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High-pressure sintering of cubic boron nitride

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Cubic boron nitride (cBN) powder was compacted at high pressure and high temperature using a solid solution of titanium carbide and titanium nitride (TiC_xN_{1-x}) as binding material in the presence of a small amount of aluminium. Different compositions of TiC_xN_{1-x}, $0 < x < 1$ were used as binders. The weight percentage of cBN, TiC_xN_{1-x} and aluminium were optimized and found to be critical; any marked deviation from these optimized values deteriorated the quality of compacts. Various high-pressure sintering parameters such as pressure, temperature and sintering time, etc, were optimized for this binder. The compacts were also characterized using X-ray diffraction, scanning electron microscopy and microhardness measurements. The microstructural and X-ray diffraction observations indicated no marked changes in the compacts as the value of x in TiC_xN_{1-x} was varied, but the microhardness was found to depend on the value of x.

1. Introduction

Cubic boron nitride (cBN) crystals are synthesized by subjecting the hexagonal form of boron nitride to high pressure and high temperature [1–5]. Single crystals of cBN are generally used in industry for cutting and grinding operations because its hardness is comparable to diamond. It also has an additional advantage over diamond as it is more temperature resistant and chemically inert towards ferrous metals. Commercial applications of cBN crystals are restricted due to the limited size to which they can be grown [6] and because they do not have the required fracture toughness as desired in the ceramic cutting tool industry [7]. To enhance the utility of these small particles they are compacted into a conglomerate mass of sufficient size, toughness, hardness and chemical stability. The above process is, in practice, visualized by subjecting cBN powder to high pressure and high temperature in the presence of a binding material which also introduces desired cutting tool characteristics in the compact. The resultant cBN compact thus produced is a hard, tough composition with sufficient thermal and shock resistance to withstand interrupted cuts at high speeds, feeds and stand high tip temperatures.

A considerable amount of work on the high-pressure sintering of cBN has been done at the General Electric Company, USA [8–12]. Wentorf and Delai [8] first reported the successful compaction of cBN under high pressure–high temperature conditions using binding materials selected from the group of elements tungsten, nickel, beryllium, rhenium, titanium, zirconium, chromium, etc. They also tried Al_2O_3 and B_4C as binders in its compaction. Bovenkerk and Kibler [9] reported the compaction of cBN powder at pressure of about 55 kbar and a temperature of about 1300 to 1600° C for 3 min in the presence of aluminium and an alloying metal selected from the group consisting of nickel, cobalt, iron, manganese, vanadium and chromium. Hibbs and Wentorf [10] have briefly reviewed various mechanical properties of cBN compacts and observed that cBN compacts give better cutting tool characteristics as compared to other conventional cutting tool materials. Fukunaga *et al.* [13] have used different compositions of Co–Al alloy as the binding material and carried out high-pressure sintering at 55 kbar and 1300 to 1600° C for a period of 1 h and conclude that the dominant factor affecting toughness and wear resistance of cBN compact is the microstructure of the matrix phase which bonded cBN grains. A new method of high-pressure sintering of cBN has been reported by Akaishi *et al.* [14]. In this method partially graphitized cBN has been used as the starting material and subjected to high pressure and temperature in presence of $Mg_3B_2N_4$ and the resultant compact had high hardness and was optically translucent.

Although a considerable amount of work has been done in the compaction of cBN, in general the details regarding the binder and the various process parameters are not disclosed due to their commercial implications. It is well known that the borides, nitrides and carbides of metals of group IVa, Va and VIa are used as binders in the compaction of cBN [15]. These compounds have high melting points and are quite hard. The present paper reports the high-pressure sintering of cBN using solid solutions of different compositions of TiC and TiN (TiC_xN_{1-x}) and the various optimized process parameters. The sintered compacts have also been extensively characterized using X-ray diffraction, scanning electron microscopy and microhardness measurements.

2. Experimental procedure

2.1. Equipment

The high-pressure sintering was carried out on a 200 tonne cubic press of Tracy Hall's design [16]. As shown schematically in Fig. 1, the press consists of three pairs of identical tungsten carbide (WC) anvils

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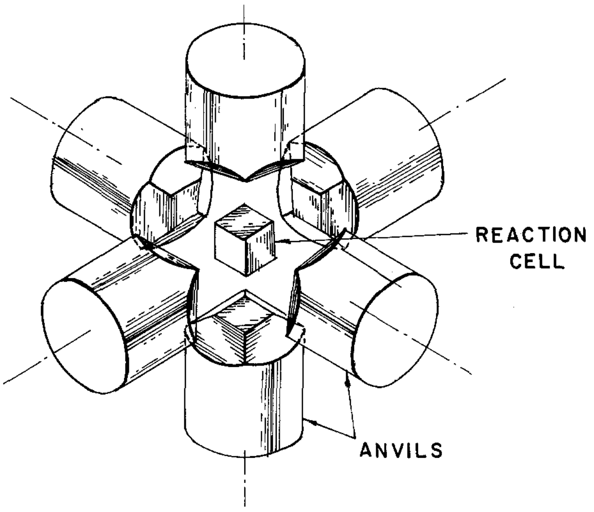

Figure 1 Reaction cell in a cubic press.

supported by hydraulic rams having equal square faces with edges 12.5 mm long, each pair mounted for rectilinear movement along a common axis and the axis of each pair being normal to the other. The three pairs of anvils converge to a common intersection and these would define the faces of the cube at their position of contact.

The reaction cell is fabricated from pyrophyllite in the form of a cube, a cross section of which is shown in Fig. 2. As illustrated in Fig. 2, within the body of the cell are steel current rings and molybdenum discs; contacting the molybdenum discs is a cylindrical graphite tube (o.d. 8 mm and i.d. 6 mm) which is used as a heater and the charge to be subjected to high pressure and temperature is contained in this tube. The edge of the cubic reaction cell (16 mm) is slightly larger than the WC anvil edge (12.5 mm). This oversize of the cell prevents the anvils from coming into direct contact with each other and also leaves ample allowance on the cell edges where it becomes extruded into the interanvil spaces on the application of pressure to form a gasket with a sloping shoulder on the anvils. The pressure calibration was carried out using standard pressure fixed points of phase transitions of bismuth (I–II) at 25.4 kbar, ytterbium (fcc → bcc) at 39 kbar [17] and barium (I–II) at 55 kbar. Heating was achieved by passing a high current through one pair of anvils via a current ring, a molybdenum disc and a graphite tube. The relatively high resistance of the graphite heater and molybdenum end disc caused the charge to heat up quickly. The temperature was calibrated in terms of electric power input in watts using a Pt–Pt/Rh 10% thermocouple placed at the centre of the reation cell.

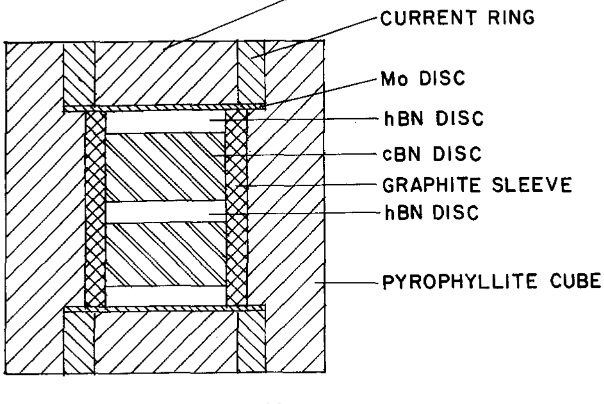

Figure 2 Reaction cell assembly.

2.2. Process

The starting materials used in the compaction of cBN are: commercially available cBN powder 6 to 9 μm (General Electric Company, USA), TiC_xN_{1-x} 2 to 5 μm, and aluminium powder 1 μm (NRD Corporation, Japan). Various mixtures of cBN and binders (different compositions of TiC_xN_{1-x}) and aluminium powder were made, using methyl alcohol as a mixing agent, in an agate mortar. The precompression of these powders was carried out initially in a steel die at about 3 tonne cm^{-2}. The thickness of the cBN disc was 3.5 mm and diameter 6 mm. The discs of cBN mixture were packed in the reaction cell as shown in Fig. 2.

3. Results and discussion

Out of the vast majority of binders reported in the literature, i.e. refractory compounds such as nitrides, borides or carbides of high melting metals, TiC_xN_{1-x} ($0 < x < 1$) was chosen in the present work. It is generally recognized that the overall performance of a cutting tool is mainly judged by its hardness, toughness, mechanical strength and wear resistance. It is difficult to identify a binder which can introduce all these cutting tool characteristics in the compacts, hence necessitating the use of the solid solution of two or more compounds. Therefore, in the present work a solid solution of TiC and TiN, i.e. TiC_xN_{1-x}, $0 < x < 1$, was used as the binder. TiC is used because of its high hardness, high melting point, toughness and its ability to inhibit the grain growth, whereas TiN has been used to give sufficient chemical stability and high fracture toughness [18–20]. Thus their solid solution incorporates all their individual mechanical properties and hence enables the microstructure of the compact to be engineered by varying the ratio of TiC and TiN, to obtain the desired cutting tool characteristics depending upon the operation it is required to perform.

Different compositions of TiC_xN_{1-x}, (x = 0.3, 0.5 and 0.7) were used as binder in the high-pressure sintering of cBN and the ratio by weight percentage of cBN:TiC_xN_{1-x}:Al was optimized at 50:45:5. Although in some experiments the weight percentage of cBN was varied from 40 to 60% and aluminium from 2 to 10%, it was found that the wt % cBN was critical within reasonable limits and any large deviation from this value yielded compacts which were either too brittle or lacked hardness depending upon whether the wt % cBN was increased or decreased.

It is known that the sintering of cBN or refractory compounds in the absence of liquid phase occurs at the expense of recrystallization, and hence a residual porosity is generally observed in the resulting compact. Furthermore, powders of cBN absorb a substantial amount of water and oxygen which during the high pressure sintering can result in the formation of boron oxide (B_2O_3) and other compounds which are

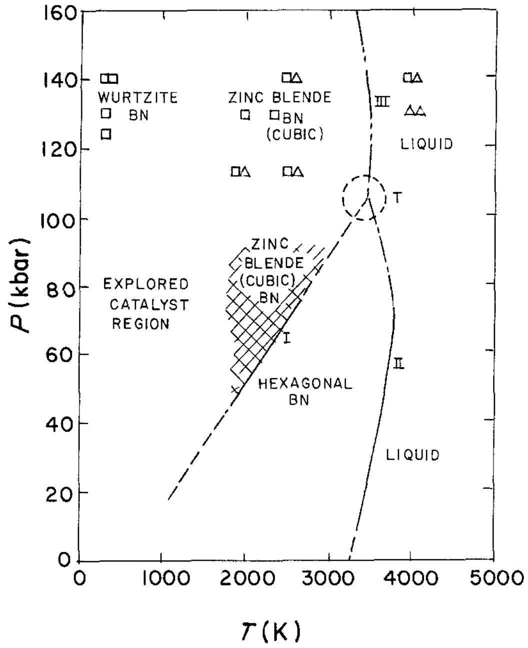

Figure 3 Phase diagram of boron nitride [4].

detrimental to mechanical strength and consequently to wear resistance of the compact. To avoid this, aluminium in the form of fine powder is included in the reaction charge; this aluminium reacts with vapours of water and absorbed gases for the formation of very durable compounds such as Al_2O_3 or AlN which do not substantially reduce the mechanical strength of the compact. Furthermore, the presence of aluminium noticeably accelerates and stabilizes the sintering process. The amount of aluminium to be added is critical so that the whole of it is converted into relatively harder phases (Al_2O_3, AlN). Therefore, in the present work the wt % aluminium to be added was found to be reasonably critical at around 5 wt %.

High-pressure sintering was carried out in the pressure range 55 to 62 kbar and temperature range 1300 to 1600° C; however, satisfactory compacts were obtained at 58 kbar and 1450° C. The sintering time at these pressure and temperature conditions was optimized at 20 min, although the results were not very sensitive to the sintering time within reasonable limits. The pressure for all the experiments was kept at 58 kbar because although higher pressures could be used, the service life of the high-pressure chamber where the sintering is performed is greatly reduced without any significant improvement in the quality of the compact.

As is evident from the phase diagram of boron nitride (Fig. 3) the value of 58 kbar and 1450°C is well within the stable region of the cubic form, although quite far away from the equilibrium line.

Because of the high hardness of cBN, even at high temperature and pressure conditions, it is difficult to squeeze out the empty space from a mass of cBN crystals in the absence of a liquid phase, irrespective of the sintering period. Hence when sufficiently high pressure is applied to the sample with high porosity, heterogeneous pressure distribution occurs. The regions where cBN–cBN grains are in contact experience higher pressure than the regions where the particles are not in contact. Thus if the pressure and temperature conditions are kept near the equilibrium line in the stable regions of cBN, then there is every possibility of cBN becoming converted to hBN – a softer form. This is even evident from our experiments when the compaction of cBN is carried out at 58 kbar and 1600° C, where it was estimated from quantitative X-ray analysis that back conversion from cBN to hBN was about 40% by weight of cBN. Thus in order to eliminate the back conversion from cBN to hBN, as mentioned above, our experiments were made at pressure–temperature conditions far from the equilibrium line.

3.1. X-ray characterization

The surfaces of the as-sintered compacts were ground with no. 200 diamond wheel and finally lapped with fine diamond paste. X-ray diffraction patterns of all three compositions of TiC_xN_{1-x} ($x = 0.3$, 0.5 and 0.7) were recorded with powder X-ray diffractometer using Cu$K\alpha$ radiation. The general features of diffraction patterns of all the three compositions of TiC_xN_{1-x} are broadly the same and a typical diffraction pattern for the compositions $x = 0.5$ is shown in Fig. 4a.

As can be observed from Fig. 4a there is no diffraction peak due to hBN which should have occurred at $2\theta = 26.7°$, confirming that there was no back conversion from cBN to hBN in all the compositions sintered at 58 kbar and 1450° C. The (1 1 1) diffraction peak of cBN is observed at $2\theta = 43.3°$ ($d = 0.2089$ nm). In addition, the diffraction maxima observed at $2\theta = 36.2°$ ($d = 0.2481$ nm), 42.3° ($d = 0.2136$ nm), 61.4° ($d = 0.1510$ nm), 73.2° ($d = 0.1293$ nm) and 77° ($d = 0.1238$ nm) correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections of the TiC_xN_{1-x} which is used as the binder material.

However, formation of an additional phase of TiB was observed as the diffraction maxima identified at $2\theta = 37.9°$ ($d = 0.2374$ nm), 51.9° ($d = 0.1760$ nm) and 61.2° ($d = 0.1514$ nm) correspond to (1 1 1), (3 0 1) and (0 2 0) reflection of TiB. The strongest line (1 0 2) of TiB at $2\theta = 42.2°$ could not be resolved as it overlaps with the strongest reflections (2 0 0) of TiC_xN_{1-x}. However, the small amount of TiB detected, will not greatly affect the mechanical properties of the compact as it possesses good hardness and toughness. No formation of Al_2O_3 or AlN could be detected.

Fig. 4b shows the diffraction pattern of the compact sintered at 58 kbar and 1600° C. The back conversion from cBN to hBN has obviously taken place as the diffraction peak at $2\theta = 26.7°$ corresponds to the hBN phase.

3.2. Microstructural observations

Figs 5a to c show the scanning electron micrographs of the cBN compact for compositions $x = 0.3$, 0.5 and 0.7, respectively. The black regions in the micrograph represent the cBN particles while the brighter regions correspond to the TiC_xN_{1-x} particles. The cBN particles are seen to be uniformly distributed in the TiC_xN_{1-x} matrix. Furthermore, in most of the regions the grain-to-grain bonding is between cBN and TiC_xN_{1-x} particles, although cBN–cBN bonding is also observed occasionally. In some regions clustering

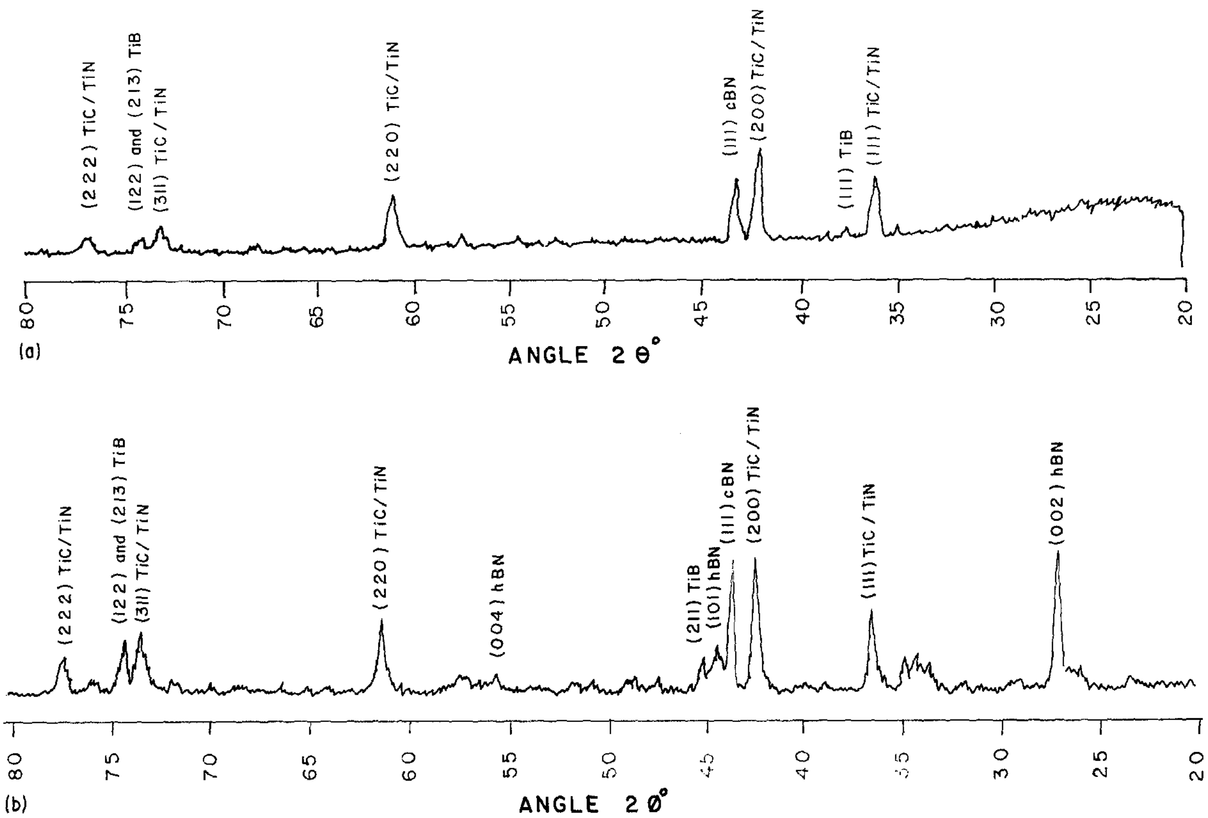

Figure 4 X-ray diffraction pattern of cBN compact for composition $x = 0.5$ sintered at (a) 58 kbar and 1450° C, (b) 58 kbar and 1600° C.

of cBN and TiC_xN_{1-x} is also observed, clusters of cBN particles being bonded by clusters of TiC_xN_{1-x} particles.

It is generally presumed that direct grain-to-grain bonding between cBN particles may improve its hardness and wear resistance but decreases its toughness. However, in our compacts major part of the grain-to-grain bonding is between cBN and TiC_xN_{1-x} particles although cBN–cBN bonding is also observed occasionally, thus indicating that the compacts have good hardness as well as reasonable toughness.

A detailed study of particle size analysis indicated that there is no significant grain growth in the as-sintered compacts during the sintering process.

3.3. Microhardness measurement

The Knoop microhardness of the compacts was measured under a load of 500 g on a Zwick 3212 microhardness tester. Prior to the measurement the samples had to be lapped and polished by fine diamond paste to obtain a mirror-like finish on the surface so that the indentation could be measured accurately. The average Knoop hardness of the compacts with different compositions of TiC_xN_{1-x} is tabulated in Table I.

TABLE I Microhardness of the cBN compact with different values of x in TiC_xN_{1-x}

x	Microhardness (kg mm^{-2})
0.3	2400 ± 200
0.5	2800 ± 200
0.7	3600 ± 300

The average Knoop microhardness is found to be maximum (3600 kg mm^{-2}) for the composition $x = 0.7$ and minimum (2400 kg mm^{-2}) for $x = 0.3$. This is quite expected because as the weight percentage of TiC in TiC_xN_{1-x} is increased the hardness is expected to increase as TiC is relatively harder than TiN.

The relatively large deviation in the value of microhardness may be attributed to the difficulty in visually locating the boundary of the indentation which is around 45 μm. It is further expected that these values refer to the microhardness of the compacts and not only cBN, as the grain size of the sample is much less than the length of the indentation. The indentation indeed envelops a few grains of cBN, together with those of the relatively soft binder. Therefore, if the grain at the indentation boundary happens to be that of the binder then the indent tends to elongate whereas if the boundary is occupied by a cBN grain the indent tends to shorten. This causes some variation in the measured value of the microhardness.

4. Conclusions

Well sintered compacts of cBN were obtained using TiC_xN_{1-x} as the binder material at 58 kbar and 1450° C in the presence of a small amount of aluminium. At temperatures lower than this good compacts were not formed and any further increase in pressure did not show any marked improvement in the quality of compacts. The wt % TiC_xN_{1-x} and aluminium in cBN compacts were optimized and found to be critical, and any marked deviation from this optimized value deteriorates the quality of the compacts. The X-ray characterization results clearly indicate the dominance of the cBN and TiC_xN_{1-x} phase but the formation of an additional TiB phase is

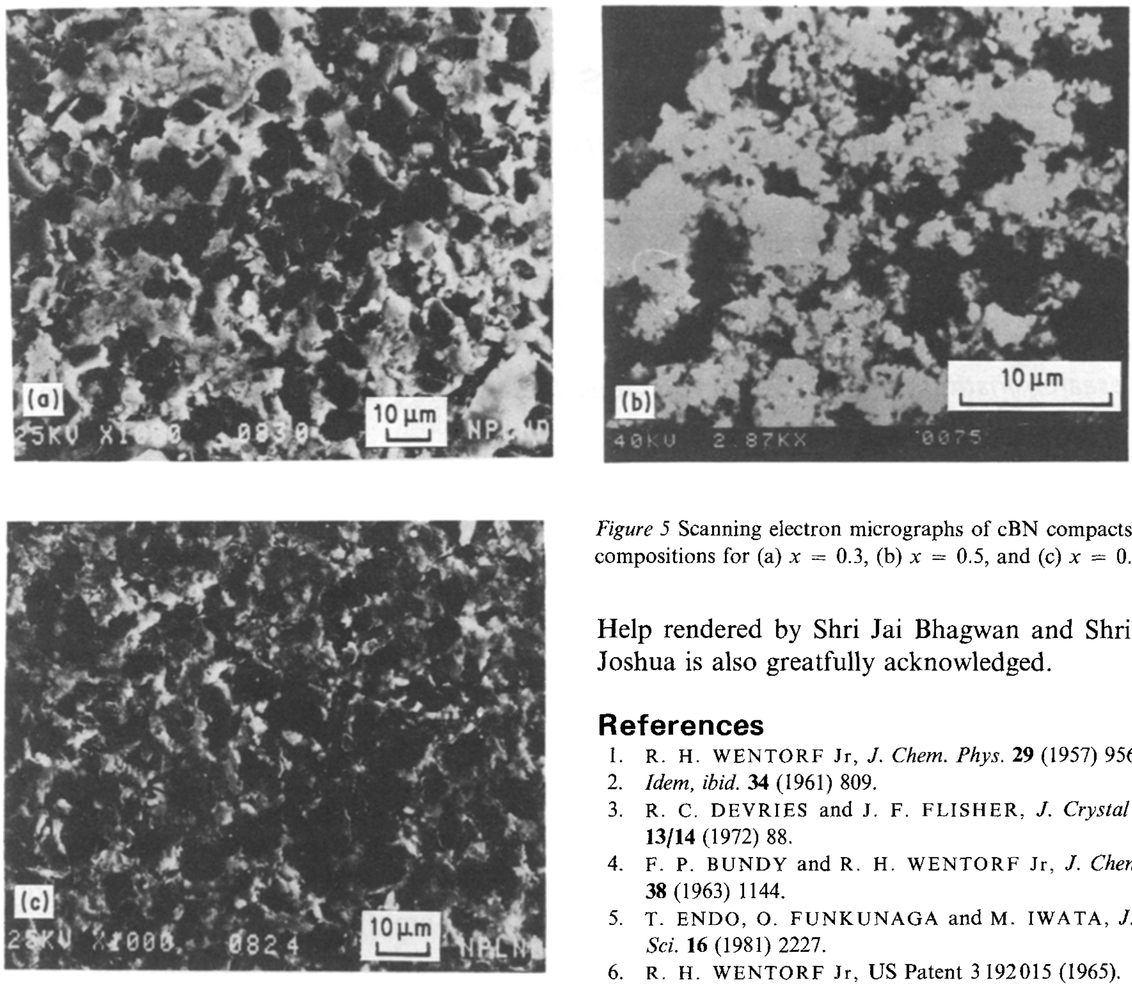

Figure 5 Scanning electron micrographs of cBN compacts for the compositions for (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$.

also detected which, however, does not greatly affect the mechanical properties of the compact. From the microstructural examination it was concluded that the major grain-to-grain bonding is between cBN and TiC_xN_{1-x} particles, although an occasional cBN-to-cBN bonding is also present. Microhardness of the cBN compacts was found to increase as the value of x in TiC_xN_{1-x} is increased and for the composition $x = 0.7$ the microhardness was found to be $3600 \pm 300\,kg\,mm^{-2}$. However, the toughness is expected to decrease as the value of x in TiC_xN_{1-x} is increased.

Thus the cBN compact characteristics can be engineered to suit a particular type of cutting operation and can be controlled by suitably selecting the value of x in TiC_xN_{1-x} to obtain the required compromise between hardness and toughness.

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