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Reaction sintering of diamond using a binary solvent-catalyst of the Fe–Ti system

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Reaction sintering of diamond was investigated using a starting mixed powder of purified natural graphite and a binary solvent-catalyst of the Fe–Ti system under high pressure (7 GPa) and temperature (1700° C) conditions for a treatment time of 1 to 15 min. Diamond sintered compact of about 100% conversion ratio from graphite to diamond was obtained with the binary solvent-catalyst content: 11.4 to 17.0 vol % (30 to 40 wt %) Fe and 6.6 to 7.7 vol % (10 wt %) Ti. The sintered compact having the bulk density of 4.1 to 5.5 g cm^{-3}, consisted of diamond phase and metal carbide (Fe_3C and TiCx) phase. The Vickers microhardness (under 1000 g load) of the sintered diamond phase was >8000, while that of the metal carbide phase was 1000 to 2000. The transformation from graphite to diamond proceeded in a short time (<1 min), which was followed by a particle joining between the formed diamond grains, when the densification would be attained at the reaction time of 15 min by pooling out the melt of carbon and solvent-catalyst.

1. Introduction

Preparation of diamond sintered compact with a polycrystalline microstructure analogous to natural carbonado diamond [1], has received an intensive interest in the industrial application to cutting tools, rock-drilling bits, high thermal-conductive i.c. substrates, etc. [2, 3]. Extensive investigations have been carried out on diamond sintering using diamond powder as starting carbon in the presence of additives [4–7] or no additive [8–10]. The sintered compact with additives contains metal or its metal carbide bonded diamond aggregates, so that the hardness of the sintered compact is comparatively low. On the other hand, a detailed description on the sintering phenomenon of no additive compact has not been reported.

Naka *et al.* [11] reported recently in their study on diamond formation from graphite, that the grain growth of diamond could be considerably depressed by using a binary solvent-catalyst system such as the Fe–Ti system. They pointed out also [12], that a particle joining between diamond grains was promoted by a careful ambient pretreatment of graphite and solvent-catalyst in an argon atmosphere.

In the present work, a diamond sintered compact was prepared successfully by the reaction sintering which is accompanied by transformation from graphite to diamond in the presence of solvent-catalyst. The reaction sintering of diamond was carried out under constant high pressure and temperature conditions, using a starting mixed powder of purified natural graphite and a binary solvent-catalyst of the Fe–Ti system. The phase transformation and sintering process, as well as the bulk density, microhardness and microstructure of the sintered compact were examined as a function of the starting powder composition and the high pressure and temperature treatment time.

2. Experimental procedure

Natural graphite powder (285–325 mesh) which was highly-purified at 2800° C in a Cl_2 atmosphere, was used as starting carbon to obtain a high yield of diamond [13]. The solvent-catalyst metals were commercially available as iron and titanium powders (about 300 mesh), both purities of which were above 99.8 wt %. The composition of the starting powder is summarized in Table I, where the weight concentration of titanium is constant at 10 wt % (5.6 to 7.3 vol %), and the relative contents of iron and purified natural graphite are varied. Thus assorted powder was mixed for 30 min in a V-shaped rotary mixer. The mixed powder was first pretreated in vacuum (at

TABLE I Composition of starting powder and conversion ratio from graphite to diamond

	Graphite		Iron		Titanium		Conversion ratio (%)
	(vol %)	(wt %)	(vol %)	(wt %)	(vol %)	(wt %)	
a	91.2	80	3.2	10	5.6	10	75
b	86.9	70	7.0	20	6.1	10	85
c	82.0	60	11.4	30	6.6	10	~ 100
d	75.7	50	17.0	40	7.3	10	100

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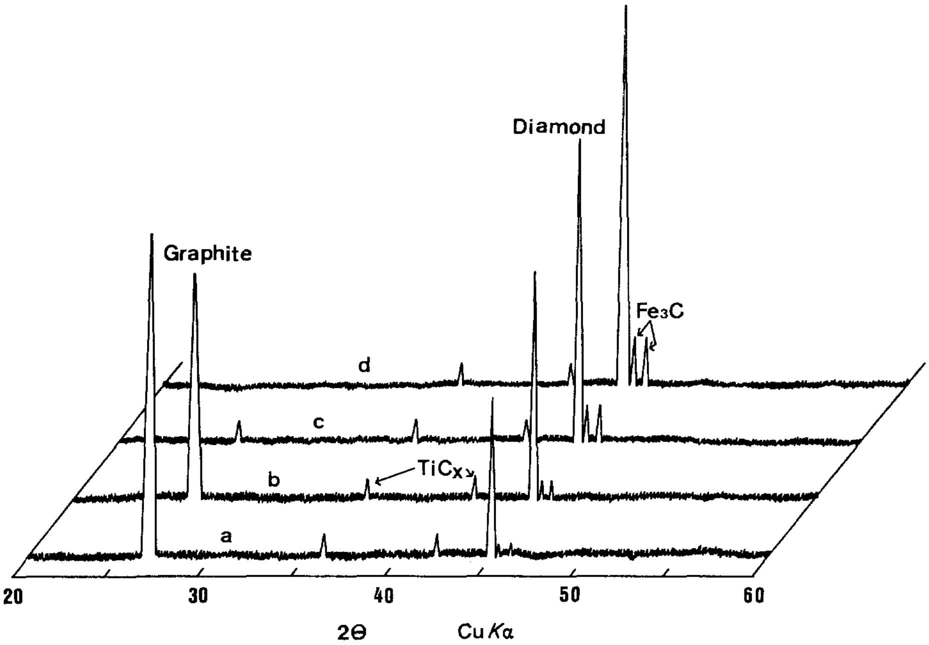


Figure 1 X-ray diffraction pattern of the specimen surface of sintered diamond treated at 7 GPa and 1700° C for 15 min in the Fe–Ti solvent-catalyst system (specimens, a, b, c, and d correspond to those in Table I).

2×10^{-5} torr) at 400° C for 1 h, and subsequently in an argon flow (flow rate: 100 ml min^{-1}) for 1 h at 760 torr at 1000° C [12].

The pretreated mixed powder was packed into the specimen cell quickly in a globe box and set in the girdle-type high pressure apparatus. The cell assembly was the same as that in the previous paper [14] except that molybdenum plates (0.1 mm in thickness) were arranged between the graphite plate and SKH-9 disk. Constant high pressure (7 GPa) and temperature (1700° C) conditions were chosen so as to give an appropriate yield of diamond with reference to previous papers [11, 15]. The specimen was compressed to 7 GPa (accuracy: ± 1.5 %) and then electric power was applied to the glassy carbon heater to heat the specimen up to 1700° C (accuracy: ±20° C) in about 7 min. After the heat treatment for a desired reaction time (1 to 15 min), the specimen was quenched to room temperature under high pressure and then decompressed. The calibration of pressure and temperature was carried out by the same techniques as previous reports [14, 15].

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 by using a calibration curve.

Surface of the diamond sintered compact was abraded by a rotary diamond disk and then mirror-polished with diamond paste. The microstructure of the specimen was examined by an optical microscope or scanning electron microscope (SEM). The bulk density of the specimen was measured by Archimedes' method. The Vickers microhardness of the polished surface was measured under 1000 g load.

3. Results and discussion

3.1. Reaction sintering conditions of diamond

Fig. 1. shows a series of X-ray diffraction patterns of the specimen surface, where the pattern symbols (a to d) correspond to the specimens in Table I. The treatment time was kept constant at 15 min. One can see the variation of conversion ratio from graphite to diamond (see also the last column in Table I) and the relative amount of coexisting carbides (Fe_3C or TiCx) with a progressive increase in the added iron content from 3.2 to 17.0 vol %.

In the solvent-catalyst system of 3.2 vol % Fe–5.6 vol % Ti (see specimen (a) in Table I and Fig. 1), the specimen was broken into a few pieces of fragments after the high pressure and temperature treatment, although each fragment was collected as a sintered matter. Residual graphite phase in the grain boundary of the sintered compact would possibly cause the fracture of the specimen. A single sintered compact that was not broken was obtained above the iron content of 7.0 vol %. The conversion ratio was 85%, however, in using the solvent-catalyst of 7.0 vol % Fe–6.1 vol % Ti (specimen (b)) in which the compact would be loosely sintered. At higher concentrations of catalytic active iron ((c) 11.4 vol % and (d) 17.0 vol %), the conversion ratio increased up to about 100% with a result of the formation of a solid sintered compact. The coexisting chemical species other than diamond and graphite were TiCx and Fe_3C in every case with the yield of Fe_3C increasing with an increase in the added iron content.

Fig. 2 shows the appearance of as-sintered compact of diamond in the solvent-catalyst system of 11.4 vol % Fe–6.6 vol % Ti. Most of the sintered compacts were

TABLE II Bulk density and microhardness of sintered compact.

Composition (vol %)			Bulk density ($\mathrm{g\,cm^{-3}}$)	Microhardness Hv	
Graphite	Iron	Titanium		Diamond phase	Carbide phase
82.0	11.4	6.6	4.1	> 8000	1000–2000
75.7	17.0	7.3	5.5	> 8000	1000–2000

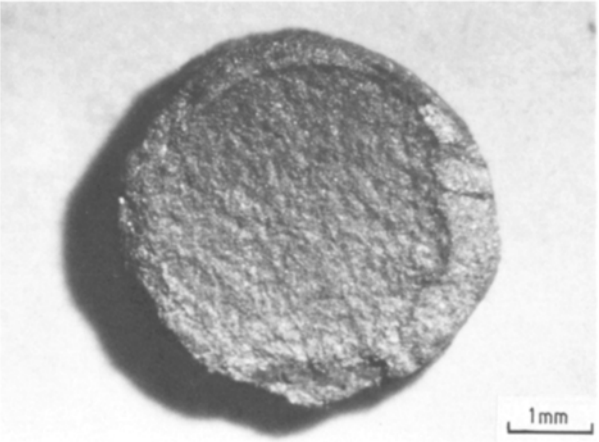


Figure 2 Appearance of the as-sintered compact of diamond treated at 7 GPa and 1700° C for 15 min in the presence of 11.4 vol % Fe–6.6 vol % Ti.

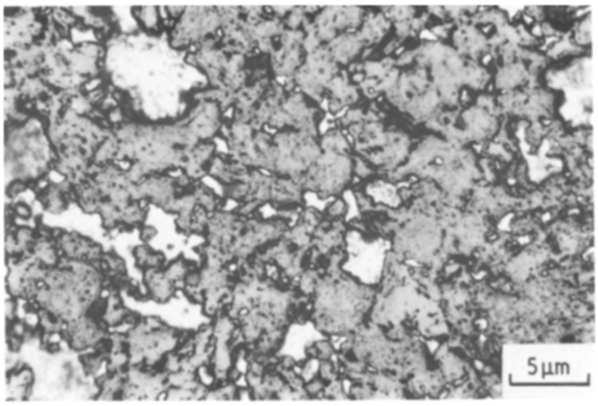


Figure 3 Optical micrograph of the polished surface of sintered diamond treated at 7 GPa and 1700° C for 15 min in the presence of 11.4 vol % Fe–6.6 vol % Ti.

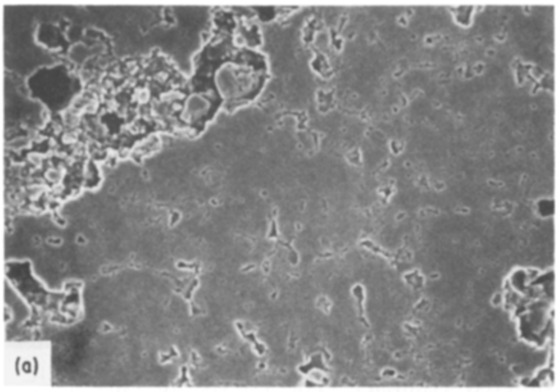
4 to 5 mm in diameter and about 2 mm in thickness. The bulk densities of the sintered compacts for two starting compositions (c) and (d) in Table I), are shown in Table II, where the respective measured densities were 4.1 and 5.5 g cm^{-3}. Supposing that natural graphite, iron and titanium converted into diamond, Fe_3C and TiC, respectively after the high pressure and temperature treatment, the relative bulk densities to the theoretical density were 82% for the specimen (c) and 93% for the specimen (d).

It is necessary, therefore, to increase the amount of catalytic active iron in order to obtain 100% of conversion ratio from graphite to diamond and a high bulk density of the sintered compact.

3.2 Microstructure and formation process of sintered diamond

Fig. 3 shows an optical micrograph of the polished surface, where several white portions with metallic luster are scattered on the grey background area. The white portions would be a carbide phase (Fe_3C and TiC_x), since the Vickers microhardness of this portion was 1000 to 2000 (Table II). On the other hand, the background portion gave no indentation even under 1000 g load which verifies the background portion consists of a tightly bonded diamond phase by reaction sintering. The microhardness of this phase is evaluated to exceed 8000, because the hardness of a commercial diamond sintered compact was 7000 to 8000 under the same measurement condition.

The polished sintered compact was treated in hot aqua regia for 1 h to dissolve the carbide phase or residual graphite. Fig. 4 shows the SEM photographs of a thus treated surface for the three different solvent-catalyst systems. There can be observed relatively large voids where the carbide phase had been pooled and corroded out entirely by the acid treatment. Apparently these voids increase in number with an increase in the concentration of catalytic active iron. Comparatively large diamond crystals with developed facets were observed on the inside walls of the voids. Fig. 5 shows an example of a magnified portion of the sintered diamond, where the particle joinings are considerably developed so that the grain boundaries are rather difficult to distinguish owing to the formation of diamond–diamond direct bonding.



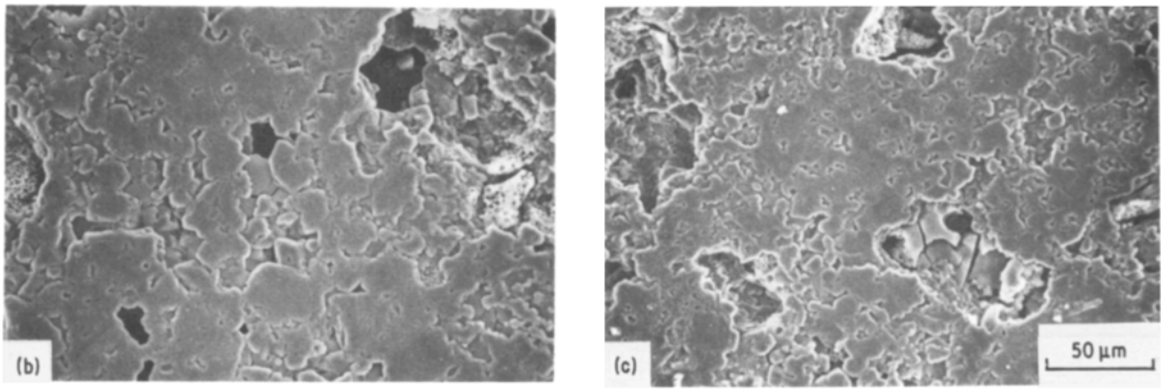


Figure 4 SEM photographs of the polished and acid-treated surface of sintered diamond treated at 7 GPa and 1700° C for 15 min in the presence of the solvent catalyst: (a) 7 vol % Fe–6.1 vol % Ti, (b) 11.4 vol % Fe–6.6 vol % Ti and (c) 17.0 vol % Fe–7.3 vol % Ti.

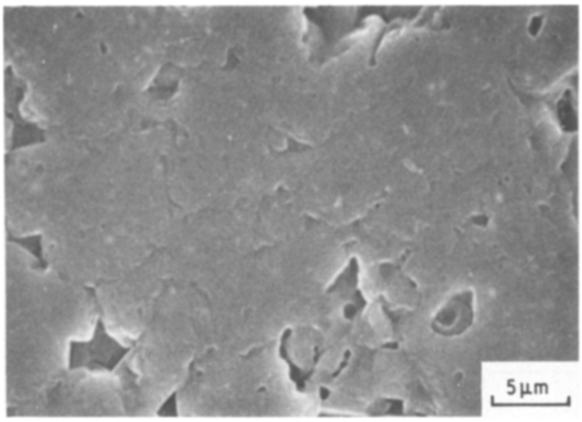


Figure 5 SEM magnified photograph of the sintered diamond phase (solvent-catalyst: 17 vol % Fe–7.3 vol % Ti).

Reaction sintering process was examined as a function of treatment time under the constant high pressure and temperature treatment conditions (7 GPa, 1700° C) using the solvent-catalyst of 17 vol % Fe–7.3 vol % Ti. Figs. 6a, b and c show the SEM photographs of the specimen surface of the sintered diamond which is subject to no mechanical finishing, but is treated in hot aqua regia for 1 h. Even at the high pressure and temperature treatment time of 1 min (Fig. 6a), the conversion ratio from graphite to diamond was found to be 100%. This indicates that the transformation from graphite to diamond occurs very rapidly in less than 1 min, which is followed by the subsequent sintering process. Fine-grained diamond particles appears between the larger diamond grains (grain size: 5 to 10 μm). In case of the treatment time of 5 min (Fig. 6b), the diamond grain grows slightly with an incorporation of smaller grains. The neck growth between many of the diamond grains is observed at the treatment time of 15 min (Fig. 6c). The densification would occur simultaneously by pooling out the melt of carbon and solvent-catalyst from the joining parts. A typical neck growth is formed also in the Ni–Zr solvent-catalyst system [16] as shown in Fig. 6d, where the graphitized pitch coke (GPC) is treated at 7 GPa and 1700° C for 10 min. Therefore, the reaction sintering is concluded to proceed by the neck growth between the transformed diamond grains with pooling out the melt.

4. Conclusions

Reaction sintering of diamond using natural graphite and a binary solvent-catalyst of the Fe–Ti system was investigated under high pressure and temperature conditions (7 GPa, 1700° C). The following conclusions are obtained from the examinations of the effect of the starting powder composition and the high pressure and temperature treatment time on the reaction sintering process and microstructure of the sintered diamond.

1. A single compact of sintered diamond (4 to 5 mm

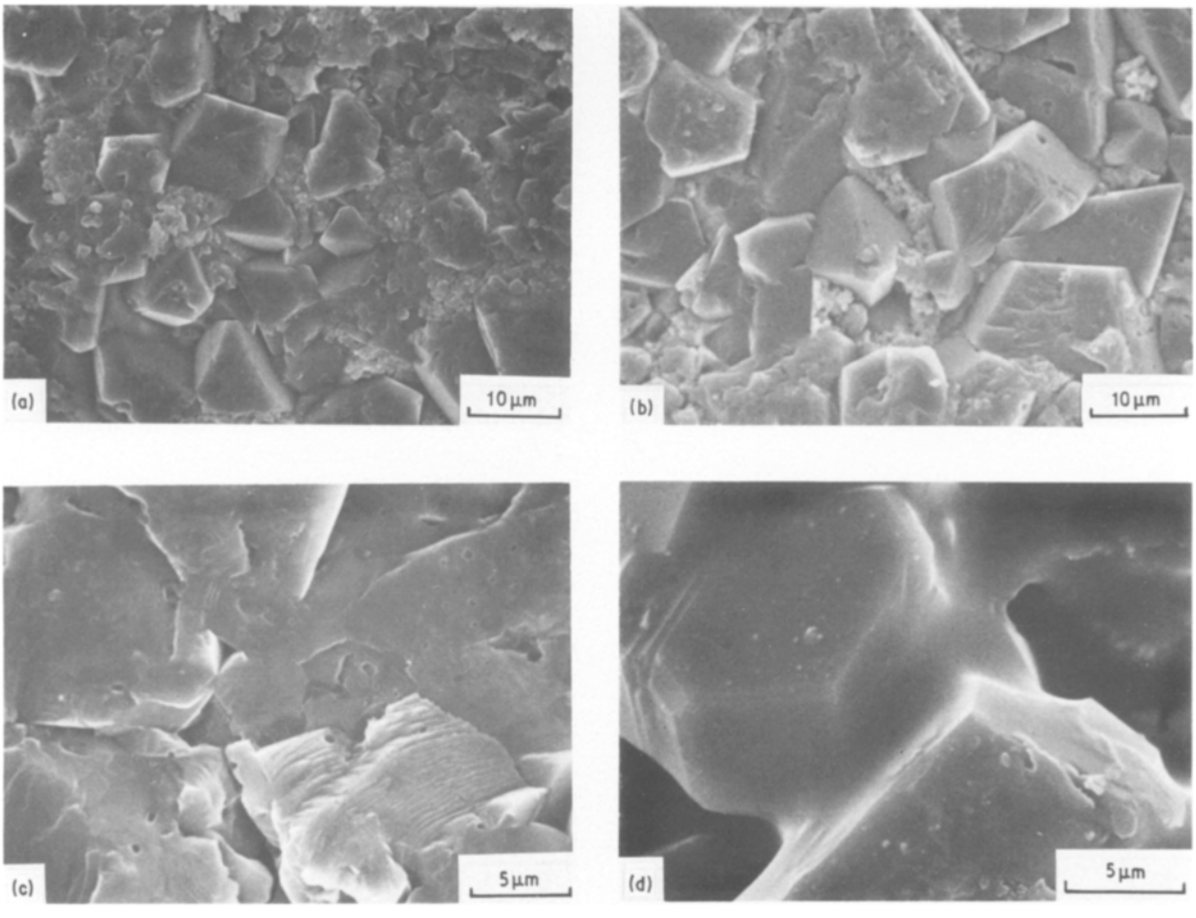


Figure 6 SEM photographs of the specimen surface of sintered diamond treated at 7 GPa and 1700° C in the presence of 17 vol % Fe–7.3 vol % Ti for (a) 1 min, (b) 5 min and (c) 15 min. (d) Starting carbon: GPC, Solvent-catalyst: 50 wt % Ni–10 wt % Zr, Treatment conditions: 7 GPa, 1700° C, 10 min [16].

in diameter, about 2 mm in thickness) with the conversion ratio of about 100% from graphite to diamond was prepared using the solvent-catalyst containing 11.4 to 17.0 vol % (30 to 40 wt %) Fe and 6.6 to 7.7 vol % (10 wt %) Ti.

2. The bulk density of the sintered compact prepared under the above conditions was 4.1 to 5.5 g cm^{-3} (the relative density: 82 to 93% of theoretical). The sintered compact consisted of the sintered diamond phase and the metal carbide phase. The microhardness of the former was above 8000, while that of the latter was 1000 to 2000.

3. The transformation from graphite to diamond will proceed in a short time less than 1 min, which is followed by sintering process of the formed diamond grains. At the initial stage of sintering, the diamond grains grow slightly with an incorporation of smaller grains. The neck growth between the grains and the densification will be attained at the reaction time of 15 min by pooling out the melt of carbon and solvent-catalyst from the joining parts.

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