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Surface structures of synthetic diamonds

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Diamond crystals of about 2 mm in size were grown by the temperature gradient method using Ni, Ni–Fe alloy and Fe as solvent metals. Several characteristic patterns were seen on the surfaces of the grown diamonds and were found to correspond to the texture of the quenched solvent metals. A vague vein-like pattern appeared when Ni was used. The surface patterns became finer with the increase of the content of Fe in Ni–Fe alloy, and when 70 wt % Fe–30 wt % Ni alloy was used, very fine dendritic patterns were seen on all of the faces of diamond in accordance with the symmetries of the lattice. The patterns are formed by the precipitation of carbon atoms in the space of the dendrites of the solvent metals during the quenching process. Lamellar patterns and etch pits were seen when Fe was used. The patterns are formed when Fe dissolves the diamond surfaces to produce Fe_3C during the quenching process.

1. Introduction

One of the characteristic features of synthetic diamonds is a dendritic or a vein-like pattern seen on its surfaces. These patterns can commonly be seen on the surfaces of almost all the synthetic diamonds. These patterns were referred to in the several papers [1–4] of the early studies of synthetic diamonds which were made by the "thin film movement" of solvent metals mechanism [5].

Bovenkerk [1] observed such patterns on both the {1 1 1} and {1 0 0} faces and considered that they were formed by the migration of carbon in semi-solid metal during the last stage of growth. Wentorf [2] also observed such patterns on the diamond surfaces grown in Ni and presented almost the same origin as Bovenkerk. Tolansky [3] observed a veined structure on the {1 1 1} surfaces and dendritic patterns with definite orientation on the {1 0 0} surfaces, and conjectured that they were formed by dendritic overgrowth of diamond. Giardini *et al.* [4] also observed the dendritic patterns and concluded that they were depositional patterns of carbon from metal solution during the coalescence process. Because their discussions are only based on the observations of the diamond surfaces without consideration of the growth conditions, this explanation for the origin of the surface patterns is not sufficient.

In this work diamond crystals were made of about 2 mm in size using several kinds of metal solvent by the temperature gradient method first presented by Wentorf [6]. The crystals were grown more slowly and steadily than those made by the thin film method. However, the same dendritic or vein-like pattern could be observed on the diamond surface in spite of the slow growth rate. The patterns varied considerably with the solvent metal. Then we turned our attention to the relation between the surface patterns and the solvent metals.

In this paper the surface patterns of synthetic diamond will be described and their origin discussed using the texture of the frozen solvent metals and the metal–carbon phase diagrams.

2. Experimental procedure

The cell assembly for diamond growth is shown in Fig. 1, which was composed on the basis of the GE patent [7]. A carbon source was placed on the upper end of a metal solvent and a seed crystal on the lower end. In order to prevent the seed crystal from dissolving into the metal solvent

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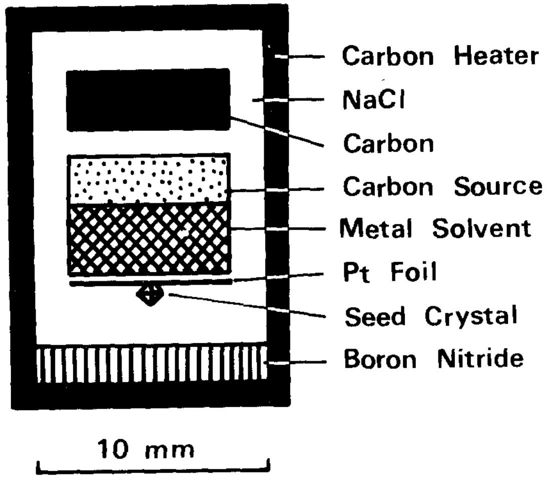

Figure 1 The sample assembly for diamond growth.

before the deposition of carbon atoms starts, a platinum foil was inserted between the two. The powder mixture of diamond and graphite was used as a carbon source, which was wrapped in aluminium foil and pressed into a cylindrical shape (7 mm in diameter and 2 mm thick). Synthesized diamonds 0.5 mm in size were used as seed crystals. Four kinds of solvent metals, Ni, 70 wt % Ni–30 wt % Fe, 30 wt % Ni–70 wt % Fe and Fe, of size 7 mm diameter, and 3 mm thickness were used. The sample assembly was placed in such a way that the carbon source was at the centre of a carbon heater in order to keep the temperature of the carbon source higher than that of the seed crystal.

This cell assembly was brought up to pressures of 5.5 to 6.0 GPa by a modified belt-type high pressure apparatus and then heated to a temperature of about 1400° C. After keeping the sample at this temperature for 5 h, the temperature was decreased rapidly by turning off the electric power. The diamond grown in the solvent metal was recovered by dissolving the metal in acids. Before solvent metals were dissolved, they were cut and polished, and the internal structures were observed. The surfaces of the grown diamonds and the polished solvent metals were examined by a differential interference microscope and a scanning electron microscope.

3. Results

3.1. Crystal shapes

Crystals grown for 5 h had a size of between 1 and 2 mm which depended on the growth temperature and temperature gradient in the metal bath. The crystal shape was generally octahedral truncated by {1 0 0} faces. Although the crystals were mainly composed of {1 1 1} and {1 0 0} faces, {1 1 3} and {1 1 0} faces frequently appeared in addition. The appearance of the latter faces depended on growth conditions such as temperature, temperature gradient and solvent metal. For example, in Fe-rich metal solvent they were easily developed and sometimes became larger than the {1 0 0} faces. On the other hand, such faces were rarely seen on the diamond grown in Ni.

3.2. Surface patterns of the grown diamonds

Surface patterns varied considerably with the solvent metal. When Ni was used as a solvent metal, a vague pattern of veined structure appeared. Fig 2a shows the surface structure on a {1 0 0} face, where indistinct dendrites as well as veined structure can be seen. The veins seemed to be constructed by linking the space of dendrite arms. A {1 1 1} face has a nearly flat surface but a slight dendritic or vein-like pattern can sometimes be seen as shown in Fig. 2 b.

As for the diamonds grown in the solvent of 70 wt % Ni–30 wt % Fe alloy, surface patterns became much clearer than those in Ni metal. On a {1 0 0} face, dendritic patterns with an arm direction of [1 0 0] appeared and, on a {1 1 1} face, those which extend in [1 1 0] directions appeared, as shown in Figs 3 a and b. On {1 1 0} and {1 1 3} surfaces, however, only irregular structures of veins are observed as shown in Figs 3 c and d. When 70 wt % Fe–30 wt % Ni alloy was used, dendritic patterns could similarly be seen on {1 0 0} and {1 1 1} surfaces as shown in Figs 4 a and b. They are more distinct and have more clearly defined orientation than those in the case of 70 wt % Ni–30 wt % Fe alloy. On the {1 1 0} and {1 1 3} faces, dendritic patterns can also be observed with crystallographic orientation as shown in Figs 4 c and d. Fig. 5 is a SEM photograph of a part of the {1 1 1} face in Fig. 4 b, showing that the dendrite arms and their spaces are valleys and ridges, respectively.

On the other hand, a lamellar pattern was observed on all of the faces of diamonds grown in Fe metal solvent, as shown in Fig. 6 a. This pattern has no similarity to the dendritic or vein-like patterns described above. In addition to the lamellar pattern, small etch pits of a few micro-

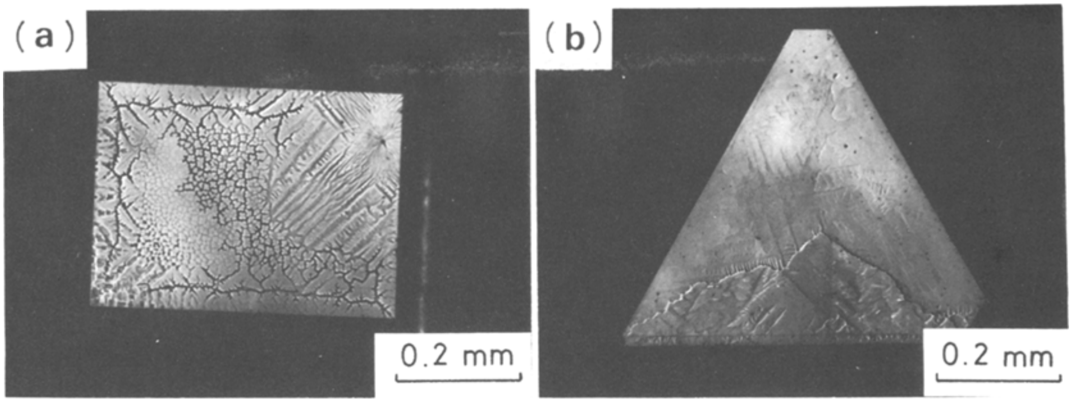

Figure 2 Surface patterns of a diamond grown in Ni solvent showing (a) {1 0 0} and (b) {1 1 1} surfaces.

metres in size can be observed on the {1 1 1} and {1 0 0} faces as shown in Fig. 6 b. They are triangular on {1 1 1} and square on {1 0 0}. The orientation of the triangular pits is the same as that of so-called "trigon" seen on natural diamonds.

3.3 Textures of the frozen solvent metals

Polished cross-sections of the frozen solvent metals after the diamond growth experiments were observed. Fig. 7 a shows the texture of the frozen Ni metal solvent. It is composed of two kinds of regions: large white regions lying parallel to each other, each of which is surrounded by a black stripe. The black region was found to be rich in carbon atoms by an electron probe micro analyser (EPMA) showing that it is a segregated carbon region and also that this texture shows a eutectic structure of the Ni–C system presented by Strong and Hanneman [8]. Fig. 7 b also shows the

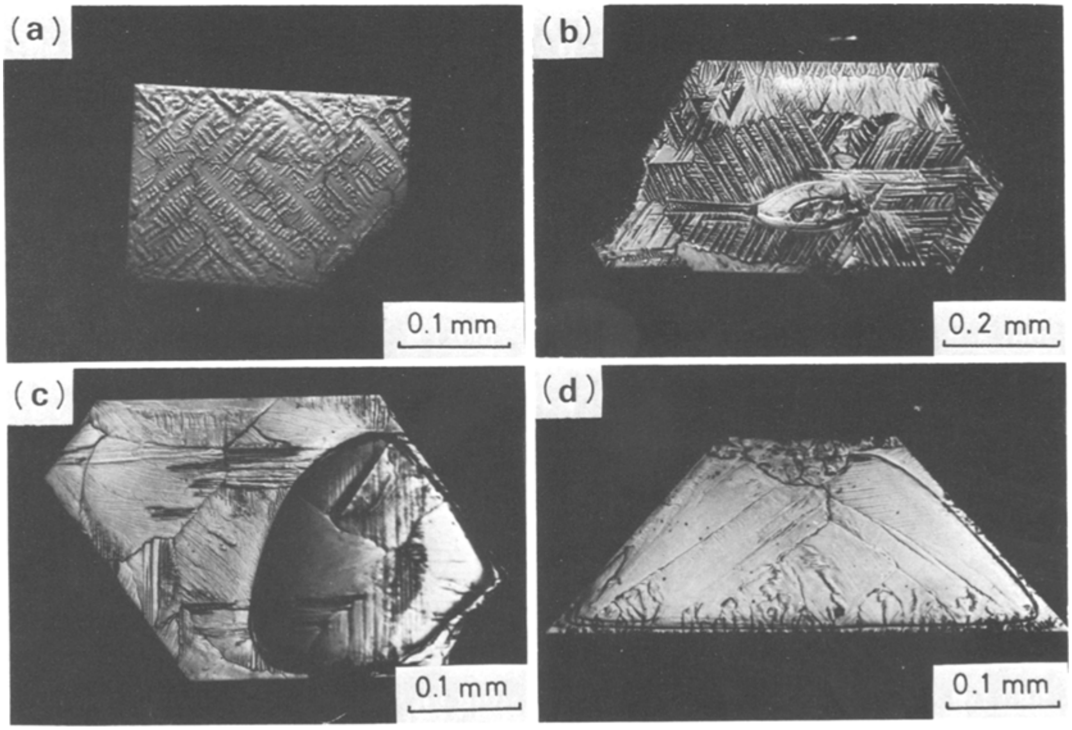

Figure 3 Surface patterns of a diamond grown in the solvent of 70 wt % Ni–30 wt % Fe alloy showing (a) {1 0 0}, (b) {1 1 1}, (c) {1 1 0} and (d) {1 1 3} surfaces.

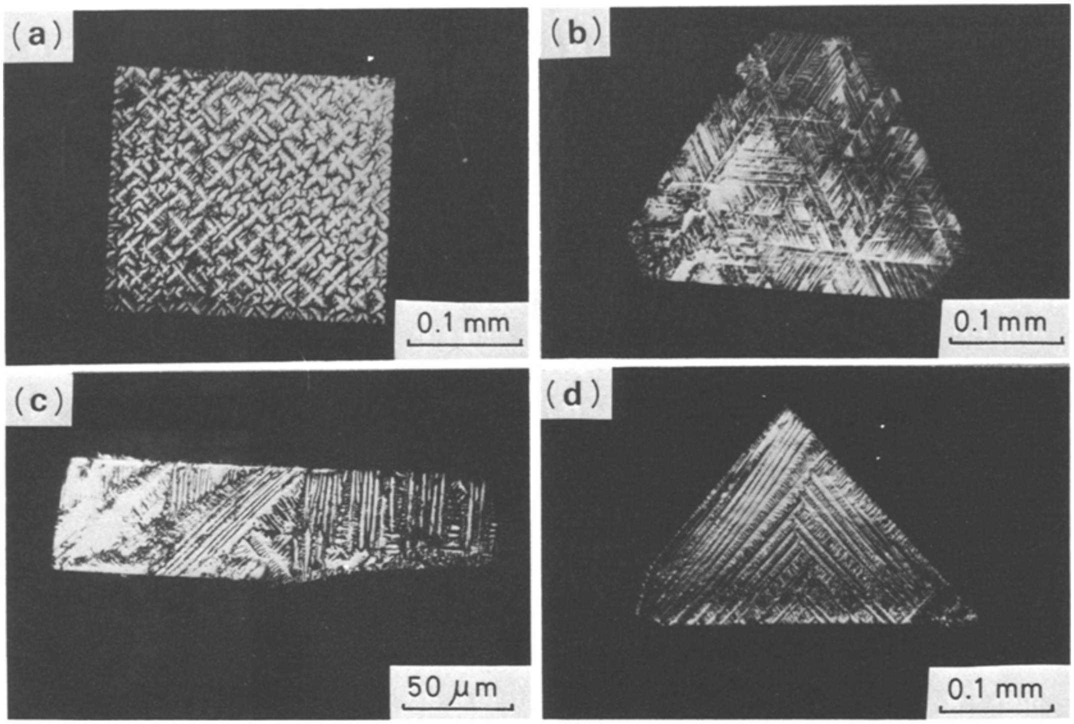

Figure 4 Surface patterns of a diamond grown in the solvent of 70 wt % Fe–30 wt % Ni alloy, showing (a) {1 0 0}, (b) {1 1 1}, (c) {1 1 0} and (d) {1 1 3} surfaces.

texture of the frozen solvent of 70 wt % Ni–30 wt % Fe alloy. Although the pattern is a little finer compared to that of Fig. 7 a, it is almost the same and is considered to be a eutectic structure of (Ni–Fe alloy)–C system. Fig. 7 c shows the frozen texture of 70 wt % Fe–30 wt % Ni alloy. Although dendritic patterns are observed, the structure is so fine that EPMA cannot resolve the heterogenity of component distribution.

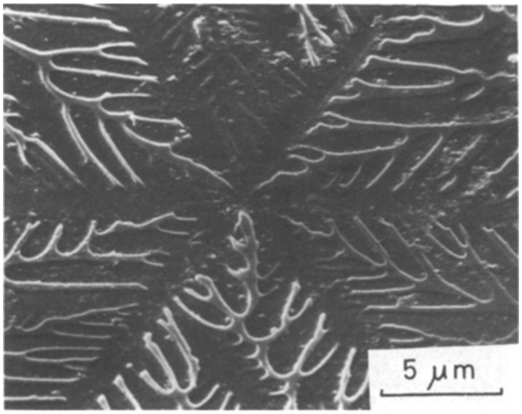

Figure 5 A scanning electron micrograph of a {1 1 1} surface grown in 70 wt % Fe–30 wt % Ni alloy.

Fig. 7 d shows the frozen texture of the Fe solvent, where a lamellar structure is observed. According to the phase diagram of the Fe–C system at high pressure, by Strong and Chrenko [9], this texture must be of a eutectic of the Fe–Fe_3C system.

4. Discussion

The surface patterns seen on a grown diamond can be said to be formed during the quenching process after the growth experiment because they correspond fairly well to the texture of the frozen metal solvent used. The solvent metals are classified into two groups to discuss the origin of the surface patterns: one is a group of Ni and Ni–Fe alloys and the other Fe. Those in the former group produce surface patterns like veins or dendrites and those in the latter group produce a lamellar structure, which is independent of the crystal orientation of the diamond. The origin of the surface patterns is suggested to be as follows on the basis of the phase diagrams of the metal–carbon system at high pressure.

The solvent metals of Ni and Ni–Fe alloy crystallize epitaxially on the diamond surface to

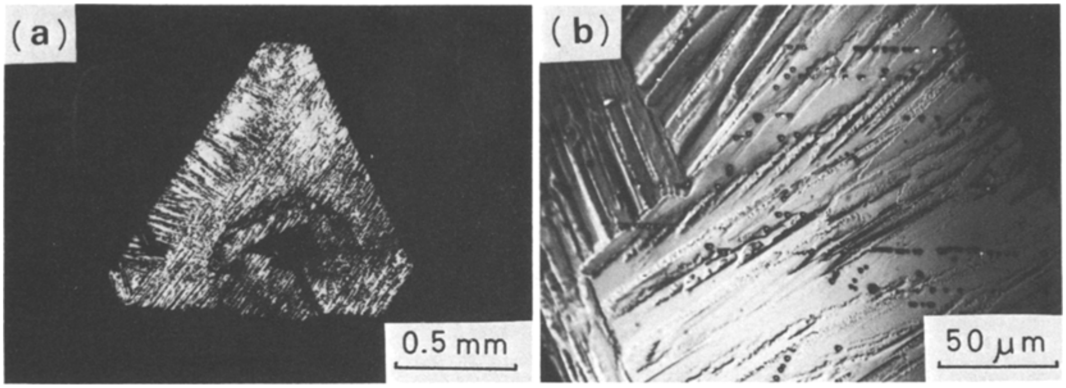

Figure 6 Surface patterns of a diamond grown in Fe metal showing (a) {1 1 1} face and (b) an enlargement of (a).

form dendrites at the eutectic temperature of the metal–carbon system in the quenching process. At the same time, carbon atoms segregate from the liquid and precipitate as diamond in the spaces of the dendrite arms on the diamond surface. After metal alloy is dissolved in acid, the traces of the dendrites can be observed as the surface depressions on the diamond surface. Clarity of the surface patterns may be related to the compatibility of the crystal structure of the solvent metal with the diamond lattice. It is suggested that 70 wt % Fe–30 wt % Ni alloy, where distinct dendritic patterns with definite orientation are produced, matched diamond fairly well and that the structural compatibility of the solvent metal with diamond becomes lower as the content of Fe decreases from 70 wt %.

The origin of a lamellar structure with etch pits, seen on the diamond grown in Fe solvent, is explained using the phase diagram of the Fe–C

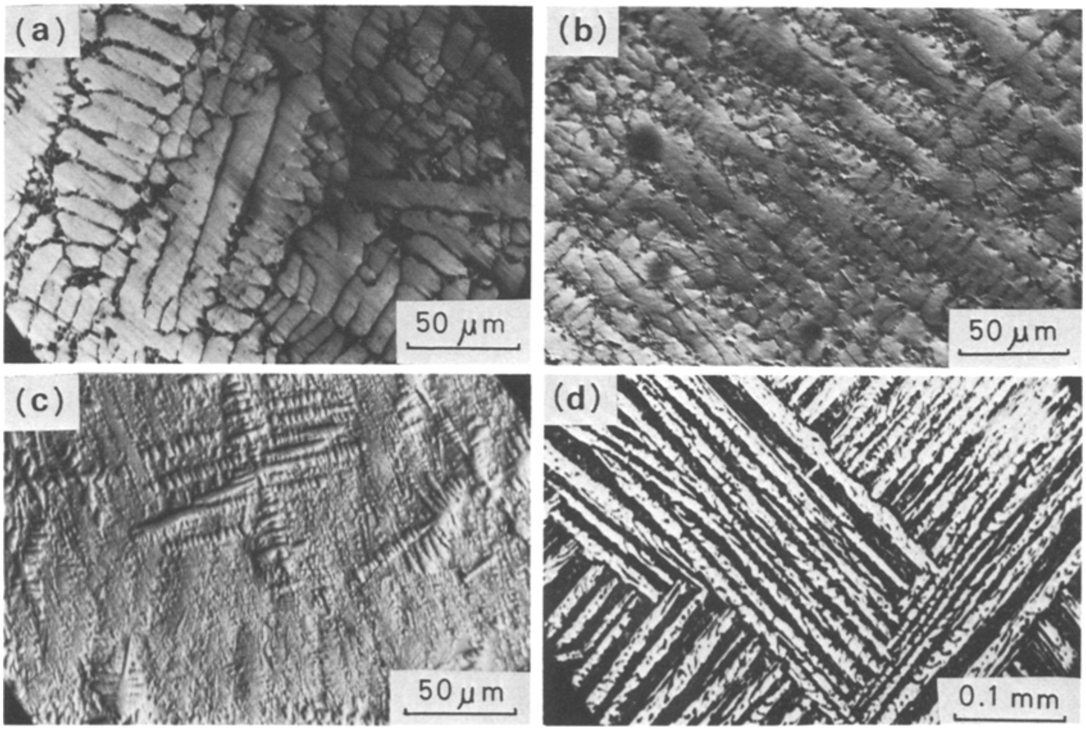

Figure 7 Textures of the frozen solvents of (a) Ni, (b) 70 wt % Ni–30 wt % Fe alloy, (c) 70 wt % Fe–30 wt % Ni alloy and (d) Fe.

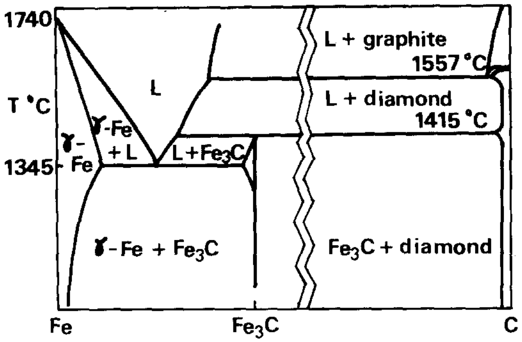

Figure 8 A phase diagram of the Fe–C system at 5.7 GPa after [9].

system at 5.7 GPa illustrated in Fig. 8 [9]. The phase diagram of Fe–C system is different from that of the Ni–C system at the point where a carbide has a stable region. As shown in Fig. 8, Fe_3C is stable at temperatures lower than the peritectic temperature of 1415° C. Below that temperature, diamonds are consumed by the reaction with Fe forming Fe_3C. From the diagram, the reaction must have two stages during the quenching process as follows:

$$\text{Fe (in liquid)} + \text{diamond surface} \rightarrow Fe_3C \quad (1)$$
$$(\text{between } 1415^\circ \text{ C and } 1345^\circ \text{ C})$$

$$\gamma\text{-Fe} + \text{diamond surface} \rightarrow Fe_3C \quad (2)$$
$$(\text{below } 1345^\circ \text{ C})$$

A diamond surface is dissolved by Reaction 1, and etch pits are formed, because Fe is still in a liquid state. At the eutectic temperature of 1345° C, molten Fe freezes with the formation of the lamellar structure composed of γ-Fe and Fe_3C as shown in Fig. 7 d. Below the eutectic temperature, the part of the diamond surface which contacts with γ-Fe in the lamellar structure is eroded by Reaction 2, but the part of surface in contact with Fe_3C is not eroded. Therefore, the lamellar structure of the frozen metal solvent is printed on the diamond surface.

5. Conclusions

Characteristic surface patterns were seen on the grown diamond and the patterns corresponded to the textures of the frozen metal solvent used. The diamond surfaces grown in the Ni or Ni–Fe alloy had dendritic or vein-like patterns. Only a vague pattern of veined structures appeared on the surfaces of a diamond grown in Ni. Surface patterns became finer with increased Fe content in the Ni–Fe alloy. Fine dendrites with crystallographic orientation finally appeared on all of the surfaces of diamond grown in 70 wt% Fe–30 wt% Ni alloy. The origin of the patterns is considered to be as follows. The molten solvent metal crystallizes expitaxially as the dendrites form on the diamond surfaces at the eutectic temperature during the quenching process. Carbon atoms precipitate as diamond in the space of the dendrite arms and so the trace of the dendrite of the solvent metal is printed. The direction of the dendrites is restricted by the symmetry of diamond lattice and the crystal structure of the solvent metal must therefore match the diamond structure well. The 70 wt% Fe–30 wt% Ni alloy is especially well matched in this respect.

There are two kinds of patterns on the diamond surface grown in molten iron. One is a lamellar pattern running in a random direction and the other is a lamellar pattern with etch pits. These patterns are formed when Fe dissolves the diamond surface to produce Fe_3C during the quenching process.

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