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High pressure sintering of diamond-SiC composite

Y. S. KO, T. TSURUMI, O. FUKUNAGA
Department of Inorganic Materials, Tokyo Institute of Technology 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

T. YANO
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan
E-mail: tyano @nr.titech.ac.jp

Sintered polycrystalline compacts in the system diamond-10–50 wt% SiC having average grain size of less than 1 μm were prepared at pressure of 6 GPa and temperature between 1400 and 1600 °C. Knoop indentation hardness of the compacts increased with diamond content and sintering temperature, and specimens with a Knoop indentation hardness greater 40 GPa were obtained. It was found that small amount of Al addition into the starting diamond-SiC powder was effective to improve relative density and Knoop indentation hardness of the compacts. The formation of graphite was also suppressed by the addition of Al. Microstructure observation by SEM and TEM suggested that Al segregated at the grain boundary and promoted the bonding between grains. Thin microtwins were observed in diamond grains, whereas fine wavy structures with slightly different orientations were observed in SiC grains, with or without Al addition.

1. Introduction

Two methods for fabricating diamond compacts, namely solid state and liquid phase sintering have been developed in the early 1970s. Hall [1] has reported solid state sintering of diamond powder without additives under high pressure. He reported that the density of sintered compact was 3480 kg/m^3 (99% of relative density) when it was sintered at 8.5 GPa and 2170 °C for 3 min. Stromberg and Stephens [2] have reported diamond sintering at 6–6.5 GPa and 1800–1900 °C. They have studied the effect of B and Si additives and reported that both B and Si were effective to increase the relative density of the compacts.

Katzman and Libby [3] have reported liquid phase sintering of the system diamond-Co. They prepared diamond-Co composite having 27–30 GPa of microhardness with adding 20% cobalt. Bex and Wilson [4] and Walmsley and Lang [5] also obtained diamond compacts sintered under $\sim$6 GPa and temperatures above 1400°C with 8 vol% cobalt. Hibbs and Wentrof [6] have developed the cobalt infiltration method into diamond layers at high pressure sintering condition. They succeeded in making a WC-Co and diamond laminated compact suitable for cutting tool application. Yao *et al*. [7] reported the consolidation of diamond powder with Si-18wt%Ti-2wt%B alloy under 4.5–6.0 GPa at 1400–1600°C. On the other hand, dynamic or shock consolidation of diamond powder [8] or mixture of diamond and ceramic powders [9] have been reported.

So far, a few studies have been reported on the high pressure sintering of diamond and ceramic system. The diamond-ceramic composites are possibly used as high temperature abrasive materials because they do not form liquid phase at high temperature. We can also expect lower internal-strain bodies as a result of minimizing the difference of thermal expansion between diamond and matrix ceramic phase. SiC can be considered as a candidate for the matrix phase, because SiC is known as a very hard material with strong covalent bonds having similar structure with diamond.

In this paper we present experimental results of high pressure sintering of diamond-SiC or diamond-SiC-Al systems to explore diamond-ceramic composites, and microstructure of the obtained composites are investigated.

2. Experimental procedure

2.1. Starting materials

Starting materials used in this study were diamond powder (0.1–1 μm grade, GE, USA), β-SiC powder (0.1–1 μm grade, Ibiden, Japan) and Al powder (average 3 μm grade, Rare Metallic, Japan).

2.2. High pressure sintering and characterization of the compacts

The SiC powders ranging 10 to 50 wt% were mixed into diamond powders. The starting powders were mixed with ethanol for 1 h in an agate mortar. Mixing was

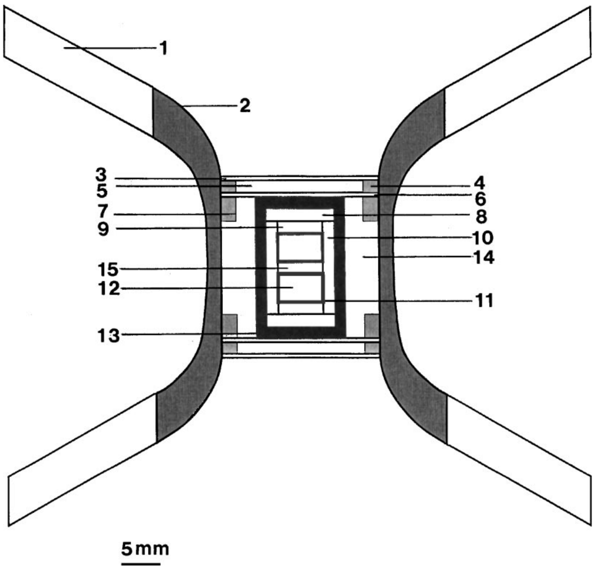

Figure 1 Sample assembly for high pressure sintering. 1. paper gasket, 2. pyrophyllite gasket, 3. stainless steel plate, 4. current ring, 5. zirconia plate, 6. Mo plate, 7. steel ring, 8, 10, 14 NaCl + 10 wt% zirconia, 9, 15 NaCl, 11. zirconium foil, 12. sample, 13. graphite heater.

carried out with care to avoid contamination from agate mortar. In some case, 1 wt% Al was added to the diamond and SiC mixture. Here after, the samples were denoted as 9D1S for 90 wt% diamond and 10 wt% SiC mixture and as 9D1SA for the mixture of (90 wt% diamond and 10 wt% SiC) plus 1 wt% Al. The dried powders were sieved through an 83 mesh sieve. Green disks of 7 mm in diameter and 2 mm in thickness were formed with a compacting pressure of 400 MPa.

A flat belt type high pressure apparatus of 25 mm of bore diameter [10, 11] was used for high pressure sintering. Sample assembly of the sintering is illustrating in Fig. 1. The green bodies were surrounded with 0.04 mm thick Zr foils to prevent contamination from the pressure medium. The samples were loaded to 6 GPa at room temperature, then heated to the designed temperature between 1400 and 1600 °C and kept for 1 h. The sintered compacts were ground with a diamond grinding wheel to remove the Zr capsule. The surface of the compacts was analyzed by X-ray diffraction method (XRD).

The Knoop indentation hardness was measured on the polished surface of the samples with 9.8 N load. The microstructure of the fractured surface was analyzed by SEM, after breaking the specimens.

Preparation of the specimens for TEM observation were carried out as follows: Sintered bodies were ground to under 40 μm thickness, the disks were dimpled and then these were Ar-ion-beam thinned with 2.3 mA of current at 4.2 kV of voltage for about 48 h. TEM observation was carried out using a 300 kV TEM apparatus (Type H-9000, Hitachi Ltd., Japan) with an attached EDX micro-analyzer (Analyst-8000, Kevex Co., USA).

3. Results and discussion

3.1. Relative density of the sintered body

Densities of the sintered bodies were measured by the Archimedes method. As shown in Fig. 2, the relative densities of the samples were increased with increase of the sintering temperature. The relative density of the series increased remarkably with 1 wt% Al addition. The density of the other composition specimens with higher SiC content was not measured, but it was supposed that these densities reached similar relative densities as shown in Fig. 2.

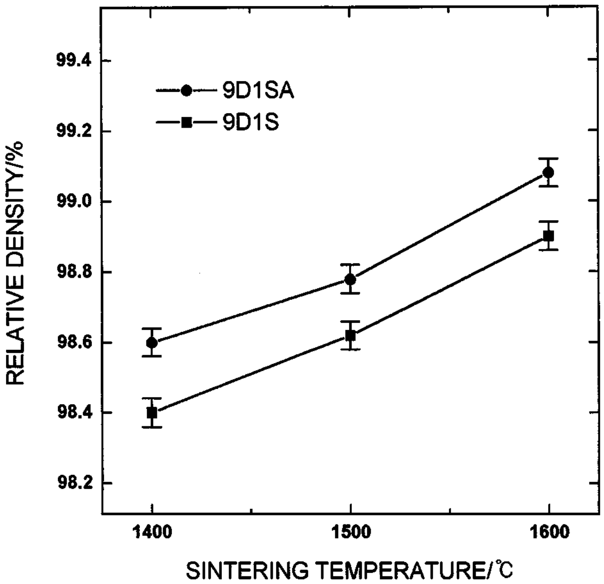

Figure 2 Relative densities of the samples 9D1S and 9D1SA with different sintering temperature.

3.2. XRD analysis

Fig. 3 shows the XRD patterns taken from the surface of the mechanically polished specimen of 5D5S, 9D1S, 5D5SA and 9D1SA sintered at 1600 °C. The major XRD peaks were identified as diamond and β-SiC, but weak diffraction peaks of graphite and α-SiC were detected. We could not find NaCl-type SiC, which was reported to be formed during high pressure sintering of diamond with Si-Ti-B alloy at 1400–1600°C under 4.5–6 GPa [7]. The intensity of the graphite peak was decreased with increase of SiC content and Al addition. It was considered that graphite free compacts could be prepared by adjusting the ratio of SiC and Al content to the diamond.

3.3. Knoop indentation hardness

The results of Knoop indentation hardness of the polished surface of the diamond-SiC composites are illustrated in Fig. 4. The range of the hardness was between 24 and 36 GPa with standard deviation of 0.9 GPa. The hardness increased with increase of the content of diamond. Higher sintering temperature gave higher hardness. For the sample 9D1S, the increment of hardness with increase of sintering temperature was small. Degradation of micro-hardness of the sample 9D1S sintered at 1600 °C could be attributed to formation of the graphite phase, which was confirmed by XRD analysis.

Fig. 5 shows the micro-hardness of diamond-SiC-Al system. The hardness values were ranging 23–40.5 GPa with standard deviation of 0.7 GPa. The hardness values

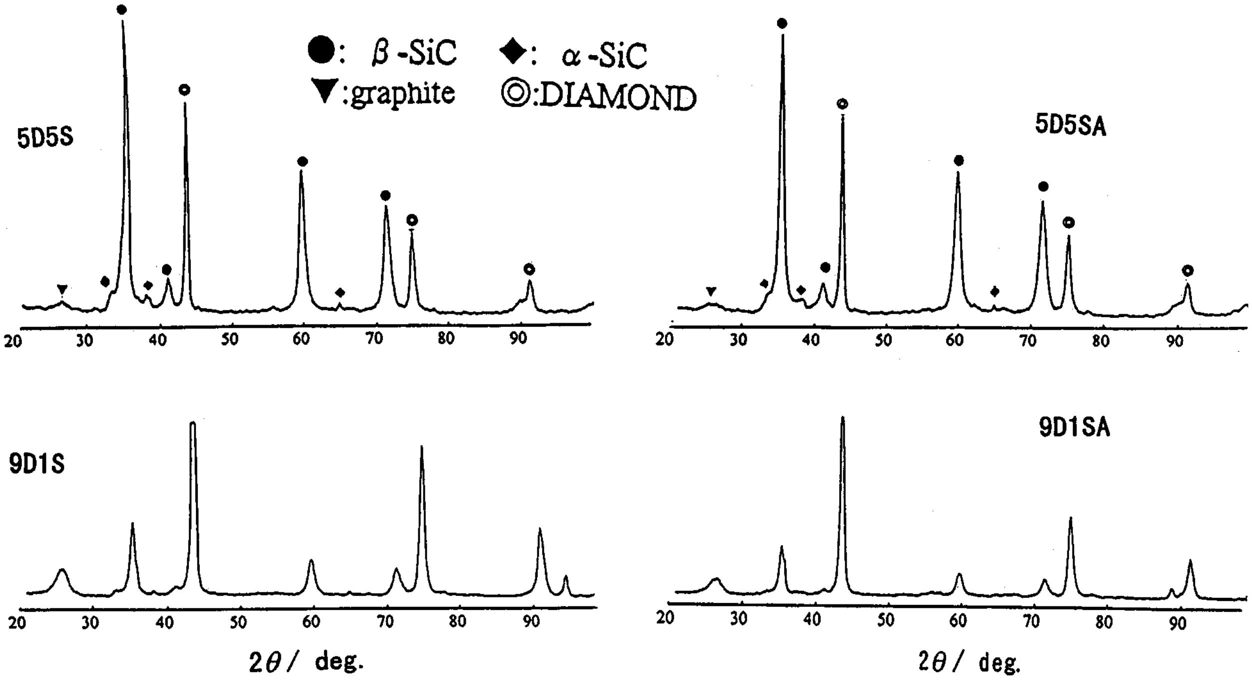

Figure 3 XRD diffraction patterns of 5D5S, 5D5SA, 9D1S and 9D1SA samples sintered at 1600 °C.

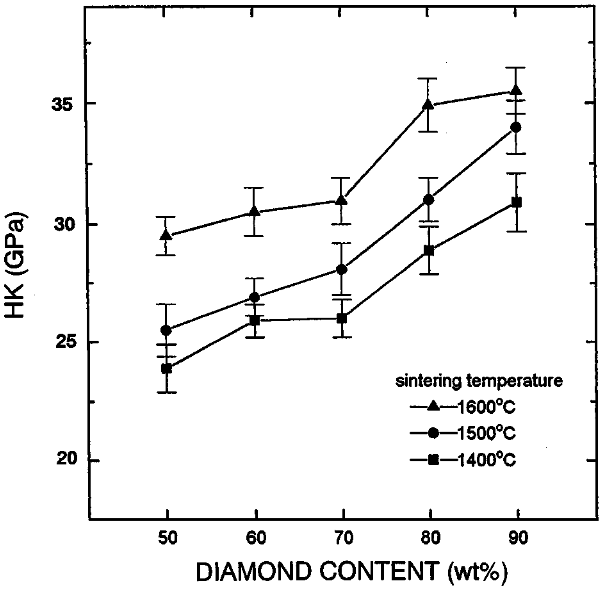

Figure 4 Knoop indentation hardness of the samples in the system diamond-SiC with different diamond content and sintering temperature.

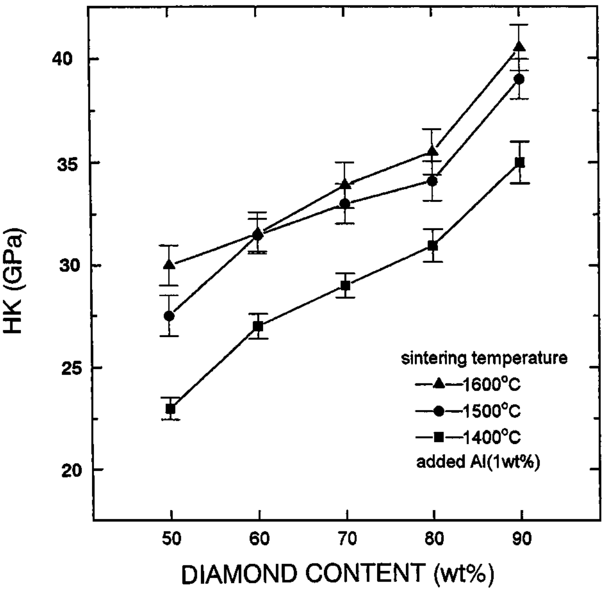

Figure 5 Knoop indentation hardness of the samples in the system diamond-SiC-Al with different diamond content and sintering temperature.

were increased with increase of the content of diamond, as in the system of the Al free composite. It was obvious that the hardnesses of diamond-SiC-Al composites were higher than those of diamond-SiC. The hardness of the sample 9D1SA sintered at 1600 °C was about 14% higher than that of 9D1S. It was found that small amount of Al addition was effective to improve intergranular bonding between diamond and SiC, which was confirmed by TEM observation as mentioned later.

Ideal hardness of diamond and SiC were reported to be 70 GPa and 25 GPa, respectively. From these data and simple rule of mixtures, the ideal hardness of 9D1S was estimated to be about 55 GPa. The maximum hardness of 9D1SA is about 75% of the estimated value. The degradation of hardness of 9D1SA sample may be attributed to the relatively weak intergranular bonding strength.

3.4. Observation of the fractured surface

SEM micrographs of the fractured surface of 5D5S and 9D1S specimen sintered at 1400 °C and 1600 °C are shown in Fig. 6a, b and c, d, respectively. It can be seen that the microstructure of the samples sintered at 1600 °C suggested denser and pore free structure. It was suggested that the densification of the compacts of diamond-SiC system may be promoted mainly by

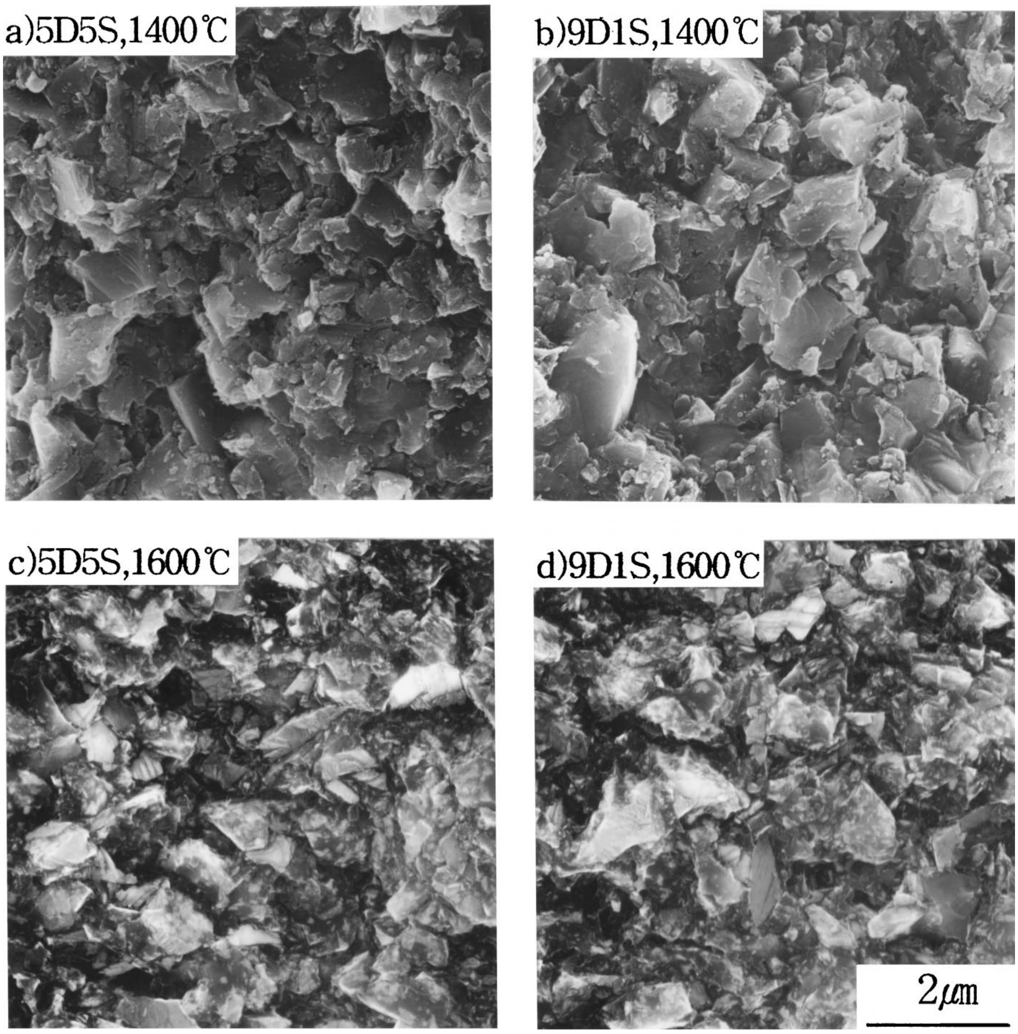

Figure 6 SEM micrographs of the fractured surfaces of diamond-SiC composites. (a) 5D5S sintered at 1400 °C (b) 9D1S sintered at 1400 °C, (c) 5D5S sintered at 1600 °C, (d) 9D1S sintered at 1600 °C.

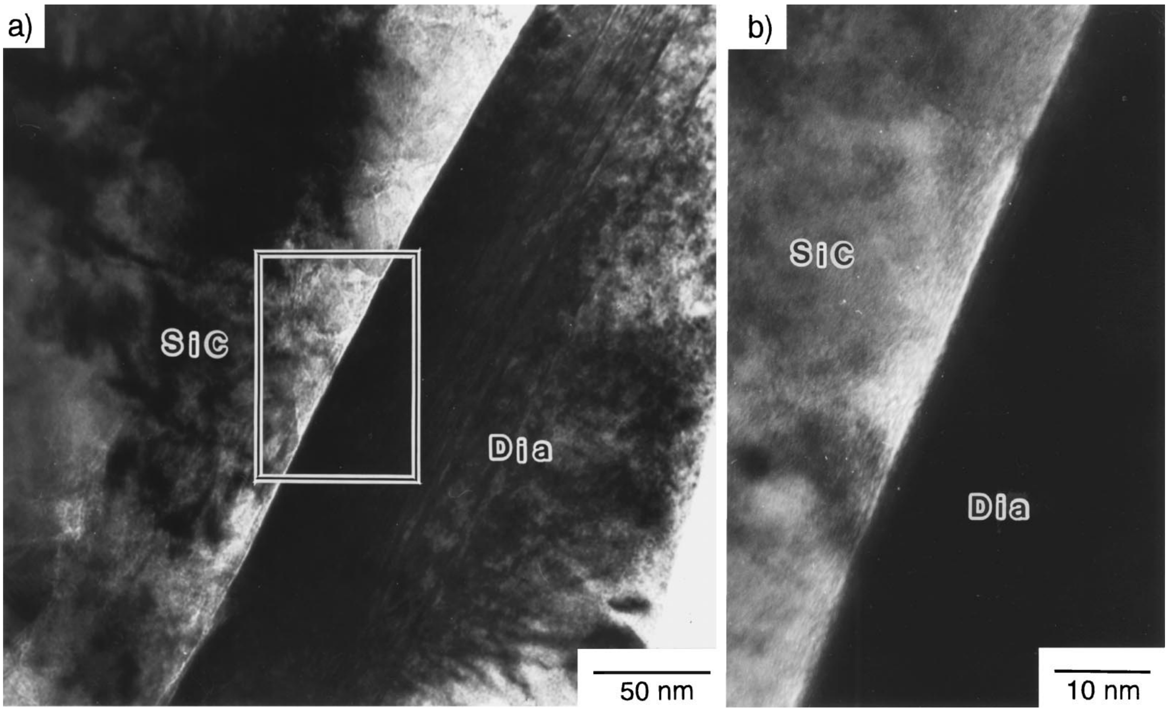

Figure 7 TEM micrographs of the grain boundary of the 50%diamond-50%SiC composite sintered at 1500 °C. (a) Bright field image of the grain boundary, and (b) higher magnification photograph of the area indicated in (a).

sintering temperature. Whilst change in sintering temperature makes a significant difference to the density of the compact, the ratio of diamond to silicon carbide is not an effective factor to obtain denser microstructure. From SEM micrographs of Fig. 6, no abnormal grain growth was observed and the grain sizes were the same order of magnitude with those of from starting powders. The fracture mode observed was mainly transgranular. There was no evidence of melting of the SiC phase. Dynamic consolidation of admixture of diamond and SiC [9] or c-BN and SiC [12] resulted in extensive melting of SiC phase. In the case of dynamic consolidation, the maximum pressure was reported to be higher than 10 GPa and maximum specimen temperature to be up to 2700°C, and then melting of SiC would be observed. In the case of static high pressure sintering of this study, specimen temperature was controlled by heater more accurately [11], and melting of SiC is not expected.

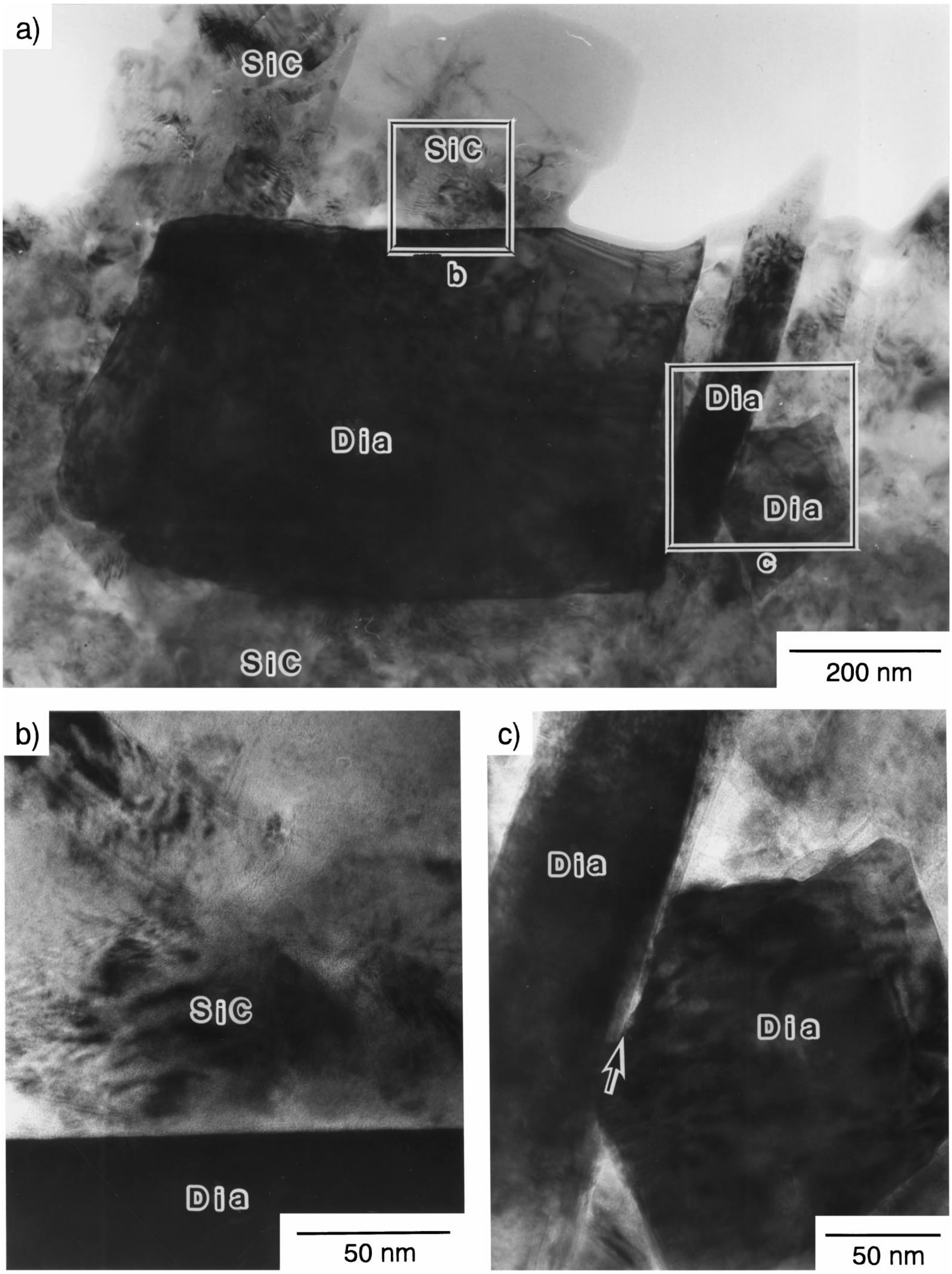

Figure 8 TEM micrographs of the grain boundaries of the 50%diamond-50%SiC-Al composite sintered at 1500 °C. (a) Bright field image, (b) higher magnification photograph of the grain boundary marked as b in Fig. 8a. (c) Higher magnification photograph of the grain boundary where diamond-diamond formed grain boundary. The TEM taken the portion marked as c in Fig. 8a.

The microstructure of the Al-containing samples 5D5SA and 9D1SA corresponding Fig. 6 data (not shown here) suggested a similar trend to the sample without Al addition. No considerable difference was recognized between the diamond-SiC and the diamond-SiC-Al system's sample.

3.5. TEM observation

Fig. 7 shows TEM micrographs of grain boundary regions of the diamond-SiC composite. The sample examined was 5D5S sintered at 1500 °C. Fig. 7b is higher magnification photograph of the outlined region of Fig 7a. Identification of diamond grains and SiC grains was carried out by selected area diffraction technique and by EDX analysis. Grains identified are labeled in the figures. Strain contrast was observed both in diamond and SiC grains almost throughout the specimen, probably caused by ultra-high pressure during the sintering. Between diamond and SiC grain, neither reaction products nor glassy grain boundary phase was observed. In contrast, interstices between two grains were observed frequently. It is suggested, therefore, that intergranular fracture observed by SEM was due to interstice between grains.

Fig. 8 shows TEM micrographs of the diamond-SiC-Al composite. The sample was 5D5SA sintered at 1500 °C. Fig. 8b and c are higher magnification photographs of the outlined regions in Fig. 8a. An interphase with thickness of about 5 nm between diamond and SiC grains was observed in Fig. 8b. As shown in Fig. 8c, the contact parts between diamond grains formed good bonding while there is the interstice in other parts as indicated by the sign of the arrow. It can be thought of as a cause of the grain boundary fracture. The aspects of bonding between grains affected the properties of fracture. As stated above, the fracture mainly depends on the existence of interstices for sintered diamond-SiC composite.

In order to examine the role of Al addition, the microstructure of 5D5SA sample sintered at 1500 °C was further observed by EDX as shown in Fig. 9a and b. The results of EDX analysis of the grain boundary between diamond and SiC, at the point marked by arrow in Fig. 9a, indicates segregation of Al in the grain boundary phase. The role of Al precipitates at the grain boundary was not fully analyzed but Al may play a role to promote the bonding between diamond and SiC grains. As mentioned in the fracture surface observation, melting of not only SiC [9] but also diamond [8] is not confirmed also by TEM observation. On the other hand, the fracture of large diamond particles and deformation of SiC grains are observed generally, as shown in Fig. 8a, irrespective of whether the sample contained aluminum addition.

The microstructure of diamond and SiC grains observed with incident beam direction of [110] are represented in Fig. 10a and c, respectively. Corresponding electron diffraction patterns are shown in Fig. 10b and d, respectively. In the diffraction pattern of diamond, diffuse streaks along the $[\bar{1}11]$ direction were observed, corresponding with the stacking faults observed

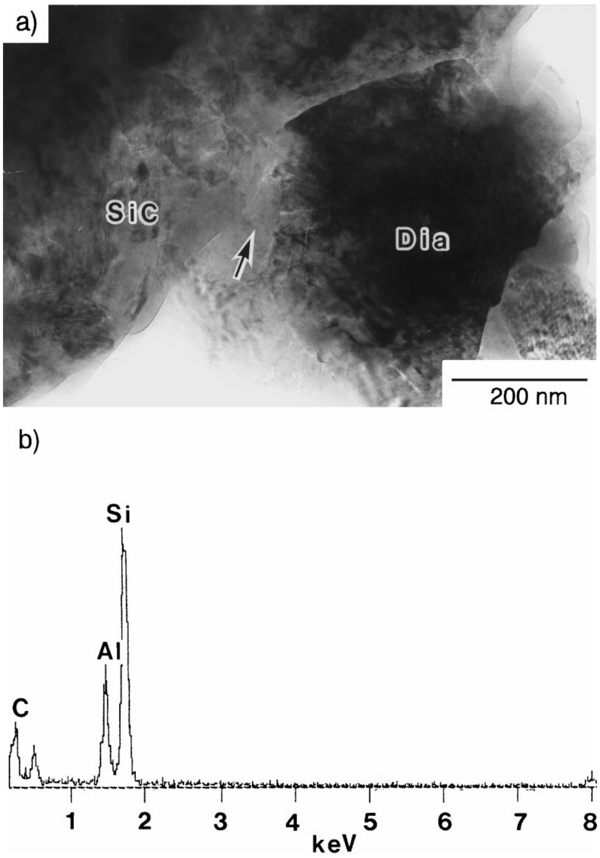

Figure 9 TEM and EDX analysis of the sample 5D5SA sintered at 1500 °C. EDX was taken at the portion marked by an arrow in Fig. 9a.

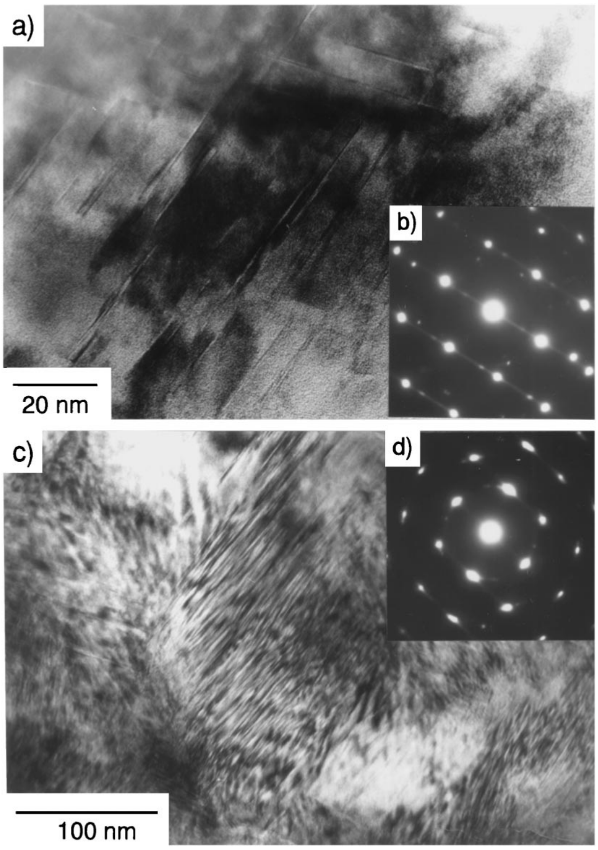

Figure 10 TEM micrographs of grains in the sintered body of 5D5S sintered at 1500 °C under 6 GPa. (a) Diamond, (b) diffraction pattern of diamond, (c) SiC, and (d) diffraction pattern of SiC.

in Fig. 10a. Walmsley and Lang [5] reported the formation of thin microtwins parallel to {111} directions in synthetic diamond compacts under nearly the same sintering conditions as used in the present study, i. e., at pressure of ∼6 GPa and temperature above 1400°C, but more larger size (30–40 μm) diamond powders was used. They mentioned that the thinnest twins may be only 1.0 nm thick. The diffraction pattern of diamond shown in Fig. 10b indicates the presence of reflections caused by {111} twins, overlapping onto the diffuse streaks. Furthermore, many of the line-contrasts indicating the presence of stacking faults were observed as a parallel pair lines, with separation of around a few nm, as shown in Fig. 10a. This result is in good agreement with the above mentioned report [5].

In SiC grains, abnormal fine wavy contrast with slightly different orientations was frequently observed as shown in Fig. 10c. It probably gives concentric circular diffuse streaks, as shown in Fig. 10d. From these observations, both diamond and SiC grains were deformed due to very high pressure during sintering, since such contrast was not observed with the starting powders. The degree of deformation of SiC grains was more severe than that of diamond grains. The crystalline lattice deformation of diamond as shown above may induce higher abrasion resistance, as reported by DeVries [13].

4. Conclusion

To study high pressure sintering of diamond-ceramic composite, diamond-SiC system was examined for the composition between 50 wt% and 90 wt% of diamond. The mixtures were sintered at 6 GPa and between 1400 and 1600 °C for 1 h. The effect of Al addition (1 wt% for the mixture) was also examined. The samples were analyzed by relative density, XRD, Knoop micro-hardness, SEM and TEM. Obtained results are summarized as follows. (1) Relative densities of about 99% were obtained for the samples 90% diamond-10%SiC and 90%diamond-10%SiC +1 wt%Al sintered at 1600 °C, and slightly higher densities were obtained for Al added samples. (2) Small amounts of graphite precipitation were observed from diamond-SiC samples, but the graphite content was decreased with addition of 1 wt% Al. (3) SEM observation of the fractured surface suggested no abnormal grain growth and intergranular fracture. Homogeneous microstructure was obtained by higher temperature sintering. (4) Knoop indentation hardness was increased with increase of the content of diamond. Al addition was effective to increase hardness. (5) TEM observation revealed interstices between diamond and SiC grains for diamond-SiC compact. It may induce grain boundary fracture. Al addition formed interphase at the grain boundary. (6) SiC grains deformed more severely than diamond grains both with and without Al addition. Thin microtwins were observed in diamond grains, whereas a fine wavy structure with slightly different orientations was observed in SiC grains.

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