Materials Letters 183 (2016) 14–18

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Nano-diamond obtained from adipic acid at ultra-high pressures

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ARTICLE INFO

Article history:
Received 11 July 2016
Accepted 15 July 2016
Available online 16 July 2016

Keywords:
Nanocrystalline materials
Grain boundaries
Carbon materials
Nano-diamond
Ultra-high pressures

ABSTRACT

Adipic acid was used in this work as a carbon-containing precursor for the HPHT synthesis of a carbon sample containing nano-diamond. The carbon sample consists of lamellar diamond nano-grains of about 30–50 nm embedded in an amorphous or poorly crystallized carbon matrix. The carbon sample comprises mainly sp^2-hybrydized carbon in form of graphite or amorphous carbon.

1. Introduction

Traditionally, synthetic diamond grits and diamond-based materials, polycrystalline diamond containing a Co-based binder (PCD), are manufactured by high-pressure high-temperature (HPHT) processes at pressures above 5 GPa with the aid of Fe-group metals having a catalytic effect on the transformation of sp^2-hybridized carbon into diamond.

Another route for the diamond fabrication is based on the direct conversion of carbon-based precursors, usually graphite or amorphous carbon, at pressures of above nearly 12 GPa [1,2]. In the beginning of the 2000's it was shown that it is possible to fabricate nano-diamond with a mean grain size of below 100 nm by the direct conversion of graphite into pure polycrystalline diamond (see e.g. refs. [3,4]). The nano-diamond obtained in such a way is characterized by superior hardness, cutting performance and other properties [5–8]. Different carbon-based sp^2-hybridized precursors were employed for the fabrication of nano-diamond by use of the direct conversion process [3,9–11] and it was established that their behavior is different with respect to the nano-diamond formation.

It can be expected that the employment of organic precursors could facilitate the formation of nano-diamond at high temperatures and ultra-high pressures, especially when the precursors contain significant amounts of oxygen. Oxygen is thought to react with hydrogen during the decomposition of such organic precursors resulting in the formation of high-pressure water vapor in a capsule employed for HPHT experiments at high temperatures and ultra-high pressures. As a result, the formation of nano-diamond can be enhanced and also metastable forms of carbon might be obtained.

The major objective of this work was to evaluate the possibility of the nano-diamond formation by use of an organic oxygen-containing precursor at ultra-high pressures.

2. Experimental details

Adipic acid with the formula $(CH_2)_4(COOH)_2$, which is a powder at room temperature, was used in this work as a precursor for the direct conversion into a carbon sample containing nano-diamond grains. The sample was compressed using a custom-built 5000-ton multi-anvil press at a temperature of 1235 °C and pressure of 14 GPa for 1 h. The adipic acid powder was placed inside a thin graphite sleeve and welded into a 2 mm diameter gold capsule. A 0.025 mm thick piece of molybdenum foil was placed at the bottom of the capsule to fix the oxygen fugacity. The capsule was carefully compressed to produce a cylinder 3.5 mm long and placed inside a cylindrical sleeve made of hexagonal boron nitride (h-BN). The capsule and sleeve was placed at the center of a LaCrO3 (Sr-doped) cylindrical heater. Space below the capsule was filled with an MgO cylinder, while from above a W3%Re-W25%Re (type d) thermocouple inside a 4-bore alumina tube was inserted through a further MgO sleeve. The furnace was surrounded by a ZrO2 insulator. The entire assembly was placed into a 6.8 mm diameter hole bored into an 18 mm edge length MgO (Cr2O3-

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http://dx.doi.org/10.1016/j.matlet.2016.07.065
0167-577X/

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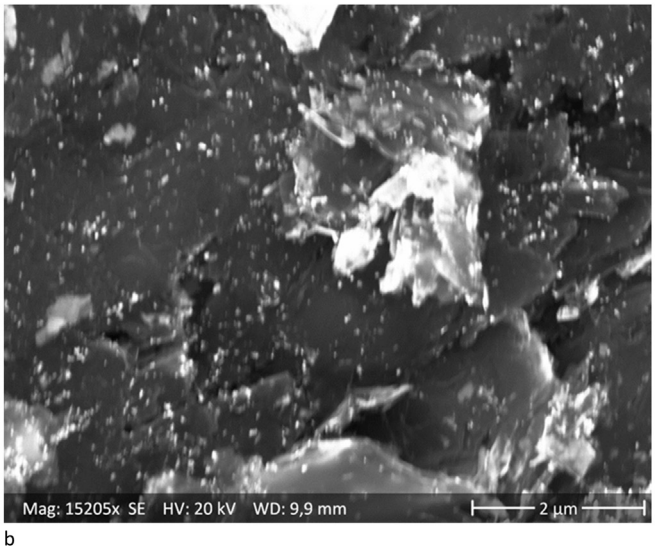

b

Fig. 1. Appearance of the carbon sample after the HPHT process: a – golded capsule with the carbon sample, and b – HRSEM image of the carbon sample.

doped) octahedral. The octahedral was compressed at the center of 8 tungsten carbide cubes, each with an 11 mm corner truncation. Further experimental details can be found in ref. [12].

After HPHT equilibration, the recovered carbon sample was examined by high-resolution scanning electron microscopy (HRSEM) by use of a Philips XL30S instrument, transmission electron microscopy (TEM) and electron diffraction by use of a JEOL 3000F instrument. A JEOL ARM 200F aberration corrected TEM operating in the STEM mode was used to acquire the Electron Energy Loss Spectra (EELS).

3. Results and discussion

After performing the HPHT experiment it was possible to easily cut the golden capsule by a steel blade, so that the carbon sample was relatively soft providing evidence that it consists of mainly sp^2-hybrized carbon. Fig. 1a shows the appearance of the capsule with the carbon sample in the middle indicating that the carbon sample has a dark-grey color. Fig. 1b shows its HRSEM image indicating the presence of fine precipitates (below roughly 100 nm) embedded in an apparently amorphous matrix.

Fig. 2a to Fig. 2c show TEM images of the carbon sample taken at different magnifications. It can be seen that there are a number of apparently crystalline lamellar nano-grains in the sample of nearly 30–50 nm in size. It would appear that the nano-grains are embedded in a poorly crystalline or amorphous carbon matrix.

A number of diffraction patterns, a typical example of which is shown in Fig. 3d, were taken from different areas of the sample. Most areas display the typical pattern of diamond or hexagonal carbon structures. The diffraction pattern shown in Fig. 3d provides clear evidence for the presence of nano-diamond in the sample, as all the reflections of cubic diamond indicated in Fig. 3d can be seen in the electron diffraction pattern.

Fig. 3a and Fig. 3b show STEM images of two areas of the carbon sample, where EEL spectra were taken. Fig. 3c and Fig. 3 d show the EEL spectra indicating the presence of mainly amorphous carbon in the sample.

Using equation of state data [13] and under the assumption of ideal mixing it is possible to calculate that under the conditions of the experiment where the oxygen fugacity was buffered by the presence of Mo-MoO_2, the composition of the fluid formed by the breakdown of adipic acid comprised 60% H_2O and 40% CH_4.

Thus, the carbon sample obtained from adipic acid at ultra-high pressures consists of diamond nano-grains embedded in the amorphous or poorly crystallized carbon matrix. The carbon sample comprises mainly sp^2-hybrydized carbon in form of graphite or amorphous carbon. No additional metastable forms of carbon, which were expected to form as a result of the presence of high-pressure water vapor in the capsule during the HPHT experiment, were found in the sample. Nevertheless, the formation of nano-diamond at the relatively low temperature used in this work (1235 °C) provides evidence that the employment of adipic acid as a precursor can simplify the nano-diamond synthesis, as conventionally nano-diamond is obtained at significantly higher temperatures (usually above 1600 °C) [11].

4. Conclusions

Adipic acid was used in this work as a precursor for the HPHT synthesis of the carbon sample containing grains of nano-diamond. The carbon sample consists of lamellar diamond nano-grains of nearly 30–50 nm embedded in the amorphous carbon matrix. The majority of the carbon sample comprises sp^2-hybrydized carbon in form of graphite or amorphous carbon.

Please cite this article as: I. Konyashin, et al., Nano-diamond obtained from adipic acid at ultra-high pressures, Mater Lett (2016), http://dx.doi.org/10.1016/j.matlet.2016.07.065