Sintered Superhard Materials

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Summary. Diamond or cubic boron nitride particles can be sintered into strong masses at high temperatures and very high pressures at which these crystalline forms are stable. Most of the desirable physical properties of the sintered masses, such as hardness and thermal conductivity, approach those of large single crystals; their resistance to wear and catastrophic splitting is superior. The sintered masses are produced on a commercial scale and are increasingly used as cutting tools on hard or abrasive materials, as wire-drawing dies, in rock drills, and in special high-pressure apparatus.

In the hierarchy of hardness one may recognize three broad classes of materials:

1) The common materials of construction, such as organic materials, some ceramic materials, and metals, including most steels.

2) The harder materials, such as aluminum oxide and silicon carbide, which are used mostly as abrasives, and the cemented carbides of tungsten and titanium, which are used mostly as cutting tools. These harder materials are used to shape the common materials of construction into useful articles. Much of our material wealth and productivity depends on the effective use of these harder materials.

3) The superhard materials, diamond and cubic boron nitride (CBN). The best ways to shape or sharpen the harder materials widely used as tools in modern industry generally involve the use of diamond as a component of an abrasive wheel or a fixed tool. For example, approximately a quarter carat (0.05 gram) of diamond is used up in shaping the tools used to manufacture a typical automobile.

Diamond is also widely used in tools for the cutting and shaping of the harder materials of construction such as stone, concrete, glass, ceramics, and other hard or abrasive materials which chemically react only slightly with carbon at the cutting edge. Cubic boron nitride, which is somewhat softer than diamond, finds use in shaping hard iron or nickel-containing metals that chemically attack diamond rapidly at the hot cutting edge and thereby make a diamond tool deteriorate at uneconomic rates.

Both diamond and CBN are thermodynamically stable only at very high pressures, as indicated in Fig. 1. Diamond is found naturally, presumably brought to the earth's surface after being formed at great depths. Most of the industrial diamond used today is synthesized at high pressures from graphite (*1*); CBN is formed under similar conditions of temperature and pressure from graphitic hexagonal boron nitride (*2*). One of the factors affecting the extent of use of these materials is the high cost of the apparatus required to synthesize them. Other factors are their size, shape, and coherence. Until recently, most of the synthetic materials came in pieces whose maximum size was less than about 1 millimeter. This was suitable for sawing and grinding purposes but the great need for larger pieces to be used as cutting tools or wire-drawing dies remained unsatisfied by the synthesized material. This need was met as much as possible by natural single crystals of diamond despite their limitations of costliness, variability, susceptibility to massive fracture along easy cleavage planes, and uneven wear.

These limitations arise from the crystal structure of diamond, which is such that each carbon atom has four nearest neighbors at the corners of an imaginary tetrahedron. They are stacked together so that the entire array has the same symmetry properties as a cube. The carbon atoms are small and the carbon-carbon bonds are stiff and highly directional, so that the bond energy per unit volume of diamond exceeds that of any other substance, hence the surpassing hardness. However, if one makes imaginary slices through the crystal on various planes, one finds that there are four different planes across which the number of bonds per unit area is the least. Furthermore, impurities are most easily accommodated on these planes, because most impurity atoms are larger than carbon atoms and so prefer positions where the misfit strain is the smallest. Thus the crystal tends to separate most easily across these less strongly bonded planes. These planes are the (111) or octahedral face planes. They pass through three (but not four) corners of a cube.

The so-called "grain" as well as many of the wear and fracture properties of diamond crystals may be explained by invoking the lower resistance of (111) planes to tensile or cleavage failure (*3*). In the gem trade, the "easy" polishing directions on different crystal faces are determined mainly by the ease with which microscopic octahedral-faced fragments can be pulled out of the surface being polished. In single-point cutting tools or wire-drawing dies, attention is paid to the orientation of the crystal to minimize the possibilities of catastrophic cleavage and rapid or uneven wear. For example, the hole in a single-crystal wire-drawing die wears to an out-of-round shape owing to the differing resistance to abrasion along different crystal directions as the wire rubs the diamond. Usually, a single diamond crystal bears some obvious natural crystal faces to permit easy identification of the weak planes; otherwise an x-ray diffraction pattern is needed to indicate them because the crystal is optically isotropic, except for residual strains.

Several kinds of natural polycrystalline diamond masses are also available and find some use despite their relative scarcity and the difficulties of shaping and holding them. For example, framesite is weak, composed of relatively large crystals held together more by impurities than by diamond-diamond bonding, and is not widely used. A more durable category, called carbonado, has extensive diamond-diamond bonding despite mineral oxide impurities. Ballas contains very little impurity, is generally white instead of dark in color, and is extremely strong (*4*). The natural formation processes for these materials remain largely unknown.

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←Oil well drilling bit armed with sintered diamond teeth. [R. H. Wentorf, General Electric Co., Research and Development Center, Schenectady, New York]

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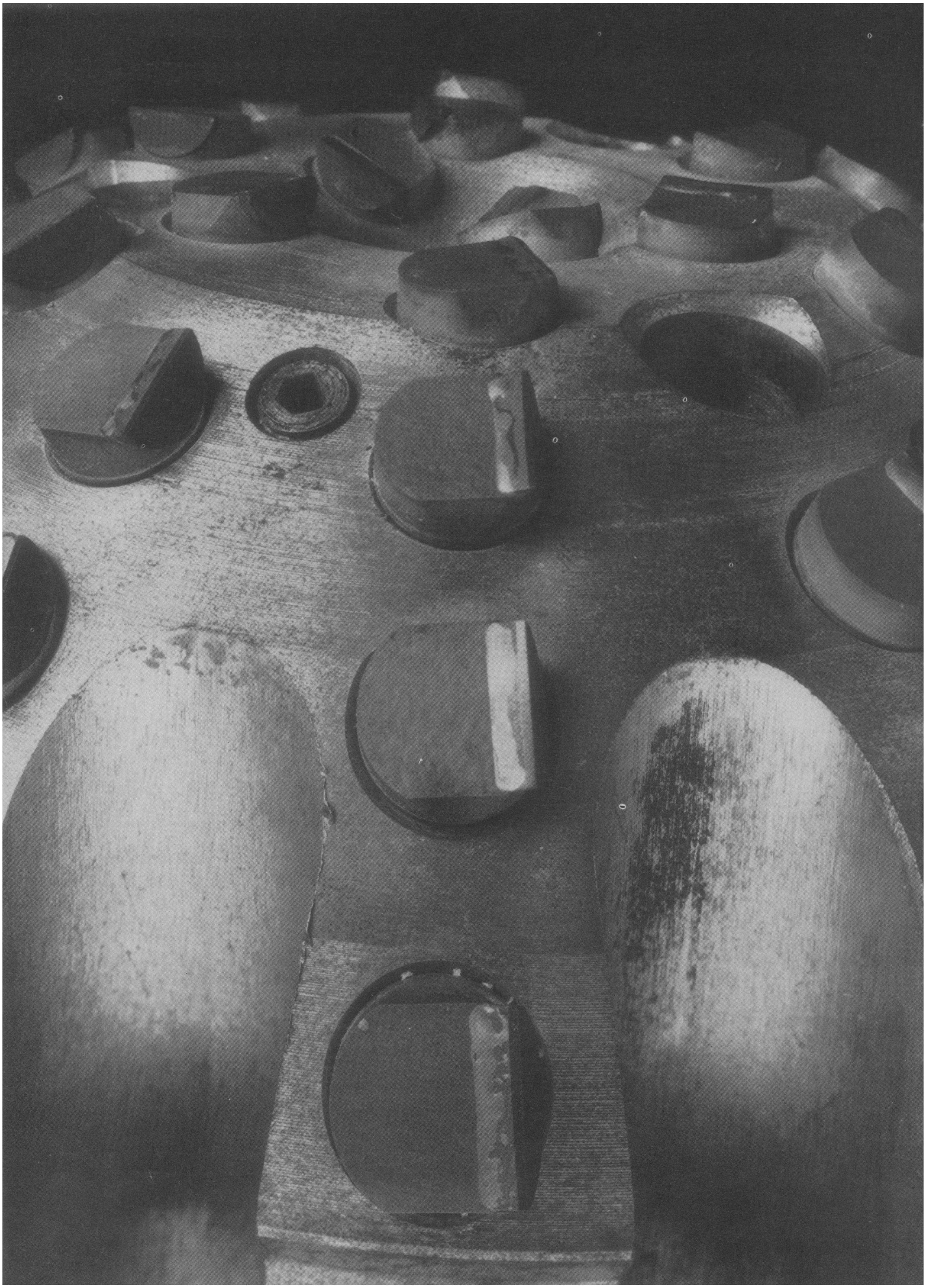
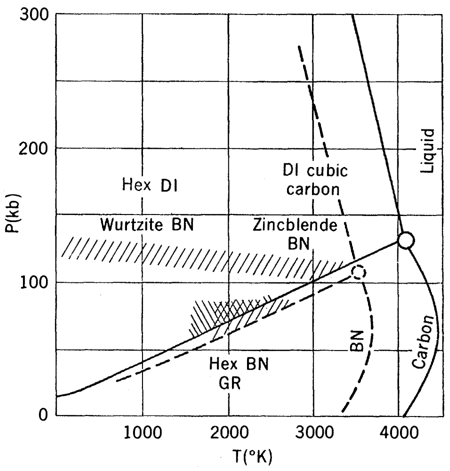




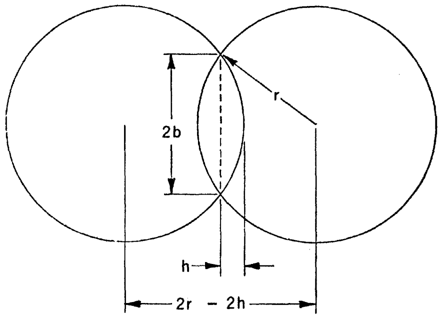


Fig. 1 (left). Pressure-temperature phase diagram for carbon and boron nitride (*BN*). (*DI*, diamond; *GR*, graphite.) Fig. 2 (right). Overlapping spheres.

The advantages of a strong, polycrystalline mass are its greater "toughness" (the easy cleavage planes of its component crystals lie randomly toward one another, so that propagation of a crack throughout the mass is difficult) and its more uniform wear, independent of direction. Such masses lack the aesthetic appearance of single crystals but their greater utility makes efforts to prepare them worthwhile.

Aspects of Sintering Superhard Materials

By sintering one means the bonding together of a mass of small particles into a larger, coherent piece. During this process the contact patches between particles grow and the total volume of the mass shrinks. Eventually the mass becomes sufficiently dense and strong even though some voids may remain.

As a simple model of a sintered mass, consider a face-centered cubic array of close-packed spheres, each of radius r, which have common circular contact patches of radius b, and center-center distances of $2r - 2h$, as shown in Fig. 2. Then a cap of volume $(3r - h)\pi h^2/3$ is missing from each sphere. A unit cell, of edge length $a = 2\sqrt{2}\,(r - h)$, contains four spheres, each with 12 nearest neighbors. Then F, the actual volume fraction of the cell occupied by spheres will be

$$F = 4[4\pi r^3/3 - 12(3r - h)\pi h^2/3]/16\sqrt{2}(r - h)^3 \qquad (1)$$

When the spheres are flattened so that the contact patches from six coplanar spheres touch, the voids between spheres will no longer be connected. This occurs for $2(r - h) = \sqrt{3}\,r$, or $h/r = 0.134$. The total contact patch area, C, per unit cell, arises from 12 patches on each of four spheres, or 24 net patches, each of area πb^2, so that

$$C = 24\,\pi b^2 = 24\,\pi h(2r - h) \qquad (2)$$

For mechanical strength and transmission of heat, one considers the ratio $C/a^2 = M$. Table 1 shows that M increases rapidly at the higher values of F. A practical lower limit for carrying most of the strength of the grains might be $M = 2$, where F is about 0.92. Foreign material among the spheres will be trapped when F exceeds 0.962.

Table 1. Values of F and M for various values of h/r up to 0.134, above which the analysis is irrelevant.

	Values of h/r						
	0	0.04	0.06	0.08	0.10	0.12	0.134
F	0.704	0.826	0.863	0.895	0.927	0.953	0.962
M	0	0.801	1.242	1.715	2.21	2.75	3.14

Table 2. Properties of diamond and steel.

Property	Diamond	Steel
Melting point (K)	4000	1800
Hardness (kg/mm^2)		
At 25°C	7000+	1000
At 1300°C	1500	10
Youngs' modulus (dyne/cm^2 at 25°C)	8 to 12 $\times$ 10^{12}	2 $\times$ 10^{10}
Thermal conductivity (watts cm^{-1} K^{-1} at 25°C)	7 to 20	0.7
Linear thermal expansion coefficient 10^{-5} K^{-1} at 25°C	0.1	1

The driving forces for sintering are the decreases in free energy accompanying reductions of stresses and surface area. Pure materials usually sinter reasonably rapidly at absolute temperatures about 0.6 to 0.7 that of melting. Solvent impurities may assist sintering but they may also affect the sintered mass undesirably.

The embedding of diamond particles in some kind of a tough matrix (usually metal) to form a hard composite mass is satisfactory for many uses of diamond, but it is not a substitute for direct sintering between diamond grains when the properties necessary for a cutting tool, such as high hot strength and good thermal conductivity, are desired. The conductivity, strength, stiffness, hot hardness, and thermal expansion of possible matrix materials are so inferior to those of diamond that the properties of the composite tend more to those of the matrix than of diamond (see Table 2).

The melting point of diamond is about 4000 K (see Fig. 1), so that a suitable sintering temperature would be about 2400°C, about the same temperature as that used in the manufacture of graphite from coke. The required pressure for diamond stability then would be about 70 kilobars.

However, the hardness of diamond is a practical obstacle to achieving this pressure over the entire surfaces of all the consolidating particles. A vessel into which diamond grains have been poured may contain about 30 percent voids, depending on grain shape and size distribution. Tamping or squeezing the vessel scarcely affects the void fraction because the hard particles do not crush much; instead they indent the walls of the vessel. Where the diamond particles touch each other, the local pressures are very high, in the range 300 to 1000 kbar. In other places (most places) the local pressure is that of the voids. Thus, at an average pressure of, say, 70 kbar on the vessel, one has heavily indented vessel walls, a network of local high-pressure contact patches, and a large area at a relatively low pressure. As the sintering temperature is reached, some reduction in strength and hence local pressure will occur, and the contact patch area will increase slightly. But at 2400 K the transformation of diamond into graphite is rapid at low pressures. One volume of diamond expands to about 1.6 volumes of graphite, and so the low-pressure voids become filled with graphite until the local graphite pressure is high enough to repress further graphite formation. However, this pressure is not necessarily high enough to force the graphite back into diamond. Thus the 70 kbar of external pressure is borne by a mixture of diamond and graphite, and in order to increase the fraction of diamond, an increase in pressure will be necessary so that the diamond grains yield and the graphite pressure increases enough to form some diamond. From separate experiments on the simple conversion of graphite into diamond, it appears that pressures on the order of 100 to 130 kbar are required (*5*). Such pressures are difficult to achieve on a practical commercial scale.

The presence of solvent catalyst metals, such as manganese, iron, or nickel facilitates the transformation between diamond and graphite (*1*). These molten metals are also excellent solvents for most other metals and their carbides and hence might be expected to attack the walls of the vessel containing the mass to be sintered. Too much metal among the diamond grains reduces the stress gradients that can drive the consolidation process.

Another difficulty that occurs with a mixture of catalyst metal and diamond is the formation of stable arches or shells before the entire mass is consolidated. Such a shell is essentially all diamond in perfect mechanical contact and hence changes shape very slowly. Inside it the pressure falls to that of the diamond-graphite equilibrium; no consolidation occurs and graphite may form from diamond there. Suitable vessel design can frequently eliminate this problem, thereby reducing the overall pressure required for consolidation.

Finally, let us consider a mass of sintered diamond embedded in a pressure-transmitting medium at high pressure. This medium is necessarily a solid at the low temperatures (20° to 200°C) prevailing during the reduction of pressure to 1 atmosphere. Since nothing expands so little as diamond during pressure reduction, the outer surfaces of the sintered diamond mass are exposed to strong tensile stresses as the pressure-transmitting medium tries to expand more rapidly. These stresses can be high enough to tear the sintered mass apart if it is not strong enough or convex enough.

From the foregoing comments one may conclude that the production of sintered superhard materials is beset with several peculiar and difficult problems. Indeed, they blocked the development of practical production of sintered diamond bodies for many years despite numerous attempts and much experimentation in many laboratories.

Progress Toward Practical Solutions

The availability of apparatus capable of maintaining temperatures of 1500 to 2000 K together with pressures of 50 to 70 kbar, where diamond is stable, fostered new work on sintering diamond.

Katzman and Libby (*6*) described the formation of sintered diamond compacts with a cobalt binder. They found the best conditions to be about 20 minutes at 1600°C and 62 kbar using a mixture of cobalt and diamond powders (20:80, by volume) of particle sizes 1 to 5 micrometers held in a tantalum vessel. The sintered masses were about 6 millimeters in diameter and 3 to 8 mm long. There appeared to be some grain growth or diamond-diamond bonding. The masses had about half the life of a single-crystal diamond when used to dress abrasive wheels. The process never reached commercial production.

Stromberg and Stevens (*7*) reported on the sintering of diamond at 1800° to 1900°C and 60 to 65 kbar. They loaded cleaned natural diamond powder of sizes 0.1 to 10 μm into tantalum containers. The vessels, about 3 mm in size, were heated in vacuum to remove gases and then sealed by electron beam welds before being loaded into a high-pressure apparatus and exposed to high pressure and temperature for about an hour. In some experiments about 1 percent of boron, silicon, or beryllium powder was added to react with residual gases and form strong carbides for bonding. An indium sheath surrounding the vessel helped prevent tearing apart of the mass as the pressure was reduced. The diamond masses obtained had densities of up to about 99 percent and microhardnesses of 75 to 90 percent that of solid diamond. Efficient mixing of diamond particles in a range of sizes suitable for high packing density produced the highest final densities. No tests of strength or wear resistance were reported. The process was never practiced on a commercial scale.

Hall (*8*) found that strong diamond compacts could be made at about 2000 to 2500 K and 65 kbar using short sintering times of 20 to 200 seconds. The diamond powder is contained in graphite tubes and no special cleaning procedures are mentioned. The products are usually black cylinders with densities of about 3.2 grams per cubic centimeter. Extra bonding agents (borides, nitrides, carbides, and oxides) may be added to the diamond before sintering. Such diamond compacts are available and have found

Table 3. Mechanical properties of sintered superhard materials [from (*11*, *16–19*)].

Type of compact	GPa						Sound velocity (V_1, m/sec)	Poisson's ratio, ν	Relative wear resistance
	Compressive strength	Modulus of elasticity, *E*	Transverse rupture strength	Simple compressive stress	Simple shear stress	Knoop hardness			
				Diamond					
Regular (two-phase)	6.9 (*11*)	890 (*11*)	1.35 (*11*)			63.7 to 78.4 (*19*)	16330 (*18*)		200 (*19*)
"Treated"	—	840 (*11*)	0.83 (*11*)						
Anvils				35 (*16*)	20 (*16*)				
				Cubic boron nitride					
Single-phase		890 (*18*)				44	16365 (*18*)	0.138 (*18*)	20 (*19*)
				Comparative materials					
Cemented tungsten carbide	3.7 to 5.5	460 to 675 (*18*)	1.7 to 2.7	7 (*16*)	4 (*16*)	18 to 22	6400 to 7000 (*18*)	0.20 to 0.24 (*18*)	2 (*19*)
Single-crystal diamond	8.69 (*17*)	950 (*17*) to 1100 (*11*)	1.05 (*11*)			≤ 88	17780 (<100>) 18620 (<111>) (*18*)		95 to 245 (*19*)

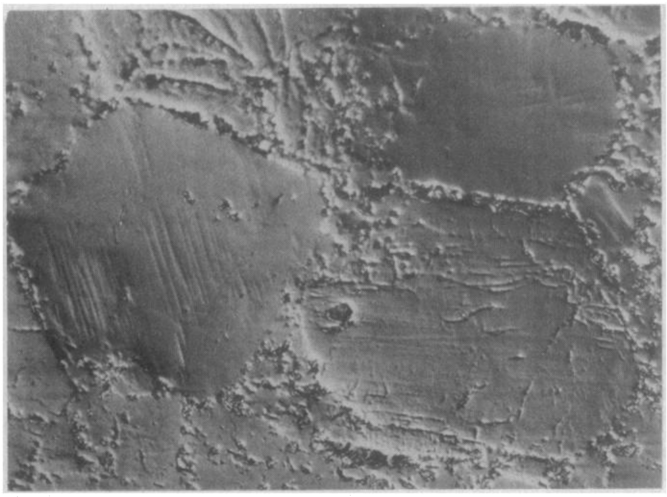


Fig. 3. Photomicrograph of polished surface of man-made sintered diamond mass.

uses as cutting and dressing tools, and as gauge blocks.

Hibbs and Wentorf (*9*) described commercially available diamond and CBN compacts and some of their uses in cutting and shaping hard materials. These sintered masses are characterized by extensive direct bonding between the hard particles and a minimum of second phase. Temperatures in the range 1500° to 2000°C are suitable for their formation and these temperatures require pressures of the order of 50 to 70 kbar so that the cubic crystals are thermodynamically stable during sintering. The grain size in the diamond and CBN compacts can range from a few to several hundred micrometers in size. Smaller grain sizes permit finer cutting edges on the finished tool. Usually the hard materials are consolidated as a layer about 0.5 mm thick on the circular face of, or as a core within, a cylinder of cobalt-cemented tungsten carbide which provides strength and convenience in use (*10*). Cutting tool blanks are commercially available in disks up to about 14 mm in diameter and wire-drawing die blanks of comparable sizes are also available. The General Electric Company has been manufacturing sintered diamond materials since 1972, and these materials enjoy wide utility and acceptance for many industrial purposes, where they replace not only large single crystals but also often other hard sintered materials such as tungsten carbide and aluminum oxide.

Table 4. Machining performance of sintered diamond and CBN.

Material	Total number of pieces cut per tool
Machining silicon-aluminum SAE 332 (*33*)	
Compax diamond tool	412,000
Cemented carbide	2,400
Turning rubber filled with nickel and aluminum powder (*34*)	
Compax tool	6,000
Cemented carbide	140
Machining flame-sprayed alloys (Colmonoy No. 43) (*35*)	
CBN tool	3,000
Cemented carbide	9
Milling of type 380 aluminum line bore crankcase (*36*)	
Compax tool	12,000 to 14,000
Cemented carbide	3,000
Machining glass filled polypropylene (facing operation)* (*37*)	
Compax tool	7,000
Cemented carbide	400

*Cutting speed for Compax is approximately two times that of carbide.

Relation of Microstructure to Property

Although sintered superhard materials are relatively new, some understanding of the microstructural features and their relation to macroscopic properties has been developed. The stronger and more successful man-made sintered diamond compacts are brittle, two-phase materials—predominantly randomly oriented diamond ($\geq$ 90 percent by volume) with the remainder a metallic phase (Fig. 3). The former is continuous and the latter essentially continuous as determined by its etching behavior (*11*). The modulus of elasticity of the two-phase composite was found to be 890 gigapascals (*11*), which approaches that of single-crystal diamond.

When the metal phase was dissolved away, the modulus of the polycrystalline diamond, corrected for porosity, was 840 GPa (*11*). (The pores were uniformly distributed and were less than 1 μm in diameter.) This value is only about 5 percent lower than that for the original material containing the metallic phase. This result strongly suggests that there is diamond-diamond bonding in the composite and that the metallic phase is a minor contributor to the strength of the material acting only as a mechanical filler. Besides this indirect evidence, there is convincing direct support for diamond-diamond bonding from microscopic observations of grain boundaries.

Another prominent microstructural feature of some sintered diamond is deformation twinning, which is seen as groups of lines within grains (Fig. 3). When diamond is deformed under conditions that inhibit brittle fracture, it can deform by twinning on (111) planes. This has been observed in the naturally occurring polycrystalline aggregate called framesite (*12*) and has purposely been introduced into single crystals (*13*). Similar structures have been reported in single-crystal diamond indentors (*14*) and in anvils subjected to high pressures (*15*). The deformation twins within grains in Fig. 3 are visible because of relief polishing which emphasizes the greater wear resistance of the twinned region compared to the rest of the crystal. If the pressure-temperature conditions are adequate, this type of deformation structure can be expected when the diamond grains are large enough to sustain such deformation, and this microstructural feature may be significant in grains that are less than about 1 μm in size. In addition, under semihydrostatic conditions, as might exist with the presence of a softer phase, the deformation structure will probably not be generated everywhere in the compacted aggregate.

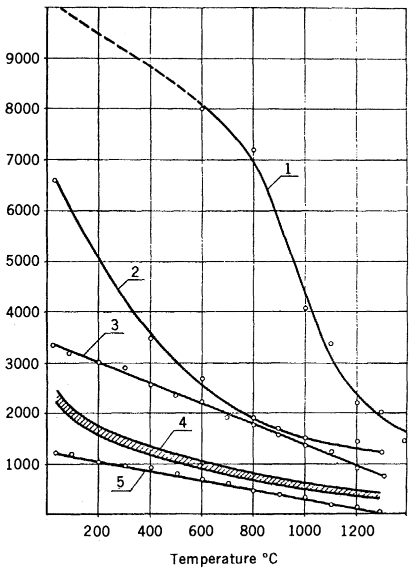


Fig. 4. Hot hardness of sintered superhard materials. Curve 1, diamond; curve 2, CBN; curve 3, silicon carbide; curve 4, different kinds of electrocorundum; curve 5, carbide VK-8 (92 percent tungsten carbide, 8 percent cobalt).

Mechanical Properties

A summary of the mechanical properties of sintered diamond with some comparisons with single-crystal diamond and with cemented tungsten carbide is shown in Table 3. These data, which are from several sources (*11*, *16-19*), are primarily for the same sintered material (*20-25*).

The effect of grain size on mechanical properties has been reported (*21*). In common with other brittle polycrystalline materials, an inverse relation exists between grain size and ultimate tensile strength.

A direct relation between remanent magnetism of sintered diamond and hardness in material sintered with cobalt has been reported (*25*). The intensity of the remanent magnetization is thought to be related to the residual graphite. As the amount of decomposed diamond (that is, as graphite in the pore regions) increases, the hardness and magnetic intensity decrease, unless the graphite reprecipitates as diamond from the cobalt-carbon liquid.

Dunn and Lee studied the fracture and fatigue of sintered diamond compacts with a cemented carbide substrate (*26*). The conclusions from their study are: (i) that the failure load falls from 1900 pounds at 5000 cycles to 1200 pounds at 200,000 cycles; (ii) fracture stress is reduced under cyclic loading; (iii) failure is by shear mode brittle fracture; (iv) there is no appreciable difference in results at 20°C and at 300°C; (v) the failure load corresponding to an infinite number of cycles is far above reported values of force for cutting rocks under similar geometric conditions.

Thermal Properties

Thermal degradation of some sintered diamond compacts is a well-documented phenomenon. Lee and Hibbs (*27*) and Dennis and Christopher (*28*) cited a 700°C temperature limit, and it is recommended that this temperature not be exceeded in brazing other sintered diamond compacts (*22*). Thermal cracking is related to the thermal stresses set up by the differential thermal expansion of diamond and the metallic second phase.

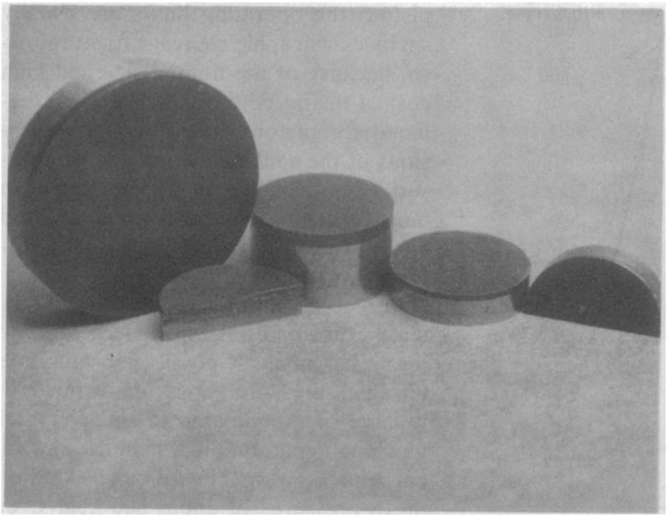
Hot hardness data on sintered superhard materials (*29*) are shown in Fig. 4. On the basis of comparative hot strength data, Hibbs and Wentorf (*9*) cited the advantages of sintered diamond and CBN tools over tungsten carbide-based materials with respect to machining hard alloys. Machining of these materials at temperatures of their yield strengths is clearly possible with sintered CBN. Cubic boron nitride has the distinct added advantage over diamond of greatly reduced reactivity with tool steels and superalloys (*30*).

There are claims of increased fracture toughness and improved strength of CBN ceramics if they contain some of the wurtzite form of boron nitride (*31*). This form is as hard as the cubic form but appears to be less stable than CBN with respect to conversion back to the soft graphite form. The toughening mechanism suggested is by the stress-induced phase transformation of the metastable wurtzite boron nitride to the graphitic form of boron nitride. The high internal stresses thus created control the extent of further transformation of the constrained metastable form. In grinding applications, the tensile stresses release the compressive stress around the potential graphitic boron nitride. This explanation may be valid, but it ignores grain size effects and the fact that the cleavage systems of the two types of hard boron nitride are quite different. It may also be that the longer life of the cutting tools containing wurtzitic boron nitride is simply related to the lubrication provided by the soft form of boron nitride as it forms from the less stable wurtzite form. There's room for additional study of this and other physical "metallurgy" phenomena in sintered superhard materials.

Sintered diamond and CBN have been proposed as heat sink materials because of the intrinsic high thermal conductivity of single crystals of these materials. Values as high as 9 watts per centimeter per degree Celsius have been reported for sintered CBN (*32*), but there is little evidence for application of these materials because of cost considerations.

Applications of Sintered Superhard Materials

In the short time since their introduction to technological applications, sintered superhard materials have successfully established places as both cutting tools and wire-drawing dies, and encouraging results have been achieved in some rock-drilling applications. Examples of a layer of sintered diamond on cemented carbide are shown in Fig. 5. Wire-drawing dies with sintered diamond cores are shown in Fig. 6. Single-crystal diamond is being replaced in many cutting and dressing operations in-



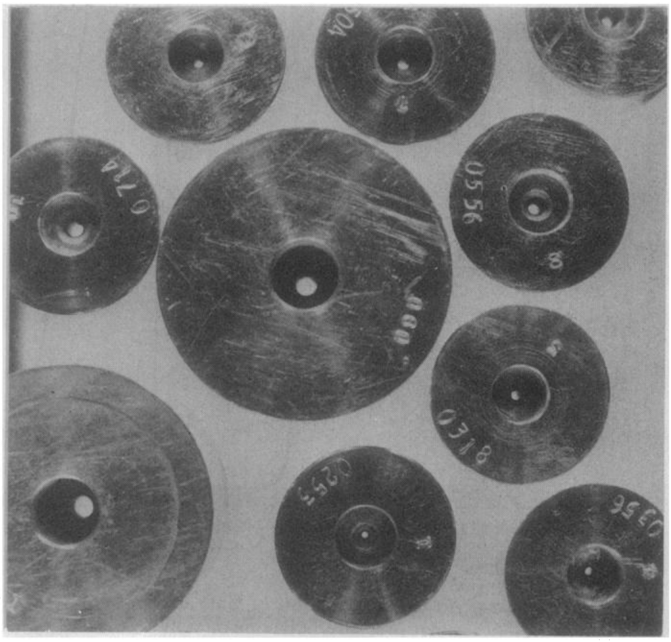
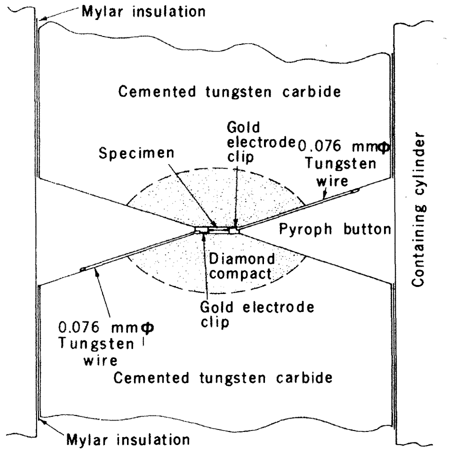


Fig. 5 (left). Sintered diamond layers on cemented tungsten carbide substrates. Fig. 6 (right). Sintered diamond wire-drawing dies.

volving ceramics, glass, concrete, plastics, fiberglass composites, presintered and sintered tungsten carbide, and nonferrous metals such as copper, or aluminum-silicon alloys that contain hard particles. Sintered diamond is practically as hard as single-crystal diamond and in addition is not plagued by catastrophic single-crystal cleavage and anisotropic wear. The availability of large-size pieces of different shapes is another asset. The most severe restriction for diamond is still chemical reactivity under cutting and grinding conditions with iron-, cobalt-, and nickel-based alloys. For these materials sintered CBN may be used. As a general rule, for finer finishes a finer grain size compact should be used in both cutting and wire-drawing operations. There is as yet no published data on turning optical finishes with sintered materials, but the prospects look attractive. Table 4 gives some typical examples of the performance of sintered diamond in cutting tools (*33-37*).

Perhaps the most spectacular comparison of single-crystal diamond with the sintered aggregate is as wire-drawing dies. Here the isotropic wear characteristic and the lack of extensive easy cleavage planes of the sintered material results in outstanding performance. Enough copper wire to circle the earth at least seven times has been drawn through one 0.203-cm die without change in roundness or dimension. With the recent availability of larger size die blanks, cemented carbide is also being replaced in this application. For a summary of the performance of these materials, see Table 5 (*38*).



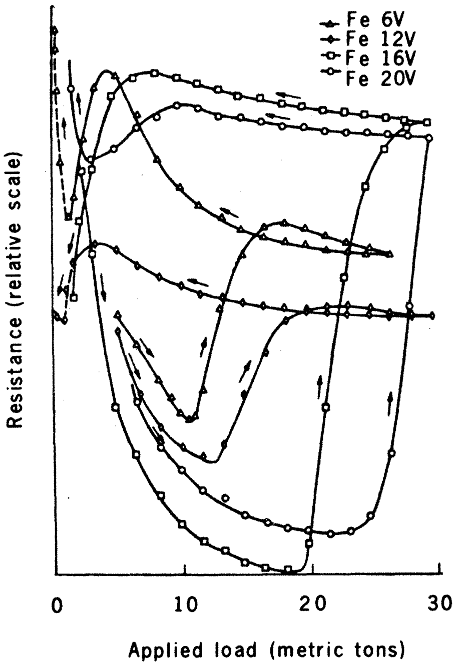


Fig. 7 (left). Section of the center part of the sintered diamond-tipped piston apparatus. Fig. 8 (right). Resistance plotted against apparatus loading for four Fe-V alloys. The up-jump of resistance indicates transformation from the α to the ϵ state, and gives a calibration of the cell pressure.

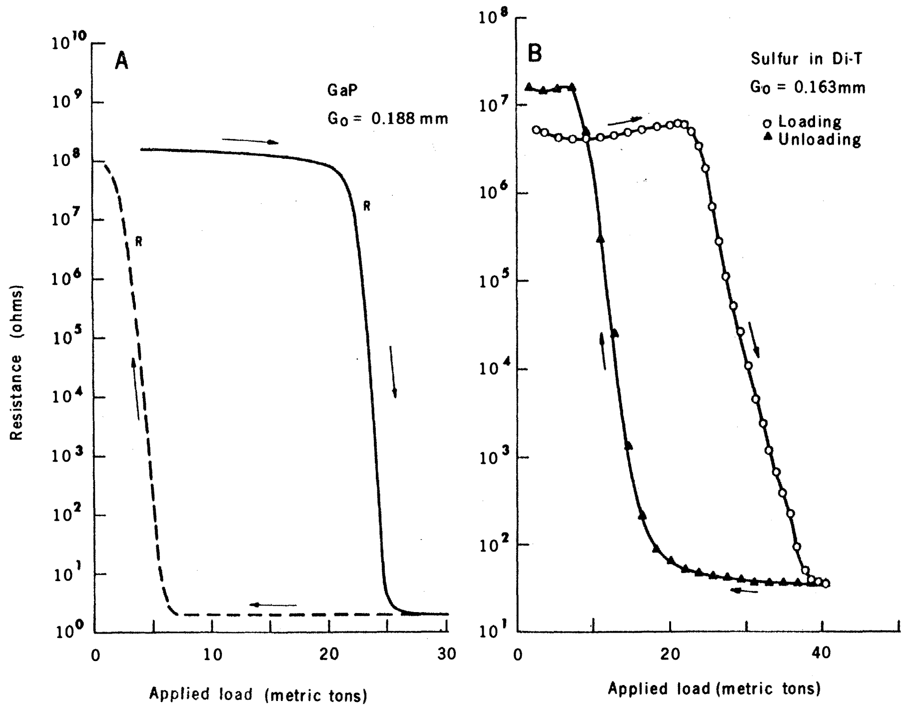


Fig. 9. (A) Insulator-to-metal transition in GaP at room temperature at about 220 kbar. (B) Resistance plotted against pressure behavior of sulfur.

Sintered Diamond for Ultrahigh-Pressure Apparatus

To generate the highest possible static pressures in specimens for scientific experiments the specimen material must be confined between the faces of pistons of very hard, strong material and compressed to smaller volume. In the past, the most useful ultrahigh-pressure apparatuses have included pistons made of cemented tungsten carbide (*39-41*) or of single-crystal diamond (*42*), and these materials are still being used extensively today. Even in the best designs, in respect to keeping shear stress as low as possible, it has been determined that some plastic flow begins in carbide apparatus at about 52 kbar (*43, 44*), and in single-crystal diamond at 700 to 1500 kbar (*45, 46*). Cemented tungsten carbide apparatus, properly used, can be made to operate up to 200 to 230 kbar, but loading beyond that results only in extensive plastic distortion without increase of cell pressure.

In the case of single-crystal diamond pistons the operating limits are usually set by catastrophic cleavage fracture. Also, because of the limited size and high cost of nearly perfect single-crystal diamond for pistons, the physical dimensions of the specimens that can be pressurized in this manner are very small. In most cases the specimens are monitored by optical, spectroscopic, or x-ray diffraction methods.

In recent years the availability of sintered diamond in special geometric forms has made it possible to fabricate ultrahigh-pressure apparatus of relatively large size (compared to single-crystal diamond apparatus) in which the electrical behavior of specimens can be studied up to pressures of about 600 kbar over the temperature range of about 400 to 2.6 K. We will illustrate this type of equipment and its use by an apparatus developed at the General Electric Research and Development Center in recent years (*47*). Other experimenters have developed versions that utilize the basic principles, but differ in detail.

Figure 7 shows the details of the center part of the apparatus, particularly the specimen and electrode arrangements in the high-pressure zone between the flat faces of the pistons. In this case the pistons were about 13.7 mm in diameter and the flat-pressure face about 1.25 mm in diameter. In most cases the specimen was in the form of a thin rectangular flake less than 0.025 mm thick and 0.60 mm long, resting in the plane of the equator sandwiched between two pyrophyllite stone disks, and with each end in contact with a tiny gold foil electrode. The gold electrodes in turn were connected by very thin tungsten wires to the metallic part of the piston because the sintered diamond is essentially an electric insulator. One electrode made contact with the top piston and the other with the bottom piston. The pistons themselves were electrically insulated from the cylinder wall by 0.025-mm Mylar film so that they could serve as part of the electrical monitoring circuit. The pyrophyllite stone gasket between the adjacent ends of the pistons served as a gasket and as pressure gradient medium, as well as an electric insulator.

For experimentation to very low temperatures this apparatus was fitted with a "squirrel-cage" clamping arrangement (*48*) so that it could be loaded at room temperature to a desired pressure in a hydraulic press, clamped at that loading, removed from the hydraulic press, and inserted in a cryogenic container and cooled to temperatures as low as 2.6 K with liquid helium. This arrangement was used particularly to study the behavior of "high-pressure metals" derived from insulator or semiconducting substances (such as silicon, tellurium, or selenium), especially in respect to electrical superconduction.

Some examples of very-high-pressure phenomena that have been observed with this type of apparatus are as follows. Some ordinary metals change to different metallic structures when subjected to high pressures. For example, iron and many of its alloys take the α (body-centered cubic) structure under ordinary conditions, but upon application of high pressure, transform to a more dense ϵ (hexagonal close-packed) structure with higher electrical resistivity. When iron is alloyed with cobalt or with vanadium, the pressure of the transition is increased by an amount roughly proportional to the fraction of the alloying element. Shock compression tests of such alloys at Los Alamos Scientific Laboratory by Loree *et al.* in 1966 (*49*) showed that the transition in Fe20V is at about 500 kbar.

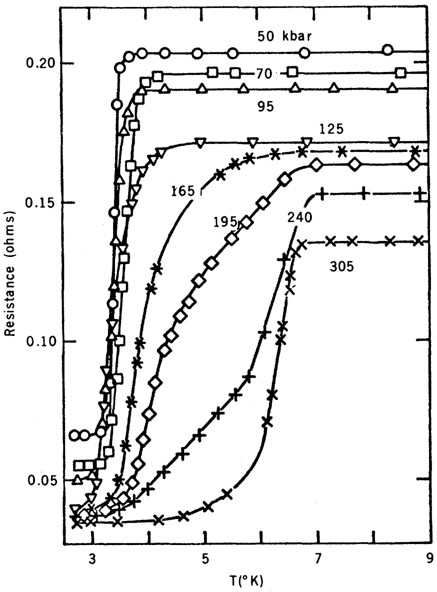


Fig. 10. Recent General Electric data on the pressure dependence of the T_c of tellurium, presented as $R(T)$ for various pressures. Note the large increase of T_c in the 110 to 190 kbar pressure region.

Figure 8 shows the α → ϵ transition as observed by a resistance-jump in a sintered diamond-tipped apparatus for four different Fe-V alloys. This is the first time these high-pressure transitions had been observed in a static high-pressure apparatus.

An example of the transformation of an insulator to a metal at room temperature is gallium phosphide, shown in Fig. 9A. In this experiment the resistance remained at about 10^8 ohms, the insulation resistance of the apparatus, up to a loading of about 22 tons, beyond which it dropped quite abruptly by eight orders of magnitude to about 2 ohms. This is the result of a change of structure from a covalent-bonded diamond cubic form to a tinlike metallic form. Upon unloading, the GaP reverts to an insulating, covalently bonded structure.

Figure 9B shows the electrical behavior of sulfur when compressed at room temperature to over 500 kbar pressure (*50*). As in the case of GaP the indicated resistance remained constant at the apparatus insulation value until, at about 25 tons of loading, the resistance of the sulfur specimen started decreasing below that value. Beyond a loading of about 37 tons the resistance leveled out at about 30 ohms with the specimen in a semimetallic state, having a positive temperature coefficient of resistance. Temperature cycling experiments at pressures in the range of 250 to 450 kbar showed that in this interval sulfur acts as a semiconductor with the band gap, or activation energy of conduction, decreasing rapidly with pressure. This band gap went to zero between 450 and 500 kbar, and for greater pressures the sulfur acted as a semimetal.

Some of the "high-pressure-induced metals" become superconducting at low temperatures. One of the most interesting examples is tellurium, which goes from a semiconductor form to a metallic form at about 40 kbar. Soviet studies (*51*) of the superconduction critical temperatures, T_c, of this material up to about 150 kbar indicate three different metallic forms. More extensive studies of the su-

Table 5. Compax diamond die blank performance (*38*). These results were obtained under production conditions in different wire manufacturer's plants and are believed to be representative of the performance that can be expected by others. However, variables such as rod quality, type of wire machinery, lubrication systems, die fabrication techniques, die practices, and drawing speed can alter performance.

Application	Wire sizes (mm)	Relative performance
Aluminum	0.64 to 2.6	3 times over natural diamond
Copper	1.84 to 4.6	200 times over carbide
Copper	0.40 to 2.05	10 times over natural diamond
Tin-plated copper	0.50 to 1.45	8 times over natural diamond
Nickel-200	0.33 to 1.45	10 times over natural diamond
Aluminum (5056)	3.05 to 4.76	150 times over carbide
Tungsten	0.18 to 0.62	4 times over natural diamond
Molybdenum	0.38 to 1.02	70 times over carbide
Molybdenum	0.18 to 1.02	5 times over natural diamond
Brass-plated steel (tire cord)	0.17 to 0.96	4 times over natural diamond
Brass-plated steel (tire cord)	0.17 to 0.96	20 times over carbide
Galvanized high carbon steel	0.17 to 1.05	36 times over carbide
Stainless steel (304 and 316)	0.41 to 1.6	6 times over natural diamond
Stainless steel (302)	0.36 to 0.71	3 times over natural diamond
Stainless steel (302)	1.1 to 1.6	10 times over carbide
Nickel-chrome-iron alloy (60-15-25)	0.23 to 0.91	5 times over natural diamond
Low carbon steel	1.55 to 3.2	40 times over carbide

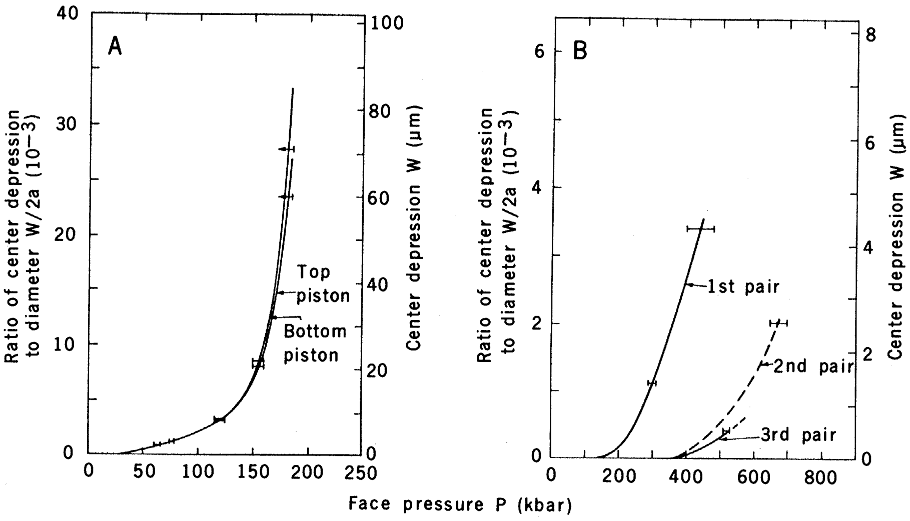


Fig. 11. Face center deformation plotted against face loading pressure for (A) 3 percent cobalt cemented carbide pistons, and (B) sintered diamond-tipped pistons. Note that the yield stress in (B) varies significantly with the quality of sintering of the diamond in the three different cases.

perconduction temperature of high-pressure tellurium metal, done recently with the sintered diamond-tipped apparatus to pressures over 300 kbar, indicate that there is an additional phase change in the 160- to 190-kbar pressure region, as shown in Fig. 10 (*52*). Note from the $R(T)$ curves shown that the resistance jump associated with the specimen going superconducting goes from about 3.5 K at 125 kbar to about 6.5 K at 195 kbar. Such a large change in T_c almost certainly means a significant change in the structure of the metallic phase.

Recently, quantitative studies of the permanent deformation of piston faces subjected to known pressures have yielded information on yield strength of the piston materials. The results for 3 percent cobalt-cemented tungsten carbide are shown in Fig. 11A (*44*). Taking the definition of the plastic yield stress as that at which there is 0.2 percent permanent deformation, it is found that the yield stress of this hard grade of carbide is about 50 ± 5 kbar. Figure 11A indicates that plastic yielding limits the face pressure of Bridgman-type or Drickamer-type opposed piston apparatus to about 200 kbar.

The same kind of tests applied to pairs of sintered diamond-tipped pistons gave the results shown in Fig. 11B. Such tests show the difference in the completeness and quality of the sintering of the diamond particles of these development pieces. The first pair showed a nominal yield strength of only a little over 200 kbar, while the third pair was much better at about 500 kbar. Thus a well sintered set of such pistons, properly used, is capable of a few experiments up to the 600 to 800 kbar range.

Somewhat higher pressures are attainable by going to much smaller pressure face diameters at the expense of reducing the specimen size by a large factor, and hence also at the expense of the possibility of getting good electrical measurements. This size effect on the maximum attainable pressures applies to single-crystal diamond apparatus as well as to the sintered diamond kind. To date the highest reliably reported static pressure experiments extend up to about 700 kbar with sintered diamond apparatus and electrical monitoring, and to 1700 kbar with gasketed opposed single-crystal pistons with optical and x-ray monitoring. Since diamond is the hardest and strongest known material, both theoretically and practically, the attainment of higher static pressures can result only from improved geometrical stress designs. The pressure gains by this means probably will be only incremental.

References and Notes

1. F. P. Bundy, H. M. Strong, R. H. Wentorf, Jr., in *Chemistry and Physics of Carbon*, P. L. Walker, Jr., and P. A. Thrower, Eds. (Dekker, New York, 1973), vol. 10, pp. 213-263; R. H. Wentorf, Jr., *Ber. Bunsenges. Phys. Chem.* **70**, 975 (1966); H. M. Strong and R. H. Wentorf, Jr., *Naturwissenschaften* **59**, 1 (1972).
2. R. H. Wentorf, Jr., *J. Chem. Phys.* **34**, 809 (1961); F. P. Bundy and R. H. Wentorf, Jr., *ibid.* **38**, 1144 (1963).
3. E. M. Wilkes and J. Wilkes, *Philos. Mag.* **4**, 158 (1958); R. H. Wentorf, Jr., *J. Appl. Phys.* **30**, 1765 (1959); F. P. Bundy, *Sci. Am.* **231**, 62 (August 1974).
4. F. L. Trueb and W. C. Butterman, *Am. Mineral.* **54**, 412 (1969).
5. F. P. Bundy, *J. Chem. Phys.* **38**, 631 (1963); *K. Ned. Akad. Wet.-Amsterdam Proc. Ser. B* **72** (No. 5), 302 (1969).
6. H. Katzman and W. F. Libby, *Science* **172**, 1132 (1971).
7. H. D. Stromberg and D. R. Stevens, *Ceram. Bull.* **49**, 1030 (1970); U.S. Patent 3,574,580, 13 April 1971.
8. H. T. Hall, *Science* **169**, 868 (1970).
9. L. E. Hibbs, Jr., and R. H. Wentorf, Jr., *High Temp.-High Pressures* **6**, 409 (1974).
10. R. H. Wentorf, Jr., and W. A. Rocco, U.S. Patents 3,745,623, 17 July 1973, and 3,767,371, 23 October 1973, assigned to General Electric Company.
11. P. Gigl, in *High Pressure Science and Technology, 6th AIRAPT Conference, July, 1977, Boulder, Colorado*, K. D. Timmerhaus and M. S. Barber, Eds. (Plenum, New York, 1979), vol. 1, pp. 914-922.
12. R. C. DeVries, *Mater. Res. Bull.* **8**, 733 (1973).
13. ______, *ibid.* **10**, 1193 (1975).
14. C. Phaal, *Philos. Mag.* **10**, 887 (1964).
15. H. K. Mao *et al.*, *Rev. Sci. Instrum.* **50** (No. 8), 1002 (1979).
16. F. P. Bundy and K. J. Dunn, in *High Pressure Science and Technology, 6th AIRAPT Conference, July 1977, Boulder, Colorado*, K. D. Timmerhaus and M. S. Barber, Eds. (Plenum, New York, 1979), vol. 1, pp. 931-939.
17. R. Chrenko and H. M. Strong, *Physical Properties of Diamond* (Rep. 75CRD089, General Electric Company, Schenectady, N.Y., 1975).
18. R. H. Gilmore, private communication.
19. J. F. Spanitz, paper presented at *Diamond, Partner in Productivity*, symposium of Industrial Diamond Association of America, November 1979.
20. Because of the inherent variability of the product from different processes and the difficulty of comparing results from different testing procedures, we have chosen essentially "in-house" data. For procedures and property data on other sintered products see (*21-25*).
21. D. C. Roberts, *Ind. Diam. Rev.* (July 1979), pp. 237-245; P. A. Bex and D. C. Roberts, *ibid.* (January 1979), pp. 1-7.
22. P. A. Bex, *ibid.* (August 1979), pp. 277-283.
23. M. D. Horton, in *High Pressure Science and Technology, 6th AIRAPT Conference, July 1977, Boulder, Colorado*, K. D. Timmerhaus and M. S. Barber, Eds. (Plenum, New York, 1979), vol. 1, pp. 923-930.
24. Y. Notsu, T. Nakojima, N. Kawai, *Mater. Res. Bull.* **12**, 1079 (1977).
25. ______, *ibid.* **14**, 1065 (1979).
26. K. J. Dunn and M. Lee, *J. Mater. Sci.* **14**, 882 (1979).
27. M. Lee and L. E. Hibbs, Jr., in *Wear of Materials—1979*, K. C. Ludema, W. A. Glaeser, S. K. Rhee, Eds. (American Society of Mechanical Engineers, New York, 1979), pp. 485-491.
28. M. D. Dennis and J. D. Christopher, Technical Paper MR75-986, 17th Annual Seminar of Society of Manufacturing Engineers, Kansas City, Mo., 17 May 1975.
29. T. N. Loladze and G. V. Bockuchava, in *Proceedings of the International Grinding Conference, 18-20 April*, M. C. Shaw, Ed. (Carnegie-Mellon Univ. Press, Pittsburgh, 1972).
30. A. Furst, *Am. Met. Mark. Metalwork. News Ed.* **87** (No. 249), (24 December 1979).
31. A. N. Pilyankevich and N. Claussen, *Mater. Res. Bull.* **13**, 413 (1978).
32. F. R. Corrigan, in *High Pressure Science and Technology, 6th AIRAPT Conference, July 1977, Boulder, Colorado*, K. D. Timmerhaus and M. S. Barber, Eds. (Plenum, New York, 1979), vol. 1, pp. 994-999.
33. F. W. Krumrei, Industrial Diamond Association of Japan, 30th Anniversary Meeting and Seminar, Tokyo, 17 May 1978.
34. Specialty Materials Department, General Electric Company, Worthington, Ohio 43085, Case History 107.
35. ______, Case History 202.
36. T. Ford and E. Krumrei, *Am. Mach.* (July 1976).
37. Specialty Materials Department, General Electric Company, Worthington, Ohio 43085, Case History 113.
38. Product data sheet SMD 85-324, General Electric Company, December 1979.
39. P. W. Bridgman, *J. Appl. Phys.* **12**, 461 (1941).
40. A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instrum.* **32**, 308 (1961).
41. F. P. Bundy, *J. Chem. Phys.* **38**, 631 (1963).
42. C. E. Weir *et al.*, *J. Res. Natl. Bur. Stand. Sect. A* **63**, 55 (1959).
43. K. J. Dunn, *J. Appl. Phys.* **48**, 1839 (1977).
44. ______ and F. P. Bundy, *ibid.* **49**, 5865 (1978).
45. A. L. Ruoff, in *High Pressure Science and Technology, 6th AIRAPT Conference, July 1977, Boulder, Colorado*, K. D. Timmerhaus and M. S. Barber, Eds. (Plenum, New York, 1979), vol. 2, p. 525.
46. H. K. Mao and P. M. Bell, *Science* **200**, 1145 (1978).
47. F. P. Bundy, *Rev. Sci. Instrum.* **46**, 1318 (1975).
48. ______ and K. J. Dunn, 7th AIRAPT International Conference on High Pressure, LeCreusot, France, August 1979, paper E IV 2.
49. T. R. Loree, C. M. Fowler, E. G. Zukas, F. S. Minskall, *J. Appl. Phys.* **37**, 1918 (1966).
50. K. J. Dunn and F. P. Bundy, *J. Chem. Phys.* **67**, 5048 (1977).
51. I. V. Berman, Zh. I. Binzarov, P. Kurkin, *Sov. Phys. Solid State* **14**, 2192 (1973).
52. F. P. Bundy and K. J. Dunn, in preparation.