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Growth of single crystals of diamond by a two-stage method

W. Li, H. Kagi and M. Wakatsuki

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

This paper reports a two-stage method for growth of single crystals of diamond. The new configuration contains a recess at the low temperature side of the reaction space. The seed grows to fill the recess, and then its extended top surface serves as a large seed for the second stage growth. The main part of the crystal grown in the second stage is found to contain no or only few metallic inclusions when the size of the recess is selected appropriately. Both experimental results and numerical simulations show that the growth rate is small in the first stage growth within the recess, and it becomes larger after the crystal grows out of the recess.

1. INTRODUCTION

In growing a single crystal of diamond by the conventional temperature-gradient-method [1, 2], the driving force for crystal growth is determined by the temperature difference between the source and the seed or growing crystal. Too large a temperature difference results in inclusion of the flux material (metallic solvent) into the crystal (especially at the early stage of growth while the crystal is small). This is related to a concentrated diffusion flux of carbon in the solvent on a small surface area of the seed. In order to avoid the inclusion of the solvent material even with the use of a small seed, the initial growth rate should be limited to a sufficiently small value. This is realized by giving a small temperature difference, which, however, will results in a small rate of the total growth process.

The ideal method to solve this problem should be a continuous adjustment of the supplied carbon flux according to the increasing size of the crystal under growth. However, with a conventional sample configuration, it is impossible to change, intentionally, the carbon flux during the growth.

A new sample configuration was devised in the present study, in which a small seed is put in a recess, and the diffusion of the dissolved carbon to it may be considered to be limited at first. However, the crystal gets more supply of carbon when it grows out of the seed-recess in the later stage. Since it is very difficult to characterize a diffusion field in a metallic solution by experiments, the diffusion fields and their features are examined by calculation, and used for discussing the advantage of the new method.

2. METHODS OF EXPERIMENTS AND CALCULATIONS

2.1 Experimental procedures

Figs.1 (a) and (b) show the conventional and the new reaction cells, respectively. An Fe-Ni-Co alloy (55:29:16 by wt%) was used as the growth flux, an artificial high purity graphite was used as the carbon source, and a diamond crystal of about 0.5 mm in size was used as the seed. The graphite carbon source is changed at first to a lump of diamond particles, and then works as a diamond carbon source. The diameter of the second stage flux was 6.4 mm, and the total thickness of the first stage and the second stage fluxes was 4 mm. In order to find out the best geometry of the recess for growing a sound crystal, we changed the diameter and depth of the recess, and observed the quality of the grown crystals, and also evaluated the the growth rate of crystals. Table 1 gives a list of the sample configurations examined.

A cubic anvil high-pressure apparatus [3] was used for the experiments. The reaction pressure was 5.5 GPa, the temperature at the seed was 1200 °C, and the temperature at the carbon source was 1320 °C, throughout all the experiments in this study. This heating condition corresponded to a temperature gradient of 30 °C/mm in the flux.

2.2 Calculation procedures

The situation of the diffusional transportation of carbon to the crystal is very difficult to be confirmed by experiments. Therefore, we tried to characterize the diffusion field by numerical calculation of the time-dependent diffusion equation (1). The crystal under growth is modelized as a circular disc. Carbon

transportation rate onto a surface of a crystal is determined by the concentration gradient normal to the surface. Therefore, the normal growth rate of a facet is evaluated by the normal gradient which is averaged on the concerned facet. In this way, we simulated the growth of crystals.

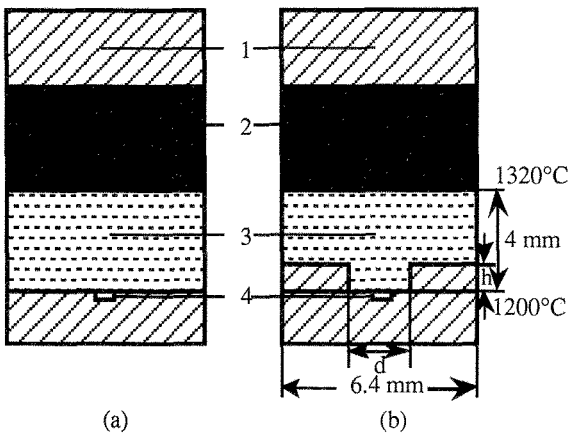

Fig.1 The reaction cells for (a) the conventional, and (b) the two-stage growth. 1. machinable ceramics, 2. carbon source, 3. metallic flux, 4. seed

Table 1 Experimental configurations and results. d and h represent the diameter and the thickness of the first stage flux, P is the ratio of runs for sound crystal to total runs of experiment.

Type	Diameter d	Thickness h	Ratio P
1	-	0.0	0/15
2	1	0.5	5/10
3	2	0.5	14/20
4	2	1.0	16/20
5	2	2.0	0/4
6	3	0.5	0/4

The equation to be solved is

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right) \qquad (1)$$

where c represents the concentration of carbon in the flux which is a function of time t, the axial coordinate z, and the radial coordinate r. D is the diffusion constant which is evaluated as 4×10^{-5} cm^2/sec [4].

3. RESULTS AND DISCUSSION

3.1 Experimental results

Fig.2 shows a schematic feature for the two-stage growth. At first, the crystal grew within the recess; then grew out of it after an enough long time. The grown crystal were found to be consisted of two parts: a smaller one buried in the recess and a larger one grown in the second stage space, and taking a shape of "mushroom". Fig.3 shows a photograph of a crystal grown in twenty hours.

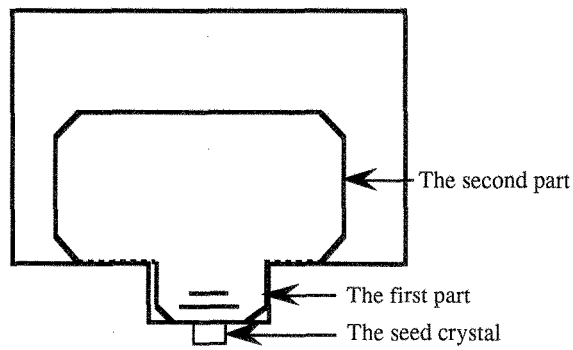

Fig.2 A schematic feature of crystal growth in a two-stage growth method

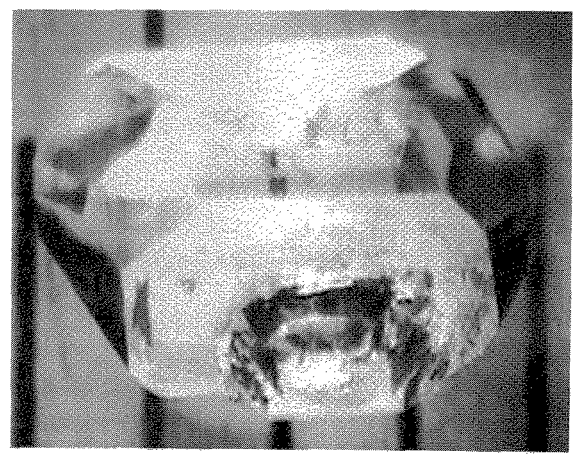

Fig.3 Photograph of a crystal grown by the type 4 configuration. (about 4 mm, grown in twenty hours)

Another interesting fact was found about the inclusions in the crystals. That is, even when the first part of crystal contained many inclusions, the

second part contained a few inclusions; and when the first part contained a few inclusions, the second part contained no inclusion.

In Table 1, the parameter P shows the ratio of the number of experimental runs which produced sound crystals to the total number of the experimental runs.

In the type 1, all of the fifteen grown crystals were found containing a lot of inclusions, sometimes accompanying by newly crystallized diamond or graphite at the peripheral zone of the seed bed. It was found out that growing of sound crystal required a lower growth rate (about 1.0 mg/h), for the same geometry of the growing space.

Configurations from the type 2 to the type 6 are for the two stage growth. No sound crystal was obtained by the type 5 and 6 configurations. This means that too shallow or too deep a recess does not work well for producing a high-quality crystal. On the other hand, with the type 2, 3 and 4 configurations, more than half of the grown crystals were found to contain no inclusion, especially the type 4 configuration gave sixteen sound crystals in twenty runs. The improvement in quality is quite evident.

Furthermore, the growth rate of the crystal in the second stage of the type 4 configuration is about the same as large as that of the type 1 configuration. The relations between the weight of the grown crystal and the growth time for the type 1 and the type 4 configurations are shown in Fig.4.

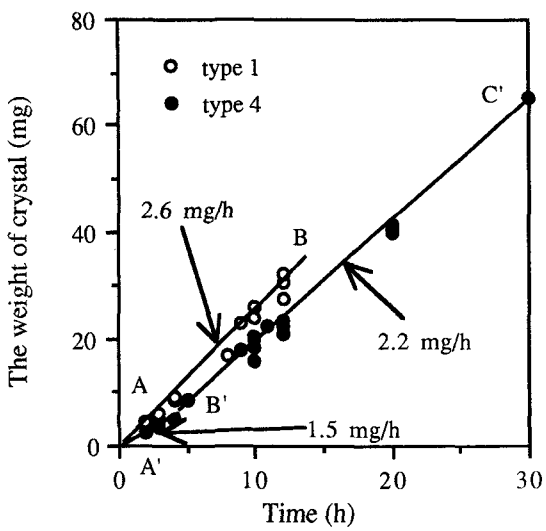

Fig.4 The experimental relation between the weight of crystal and the growth time

For the type 1, the averaged rate of weight increase was expressed as

$$W = 2.6\ (t - 0.5), \qquad (3)$$

which corresponds to a growth rate of 2.6 mg/h, and a dead time of 0.5 hours (30 minutes).

For the type 4, it took about four hours for the first stage growth. Therefore, the experimental data are fitted into two straight lines, corresponding to the averaged growth relations for the first and the second stage, respectively, as

$$W_1 = 1.5\ (t - 0.3), \qquad (t < 4 \text{ hours}) \qquad (4)$$

$$W_2 = 2.2\ (t - 1.7), \qquad (t > 4 \text{ hours}) \qquad (5)$$

It implies that the averaged growth rate in the first stage was lower than that in the second one.

The growth rate of 2.2 mg/h in the second stage is twice as large as that (1 mg/h) for producing sound crystals with the type 1 configuration. The top surface of the crystal getting out of the seed-recess plays a role of an enlarged seed for the second stage growth, which should be the reason for the growth of sound crystals with a larger rate.

There is no theoretical support for the growth curve to be a straight line. As the crystal becomes larger, the boundary conditions of the diffusion field should change. The crystal surface area available for absorbing the diffusional supply of dissolved carbon increases, and the rate of increase of the gross weight will accelerate with the increasing size of the crystal [5]. On the other hand, the decreased difference in temperature between the carbon source and the surface of the crystal (grown larger) will work to cancel the acceleration of the weight increase mentioned above. The total effect may be complicated, depending on the particular case, and the actual data show a very small curvature as seen in Fig.4 (line B'C').

3.2 Calculated results

Fig.5 shows the calculated relation between the weight of the grown crystal and the growth time for the type 1 and the type 4 configurations. The weight increase curve has a slight curvature, showing the effect of the increase of the crystal surface area [5]. For the type 1 configuration, the averaged growth rate for the main part is 6.6 mg/h. In the growth curve for the type 4 configuration, the averaged rate for the second stage growth is 5.8 mg/h. A discontinuous change in the growth rate can be seen

clearly at the boundary between the first and the second stage growth. The growth rate of the first stage is 1.4 mg/h, much smaller than that of the second stage. This supports the reason why the two stage method can produce sound crystals, with a larger net growth rate. Although there are discrepancies of factors of 2 to 2.5 in the absolute values, the qualitative features of growth are clearly reproduced.

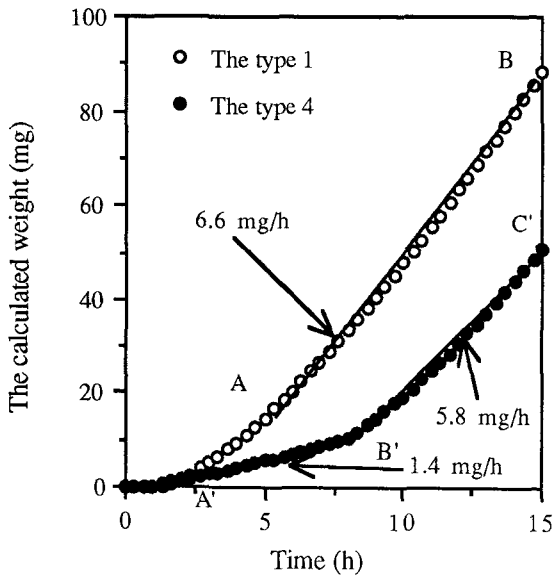

Fig.5 The calculated relation between the weight of crystal and the growth time

4. CONCLUSIONS

(1). The two-stage method can easily grow inclusion-free crystals.

(2). Carbon transportation rate onto the growing crystal is adjusted according to its size in a single growth run.

(3). The upper limit of growth rate for producing sound crystals in the later stage is twice as large as that with the conventional geometry.

(4). Numerical simulation could show the growth features with the two-stage growth.

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