12. C. A. KAGARAKIS, *J. Mater. Sci.* **13** (1978) 1594.
13. C. M. GARNER, L. R. GILBERT and C. WOOD, *J. Non-Crystalline Solids* **15** (1974) 63.

Received 21 August
and accepted 1 October 1979

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Consolidation of diamond powders by thermal decomposition of methane and benzene

Diamond is one of the most difficult materials for sintering, and commercially available sintered diamonds are made under high pressure with addition of foreign metals, e.g. [1, 2]. Vapour infiltration is a well-known method for densification of carbonecious or other materials [3]. It is also reported that diamond can be grown epitaxially on diamond by thermal decomposition of carbon source gases under pressures less than 1 atm [4–7]. The present investigation was undertaken to consolidate diamond powders by vapour infiltration of methane at low pressures. As aromatic hydrocarbons are reported to deposit non-diamond black carbon and to be unsuitable for epitaxial growth of diamond [4], for comparison, benzene was also used instead of methane. The experiments were made primarily for a practical purpose, i.e. to obtain a hard and homogeneous aggregate. As a measure of consolidation, Vickers micro-hardness was measured as a function of a distance from the surface. The hardness of the aggregates obtained was, however, too small to be used practically.

During our investigation, Fedoseev *et al.* [8, 9] applied patents for the same method and used high pressure after carbon deposition to obtain a strong compact which can be used for cutting tools. However, details of the experiments have not been described. The present communication reports the results of our investigation on the vapour consolidation.

A natural diamond powder of 0 to 0.5 μm particle size was prepressed into a disc 5 mm diameter and 3 mm thick at 1000 kg cm^{-2} and then isostatically pressed at 2000 kg cm^{-2}. This green compact was infiltrated at 700 to 900° C in three different atmospheres: 1 atm methane, 270 Pa methane, and 1 atm argon saturated with benzene at 15° C. The vapour pressure of benzene at 15° C is 8000 Pa. The weight change during deposition at 1 atm was recorded with a thermobalance. Deposition in 270 Pa methane was made in another furnace equipped with an oil rotary pump. The methane used was of reagent grade (99.95%), and the nominal purity of argon was 99.999%. The rate of flow of the gases was about 20 cm^3 min^{-1}.

The carbon-deposited compacts were cut vertically into two pieces, and the Vickers microhardness was measured along the centre axis. The instrument used was a Reihert "MeF 2" universal microscope. The intender load was 100 g, and the load duration was 30 sec.

Table I summerizes the weights and densities of

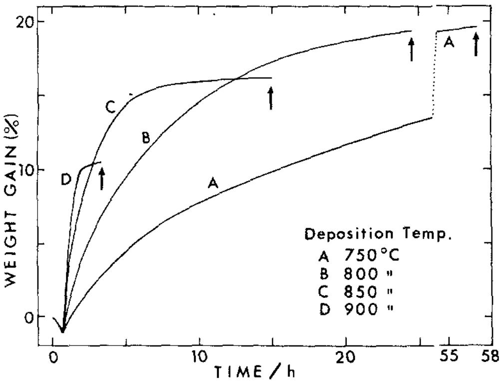

Figure 1 Rate of infiltration of diamond compacts with carbon deposited from 1 atm methane. Arrows indicate the times when the compacts were taken out.

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TABLE I Infiltration conditions and weight changes

Specimen number	Infiltration conditions				Initial weight (mg)	Weight gain (mg)	Relative density (%)		
	Vapour	(atm)	(°C)	(h)			Initial	Final‡	
								diamond	graphite
A1	CH_4	1	750° C	57	117.4	23.0	56.9	68.1	74.3
A2	CH_4	1	800	24.8	116.0	22.4	56.0	66.8	72.8
A3	CH_4	1	850	15.3	116.4	18.8	57.0	66.2	71.3
A4	CH_4	1	900	3.3	117.7	12.3	57.2	63.2	66.6
B1	CH_4	270 Pa	800	229	116.0	10.4	56.9	62.0	64.8
B2	CH_4	270 Pa	850	214	227.9†	18.4	57.1	61.8	64.4
B3	CH_4	270 Pa	900	34.5	110.0	7.6	55.4	59.2	61.4
C1	Ar + $C_6H_6^*$	1	765	25.8	126.7	24.3	57.1	68.0	74.1
C2	Ar + $C_6H_6^*$	1	815	10.5	127.8	22.9	57.6	67.9	73.6
C3	Ar + $C_6H_6^*$	1	860	5	126.8	14.6	57.2	63.8	67.4

*Partial pressure of 8000 Pa.

†Specimen size is 6 mm diameter × 4 mm, all the others 5 mm diameter × 3 mm.

‡Calculated values assuming the deposit to be diamond or graphite.

compacts before and after deposition. The relative densities were calculated from the values of weights and dimensions of the compacts. The relative densities after deposition were estimated on the basis of two assumptions: carbon deposits are exclusively (1) diamond ($d = 3.515$) or (2) graphite ($d = 2.26$).

Figs. 1 and 2 show, respectively, the weight change of the compacts during carbon deposition in 1 atm methane and in 1 atm argon saturated with benzene. A heating rate to the reaction temperatures was 20° C min^{-1}. The initial weight loss is due to the desorption of CO and CO_2 from the diamond surface. As deposition temperature increases, the increase in weight levels off with a smaller gain. This suggests that at high temperatures the deposition of carbon is faster than the diffusion of a reactant gas and closes surface pores.

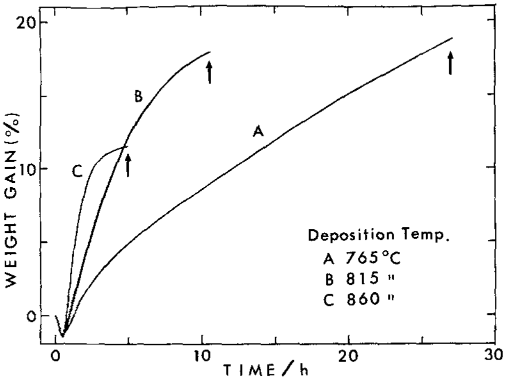

Figure 2 Rate of infiltration of diamond compacts with carbon deposited from 8 kPa benzene with 93 kPa argon.

Figs. 3 to 5 show the results of the measurements of Vickers micro-hardness for the above samples and for those heated in 270 Pa methane. The hardness of all the samples decreases with increasing distance from the surface, and the hardness gradient increases with a reaction temperature. These results are explained by a decrease in deposition of carbon due to pore narrowing at the surface, as was shown by the rapid levelling off of a weight gain.

Deposition at 750° C in 1 atm methane (Fig. 3A) and at 765° C in a benzene–argon mixture (Fig. 5A) gave nearly homogeneous distributions of hardness of 800 and 450 kg mm^{-2}, respectively.

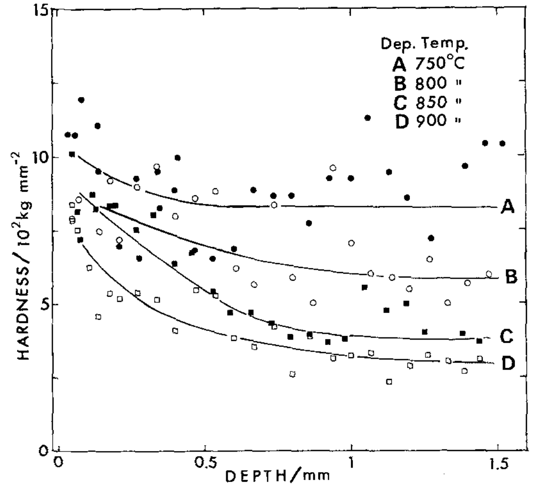

Figure 3 Variation of measured Vickers micro-hardness with distance from the surface of compacts consolidated in 1 atm methane.

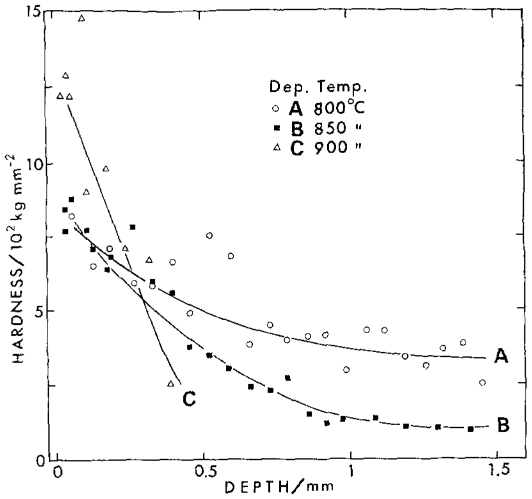

Figure 4 Variation of measured Vickers micro-hardness with distance from the surface of compacts consolidated in 270 Pa methane.

In spite of their smaller weight gains and lower hardness in the inner regions, at the surface regions the samples heated in 270 Pa methane showed nearly the same hardness as those of the samples heated in 1 atm methane (800 to 1000 kg mm^{-2}). In particular, the compact treated at 900° C in 270 Pa methane exhibited relatively high hardness (≈ 1200 kg mm^{-2}, Fig. 4C). This is the highest value obtained in this work but is far smaller than the reported value, > 8000 kg mm^{-2} of compacts sintered at high pressure with metals [1, 2].

Because the size of the original powder was 0 to 0.5 μm and the size of an indent over 10 μm, the measured Vickers hardness is considered to exhibit the strength of an aggregate rather than that of a single particle. Fig. 6 shows the variations of log(load) versus log(length of indent diagonal) for three of the compacts with carbon infiltrated as described above. Because the variations are nearly expressed as straight lines of slope 2, the hardness is believed to be load-independent.

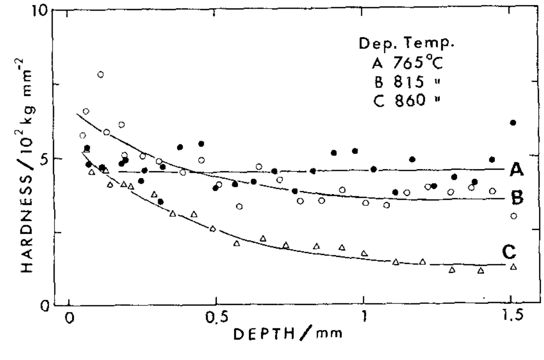

Figure 5 Variation of measured Vickers micro-hardness with distance from the surface of compacts consolidated in a mixture gas of 8 kPa benzene and 93 kPa argon.

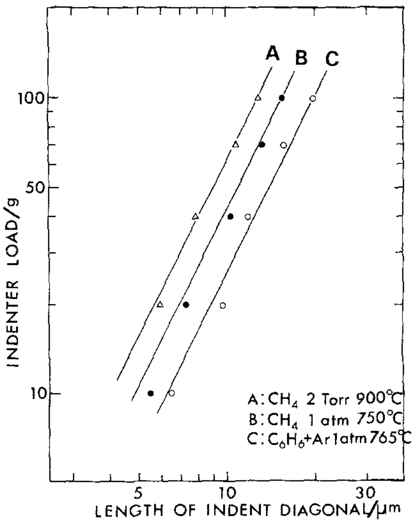

Figure 6 The relation of indent impression size to the indenter load at the polished surface (A) and at the centre region (B, C) of typical compacts. The lines of slope 2 are superimposed.

The above results suggest that the deposition conditions which have been used in the experiments of epitaxial growth of diamond on free-flowing diamond powder may be also favourable for obtaining harder aggregates; aliphatic rather than aromatic compounds and lower pressure of reactant gas are preferable. However, the latter condition results in the decrease in deposition rate. To clarify the relations between deposition conditions and the strength of the resulting body, it is necessary to investigate the distribution and the structure of the carbon deposited.

References

1. P. A. BEX and W. I. WILSON, *Ind. Diamond Rev.* 1977 (1977) 10.
2. L. E. HIBBS JR and R. H. WENTORF JR, *High Temp. High Press.* **6** (1974) 409.
3. W. V. KOTLENSKY, "Chemstry and Physics of Carbon", Vol. 9, edited by P. L. Walker Jr and P. A. Thrower (Marcell Dekker, New York, 1973) p. 173.
4. W. G. EVERSOLE, US Patent nos. 3 030 187 and 3 030 188 (1962).

5. J. C. ANGUS, H. A. WILL and W. S. STANKO, *J. Appl. Phys.* **39** (1968) 2915.
6. B. V. DERJAGUIN, D. V. FEDOSEEV, V. M. LUKYANOVICH, B. V. SPITZIN, V. A. RYABOV and A. V. LAVRENTYEV, *J. Crystal Growth* **2** (1968) 380.
7. B. V. DERJAGUIN and D. V. FEDOSEEV, *Sci. Am.* **233** (1975) 102.
8. D. V. FEDOSEJEV, B. V. DERJAGIN, V. N. BAKUL, A. J. PRICHNA, V. P. VARNIN, S. P. VNUKOV, V. K. GERASIMENKO, J. I. NIKITIN, N. V. ZYPIN and A. V. BOTSCHKO, Ger. Off. 2 533 743 (1975).
9. B. V. DERJAGUIN and D. V. FEDOSEEV, *Vestnik Akad. Nauk SSSR* **1976** (1976) 95.

Received 23 March
and accepted 16 October 1979

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