

Micro-texture and structure of high-pressure quenched graphite

Hiroaki Ohfuji[1]; Kaoru Aibara[2]; Hitoshi Sumiya[3]; Tetsuo Irifune[1]

[1] GRC, Ehime Univ.; [2] Earth science, Ehime Univ.; [3] R&D, Sumitomo Electric

Graphite is composed of loosely stacked layers of graphene sheets in which sp²-hybridized carbon atoms are arranged in a honeycomb pattern. It is well-known that graphite transforms into cubic diamond, which consists of sp³-hybridized carbons, under high pressure and high temperature conditions. The pressure induced structural change of graphite at room temperature has also been of interest to material scientists, and several experimental studies have been reported in the past decades. In-situ x-ray diffraction studies suggested that graphite transforms to hexagonal diamond (or analogous structure) upon static compression to ~18 GPa at room temperature, although the transformation is fully reversible and the high-pressure phase is not quenchable to ambient conditions (e.g. Utsumi and Yagi, 1991; Yagi et al., 1992; Mao et al., 2003). Micro-Raman investigation of graphite sample recovered from 72 GPa by Schindler and Vohra (1995) reported the formation of cubic diamond-like phase in the product, whereas in-situ Raman study by Goncharov (1991) suggested that graphite-diamond transformation does not take place below 80 GPa. So, the structural characteristics of graphite under high pressure at room temperature and its quenched form have still been controversial. Here, we investigated the micro-texture and structure of such high-pressure quenched graphite using high-resolution electron microscopy in order to visualize the local structural changes recorded in the sample.

Room temperature compression of graphite was carried out in a diamond anvil cell (DAC) with a culet size of 250 μm in the pressure range of 10-90 GPa. Highly oriented pyrolytic graphite (HOPG) sheet (45 or 70 μm thickness) was laser cut into a small disc and leaded into a 70 μm hole, drilled in a preindented Re gasket, without a pressure medium. The sample was compressed to 10 ~90 GPa at room temperature, kept at the desired pressure at least overnight, and then quickly decompressed. The recovered samples were examined by Raman spectroscopy, high-resolution scanning electron microscopy (FE-SEM) and transmission electron microscopy (HRTEM). A focused ion beam (FIB) was employed to fabricate thin cross-sections of the samples for TEM analysis.

Graphite samples recovered from pressures above 20 GPa are characterized by the formation of spherical to rod-shaped particles (dia. 100-200 nm) along cracks which occurred extensively in the sample during decompression and edges of fragmented (cleaved) graphite flakes. HRTEM observation of the FIB sections revealed that the spherical particles are composed mainly of amorphous carbon and a small amount of nano-fragments of graphene layers, which have the same interlayer spacing ($d_{002} = 0.34$ nm) as the starting material, but are considerably distorted. The interface between the particles and basal graphite is unclear and the transition from crystalline to amorphous phases seems to be continuous. In the sample recovered from the highest pressure (~90 GPa), nanometric domains characterized by linear lattice fringes with a spacing of ca. 0.21 nm, which is equivalent to that of diamond (111), were observed in the core of the spherical particles. These results suggest that (1) the breakdown of sp²-hybridized carbon atoms in graphene to form sp³-hybridized species (amorphization) occurs at pressures above 20 GPa at room temperature, and (2) local ordering of sp³-carbon atoms (diamond nucleation) may be achieved preferably at such environment.