

THE INCREASE OF SYNTHETIC DIAMOND GROWTH RATE

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The state diagram of the Mg–C system at high pressures and temperatures was investigated. It is shown that magnesium carbide (MgC_2), formed under these conditions, starts melting at higher temperatures and dissolves carbon, which precipitates in the form of diamond. The mass and linear growth rates of crystals are defined. The overgrown crystals are found to exhibit high strength ($\approx 5000 \text{ N/mm}^2$). The growth of diamond cube faces is governed by the dislocation mechanism of growth layers formation.

1. Introduction

Diamonds are produced in a specially designed apparatus at pressure above 4 GPa and temperatures above 1100°C . Solvents are chosen from transition metals.

A method is developed at our institute for the production of semiconducting diamonds in the presence of magnesium, Mg-based alloys and compounds.¹⁾ Diamond synthesis in the Mg-containing system is run at higher pressures and temperature than in the case of the presence of transition metals. Thus, for instance, diamond synthesis in the Mg–Zn-system is run at a pressure of 7.0 GPa and temperature of 1700°C , whereas in the Mn–Ni–C-system it is performed at a pressure of 4.0 GPa and temperature of 1200°C .²⁾

Diamond crystals 0.1 to 0.5 mm in size produced in the Mg-containing system appeared to be suitable for use as quick-acting temperature sensors.

To obtain diamond crystals of larger sizes, studies have been made by growing semiconducting layers on dielectric diamonds.³⁾

2. Mechanism of the diamond formation in the Mg–C-system

The interaction between magnesium and carbon at high pressures and temperatures was investigated in relation to diamond synthesis in this system.

There is little data on the Mg–C system at high

pressure. It is merely known that magnesium interacts with hydrocarbon in the temperature range $450\text{--}700^\circ\text{C}$ at atmospheric pressure giving known magnesium carbides MgC_2 and Mg_2C_3 .

The interaction between magnesium and graphite under high pressures (up to 7.7 GPa) and temperatures (up to 1800°C) was studied with their mixtures. The carbon concentration was in the range from 10 to 75 at.%.
Differential thermal analysis was made under pressure. The examination of the microstructure of pressure-hardened Mg-rich alloys have revealed the eutectic structure of the alloys. The eutectic temperature was 980°C .

With C-concentration above 15 at.%, magnesium carbide is formed in alloys. Magnesium carbide has an f.c.c. lattice with a lattice parameter of $a=5635 \text{ nm}$. This type of chemical compound (MgC) has not been observed previously. The lines of the known magnesium carbide with the rhombic lattice were revealed under pressure in the process of sintering mixtures with C-concentrations from 50 to 67 at.%. High-temperature transition to the b.c.c. lattice with a lattice parameter $a=4644 \text{ nm}$ was revealed in magnesium carbide.

At temperatures above 1680°C , magnesium carbide starts melting and dissolves carbon. At high temperatures under the conditions of supersaturation, carbon precipitates in the form of diamond.

3. Experimental procedures

Semiconducting layers were grown on yellow-coloured cubo-octahedral synthetic diamond single crystals 0.5 to 0.8 mm in size and on colourless natural diamonds.

The crystal quality is known to be dependent on the growth rate. Thus, diamonds grown at high growth rates have a great quantity of inclusions, which deteriorate their physico-mechanical properties and particularly their strength.

To measure the linear and mass growth rates, a method of temperature fluctuation was used. Internal crystal structure predetermines the characteristics of impurity distribution in crystals. In the process of overgrowth the crystal was twice thermo-cycled (every 3 minutes). It should be noted that the crystal grows irregularly.

The highest growth rate was observed along the (100) and (001) faces. Crystal growth rates measured in various directions in I, II and III zones are given in Table 1.

It is seen from Table 1 that the linear rate of growth slightly decreases with time, while the mass

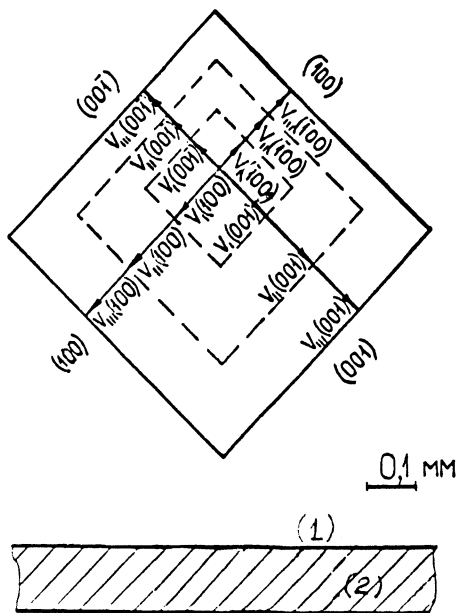


Fig. 1. The crystal position with relation to the carbon source. 1, solvent; 2, graphite.

Table 1. Diamond growth rates

Zone	Linear rate of growth, mm/min		Mass rate of growth, mg/min
	(001)	(100)	
I	0.14	0.09	0.05
II	0.13	0.08	0.30
III	0.11	0.06	0.60

rate of growth considerably increases. Due to the temperature fluctuation, the flow of crystallizing particles intensifies and gives rise to the higher growth rates.

Our interest is in the strength of the overgrown diamonds. In this context, the strength values of seed crystals and of grown ones were compared. The ultimate strength was measured as a ratio of the crystal failing load value to the crystal/substrate contact area.

It is evident that the compressive strength depends on crystal sizes.⁵⁾ The ultimate strength decreases with the crystal size.

Crystals under study were of different sizes: seed crystals (cubo-octahedrons) were, naturally, smaller in size as compared to overgrown (cubic) crystals. The ultimate strength has a practical size-independent value for crystals with an edge size above 0.5 mm.

It is seen from Table 2 that the average ultimate strength of seed crystals (contact area = 0.31 mm²) is 4480 N/mm², and that of overgrown crystals (contact area = 0.68 mm²) is 4950 N/mm².

It should be noted that the seed crystal growth rate was 0.006 mm/min. Hence, the growth rate of the crystals in the presence of a new solvent is tens of times that for diamonds produced with transition metals. The strength of the former is much the same.

X-ray diffraction analysis (the Kossel method) revealed that the grown layer has a crystalline structure with a lattice constant being coincident with that of a seed crystal to the fourth decimal place and measuring 3.5666 Å. The electrical resistance as a function of the uncontrolled boron impurity content in graphite measures from 10⁹ to 10² Ohm·cm.

Table 2. Compressive strength as measured on seed crystals and on overgrown crystals

Crystal No.	Seed crystals			Crystal No.	Overgrown crystals		
	Contact area, mm ²	P, N	σ , N/mm ²		Contact area, mm ²	P, N	σ , N/mm ²
1	0.31	1650	4950	1	0.67	3700	5490
2	0.40	1680	4300	2	0.56	4250	7560
3	0.27	880	3300	3	0.65	3060	4670
4	0.27	1250	4650	4	0.85	1610	2080
5	0.25	860	3460	avg.	0.68	3150	4950
6	0.27	2270	8270				
7	0.40	820	2050				
avg.	0.31	1340	4480				

4. Crystallographic peculiarities of crystals obtained in the Mg-based system

Crystals obtained in the Mg-based system, at practically all temperatures of synthesis, are predominantly of cubic habit.⁶⁾ The existence of well-defined positive growth steps on cube faces is the characteristic property of these crystals. The steps form concentric layers growing one upon the other, progressively smaller and well polygonized.

The steps grow from the centre of the face or shift to a crystal edge or vertex. At low growth rates the steps grow from several centres and the height does not exceed 1 μm . At higher growth rates the steps grow, mainly, from one centre, the height being up to tens μm . When carbon black was added to the mixture (20% with respect to graphite), diamond growth rate essentially decreased. Under these conditions many hillocks developed on the cube faces. The formation of growth layers at the centre of faces is characteristic when screw dislocations are the source of these layers. In the systems under study the growth of diamond cube faces is most likely governed by the dislocation growth mechanism.

When natural diamonds are used as seeds the seed/overgrown layer interface is not observed.

5. Conclusions

A mechanism of diamond growth in Mg-containing systems has been defined.

In the Mg-C-system a new high pressure phase has been detected.

Under the conditions of thermal cycling the mass rate of diamond growth increases, the crystal habit being unchanged.

The growth rate is higher in the direction of the carbon source.

The growth of diamond cube faces is governed by the dislocation mechanism of growth layers formation.

The overgrown crystals exhibit high ultimate strength values.

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