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Effects of added diamond powder on the reaction sintering behaviour of diamond in the graphite–nickel system

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Polycrystalline diamond sintered compact was prepared under high pressure and temperature conditions (7 GPa, 1700° C, 10 to 30 min) from the starting material with the composition of the system 50 wt% carbon (diamond + graphitized pitch coke (GPC))–50 wt% Ni. The effects of added diamond powder on the microstructure of the sintered compact and reaction sintering behaviour were investigated. The grain size of diamond in the sintered compact decreased remarkably from 20 to 40 μm to 2 to 3 μm on addition of 10 to 20 wt% diamond powder (grain size: $\sim$1 μm) to the GPC–Ni system. The grain size can be controlled by that of the added diamond powder. A sufficient supply of carbon from GPC plays an important role in the formation of a covalently bonded compact of diamond. The grain growth of the formed diamond is depressed by the coexistence of diamond powder, which controls the solubility of carbon in the metal–carbon system and also the grain growth process by solution-reprecipitation.

1. Introduction

Naka *et al.* [1–4] reported that diamond sintered compacts can be prepared by reaction sintering which is accompanied by transformation from graphite to diamond in the presence of a solvent–catalyst. When the starting material with the composition of the system 40 to 60 wt % (73 to 85 vol %) graphitized pitch coke (GPC)–60 to 40 wt % (27 to 15 vol %) Ni was treated at 7 GPa, 1700° C and 10 min, a polycrystalline diamond sintered compact whose conversion ratio from graphite to diamond was nearly 100%, was formed [3]. Direct bonding between the converted diamond grains was found in the sintered compact. The Vickers microhardness was above 8000 kg mm^{-2}. However, abnormal grain growth was observed in this sintered compact. It was necessary to add solvent metal such as titanium or zirconium to the catalytic active metal in order to depress the abnormal grain growth [3]. Basic investigations on the liquid-phase sintering behaviour are important to control the microstructure (grain size, grain-size distribution and grain connectivity) of the sintered compact [5]. The solubility of carbon in the metal–carbon system will be related to the neck growth and grain-growth behaviour of the nucleated diamond.

The effects of the addition of diamond powder to the starting material of the graphitized carbon and solvent–catalyst system on the reaction sintering of diamond were investigated in the present work. The microstructure of the sintered compact was examined by varying the amount and grain size of the added diamond powder and the high pressure and temperature treatment time.

2. Experimental procedure

The starting graphitized carbon used was GPC (under 325 mesh, treated at 2800° C in an argon atmosphere), which has a lattice constant $c_{0002} = 0.6722$ nm, a crystallite size $L_{c_{002}} = 91$ nm and a degree of graphitization $P = 0.92$ [6]. The solvent-catalyst metal was commercially available nickel powder (about 300 mesh, purity > 99.8 wt %). Commercially available diamond powders with four different particle sizes ($\sim$1, 5 to 10, 20 to 30 and 40 to 60 μm) were also used.

The composition of the starting powder was kept constant at 50 wt % carbon (GPC + diamond) and 50 wt % nickel. These assorted powders were mixed for 1 h in a V-shaped rotary mixer. Taking into account the ambient pretreatment effect on the promotion of particle joining of diamond grains [1], the mixed powder was first degassed in a 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 quickly packed into the specimen cell and placed in the girdle-type high-pressure apparatus [2, 4]. The procedures for high pressure and temperature treatment (7 GPa, 1700° C), as well as the calibration method for pressure and temperature, were the same as those in the previous papers [2, 4]. Treatment time was varied from 10 to 30 min.

The treated specimens were identified by X-ray diffraction. The conversion ratio from graphite to diamond was determined from the relative intensity of diamond 1 1 1 diffraction to that of graphite 0 0 2 diffraction, using a calibration curve. The treated specimen was post-treated in hot aqua regia for 1 h to

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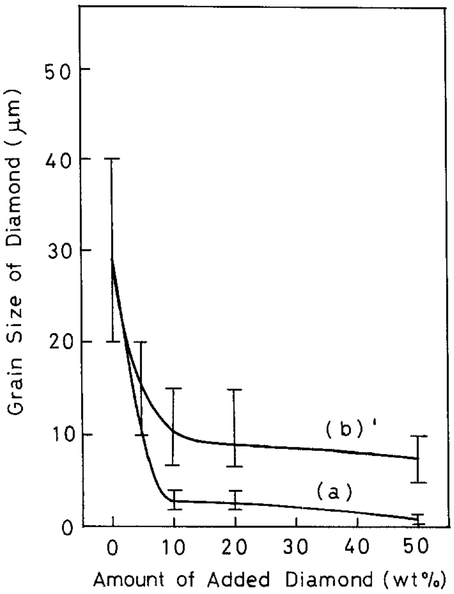
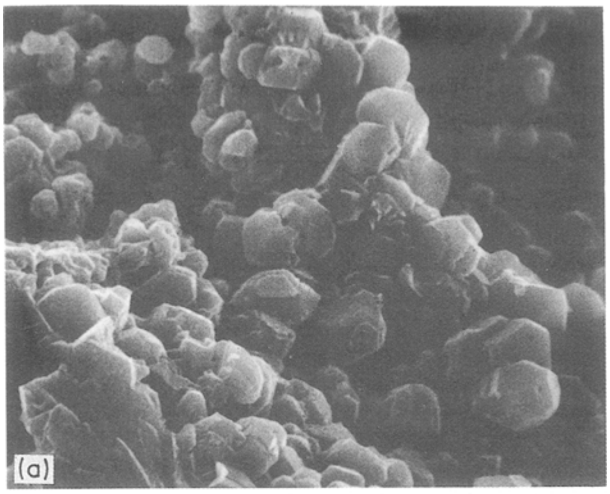


Figure 1 Relationship between grain size of diamond in the sintered compact and amount of added diamond powder. Size of added diamond. (a) ~1, (b) 5 to 10 μm. Starting powder composition: 50 wt % (GPC + diamond)-50 wt % Ni. Treatment conditions: 7 GPa and 1700° C for 10 min.

remove the residual carbon and metal carbide. The grain size of diamond and the surface microstructure of the sintered compact were examined by scanning electron microscope. The Vickers microhardness of the polished surface was measured under a 1000 g load.



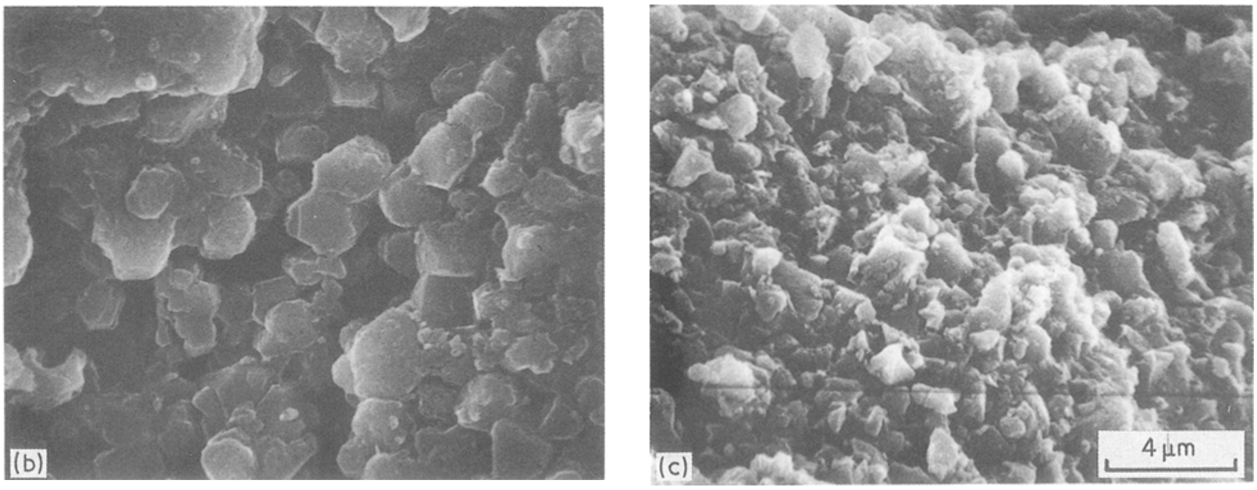
3. Results and discussion

3.1. Influence of the amount of added diamond on the grain size of diamond in the sintered compact

Fig. 1 shows the variation of grain size of diamond in the sintered compact with amount of added diamond powder. The pressure, temperature and treatment time conditions were kept constant at 7 GPa, 1700° C and 10 min, respectively. The grain size of added diamond is (a) ~1 μm and (b) 5 to 10 μm. The amount of added diamond was selected as follows: 0, 5, 10, 20, 50 wt %. Sintered diamond compact was prepared in every specimen whose conversion ratio from graphite to diamond was > 90%. The sintered compact had a wide range of grain-size distribution of 20 to 40 μm at 0 wt % of added diamond, which would be the composition of the 50 wt % GPC–50 wt % Ni system. Large diamond grains with a diameter of about 50 μm were found also in this specimen, which were formed by abnormal grain growth [3, 4]. When 10 to 20 wt % ~1 μm diamond powder was added (Fig. 1a), the grain size of diamond in the sintered compact decreased remarkably down to 2 to 3 μm. At 50 wt % added diamond, which would be the composition of the 50 wt % diamond–50 wt % Ni system, the grain size was ~1 μm, which verifies that grain growth does not occur in this specimen. An analogous tendency of a remarkable decrease in the grain size on diamond addition was confirmed using 5 to 10 μm diamond powder (Fig. 1b). However, the minimum grain size of diamond in the sintered compact was of the same magnitude as the added diamond grain size.

Fig. 2 shows the scanning electron micrographs of the sintered diamond compacts, where the grain size of added diamond powder was ~1 μm. The starting powder compositions are the systems: (a) 40 wt % GPC–10 wt % diamond–50 wt % Ni, (b) 30 wt % GPC–20 wt % diamond–50 wt % Ni, and (c) 50 wt % diamond–50 wt % Ni. Residual graphitized carbon and metal carbide are removed by acid treatment. The grain size of diamond in Figs 2a and b was 2 to 3 μm,

Figure 2 Scanning electron micrographs of the acid-treated specimens treated at 7 GPa and 1700° C for 10 min. Starting powder composition: 50 wt % (GPC + diamond)–50 wt % Ni. Diamond content: (a) 10, (b) 20, (c) 50 wt %. Grain size of added diamond powder: ~1 μm.



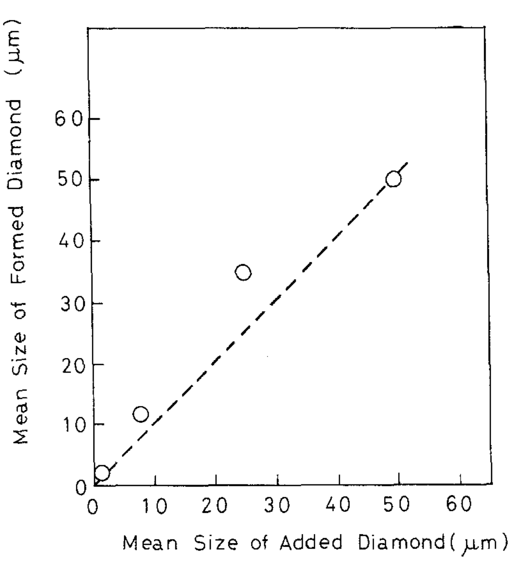


Figure 3 Relationship between the mean grain size of diamond in the sintered compact and that of added diamond powder. Starting powder composition: 40 wt % GPC–10 wt % diamond–50 wt % Ni. Treatment conditions: 7 GPa and 1700° C for 10 min.

having a homogeneous grain-size distribution with no abnormal grain growth. Neck growth can be seen between the diamond grains. The measured microhardness of these specimens was above 8000 kg mm^{-2}. These results indicated that the specimen is polycrystalline diamond, which has a strong direct bonding between diamond grains. On the other hand, Fig. 2c shows that the grain size of diamond in the sintered compact is ~1 μm. The measured microhardness of this specimen was about 4000 kg mm^{-2} and the compact pulverized by acid treatment, which suggest that this specimen is a metal-bonded sintered compact [7]. The coexistence of GPC in the specimen is indispensable for preparation of polycrystalline diamond sintered compact [8].

3.2. Influence of the grain size of added diamond powder on microstructure of diamond sintered compact

Fig. 3 shows the mean grain size of diamond in the sintered compact plotted against the mean grain size of added diamond powder. Treatment time was kept constant at 10 min. An added diamond content of 10 wt % was chosen, because the grain growth was fully depressed by 10 wt % addition, as shown in Fig. 1. The amount of GPC was 40 wt %. The mean grain size of diamond in the sintered compact increased with an increase in that of the added diamond powder. Somewhat increased grain growth was observed when using diamond powders with grain sizes of ~1, 5 to 10 and 20 to 30 μm. However, when the grain size of added diamond was 40 to 60 μm, the mean grain size of diamond in the sintered compact was as large as that of the added diamond.

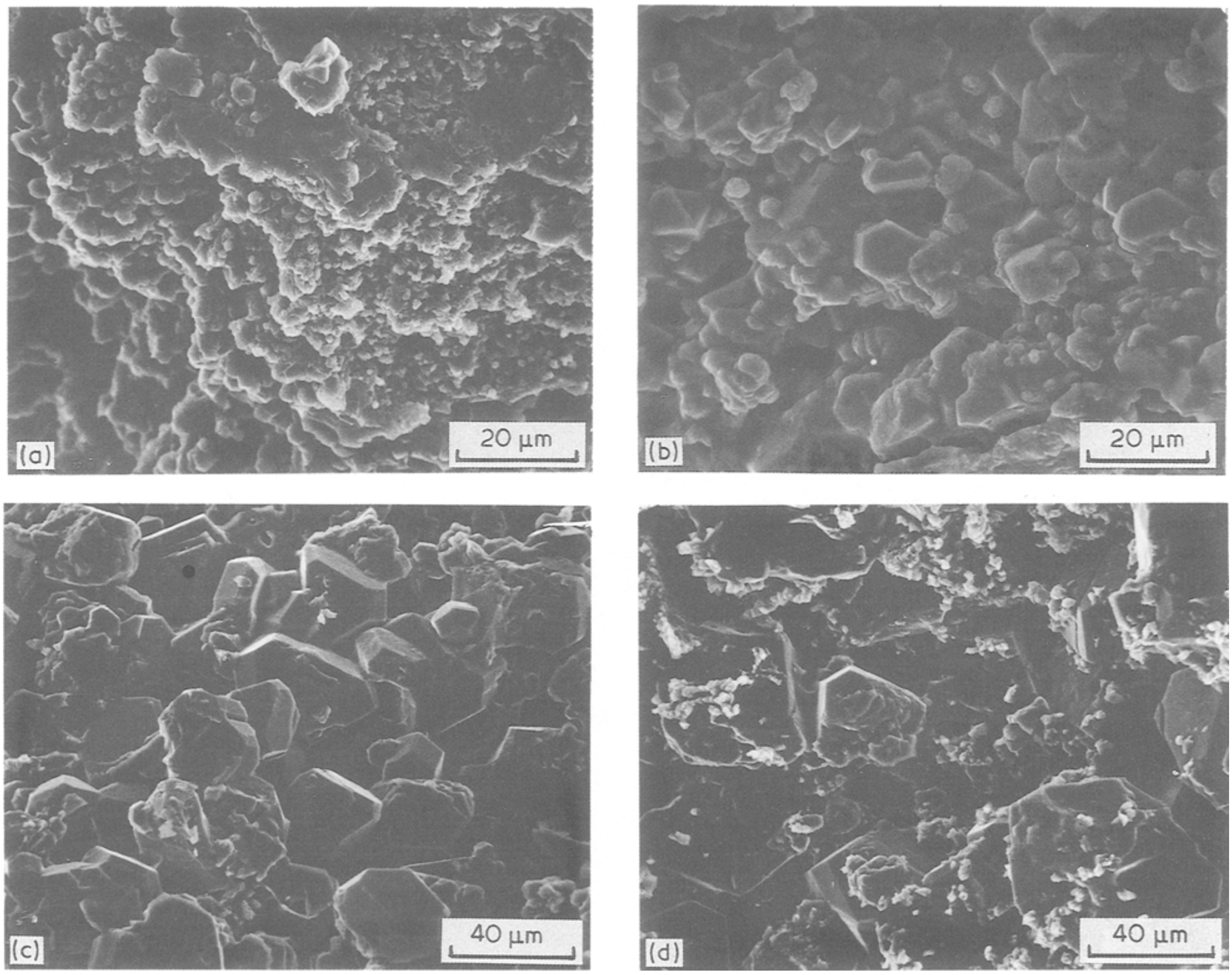
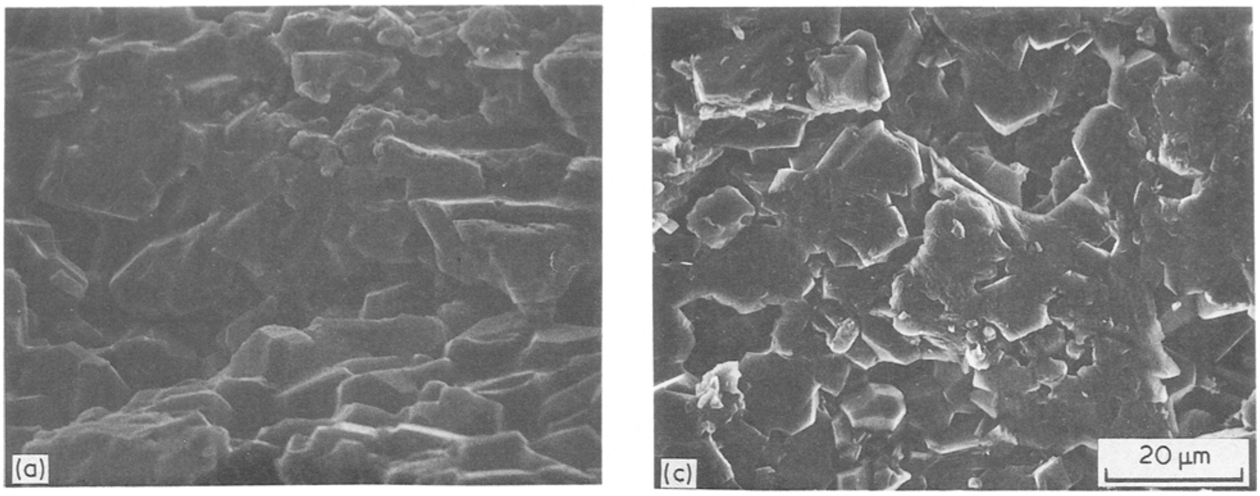


Figure 4 Scanning electron micrographs of the acid-treated specimens treated at 7 GPa and 1700° C for 10 min. Starting powder composition: 40 wt % GPC–10 wt % diamond–50 wt % Ni. Grain size of added diamond powder: (a) ~1, (b) 5 to 10, (c) 20 to 30, (d) 40 to 60 μm.



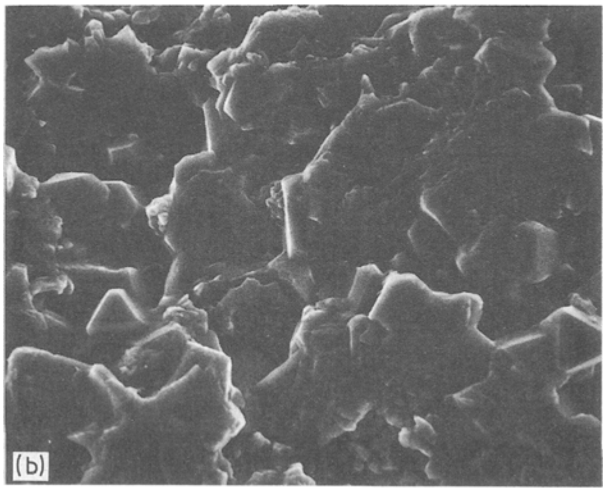


Figure 5 Scanning electron micrographs of the acid-treated specimens treated at 7 GPa and 1700° C. Starting powder composition: 40 wt % GPC–10 wt % diamond–50 wt % Ni. Grain size of added diamond powder: 5 to 10 μm. Treatment time: (a) 10, (b) 20, (c) 30 min.

Fig. 4 shows the scanning electron micrographs of the sintered diamond compacts, in which 10 wt % diamond powders with the grain sizes of (a) ~ 1, (b) 5 to 10, (c) 20 to 30 and (d) 40 to 60 μm were added, corresponding to the plots in Fig. 3. The grain sizes of diamond in the sintered compacts (a), (b) and (c) were 2 to 3, 8 to 15 and 25 to 35 μm, respectively. Homogeneous texture without abnormal grain growth was observed in the specimens (a), (b) and (c). The diamond grains converted from GPC and the added diamond grains could not be distinguished from the specimens. When adding 40 to 60 μm diamond powder, however, large diamond grains with diameters of about 50 μm were observed (Fig. 4d). Smaller diamond grains whose diameter was less than 10 μm were also observed in the space among larger grains. The microhardness of the sintered compacts of (a), (b) and (c) was above 8000 kg mm^{-2}. The exact microhardness of the specimen (d) was difficult to measure because the large diamond grains tended to fall off the compact during abrasion.

It may be stated from the results in Figs 1 to 4 that the grain size of diamond in the sintered compact can be controlled by the grain size of the added diamond powder. The grain size was somewhat larger than that of the added diamond, which suggests that the grain growth contributes to the neck growth between the diamond grains and the formation of polycrystalline diamond.

3.3. Influence of the high pressure and temperature treatment time on the microstructure of diamond sintered compact

Fig. 5 shows scanning electron micrographs of the sintered compact with varying high pressure and temperature treatment times. The pressure and temperature conditions were kept constant at 7 GPa and 1700° C. The amount of diamond added was 10 wt % and the grain size was 5 to 10 μm. The grain size of diamond in the sintered compact was about 10 to 20 μm in the specimens prepared at a treatment time of 10 to 30 min, although a slight grain growth was observed with increasing treatment time. Grain growth occurred less also in the case of ~ 1 μm diameter diamond powder.

Fig. 6 shows a scanning electron micrograph of the sintered compact at a treatment time of 30 min, where the grain size of added diamond powder was 40 to 60 μm. Other experimental conditions were the same as in Fig. 5. At a treatment time of 10 min (see Fig. 4d), small nucleated grains remained in the space between the large grains, as described in Section 3.2. However, these small grains disappeared on solution-reprecipitation [5] after a treatment time of 30 min, as shown in Fig. 6. Only large grains of diamond (grain size about 50 μm) can be observed.

3.4. Reaction sintering process of diamond

From above results in Sections 3.1 to 3.3, the reaction sintering of diamond in the GPC–diamond–Ni system is considered to proceed as follows.

During the initial stage of reaction sintering, Ni–C solution is formed above the eutectic temperature in the Ni–C system (about 1450° C at 7 GPa), followed by an immediate nucleation of many diamond grains due to the difference in solubility between GPC and diamond [9].

Neck growth between the converted diamond grains is formed by precipitation of diamond on to the adjoining part. A constant supersaturation of carbon

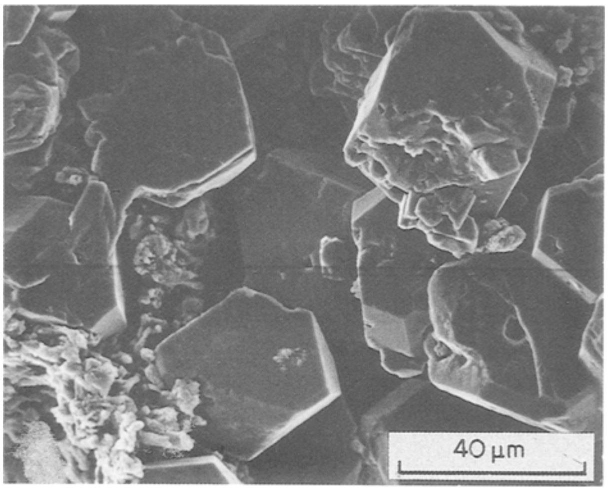


Figure 6 Scanning electron micrograph of the acid-treated specimen treated at 7 GPa and 1700° C for 30 min. Starting powder composition: 40 wt % GPC–10 wt % diamond–50 wt % Ni. Grain size of added diamond powder: 40 to 60 μm.

in the system can be maintained by solution of carbon from GPC. Grain growth of the formed diamond is depressed by the coexistence of added diamond powder, which controls the supersaturation of carbon and hence the grain growth by a solution-reprecipitation mechanism [5].

During the final stage of reaction sintering, polycrystalline diamond, which has direct covalent bonding between diamond grains, is formed with pooling of the Ni–C solution out of the grain boundary. The fact that the grain size of diamond in the sintered compact is controlled by the grain size of added diamond powder (see Section 3.2), represents a rapid growth of nucleated grains occurring preferentially by a sufficient supply of carbon to the smaller diamond grains. All the small diamond grains and GPC are spent as a material source for solution-reprecipitation, until neck growth and grain growth cease.

4. Conclusions

The effects of added diamond powder on the reaction sintering of diamond were investigated at the high pressure and temperature treatment conditions (7 GPa, 1700° C, 10 to 30 min). The following conclusions were obtained from observations of grain size, microstructure and sintering behaviour.

1. The grain size of diamond in the sintered compact decreased remarkably from 20 to 40 μm to 2 to 3 μm on addition of 10 to 20 wt % diamond powder (grain size ~ 1 μm) to the GPC–Ni system (Ni 50 wt %). An analogous tendency of a marked decrease in the grain size was observed on adding diamond powders with diameters of 5 to 10 and 20 to 30 μm. The grain size in the sintered compacts was somewhat larger than that of the added diamond powder, which shows that the grain size can be controlled by the grain size of the added diamond powder.

2. Neck growth between the small nucleated diamond grains is formed by the precipitation of diamond from a supersaturated solution of carbon on to the adjoining part. A sufficient supply of carbon from GPC in the treated specimens plays an important role in the preparation of polycrystalline diamond. Grain growth of the formed diamond is depressed by the coexistence of added diamond powder, which controls the solubility of carbon and the grain growth by solution-reprecipitation. The grain size and covalently bonded microstructure of polycrystalline diamond sintered compact can be controlled by reaction sintering in the GPC–diamond–Ni system.

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