Int. Journal of Refractory Metals and Hard Materials 62 (2017) 37–41

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

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

Precipitation mechanisms of micro-crystal graphite powder during type IIa large diamonds crystallization process

Shangsheng Li [a,*], Chunsheng Gong [a], Taichao Su [a], Menhua Hu [a], He Zhang [a], Hongan Ma [b], Xiaopeng Jia [b]

[a] School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan 454000, China
[b] State Key Laboratory of Superhard Materials, Jilin University, Changchun, Jilin 130012, China

ARTICLE INFO

Article history:
Received 19 July 2016
Received in revised form 20 September 2016
Accepted 6 October 2016
Available online 8 October 2016

Keywords:
Diamond crystal
HPHT
Micro-crystal graphite

ABSTRACT

Type IIa large diamond crystals were synthesized in FeNiCo-C system with Ti (Cu) as nitrogen getter by temperature gradient method (TGM) under high pressure and high temperature (HPHT) conditions. Diamonds grew upon (111) facet under 5.4 GPa and 1620 K while black powder appeared around the growing diamond crystal. And the black powder covered the growing crystals in cap shape and restrained the diamond growth drastically with growth time prolonged. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized to characterize the black powder described above and the regrown graphite obtained from the growth process of traditional type Ib diamonds. The black powder was proved to be micro-crystal graphite powder and the powder was similar to the regrown graphite. However, there were obvious differences between the micro-crystal graphite powder and the regrown graphite. The present discussion about precipitation mechanisms of micro-crystal graphite powder implied that the added Ti (Cu) and related reaction-products in FeNiCo-C system could change solvent property of the catalyst, which affected solubility curve of graphite. Furthermore, the practice of diamond growth indicated that the relatively high temperature and relatively low pressure conditions were remarkably responsible for the precipitation of micro-crystal graphite powder.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Natural diamonds contain many defects and stress concentrations derived from severe growth environment. An overwhelming majority of natural diamonds corresponds to type Ia with high nitrogen content. It is quite difficult to find high-quality diamond crystals free from defects or stresses, even among rare natural type IIa diamonds. The controllable diamond growth under HPHT conditions makes it attainable to obtain high-quality type IIa diamonds [1–3]. High-purity, perfect-crystallization type IIa large diamond crystals (diameter > 1 mm) without defects can be applied in many fields [1–10]. Therefore, it is meaningful to research the synthesis of type IIa large diamond crystals.

It is well known that large diamond crystals are generally synthesized by temperature gradient method (TGM) developed by GE Company in 1971 [1–3]. In this method, the carbon positioned at high temperature region became diamond and dissolved into the melting catalyst at HPHT conditions. Then the dissolved carbon was forced by a proper temperature gradient to diffuse to the low temperature region and finally crystallized as diamond upon the surface of seed crystal. Compared with traditional type Ib large diamond crystals, type IIa large diamond crystals were more difficult to grow, because nitrogen getter usually resulted in inclusions involved into diamond structures or produced craters on the surface of diamond crystal. Hence, limiting growth rate as an optimized synthesis process was necessary to avoid the above problems [9–13].

Generally speaking, if the growth rate was too high or the synthesis condition was so-called “relatively high temperature and relatively low pressure”, the excessive carbon tended to crystallize as graphite instead of diamond. The graphite has no enough time to form diamond during growth process of traditional type Ib large diamond crystals [14–15]. Zang et al. studied the formation mechanisms of regrown graphite formed during the growth process of traditional type Ib large diamond crystals and the effects of regrown graphite on crystal growth of type Ib diamond [15]. In the present study, black powders, similar to regrown graphite, were generated and restrained diamond growth drastically if type IIa large diamond crystals grew slowly at a relatively high temperature. However, there was a lack of the study about the black powders. In this paper, precipitation mechanisms of the black powders obtained from the crystallization process of type IIa large diamond crystals by TGM were discussed in details. Additionally, a route for eliminating the black powders was proposed to synthesize high-quality type IIa large diamond crystals.

* Corresponding author.
E-mail address: lishsh@hpu.edu.cn (S. Li).

http://dx.doi.org/10.1016/j.ijrmhm.2016.10.004
0263-4368/© 2016 Elsevier Ltd. All rights reserved.

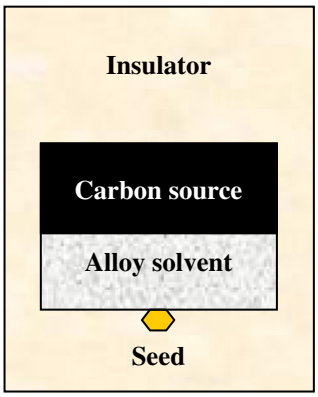

Fig. 1. The schematic diagram of the growth chamber.

2. Experiment

Experiments of diamond growth were carried out in a China-type cubic high-pressure apparatus (SPD6× 1200MN), using high-purity graphite as carbon source, FeNiCo alloy as catalyst, high-quality cub-octahedral diamond single crystal with a diameter of 0.6 mm as seed crystal, (111) facet as growth surface. High-purity Ti foil was added into the catalyst to trap nitrogen, and meanwhile Cu was added to decompose TiC.

The schematic diagram of reaction cell with a diameter of 10 mm in graphite heater was shown in Fig. 1. Based on the practical demand, the growth rate of diamond crystals could be changed by adjusting the axial temperature gradient in reaction cell [1–5]. Pressures were calculated by the relationship between the oil load and actual pressure in the compressed reaction cell, which was calibrated by investigating the electric resistance sudden changing resulted from the phase transitions in some reference materials, such as Bi, Ba and Tl [1–3]. Temperatures were calculated by the relationship between the power input and actual temperature in the compressed reaction cell, which was measured by Pt6% Rh / Pt30% Rh thermalcouple [1–3].

3. Results and discussion

3.1. The precipitation of black powder

The crystallization experiments of type IIa large diamond crystals (111)-orientated were run in FeNiCo-C system with 1.5 wt% Ti (Cu) (Ti and Cu respectively accounted for 1.5% of the catalyst weight)at pressure of 5.4 GPa and temperature of 1620 K. The growth rate must be strictly controlled about 3 mg/h to avoid the inclusions incorporation into diamond structure and the craters generation on diamond surfaces due to the addition of nitrogen getter [1–3]. Therefore, in order to synthesize high-quality type IIa large diamond crystals, the axial temperature gradient in the reaction cell was modified so that the growth rate of type IIa diamond was much lower than that of type Ib diamond. The parameters of large diamond crystal growth are listed in Table 1. It was found that some black powders (seen in Fig. 2) was collected from the sample after acid treatment for a short-time (10 h) and the amount of black powders increased gradually with growth time

Table 1
The parameters of large diamond crystal growth in Fig. 2–Fig. 4.

Sample	Growth time h	Crystal weight mg	Graphite weight mg	Axial temperature gradient k/mm	Diamond Growth rate mg/h
Fig. 2	10	30	6	15	3.0
Fig. 3	30	84	21	15	2.8
Fig. 4	30	186	26	30	6.2

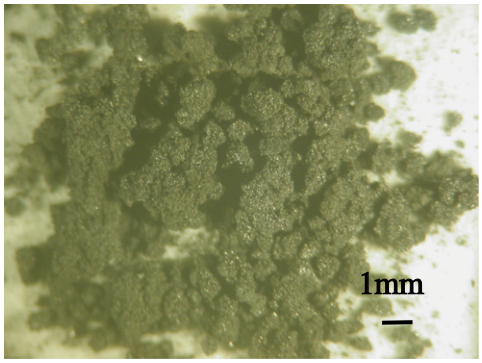

Fig. 2. The black powders of type IIa diamond grown for 10 h.

prolonged. A large amount of black powders surrounded the diamond crystal in the shape similar to cap (seen in Fig. 3) and restrained its growth drastically if the growth time arrived 30 h. However, no black powder was got after a similar synthesis (30 h) without Ti (Cu) additives at the same conditions. As shown in Fig. 4, it was noticed that a large amount of regrown graphite was collected after the similar synthesis (30 h) under pressure of 5.4 GPa and at temperature of 1620 K (discussed in Section 3.2). The production of regrown graphite was caused by enhancing the temperature gradient.

3.2. Characterizations by XRD and SEM

It is shown in Fig. 5 that black powders (seen in Fig. 3) collected after acid treatment against the catalyst used for the growth of type IIa diamond was proved to be ordinary graphite with a little Ti_2O_3. Fig. 6 shows the XRD pattern of regrown graphite (seen in Fig. 4) generated in the growth process of type Ib diamond. Considering that black powders were collected after acid treatment, we used XRD to measure the HPHT-treated catalyst before acid treatment got from growth process of type IIa diamond (Fig. 7) and to investigate the complex reactions related with additives in the synthesis system. Fig. 7 indicates that Cu, TiN and Ti_2O_3 remained in the FeNiCo catalyst after the HPHT process.

As shown in Fig. 8 (a) and (b), black graphite powders (seen in Fig. 3) were in flake shape. The dimensions were several micrometers in diameter. Regrown graphite (seen in Fig. 4) exhibited in a large sheet shape with smooth surface, as shown in Fig. 8 (c) and (d).

According to the results of XRD and SEM, black powders and regrown graphite were the same in phase structure but different in size and shape. The black powders precipitated from type IIa large diamond growth process was called the micro-crystal graphite in above test. Both micro-crystal graphite and the regrown graphite produced from the growth of type Ib large diamond were graphite phase. However, the difference between them was that the former graphite did not grow

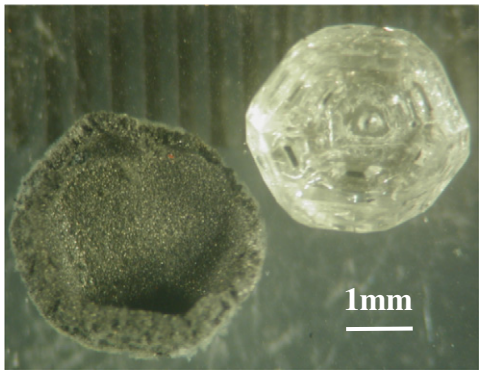

Fig. 3. Type IIa diamond grown for 30 h and the black powders in the shape similar to cap.

Download English Version:

https://daneshyari.com/en/article/5457799

Download Persian Version:

https://daneshyari.com/article/5457799

Daneshyari.com