JOURNAL OF MATERIALS SCIENCE 23 (1988) 2877–2881

Effects of starting carbon and solvent–catalyst on the reaction sintering of diamond

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Polycrystalline diamond sintered compact was prepared under high pressure and temperature conditions (7 GPa, 1700° C, 10 to 15 min) from purified natural graphite (NG) or graphitized pitch coke (GPC) using iron, cobalt or nickel as the catalytic active metal and titanium or zirconium as the solvent metal. The effects of the combinations of starting carbon and solvent–catalyst on the transformation behaviour and morphology of the converted diamond were investigated in relation to the starting powder compositions. Diamond crystals converted from NG tended to have euhedral habits, when twin crystals were occasionally found due to a relatively rapid conversion and growth rate of diamond. On the other hand, a skeletal structure of diamond was easily formed by a mild conversion from GPC in the 15 to 30 vol% ($\sim$40 to 60 wt%) nickel solvent–catalyst. The degree of catalytic action in the 8A group of 3d transition metals for the GPC system was in the order: Ni $\geqslant$ Co > Fe. The grain growth of the converted diamond was depressed by the addition of 4A transition metals (titanium or zirconium) which results in the fine-grained and homogeneous sintered microstructure.

1. Introduction

Diamond sintered compacts have been prepared from diamond powder with several kinds of additives [1–4]. The sintering mechanism has not been established especially on the formation process of a strong direct bonding between the diamond grains in the case of the melt coexisting in the carbon–metal system.

It was confirmed by Naka *et al.* [5] that a diamond sintered compact was prepared by reaction sintering which was accompanied by transformation from purified natural graphite to diamond in the presence of binary solvent–catalyst of the Fe–Ti system. The conversion ratio from graphite to diamond was nearly 100% when the specimen with a composition of 50 to 60 wt% natural graphite (NG)–30 to 40 wt% (11.4 to 17.0 vol%) Fe–10 wt% (6.6 to 7.7 vol%) Ti, was treated at 7 GPa and 1700° C for 15 min. Similarly, the diamond sintered compacts were obtained by reaction sintering from a starting powder in the graphitized pitch coke (GPC)–Ni–Zr system [6]. Among the converted diamond particles a typical neck growth was observed [5, 6] which forms a strong skeletal network of reaction-bonded diamond. A systematic investigation is important to understand the liquid-phase sintering behaviour of diamond by comparing the effects of various parameters on reaction sintering [7].

The effects of starting carbons and solvent–catalysts on the reaction sintering of diamond were investigated in the present work, using NG or GPC as the carbon source, iron, cobalt or nickel as the catalytic active metal and the titanium or zirconium as the solvent metal. The reaction sintering conditions and microstructure of the sintered compact were examined by varying the combinations of starting carbons and solvent–catalysts at constant pressure and temperature.

2. Experimental procedure

The starting carbons used were purified NG (285 to 325 mesh, treated at 2800° C in a chlorine atmosphere) and GPC (< 325 mesh, treated at 2800° C in an argon atmosphere). GPC has a lattice constant $C_{0_{002}} = 0.6722$ nm, crystallite size $L_{c_{002}} = 91$ nm and degree of crystallization $P = 0.92$. The solvent–catalyst metals were commercially available iron, cobalt, nickel, titanium and zirconium powders (about 300 mesh, purity > 99.8 wt %). These powders were combined at various compositions and mixed for 1 h in a V-shaped rotary mixer to prevent a further introduction of deformation in these highly graphitized carbon powders. According to the ambient pretreatment effect on the promotion of particle joining of diamond grains [8], the mixed powder was first degassed in vacuum (at 5×10^{-5} torr) at 600° C for 1 h and subsequently pretreated in an argon stream (at 1 atm, flow rate 100 ml min^{-1}) at 1000° C for 1 h.

The pretreated powder was packed into the specimen cell quickly in a globe box and placed in the girdle-type high-pressure apparatus. Fig. 1 shows a representative cell assembly which has a specimen volume of 6 mm diameter × 4.6 mm high. The procedures for high pressure (7 GPa) and temperature (1700° C) treatments as well as the calibration method for pressure and temperature were the same as those used in previous papers [5, 6].

The treated specimens were identified by X-ray diffraction. The conversion ratio from graphite to diamond was determined from the relative intensity

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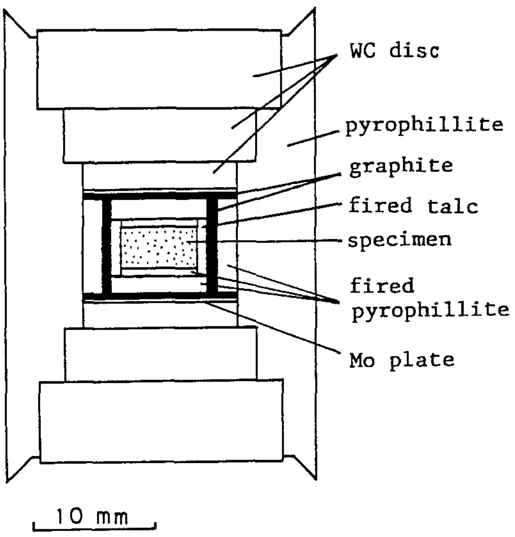

Figure 1 Cell arrangement for girdle-type high-pressure apparatus.

of diamond 1 1 1 diffraction to that of graphite 0 0 2 diffraction using a calibration curve. The surface microstructure of the specimen, which was post-treated in hot aqua regia for 1 h to remove the residual carbon, metal or metal carbide, was examined by scanning electron microscope (SEM). The Vickers microhardness of the polished surface was measured under 1000 g load.

3. Results and discussion

3.1. Reaction sintering of diamond converted from natural graphite

The conversion ratio from NG to diamond and the grain size range of the converted diamond were examined at various compositions of the starting powder which contains iron, cobalt or nickel as catalytic active metal. The pressure, temperature and treatment time conditions were kept constant at 7 GPa, 1700° C and 15 min, respectively. The conversion ratio of the specimen having the composition 80 wt % NG–20 wt % Fe was 85%, where the grain sizes of the converted diamond ranged from 50 to 70 μm. The substitution of iron by cobalt or nickel decreases the conversion ratio to 55 to 75%, while increasing the grain size up to 70 to 100 μm. It is suggested in the NG–(Fe, Co or Ni) system that iron is a better catalytic metal than cobalt or nickel. At low iron content (20 wt %), however, the treated specimen was easiy broken into fragments when removing from the high pressure cell. It was necessary to increase the iron content up to about 50 wt % (20 vol %) so as to obtain nearly 100% conversion ratio, when the specimen was recovered as a whole disc sintered compact [5].

Fig. 2a shows the scanning electron micrograph of a typical twin crystal of diamond, which was prepared from the starting powder of the 80 wt % NG–20 wt % Co system. Tiny pits can be seen on the lateral face which verifies a fast growth of the twin crystal. Such a twin crystal was observed occasionally in the specimen converted from NG, as also confirmed at a higher catalytic active metal content in the 50 wt % NG–50 wt % Ni system [6], and shown in Fig. 2b. When NG was used as a starting carbon source, diamond crystals tended to have euhedral habits and individual grain shapes [5, 9]. These morphologies would be obtained by the rapid crystallization of the converted diamond. Natural graphite, which has the highest degree of crystallinity, shows a good wettability to the solvent–catalyst metal. Fast spreading of the melt to the NG surface will promote the transformation and growth rate of diamond. The twin structure of diamond would be generated by the nucleation process from NG, which is easy to subject to deformation and stacking faults during the compression process. It is deduced from the above observations that NG is not an appropriate carbon source for controlling the sintered microstructure of the compact.

3.2. Reaction sintering of diamond converted from graphitized pitch coke

Fig. 3 shows the conversion ratio from GPC to diamond with varying the catalytic active metal content at the same treatment conditions (7 GPa, 1700° C, 15 min) as in Section 3.1. When GPC is used as the carbon source, which has somewhat lower crystallinity compared with NG, a distinct tendency of the catalytic action (Ni $\gtrsim$ Co > Fe) can be observed among the three metals. The order of catalytic action in the 80 wt % GPC–20 wt % metal (Fe, Co or Ni) system corresponds to the results in a previous paper

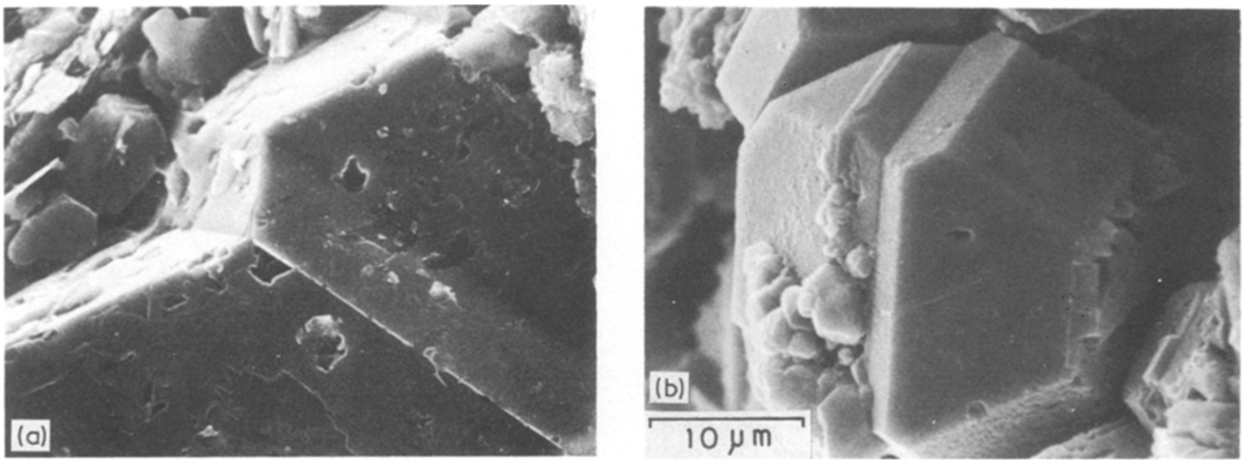

Figure 2 Scanning electron micrographs of twin crystals obtained at 7 GPa and 1700° C. Starting powder composition: (a) 80 wt % NG–20 wt % Co, (b) 50 wt % NG–50 wt % Ni [6]. Treatment time: (a) 15 min, (b) 10 min.

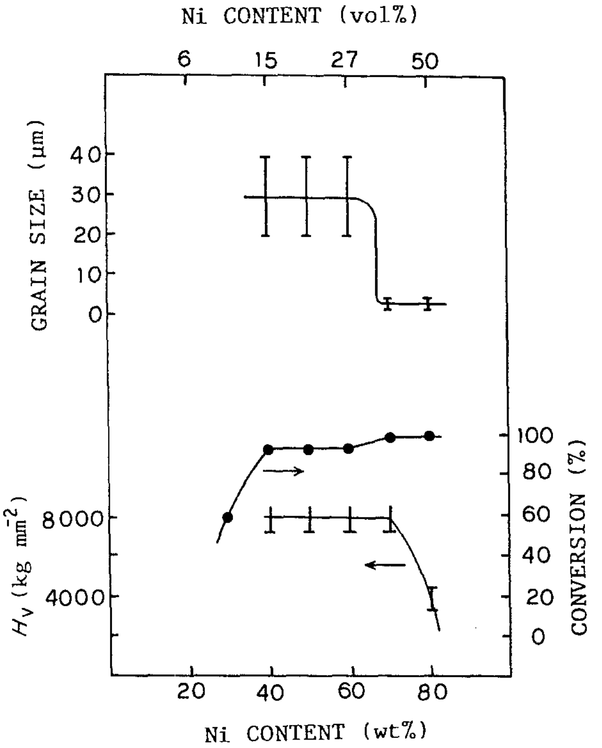

Figure 3 Conversion ratio from GPC to diamond with metal content (□, ■ Ni; △, ▲ Co; ○ Fe). Treatment conditions: 7 GPa, 1700° C, 15 min. Open symbols sintered, closed symbols: unsintered.

[10]. It was apparent that the conversion ratio of the GPC–Fe system is considerably lower even at higher contents of catalytic metal than in the NG–Fe system. This remarkable difference in the transformation reaction of the iron system could be related to the complicated formation behaviour of iron carbide [10]. In the GPC–Co and the GPC–Ni systems, the conversion ratio increased up to the metal content of 40 wt % and attained a value over 90% above 50 wt % metal content, when a sintered compact was formed in every case.

Fig. 4 shows the scanning electron micrographs of the sintered diamond compacts, which were obtained from the starting powder compositions of the 50 wt % GPC–50 wt % Co system (Fig. 4a) and the 30 wt % GPC–70 wt % Co system (Fig. 4b). The residual graphitized carbon and metal carbides are removed by acid treatment. At cobalt contents lower than 50 wt % (28.3 vol %), the grain size of converted diamond is over 20 μm, having a wide grain size distribution of diamond aggregates. By increasing the cobalt content up to 70 wt %, neck growth can be observed apparently between smaller diamond grains which constitutes the solid skeletal structure of diamond. Considerably larger voids remained where the melt of the metal–carbon phase had been pooled before acid treatment. Liquid-phase sintering by a solution–reprecipitation mechanism would proceed appropriately up to this content of catalytic metal.

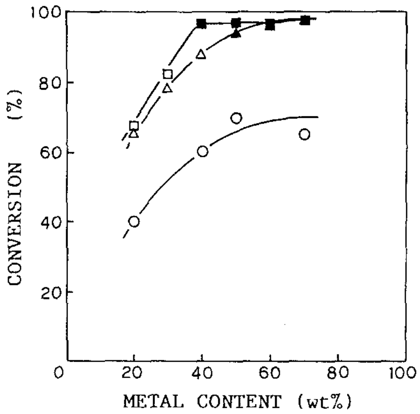

Figure 5 Grain size, microhardness and conversion ratio (1000 g load) of the sintered compacts obtained at various nickel contents. Treatment conditions: 7 GPa, 1700° C, 10 min; starting carbon: GPC).

Fig. 5 shows the grain size of the converted diamond and microhardness (1000 g load) of the sintered compact in the GPC–Ni system, which showed superior catalytic action for GPC among the three catalytic metals in Fig. 3. The treatment time was kept constant at 10 min. The conversion ratio is also plotted in the figure. A sintered compact could not be prepared below a nickel content of 40 wt % (15 vol %) because of the low conversion ratio. At a nickel content of 40 to 60 wt % (15 to 30 vol %), the grain size of diamond is 20 to 40 μm. The relatively wide range of grain size distribution would be caused by the difference in the transformation velocity, which results in the exaggerated grain growth of some of the converted diamond. The microhardness of the reaction bonded

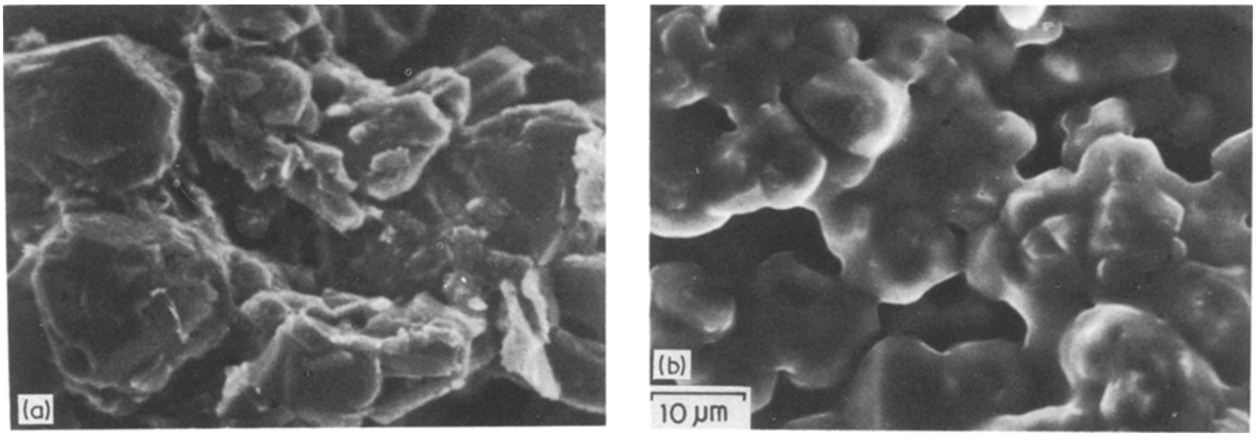

Figure 4 Scanning electron micrographs of the specimens treated at 7 GPa and 1700° C for 15 min. Starting powder composition: (a) 50 wt % GPC–50 wt % Co, (b) 30 wt % GPC–70 wt % Co.

TABLE I Grain size of the converted diamond obtained from various compositions of graphite pitch coke (GPC) and solvent-catalysts (treatment conditions: 7 GPa, 1700° C, 10 min)

Specimen no.	GPC (wt %)	Catalytic metal (wt %)	Solvent metal (wt %)	Grain size (μm)
G-1	50	Ni 50	0	20–40
G-2	50	Ni 40	Ti 10	10–20
G-2	50	Ni 40	Zr 10	10–20
G-4	50	Co 40	Zr 10	10–20
G-5	50	Fe 40	Zr 10	5–10

diamond phase is above 8000 kg mm^{-2}. Polycrystalline diamond sintered compacts would be formed with a strong direct bonding between diamond grains. At the increased content of nickel above 70 wt %, however, the grain size drops abruptly down to 2 to 3 μm, having a narrow distribution, and the microhardness decreases to about 4000 kg mm^{-2}. This shows the formation of metal-bonded sintered compact because of less connectivity between the diamond grains at such a small volume fraction of diamond in the metal matrix [7]. As a consequence, the nickel volume of 20 to 30% is found to be favourable to prepare the polycrystalline diamond sintered compact, if one can prepare the fine-grained microstructure with a narrower grain size distribution.

3.3. Effect of binary solvent–catalyst on the microstructure of reaction-sintered diamond compact

Table I shows the grain size of diamond converted from GPC using 50 wt % solvent–catalysts composed of the unary (G-1) and binary systems (G-2 to G-5). The composition of the binary system is 40 wt % Ni, Co or Fe catalytic active metal and 10 wt % Ti or Zr solvent metal. The treatment conditions were the same as those in Fig. 5. Every specimen was recovered as a sintered compact, the conversion ratio being above 90% except the Fe–Zr system. The grain size of specimen G-1 (50 wt % GPC–50 wt % Ni) is 20 to 40 μm, as also seen in Fig. 5. The addition of a solvent metal of the 4A group (titanium or zirconium) to the nickel system decreases the grain size to 10 to 20 μm (compare with G-1 to G-3) with the grain size distribution narrowed [6].

The effect of additive solvent zirconium metal on the reduced grain size can also be confirmed in the solvent–catalysts of the Co–Zr and Fe–Zr systems. Fig. 6 shows the scanning electron micrographs of the specimens (G-4 and G-5). In contrast to the GPC–Co system of the same metal content in Fig. 4a, the effects of decreasing the grain size and narrowing of its distribution are apparent in the binary solvent–catalyst system. No exaggerated grain growth can be seen. Such effects seem to be somewhat pronounced in the Fe–Zr system, where the conversion ratio enhanced to 80 to 90% on account of increasing solvent effect of zirconium (compare with Fig. 3). The difference in the formation behaviour of the solid solution or carbides in the metal–carbon system [10] is considered to affect the crystallization process (e.g. nucleation or growth) which determine the grain size and microstruture of the sintered compact.

Considering the similar effect of titanium addition on the NG–Fe–Ti system as shown in a previous paper [5], the coexistence of stable 4A transition metal carbide (TiC$_x$ or ZrC$_x$) would depress the grain growth by controlling the solubility of carbon and hence by decreasing the growth rate of diamond.

4. Conclusions

The effects of starting carbons (NG and GPC) and solvent–catalysts (nickel, cobalt, iron, titanium and zirconium) on the reaction sintering of diamond were investigated at the high pressure and temperature treatment conditions (7 GPa, 1700° C, 10 to 15 min). The following conclusions were obtained by the measurement of the conversion ratio from graphitized carbon to diamond and the observations of grain size, microstructure and sintering behaviour.

1. Diamond grains with euhedral crystal habits

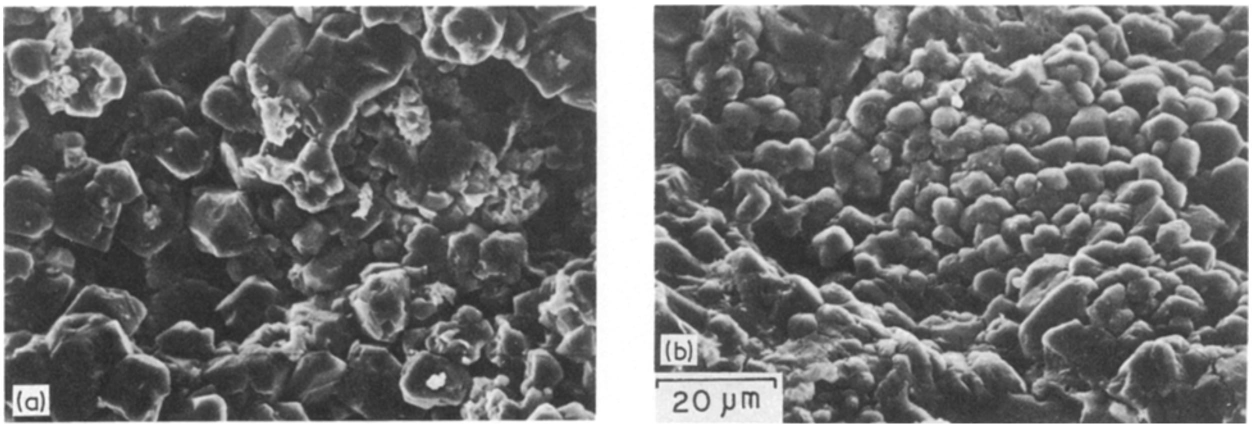

Figure 6 Scanning electron micrographs of the specimens treated at 7 GPa and 1700° c for 10 min. Starting powder composition: (a) 50 wt % GPC–40 wt % Co–10 wt % Zr, (b) 50 wt % GPC–40 wt % Fe–10 wt % Zr.

which were occasionally grown as twin crystals, were obtained from purified natural graphite using solvent–catalysts in the nickel, cobalt or iron systems. Rapid conversion and growth of diamond from NG which help the growth of twins, are unfavourable for obtaining the fine-grained microstructure of the sintered compact.

2. A skeletal strucutre of sintered diamond crystals was easily formed by a mild conversion from GPC and by promotion of neck growth of the converted diamond. A polycrystalline diamond sintered compact which has a microhardness of more than 8000 kg mm^{-2}, was prepared at the nickel solvent–catalyst content of 40 to 60 wt % (15 to 30 vol %). The degree of catalytic action for the conversion from GPC was in the order Ni $\gtrsim$ Co $>$ Fe.

3. A remarkable effect of using binary solvent–catalyst on the grain growth depression was observed with a narrow grain size distribution and no exaggerated grain growth of converted diamond. The coexistence of stable 4A transition metal carbide (TiC$_x$ or ZrC$_x$) in the solvent–catalysts would control the solubility of carbon and depress the grain growth of diamond.

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Received 24 August
and accepted 1 December 1987