



Review Article

Cubic boron nitride competing with diamond as a superhard engineering material – an overview

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Since the synthesis of the boron nitride in its cubic crystallographic structure, cBN, a material with exceptionally high hardness and special properties was developed for technical engineering applications. For practical use, cBN is, after diamond, the second known hardest material and is today being increasingly used as cutting and drilling tools in substitution for diamond-based tools owing to superior thermal stability and chemical inertness. In this study, the advances in the use of the cBN competing with diamond as a superhard industrial tooling for petroleum extraction, automobile manufacture and other engineering applications, was reviewed. The properties of both single crystals and polycrystalline cBN in the form of composites and thin films were assessed to characterize the possibilities of a next generation of superhard materials to replace diamond in tool and other technological devices.

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1. Introduction

Materials with superior hardness have since the beginning of our civilization been associated with human achievements. Hard stones were first used by our ancestors not only as simple implements such as hammers and anvils, but also as tools to shape and sharpen other stones. This was probably the most important pre-historical developed technology to break, chip, splint and finish less harder stones as well as other existing natural materials such as wood, bone and horn, for hunting and defense. At the beginning of the age of metals, bronze replaced stones as the most efficient tool material.

Around 5,000 years ago, this role was transferred to steels and remained as such until the last two centuries when diamond, hard ceramics and cermets became industrially available. Among the hard materials currently used in industrial operations related to turning, cutting, drilling, boring and grinding, diamond stands as the hardest. In fact, rock drilling for petroleum and natural gas extraction is today entirely dependent on diamond inserts placed onto the head crown of perforation tubes. Without diamond particles incorporated into these inserts it would be practically impossible to extract the petroleum with the efficiency that the modern world demands. As a wonder material, diamond has outstanding

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properties that are significantly contributing to improve our society [1,2]. In particular, synthetic diamonds allow today a commercial and relatively low cost offer to many technological applications. Here is relevant to remind that since the turn of the XIX century it was already known that diamond was an allotropic form of carbon. By then, it became clear that by applying enough pressure and temperature, it would be possible to convert the hexagonal structure of graphite into the cubic of diamond. However, it was only in 1955 that General Electric research group in the US succeeded for the first time to synthesize diamond [3,4].

In spite of its remarkable properties, as a carbon-based material, diamond has serious technological limitation. Working temperatures are restricted and degradation reactions occur with important metals including iron. For instance, the oxidation of diamond initiates at 600 °C while its conversion to graphite takes place above 900 °C [5]. The contact of diamond with a ferrous alloy, like steel, or a nickel superalloy deteriorates its properties by carbide formation [6]. As consequences of these limitations, a diamond containing tool can only be used at moderate temperatures and its application is restricted to non-metallic materials as well as a range of non-ferrous alloys. Another synthetic superhard material, the cubic boron nitride (cBN), is the solution for the adverse diamond limitations.

2. Genesis of cBN

Contrary to diamond, the allotropic cubic structure of boron nitride does not exist in a natural form, only synthetically made. Historically, the synthesis of cBN holds parallel facts to that of diamond. In 1956 [7], one year after the first synthesis of diamond [3,4], Wentorf Jr., also a GE researcher at the same laboratory in Schenectady, state of New York, USA, transformed for the first time a cubic crystalline lattice compound from mixtures containing boron and nitrogen inside a metal capsule heated by electrical resistance while subjected to high pressure in a belt-type equipment. The announcement of the cBN discovery in 1957 [8] revealed that the lowest pressure and temperatures then used were 62,000 atmospheres (6.2 GPa) and 1,350 °C. The name of 'Borazon' was proposed for the cBN and Wentorf reported that it was hard enough to scratch diamond [8]. Following the discovery, other articles by the GE group [9,10] added information on the synthesis, properties and characteristics of cBN. It was reported that high pressure and high temperature (HPHT) conditions similar to those effective for diamond synthesis were also suitable for the hexagonal structure of boron nitride (hBN) to be converted into the 'diamond-like' cubic structure of cBN. Moreover, both direct and catalyst-assisted transformations were found appropriate for HPHT conversion of the 'graphite-like', stacked sheets of hBN into the zinc-blend cubic structure of cBN. Fig. 1 compares the crystalline similarities between the graphite to diamond (G→D) synthesis and that of hBN→cBN.

Coincidences exist not only in the crystallographic transformation illustrated in Fig.1 but also in the synthesis conditions. Fig. 2 shows the pressure-temperature (P, T) diagram for both carbon and boron nitride. In this figure one

should notice the common regions of thermodynamic stability, 1,000 °C and 4 GPa for both diamond and cBN.

3. Research and development in cBN

In the years following the first synthesis not much interest was demonstrated by the application of cBN as a diamond competing superhard material. However, patents [11-13] were required for the use of cBN as inserts cutting tools. Only in the 70's considerable attention was paid to the potential of cBN as a substitute for diamond in industrial applications. In particular, it was a strong argument in favor of cBN the fact that, contrary to diamond, its structure is stable up to 2,000 °C. In addition, the decrease in the hardness of diamond

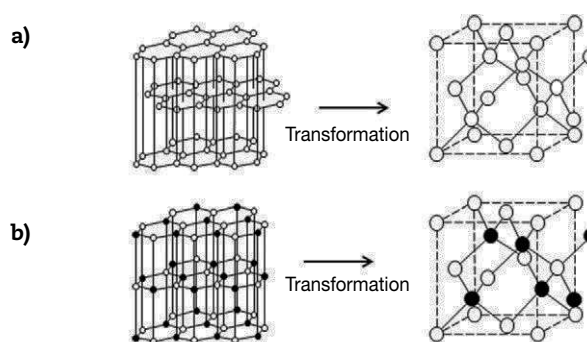


Fig. 1 – Structural transformation at high pressure and high temperature for (a) G→D, and (b) hexagonal structure of boron nitride→cBN.

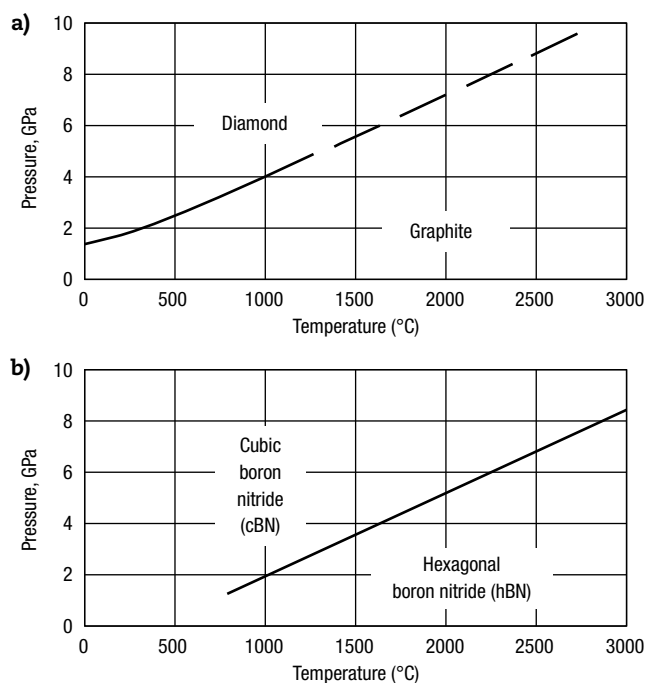


Fig. 2– Pressure vs. temperature diagrams for (a) carbon and (b) boron nitride.

Table 1 – Properties of abrasive materials.

Material	Density (g · cm ⁻³)	Knoop hardness (GPa)	Compressive strength (GPa)	Thermal conductivity (W/m.K)	Thermal expansion (10 ⁻⁶ · K ⁻¹)
cBN	3.45	45	5.33	740	1.2
Diamond	3.51	57-104	8.68	600-2,000	1.5-4.8
WC	14.7	13	4.5	100	5.4
SiC	3.20	32	3.9	120	4.0

is accentuated beyond 500 °C becoming inferior to that of cBN at 800 °C and above. Furthermore, it was realized that cBN stayed inert in contact with steels, cast irons, and superalloys at operational conditions for which diamond would react and loose machinability.

Despite its technological advantages, the cost of cBN up to the 80's was comparatively high enough to discourage a prompt substitution for diamond. Meanwhile, R&D efforts gave a significant contribution to more efficient synthesis process and motivated the expansion of composite products based on cBN. In the last decade, the industrial forms on productivity and cost reduction, created an increasing interest for high performance materials associated with long life tools. In this period, the fabrication of cBN and related sintered composites has grown more than 20 times [14].

From its creation, investigations on the properties and characteristics of cBN permitted to amass relevant data for its possible industrial applications. While the disclosure of information up to the 90's on cBN in both US [11-13,15-18] and the UK [19-21] was done mainly through patents, Russians [22-29] and Japanese [30-40] also contributed with publications in journals and conferences. In recent years, more than 40 patents and hundreds of articles including those from Chinese [41-47] and Brazilian [48-50] researchers have also been contributing to works on cBN.

Table 1 presents basic properties and characteristics of cBN and other hard materials used as abrasive, including diamond. As shown in this table, the properties of cBN are relatively close to those of diamond. The marked difference in favor of cBN is not only its thermal stability but also its inertness with respect to strong acids and ferrous alloys. In principle, these properties revealed that cBN, like diamond, can be considered as well as a superabrasive material.

4. Synthesis of cBN

A critical point regarding the commercial feasibility of cBN is the cost associated with its synthesis process. Different methods have been proposed to obtain cBN including the direct transformation [10], the high pressure chemical reaction [12] and the catalyst assisted hBN → cBN transformation at HPHT conditions [51,52]. This latter has been the most successful and is apparently becoming the viable commercial alternative to compete with synthetic diamond, which is extensively produced in a similar method. Essentially, the function of the catalyst is to decrease the thermodynamic parameters of the synthesis process [10]. Actually, the first attempts

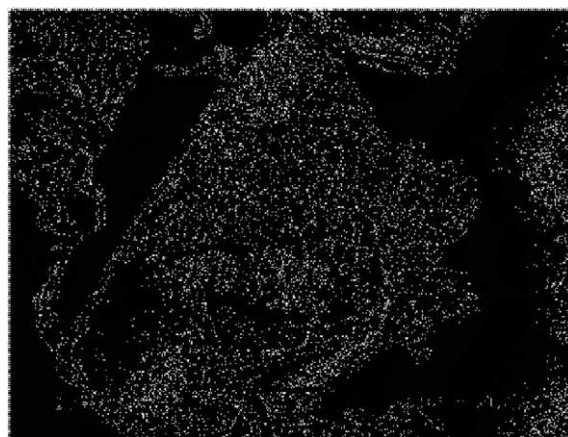


Fig. 3 – cBN crystal synthesized at 6.0 GPa and 1,500 °C with 4 wt.% of Mg as catalyst/solvent.

to synthesize cBN carried out by Wentorf [9] showed that alkali and alkali-earth metals as well as their nitrides were effective catalysts for HPHT conversion of hBN → cBN. Up to now, according to a very recent work by Guo et al. [47], about 50 kinds of solvent catalyst were used.

Not much change has occurred in the catalyst types originally investigated by Wentorf [9], with emphasis in Li, Mg and its respective nitrides as the most effective solvent/catalysts [53-56]. Furthermore, alloys such as Al-Cd, Fe-Al, Mg-Al, Ni-Al and others were also reported as possible solvent/catalyst to synthesize cBN [55].

Fig. 3 illustrates a typical cBN crystal synthesized at the Laboratory of Superhard Materials of the Universidade Federal do Norte Fluminense (UENF) by the authors of the present review article.

Fig. 4 shows an X-ray diffraction pattern obtained from hBN reaction products synthesized at 6.0 GPa and 1,500 °C with Mg as solvent/catalyst. In this figure, it is important to notice the main peak for the (111) plane of cBN, which indicates the transformation of the hexagonal to the cubic structure. Moreover, from the location of the cBN peak in Fig. 4, a lattice parameter $a = 3.615 \text{ \AA}$ was obtained.

5. cBN tool products

The growing interest for cBN as a superhard material tool is currently being translated into different forms and types of

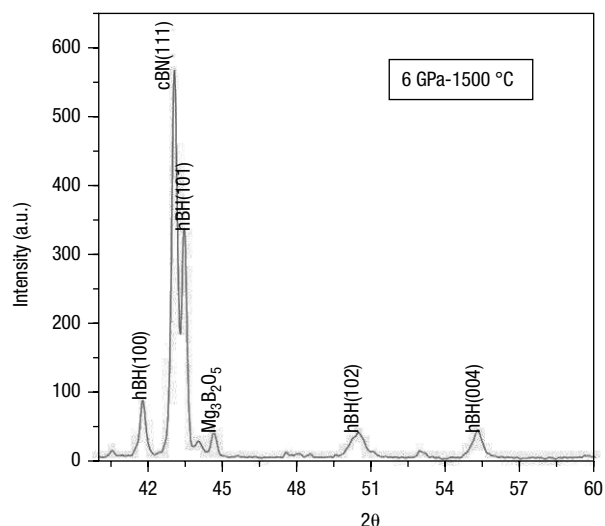


Fig. 4 – Typical X-ray diffraction pattern of the reaction products synthesized in the hBN-Mg system.

products already in the market. In general, cBN is commercially available as crystals powder and sintered composites. It is not the objective of this study to advertise products. However, brand names will here be mentioned with the only purpose to inform that cBN is today, like diamond, a commodity with technological relevance and participation in the global economy.

Crystalline powder is the basic form produced by catalyst-assisted HPHT synthesis. Depending on the processing conditions, significant differences may exist in the properties of the cBN crystals provided by distinct suppliers. GE is one of the largest companies to offer several crystal powders under the registered trademark of Borazon®, comprising many types with granulometry varying from 50/40 up to 250/200 μm and densities of 3.48 to 5.25 g/cm^3 . Another supplier is the South African Element Six with trademark Ambor®. The granulometry of Element Six cBN powder varies from 20/30 to 325/400 μm and different colors are associated with strength and uses. The Japanese supplier Sumitomo is producing the trademarks SBN® and BBN®. A heat resistant black crystal powder, SBN-F, is specific for Sumitomo sintered products. The Russian supplier Saint Petersburg Abrasive is producing crystal powders with distinct characteristics under the trademark Elbor®. In Ukraine, the IPM firm supplies powders with modified strength, with or without a metallic coating, under the trademark Kuborit®.

6. Sintered polycrystalline cBN

Like synthetic diamond powder, the crystal particles of synthesized cBN cannot be directly used in any kind of tool except as embedded particles in polishing pastes for finishing purpose. Large size pieces can only be obtained by sintering a precursor powder into a consolidated polycrystalline cBN (PcBN) insert. The first information on PcBN was released in a 1963 US Patent [11]. Since then, a growing number of articles and patents are accumulating on PcBN R&D works.

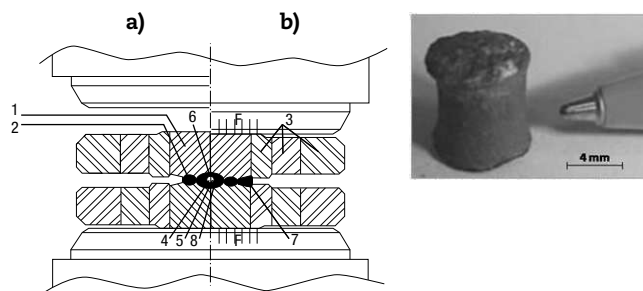


Fig. 5 – Left – Schematic of a HPD type anvils with concavity: (a) position before compression; (b) position during compression under a force ‘F’; 1: hard metal anvil; 2: container; 3: hydraulic press support blocks; 4: graphite tube; 5: reactive mixture; 6: calcite isolating lids; 7: gasket; 8: agglomerate being created during sintering. Right – Polycrystalline cBN insert sintered at the Laboratory of Superhard Materials, UENF.

The PcBN sintering process is conducted in the same HPHT equipment used for the crystal synthesis inside the region of thermodynamic stability shown in Fig. 2b. According to Novikov and Shulzhenko [57], this region corresponds to temperatures from 1,200-2,000 $^{\circ}\text{C}$ and pressures of 7-12 GPa. Fig. 5 shows both the schematic of a high pressure device (HPD) with the reactive cell containing the crystal powder (right side) and a fabricated PcBN insert (left side) at the UENF Laboratory of Superhard Materials.

Two distinct sintering procedures may be used in association with the scheme shown in Fig. 5: direct and binder assisted. The direct sintering uses only cBN crystals at relatively higher HPHT conditions for PcBN consolidation. In this procedure, the cBN particles are plastically deformed and their contact areas are increased by the applied high pressure. Surface diffusion then promotes particles adhesion and produces a sintered insert, like the one shown in Fig. 5 (right side) with the consolidated strength, density and hardness of a polycrystalline cBN [58].

The binder-assisted sintering permits to consolidate a PcBN at relatively lower HPHT conditions and yet promotes superior properties than those obtained by direct sintering. Additionally to the diffusion mechanism acting between crystals, a process of filling the pores as well as a binder/crystals interaction results in a stronger and more uniform polycrystalline cBN. Moreover, the binder has another important role, which is to prevent the formation of boron oxide that impairs the surface diffusion between cBN crystals. For this reason, a specific element like Al is used in the binder to reduce the B_2O content, allowing free B to react with other elements such as Fe, Si, Ti, Mg and other compounds that may constitute the binder [16,17,59-61].

Despite all the R & D efforts, due to high temperature atomic diffusion and reactions, the interaction mechanisms between the binder is still not completely understood owing to the difficulty in interpreting all the HPHT process stages involved in the consolidation of the PcBN [62]. Actually, it has been found that both the fast diffusion and the possibility of non-equilibrium phase transformation significantly improve

the binder interaction with the cBN crystals. As a consequence, continuous solid solution of borides and nitrides is formed. This continuous phase involving the cBN particles characterizes a true composite material with properties markedly conditioned by the choice of binder. For instance, the combination of TiN and AlN causes a fine and homogeneous microstructure to be formed with improved toughness of the insert [62] but a loss of its abrasion capacity;

The market offers many registered trademarks of PcBN composites; the following are among the most important:

- BZN compact®, GE (USA);
- Sumboron®, Sumitomo (Japan);
- Sunnit®, Amborite® and Ambrasit®, Element Six (South Africa);
- Elbor®, Saint Petersburg Abrasive (Russia);
- Belbor®, IFTT (Belarus);
- Kiborit®, ISM (Ukraine).

Table 2 shows the main properties of commercially available PcBN composites including the wear intensity associated with the turning of an AISI 4140 high strength steel.

Fig. 6 illustrates: (a) two turning bits with cBN sintered inserts that were mechanically fixed and brazed jointly with; (b) curves for the wear of different inserts. The wear curves in Fig. 5b correspond to inserts CIC-2, fabricated at the UENF Laboratory of the authors of this article, as well as a commercial brand 'Amborite', and a Russian hard metal (T30K4).

7. Thin film cBN

Most cBN tools are currently made of sintered polycrystalline inserts brazed to a hard material support. However, similar to carbon vapor deposition (CVD) diamond film, there is also the possibility of using a cBN film to coat tools for high performance machining. According to Jiang et al. [63], thin cBN film is the best candidate for coating cutting tools as well as rotary tools and wear parts. The authors indicated that their company, Durobor, together with Nanomech in partnership with the University of Arkansas, developed a technology of cBN composite coating for carbide cutting tools of various designs. They also informed that this hybrid technology combines electrostatic coating of a cBN perform followed by chemical vapor infiltration of a binder such as TiN, TiC, TiCN, HfN etc., which allows for several benefits including desired applications, specified thickness, conformability, manufacturability and cost. As conclusions from their overview study, Jiang et al. [63] indicated that this new cBN coating promotes significantly longer tool life when compared to PVD TiAlN coating, CVD multilayer coating, and bulk Al_2O_3 inserts, in tests of continuous turning of AISI 4340 hardened steel. Moreover, the outstanding performance of cBN coated inserts in turning a HSLA pre-hardened steel and nodular cast iron demonstrated the wide potential for machining other engineering materials.

Table 2 – Properties of commercial registered marks of polycrystalline cBN composites.

Commercial brand	Knoop hardness (GPa)	Density (g/cm ³)	Compressive strength (GPa)	Toughness, K_{1C} (MPa · m ^{1/2})	Elastic modulus	Thermal conductivity (Btu/m · K)	Grain size (μm)	Wear intensity (mm/W ³ · m)
BZN Compact®	35-45	3.48	3.1-4.8	8.6	740-870	50-80	1.0	11.8
BN 100®	40-45	4.25	4.6	7.0	830	34-38	0.3-2.0	12.6
BN 200®	30-35	4.25	4.3	6.6	814	24-36	0.5-1.5	12.2
Amborit®	28.5	3.37	3.7	13.1	680-720	110-135	0.1	12.1
Elbor®	32-38	3.31	2.3-3.2	3.7-4.2	660-750	60-80	0.5-1.2	12.4
Belbor®	39	3.42	4.0-5.0	10.8	730	70-85	0.2-1.5	10.6
Kiborit®	32-36	3.20	2.6-3.2	13.5	850-910	100	3.0-4.1	11.1

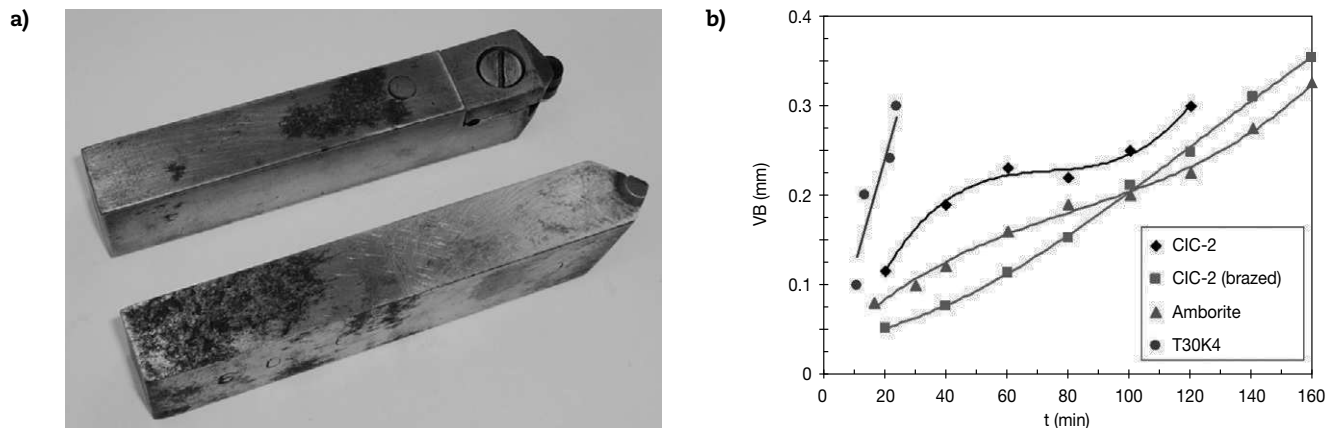


Fig. 6 – Turning bits (a) and wear curves (b) for cBN inserts.

8. The color of cBN

Although the color developed by a synthesized crystal of cBN might appear to be an irrelevant characteristic, it has nevertheless a technical importance. According to Du et al. [44], cBN crystals with different colors exhibit diversified morphologies and properties, such as thermal stability and residual strains. There seems to be a tendency that morphology becomes integrated and crystal size bigger with increasing black color. Here it is worth mentioning that the first published study [8] concerning the synthesis and preliminary characterization of cBN reported on its different colors. In that study, Wentorf [8] made a comment that 'generally the (cBN) color is black, brown or dark red, probably due to boron, though white, gray and yellow crystals can be found'. Later, the same author reported [9] that crystals synthesized with nitride as catalyst would be white if the operation was conducted at 6.5 GPa and 1,900 °C or yellow if at 5.0 GPa and 1,700 °C. Moreover, it was also reported that the addition of a few percent boron changed the color to dark brown or black.

These results have been confirmed in optical [44,64] and electronic [65,66] investigations. Today, it is known that cBN crystals may present several colors, from white to black due to different impurities and defects. Regarding the electronic properties, cBN, a periodic table group III-V compound with a relatively large, 6.3 eV, band gap, may become a p-type semiconductor by doping with Be or an n-type doped with Si. Furthermore, in terms of optical characteristics, UV light emission from a cBN p-n junction has been reported [65,66]. According to Riedel [67] these properties characterize cBN as a promising ceramic for high temperature application in microelectronics and optoelectronic devices.

9. Concluding remarks

It is unquestionable that synthetic diamond owing to both its sovereign position as the hardest material and relatively low cost will keep its present leading position in the market of machining tools. However, diamond can cut only non-ferrous materials and rocks, corresponding to a volume of 75%-80% of the total tool machining market. Conversely, cBN can cut all ferrous alloys including superalloys. Nowadays, most of the 20%-25% of the total machining market is using the traditional WC inserts, with properties shown in Table 1, for turning high strength low alloy steels. However, WC has an inferior hardness in comparison to cBN. Therefore, there is still a great potential of cBN expansion for future market. As mentioned by Jiang et al. [63], despite the increased use of Al and other non-ferrous alloys, ideally machined with diamond, steel and cast iron will remain for decades the most abundant materials in the heavy and automotive industries. With the expected decreasing costs of catalyst-assisted HPHT processed PcBN, its commercial demand may approach that of diamond. The worldwide production of cBN in the year 2,000 was around 80-100 million carats, corresponding to about 10% of synthetic diamond. Since then, the demand for cBN has rapidly grown in spite of the higher price of cBN in comparison with synthetic

diamond. By the end of this decade, the production of cBN should double and, with decreasing costs, it may take another decade for its production to equal that of synthetic diamond. Not only for the fact that sintered cBN has its own important engineering niche of dominance, but its thin film technology, if successful, will supplant the other coating materials, including CVD diamond film, for the next generation of superhard tools.

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