear to be bunched in some portions of the surface. This can be due to non-uniformity in the supersaturation caused by the irregular mass transport of the C_{60}/C_{70} vapors from the source zone to the growth zone or due to the slight thermal fluctuation on the surface of the crystal during the growth. The crystal edges and corners usually favor the nucleation of new layers and therefore be able to spontaneously generate macrosteps. Further increase in the composition of the C_{70} results in the shapeless crystalline flakes with microcrystallites embedded on the surface.

Fig. 2a and Fig. 2b show surface features of the mixed C_{60}/C_{70} crystal (Fig. 1a) after two years of exposition to atmosphere. The surface is found to be deteriorated extensively and it becomes “brownish” in color with tiny particulates embedded on the surface. Oxidation on the outer surface of the crystal must be the cause for the destruction of the surface.

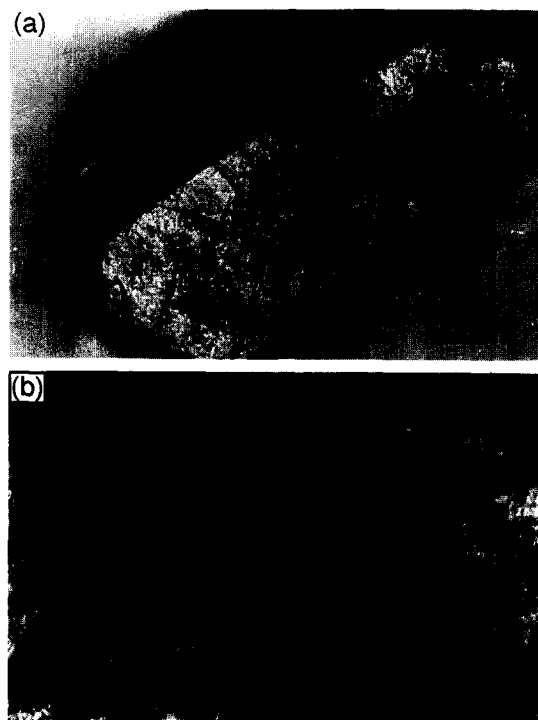


Fig. 2. Optical micrograph of (a) mixed crystal after two years of exposition to atmosphere, (b) the same surface at higher magnification.

The pure C_{60} crystals have not been affected to this extent. Also there has been no observable changes in the color of the crystal. Fig. 3a shows one of the pure C_{60} crystals exposed to the atmosphere to the same duration as that of mixed crystal. Crack lines have been observed on the surface of the C_{60} crystals. These kind of cracks have already been reported for the crystal which has been exposed to light [6–8]. In our case, the cracks have not appeared on all the crystals. The observed cracks could have developed internally due to the thermal strain during the growth and have become more significant and visible when exposed to the ambient atmosphere. The above surface features suggest that the pure C_{60} crystals offer more resistance to oxidation and the impurities such as higher fullerenes and crystal imperfection of the mixed crystals accelerate the degradation of the C_{60}/C_{70} crystal. This result is in accordance with the reports that the C_{70} is more sensitive to the oxidation than C_{60} [19–21].

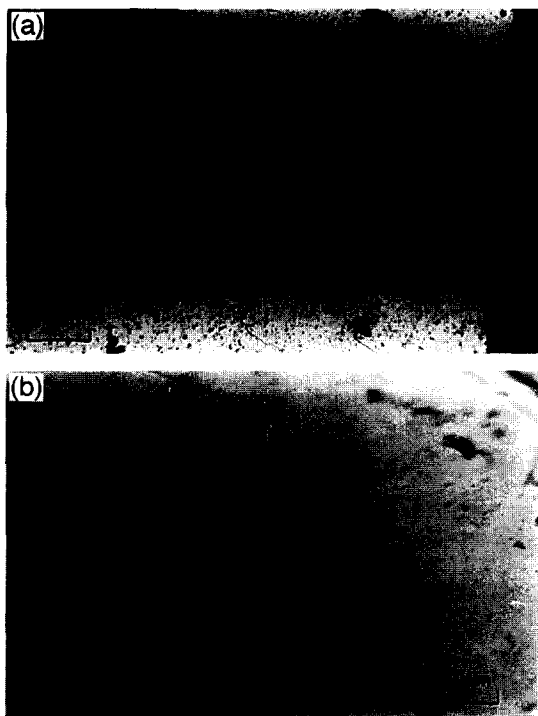


Fig. 3. (a) Crack line observed on a pure C_{60} crystal. (b) Indentation mark for a load of 100 gm on (111) face of pure C_{60} crystal.

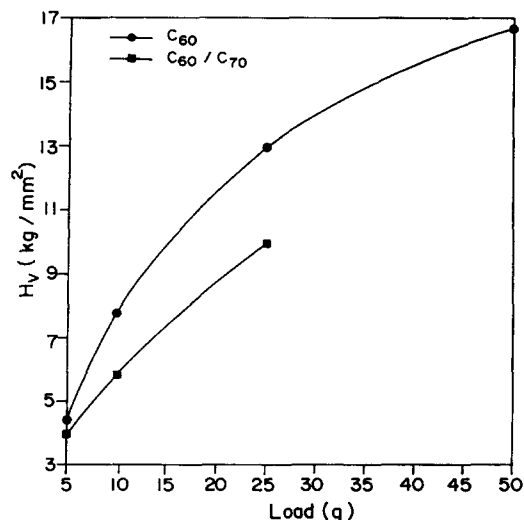


Fig. 4. Vickers hardness as a function of applied load for pure C_{60} crystals (●) and for mixed C_{60}/C_{70} crystal (■).

Fig. 4 shows the variation of Vickers hardness H_v with applied load on the (111) face of pure C_{60} crystal and mixed C_{60}/C_{70} crystal. In both the cases, the hardness value increases with the increase of the load. A systematic slip line develops at the load above 50 gm for pure C_{60} crystal (Fig. 3b) and for mixed crystals at above 25 gm. It can be noticed that the hardness value of pure C_{60} crystal is more than that of the mixed crystal. The recent report shows that the hardness value of C_{60} crystal on the (111) face is 22 kg/mm² and is independent of load at room temperature under nitrogen atmosphere for the load in the range of 3 to 14 gm [22]. The other two reports indicate the hardness values of 17.5 kg/mm² for vapor grown single crystal [10] and 1.2–1.8 kg/mm² for polycrystals grown by the solution method [23]. In the present case, the hardness value of both the crystals depends much on the applied load and can be attributed to the surface hardening due to photopolymerization.

4. Conclusion

Simple optical microscopic studies of fullerene crystals show that the purity of the material plays an important role in the surface degradation even at ambient pressure and temperature. The results indicate that C_{60} offers more resistance to oxidation than

C_{70} . Vickers microhardness studies show that the pure C_{60} crystal is harder than the C_{60}/C_{70} mixed crystal.

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