Surface Structure of Large Synthetic Diamonds by High Temperature and High Pressure

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With NiMnCo and FeCoNi alloys as solvent metals, large single-crystal diamonds of about 3 mm across are grown by temperature gradient method (TGM) under high temperature and high pressure (HPHT). Although both {100} and {111} surfaces are developed by a layer growth mechanism, some different characteristic patterns are seen clearly on the different surfaces, no matter whether NiMnCo or FeCoNi alloys are taken as the solvent metals. For {100} surface, it seems to have been melted or etched greatly, no dendritic patterns to be found, and only a large number of growth hillocks are dispersed net-likely; while for {111} surface, it often seems to be more smooth-faced, no etched or melted traces are present even when a lot of depressed trigonal growth layers. This distinct difference between {111} and {100} surfaces is considered to be related to the difference of surface-atom distribution of different surfaces, and {111} surfaces should be more difficult to be etched and more steady than {100} surfaces.

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The surface microtopography of synthetic diamonds is an important clue to understand the crystal growth mechanism under high pressure and high temperature (HPHT) indirectly. For diamond abrasives or large synthetic diamonds, the most common surface characteristic feature of synthetic diamonds is a dendritic pattern on its surfaces. Spiral patterns with high step heights, vein-like patterns, growth hillocks, as well as optically flat surfaces have also been described on all the surfaces,[1−3] especially on both {100} and {111} surfaces, which are the most common surfaces of synthetic diamonds.[4−6]

In earlier works, with the temperature gradient method (TGM) under high temperature and high pressure (HPHT), using Ni, Ni–Fe alloy, and Fe as solvent metals, Kanda *et al.*[2] also observed such dentritic and vein-like patterns on the surfaces of large synthetic diamonds, and these patterns were found to be corresponding to the texture of the quenched solvent metals. Therefore, they concluded that these patterns are formed by the precipitation of carbon atoms in the spaces of the dendrites of the solvent metals during quenching process. Maybe these conclusions are right, however, it is sure that they are not sufficient, and should be conditioned, because some other surface patterns, such as surface-pattern difference of different surfaces and the etching trace, cannot be explained with them.

Often diamond crystals synthesized under the diamond stable region and from metal solvent take on cubo-octahedral habit with well developed {100} and {111} faces. Therefore, in this Letter, the surface characteristic features of both {100} and {111} surfaces of large synthetic diamond crystals are investigated, and from the view of atomic interaction, some surface patterns are explained.

Large diamond crystals were grown by the TGM under HPHT of about 5.5 GPa and 1550 K in a china-made cubic anvil high-pressure apparatus, with the same sample assembly as shown in Ref. [7], and the details of sample assembly were reported in previous papers.[7] With high-purity Ni-based NiMnCo (70:25:5 in units of wt.%) and Fe-based FeNiCo (55:29:16 in units of wt.%) alloys as the solvent metals, no nitrogen-getter additive (such as Ti, and Al) in the solvents, and high-quality yellow type Ib diamond crystals of about 3.0 mm across and cubo-octahedral morphology were obtained in this study. The surfaces of the grown diamonds were observed and analysed with the Invia Raman microscope of Renishaw Corp.

With NiMnCo or FeNiCo as the solvent metals, all large diamond crystals grown by the TGM are mainly composed of well-developed {100} and {111} faces, sometimes no or only some {110} and {113} faces. All diamond crystals are determined by its characteristic peak at 1332 cm^{-1} in the Raman spectrum, and the typical spectrum is shown in Fig. 1, although a little shift of peak position is observed. The {100}-surface patterns of large synthetic diamond crystals grown with NiMnCo and FeNiCo alloys are shown in Figs. 2(a) and 2(b), respectively. Obviously, on {100} surfaces, a large number of growth hillocks are dispersed net-like, and the heights of growth hillocks are thicker for NiMnCo solvent metal than for FeNiCo al-

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loy. Maybe this pattern difference of large crystals grown with different alloys should be due to the solubility difference of carbon in Ni and Fe melts, and because of the larger carbon solubility in Fe melt, the protruded growth hillocks in the Fe–C system can be more easily dissolved than in the Ni–C system.

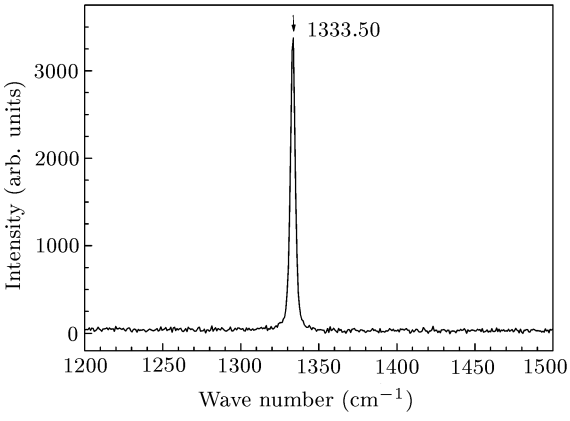

Fig. 1. Typical Raman spectrum of grown diamond crystal.

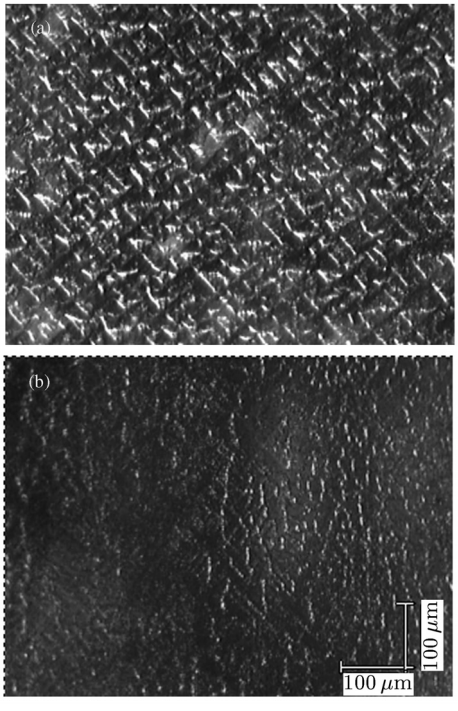

Fig. 2. {100}-surface patterns of large synthetic diamond crystals grown with NiMnCo (a) and FeNiCo (b) alloys as the solvent metals.

The {111}-surface patterns of large synthetic diamonds are shown in Figs. 3(a) and 3(b) for NiMnCo and FeNiCo alloys, respectively. Compared with {100} surfaces, {111} surfaces have nearly flat surfaces, especially when NiMnCo alloy is used as the solvent metal, as shown in Fig. 3(a). For FeNiCo alloy, only a slightly dendritic pattern could be seen as shown in Fig. 3(b). Since for the Fe–C system, Fe_3C could be formed near the diamond-growth pressures and temperatures, while for the Ni–C system, no carbide could be formed during the quenching process when HPHT is removed, maybe the surface difference appears.[2] However, the flat surface pattern does not refer to only the pattern of {111} surface, as shown in Fig. 4. Figure 4 also shows the {111}-surface pattern of large diamonds grown with NiMnCo solvent metal, compared with the crystal with the surface pattern as shown in Fig. 3(a) grown with a 0.5 mm-across seed diamond crystal, the crystal with {111}-surface pattern as shown in Fig. 4 is grown with a 1.0-mm-across seed crystal. The surface pattern exhibits a different character with a lot of depressed trigonal growth units on the {111} surface, although this surface difference may be not related to the seed crystal of different grit sizes, which should be further considered by other direct or undirect proofs. From the different surface structure, it is concluded that on the growth surface, a crystal is not grown layer by layer as a whole, but a lot of growth sectors are growing simultaneously. More importantly, it is also concluded that to grow high-quality large diamond crystals, the crystal growth on the growth surfaces should be kept at the same pace, which is determined by the carbon transportation in the solvent metals, therefore a homogeneous transportation of carbon source in the solvent metals is necessary for the growth of high-quality large diamond crystals.

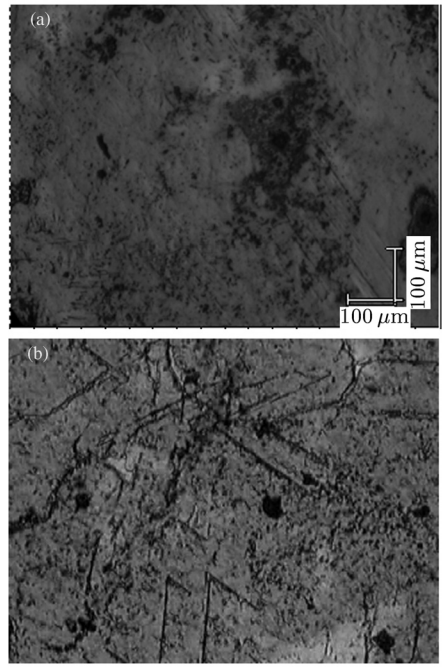

Fig. 3. {111}-surface patterns of large synthetic diamonds grown with NiMnCo (a) and FeNiCo (b) alloys as the solvent metals.

Moreover, another interesting surface appearance is also observed on the growth surfaces of large di-

amond crystals. Compared with {111} surfaces, as shown in Figs. 2 and 4, all the growth units on the whole {100} surfaces have not sharp edges and corners, and seem to be etched or melted markedly by the solvent melts, no matter whether NiMnCo or FeNiCo alloy is used. For {111} surfaces, no etched or melted trace is observed, even a lot of the trigonal growth units are present. From this surface difference, it is concluded that {100} surfaces are much easier to be etched or destroyed by the metal solvent than {111} surfaces, and {111} surfaces should be more steady than {100} surfaces.

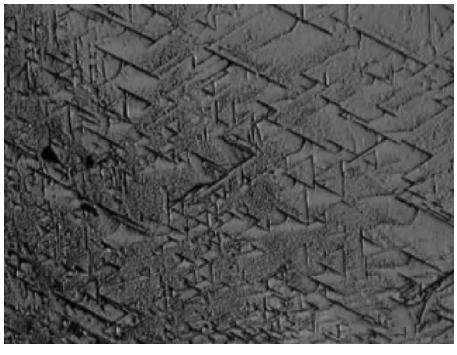

Fig. 4. {111}-surface pattern of large diamonds grown with a 1.0 mm-across seed crystal by NiMnCo alloy.

Since the etching or melting process of growth surfaces should be the embodiment of the interaction of surface atoms, therefore here the difference of {100} and {111} surface patterns could be explained from the view of atom interaction. Figures 5(a) and 5(b) are the surface atom distribution of {100} and {111} surfaces of diamond crystals, respectively. Due to the different present states of surface and inner atoms, for {100} surface, one {100}-surface atom has two dangling bonds; while for {111}-surface atoms, only one dangling bond is present. This means that the interaction between {100}-surface atoms and outside atoms or molecules should be stronger than that for {111}-surface atoms when outside atoms or molecules, such as metal solvent and nitrogen, are bonded with surface carbon atoms. Therefore, maybe two processes occur simultaneously, and they are mutually related. One process is that the {100}-surface atoms should be much easier to be drawn away from the crystal lattice by solvent metal than {111}-surface atoms, and the etching or melting process occurs on the growth surfaces, as shown in Fig. 2, so {111} surfaces should be more steady and more difficult to be destroyed or etched than {100}. The other process is that outside atoms or molecules may be much easier to be incorporated into {111} surfaces, since {111}-surface atoms are more difficult to be draw out from the crystal lattice than {100}-surface atoms. This could be proven by the difference of nitrogen-impurity concentration and the metal-impurity concentration (such as Fe, Co, Ni) in the different growth facets of {100} and {111}.[4,8−10] Generally, the above-mentioned impurity atoms are less incorporated into {100} surfaces than {111} surfaces.

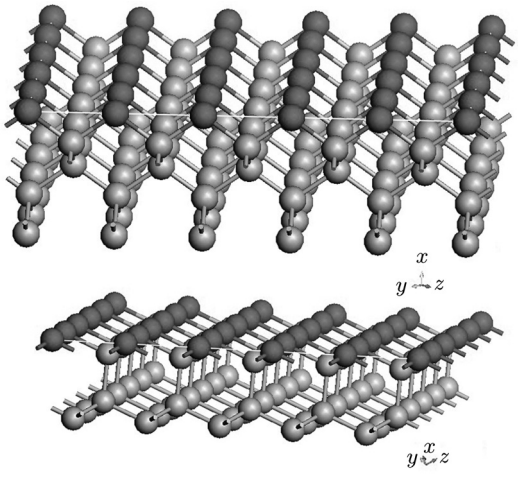

Fig. 5. Surface atom distribution of {100} (a) and {111} (b) surfaces of diamond crystals.

In summary, with NiMnCo and FeCoNi alloys as solvent metals, the different surface patterns of {100} and {111} surfaces of large diamond crystals grown by TGM are observed and discussed. On {100} surfaces, a lot of growth hillocks are dispersed net-likely, and the whole surface seems to be etched or melted by solvent metals, whether NiMnCo or FeNiCo alloy as the solvent metal; while for {111} surface, a flat surface is often observed, no etched or melted traces, even when a lot of depressed trigonal growth units, are present. Due to the different surface-atom distribution of {100} and {111} surfaces, {111} surfaces should be more steady than {100} surfaces, and thus more difficult to be etched.

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