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POLYCRYSTALLINE DIAMOND AND BORON NITRIDE CUTTING TOOLS.(U)
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(6) Polycrystalline Diamond and Boron Nitride Cutting Tools.

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Diamond Synthesis and the Bonding of Polycrystalline Diamond Masses.

The problems of diamond synthesis and the problems of bonding diamond are intimately related. ~~To the best of my knowledge,~~ no one has ever succeeded in achieving a decent polycrystalline diamond compact, bonded outside of the stability field of diamond. Further, all bonding not only must be in the stability field of diamond but must be in the presence of a molten carbon solvent such as invar, stainless steel or cobalt. Thus, the apparatus required to synthesize diamond is essentially the same as the apparatus required to bond diamond.

If precise measurements are to be made and the precision of results is to be obtained, it is necessary to know the position of graphite-diamond equilibrium boundaries. Results on the graphite-diamond equilibrium boundary was first published by F. P. Bundy in 1961. However, his work was done in "belt" apparatus where an unknown fraction of pressure was carried by the gasket and an equally unknown portion of the total load is carried on the sample. Further, the apparatus was calibrated against an assumed transition in barium at room temperature. The transition in barium was assumed to be at 60 kb and in addition no corrections were made on the effect of pressure on the electromotive force of thermocouples. Other various assumptions in this 1961 work was made. It was assumed, for instance, that the

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room temperature calibration of barium would indicate pressure at high temperature. Thus, thermal expansion or, conversely, contraction of the various parts, were set at zero. Additional data was published by Strong & Hanneman of the General Electric Company in 1967 and by Strong & Chrenko in 1971. Later data on position of the graphite diamond equilibrium boundary differed as much as 12% in the pressure term with the data of Bundy etc.

With all these uncertainties in the actual position of the graphite-diamond equilibrium boundary in mind, we elected to re-determine the position of the field. However, we first calibrated the barium transition and found it to be at 55 kb, not the 60 kb assumed by the General Electric Company and we spent a great deal of effort on measuring the effect of pressure on the emf of thermocouples. These results have been published: "Melting and polymorphism of barium at high pressures" Phys. Rev. Letters <u>10</u>, 387-389, 1963 and "The effect of pressure on the emf of chromel-alumel and platinum 10% rhodium thermocouples" J. Appl. Phys. <u>41</u>, 4552-4562, 1970.

With this preliminary data in hand we carefully re-examined the position of the graphite-diamond equilibrium boundary. Our technique was that of placing small samples which consisted of mixtures of diamond crystals, graphite and invar metal in a high pressure and high temperature environment and observing whether conversion was all to diamond or all to graphite. These results have been published in our paper entitled "The equilibrium boundary between graphite and diamond", J. Geophys. Research <u>81</u>, May 10, 1976. When we began our work on re-determining the position of the graphite-diamond equilibrium boundary we assumed that Bundy's 1961 data was probably in error by at least

10 - 15 kb. However, by some strange law of compensating errors our newly determined curve for the equilibrium boundary between graphite and diamond is essentially identical to the 1961 curve of Bundy. However, we consider this to be more fortuitous than anything else as calibration errors of at least 10 kb were made in the earlier Bundy work.

To the best of our knowledge, all diamonds made by the Russians, the Japanese, the De Beers Syndicate and The General Electric Co., are made in "belt" apparatus. The major feature of belt apparatus is that it consists of 45° tapered pistons compressing a sample which consists of a straight segment and a 45° tapered end. Obviously, an extrudible gasket is required in order to obtain pressures in this kind of apparatus. An extrudible gasket is normally made of pyrophyllite. A great number of problems are generated with the use of belt apparatus. If pressure is achieved and the extrudible gasket is greater than 0.1" in thickness, it will explosively blow out of position as it is retained only by friction. Once the pistons or the anvils have been advanced so that the gasket has been thinned to 0.05", no further pressure on the system is obtainable as larger and larger fractions of the total load are carried by the gasket and by the sides of the 45° anvil. Thus, stroke in such an apparatus is limited to about 0.1". Considering the fact that the density of diamond is circa 3.51 and the density of graphite is circa 2.25, it is clear that pressure will drop once diamond conversion begins owing to the shrinkage of the system. Thus, conical pistons in belt apparatus must be advanced to make up for this volume change on a conversion of graphite to diamond. However, only limited advance is possible and only a limited yield of diamond is possible with belt apparatus. In my many years as a consultant to the De Beers Syndicate, the largest yield we obtained per run was circa 17 carats in apparatus of circa 1" inside diameter.

The General Electric Co. patents are explicit on this point. They state that the obvious way of making diamonds is with piston-cylinder apparatus where advance of the piston throughout synthesis can be continued. They also state that these are impossible conditions to obtain inasmuch as the crushing strength of the pistons of tungsten carbide are less than the pressures required to make diamond.

With these thoughts in mind, we investigated the crushing strength of tungsten carbide. These were reported in our paper "The crushing strength of cemented tungsten carbide pistons" Rev. Sci. Instruments <u>38</u>, #11, 1590-1592, Nov. 1967. Some 56,000 atmospheres are required to synthesize diamond and we did indeed find that long carbide pistons which could fail in a 45^{0} shear plane crushed at pressures ranging from 48 to 55 kb. However, we made the relatively obvious discovery that length/diameter ratio of pistons greatly effected the crushing strength, i.e., if no 45^{0} shear plane for the crushing of tungsten carbide is available, and the pistons are crushed at a similar angle, pressures of as high as 70 kb could be achieved with cemented tungsten carbide pistons. Thus, we undertook the development of an apparatus using cemented carbide pistons of piston-cylinder design, well knowing that the aspect ratio of the pistons must be kept circa 2/1, i.e., the exposed length of a piston would only be circa 1/2 the diameter of pistons.

With this development in hand we undertook the development of proper tungsten carbide supported pressure vessels that would run routinely and economically up to 60 kb. Vast amount of effort has been devoted to this problem and we have ultimately succeeded constructing apparatus with very long life which works routinely at pressures of 60 kb and temperatures of 1350°C. The heart of our apparatus consists of a tungsten carbide pressure vessel with the outside diameter approximately four times the inside diameter, made of tungsten carbide bonded with 15% cobalt. The grade of the tungsten carbide is crucial. A fairly coarsely crystalline grade used by the mining industry for jack hammer bits appears to serve the best as some ductility is required in the pressure vessel. The tungsten carbide vessel is supported by a series of shrunk on rings made of 350 series high vanadium maraging steel, heat treated to Rockwell 48. The merits of the maraging steel is that it shows exceeding ductility as well as high hardness. The steel rings are machined and ground with a 1° taper and an interference of approximately 1%. A matching tapered shim is forced around the tungsten carbide core of the pressure vessel assemblage. All surfaces are polished and well lubricated with molybdenum disulfide or gold plated and pushed together. The resulting support on the sides of the core amount to approximately 17,000 kb. At this support, the bore diameter of the tungsten carbide pressure vessel shrinks approximately 1% as the pressure vessel is assembled. The pressure vessel must at all times be kept dry. Maraging steel's stress corrodes under the action of distilled water at an exceedingly rapid rate and stress corrosion deterioration of the maraging steel binding rings can lead to violent explosions of the apparatus.

Special attention must be made to cooling of the carbide core. During the course of a typical run using 1/8" insulation around our reaction zone, the skin temperature of your tungsten carbide can reach as much as 200°C. As these high temperatures are reached rapid deterioration of the tungsten carbide sets in. Thus, rather elaborate cooling techniques are undertaken. The shim supporting the tungsten carbide has 16 small holes axially drilled through it. The holes are manifolded together and during the course of a run water flows through these holes providing exceedingly good cooling of the carbide core. In addition, the main pressure vessel is jacketed in aluminum and water is circulated through the aluminum jacket. The cooling of the core is absolutely essential as cores properly cooled may last for several hundreds of runs; whereas an uncooled core may deteriorate in as few as three or four runs.

We have had excellent success with this type of design. Our first apparatus had a working volume of approximately 1/2" x 2". Of this volume approximately 1/4" was taken up by 1/8" thick insulating bushings around the reacting carbide invar mix so that our volume at pressures and temperatures actually amounted to approximately 1.5" x 1/4". In this small volume we were able to routinely achieve synthesis approximately 10 carats of diamonds per run. With this design behind us we scaled our design to 3/4" x 4". Inasmuch as the bushing remained the same thickness in all designs, our 3/4" x 4" apparatus synthesized approximately 40 carats of diamonds per run. We have now designed a new piece of apparatus in which the reacting volume is 1.5" x10". This design should synthesize between 500-600 carats per run. To our surprise, we anticipated a deterioration in apparatus life as we increased the size of the apparatus. However, we have noted no deterioration and the apparatus life in our 1" x 7" stage is as good or better than our initial apparatus where the carbide volume was 1/2" x 2".

Insulating bushings that separate the reacting mixture of carbon + invar from the tungsten carbide pressure vessel is kept as cool as possible. Therefore an insulating mix with the lowest possible thermal conductivity at high pressures is required. We have investigated a large number of different insulating mixes.

Various insulating mixes have been tested. Among these listed are fired pyrophyllite, pessed olivine crystals (MgO_2SiO_2) aluminum oxide, titanium dioxide, zirconium dioxide, etc. etc. However, of all the various materials we have tested for insulating properties, we have found that by far the best is potassium bromide salt stabilized with approximately 20% obsidian glass. With this particular insulating bushing the power requirement to maintain temperature at pressure is roughly one half of the power requirement for pyrophyllite or any other well advertized high temperature insulating materials. Our discovery that potassium bromide serves beautifully as insulating material was an Edisonian one. We pressed pellets of some 100 different salts and made rough measurements of their thermal conductivity. We found, for instance, that potassium bromide has approximately 1/2 of thermal conductivity of sodium chloride. Unfortunately, our theoretical understanding of why KBr has low thermal conductivity is essentially nil. We feel sure that better insulating material exist. This is the best we have found to date.

A crucial part of our apparatus is that of a 50-50 mixture of lead and zinc which serves as a driver just ahead of the piston. Inasmuch as we heat our runs by a high amperage, low voltage current, it is clear that if our piston pushes against our KBr insulating bushing and deforms the bushing it will not deform in any uniform manner and constrictions and expansions take place through the length of the run giving rise to highly non uniform temperature distributions. However, if a mixture of lead and zinc is placed in front of the piston, it extrudes as a driver pushing the carbon-invar mix forward without deforming the bushing and enable us to maintain uniform temperatures during the length of the run. The action of a lead-zinc driver is absolutely essential to the synthesis of diamonds in our piston-cylinder apparatus.

A vast number of variables affect the quality of the synthesized diamonds. It is essential to work inside the diamond stability field and at temperatures above the melting point of carbon saturated diamond solvent. These requirements dictate pressures of the order of 55-56 kb and temperatures of the order of 1350^{o}C. We have examined the inclusions in diamond synthesized by the De Beers group and the General Electric group and find that their preferred synthesis solvent is invar, a metal made up of approximately 40% nickel and 60% iron. Therefore, our first experiments were made with a mixture of invar powders and graphite powders. We have learned from such a mixture that a number of special precautions must be made as invar plus carbon makes only weak stones filled with inclusions and filled with bubbles. High purity, low surface energy graphite is required and even with the highest purity graphite the diamonds produced are not of optical quality. Milky veils are common in these stones. After a good deal of effort we have identified that the origin of these milky veils as owing to minute carbon dioxide bubbles included in the diamond. Obviously, these CO_2 bubbles within the diamonds do not strengthen the stones nor do they strengthen a polycrystalline mass made of synthetic diamond. Therefore, we have devoted a great deal of time to the problem of the origin and the problem of eliminating these CO_2 bubbles. Certain aspects of black magic appear which we do not understand at this time. For instance, if a mixture of invar carbon and an appropriate number of minute diamond seed crystals is placed in a 304 series stainless steel tube, which is placed inside our potassium bromide-obsidian bushing, without exception we find that the very best stones grow in 304 series stainless can wall. However, all attempts to grow diamonds out of 304 series stainless have failed. Mixtures of stainless steel and invar in the center of a growing run still yields stones filled with milky bubbles; whereas, the stones grown in the margin of the run inside the stainless steel can wall are essentially optical and bubble free. Our only interpretation to date is that this may be the effect of the extreme temperature gradients that exist near the margin of the run. We have not yet proved this to be the case nor have we been able to develop chemistry that would explain the very high quality of the stones grown in the can wall.

The problem of scavenging the oxygen from a run should be a very simple one. However, it proves to be difficult. Most oxygen scavengers are also nitrogen scavengers and if we add aluminum to the run we produce only poor quality diamonds as apparently aluminum also scavengers the nitrogen. Such stones are clear white and obviously not nitrogen doped but apparently also the role of the nitrogen surface absorbed on the carbon is crucial. I suspect that the surface tension of the metal to graphite is sharply different when nitrogen is present and surface absorbed on the graphite. If nitrogen is scavenged, the metals seem to disperse uniformly through the runs and small blobs of metal in which our diamonds are growing can not be maintained if the nitrogen is scavenged. We have looked at a large number of differnt scavengers and find that all scavengers which will consume oxygen and which also consume nitrogen give us very poor results.

We have developed two scavengers, however, that seem to be oxygen getters but are not nitrogen getters with rather spectacular luck. Among the two best seem to be calcium carbide which forms a stable calcium oxide and frees carbon and potassium ferrocyanide which also seems to be able to scavenge oxygen and not scavenge the nitrogen. Our current practice thus is to add about 1/10 of a gram of calcium carbide or potassium ferrocyanide to a 100 grams of mix. The quality of our diamonds have sharply improved. A large fraction of them are optical and practically one of them show magnetic inclusion.

Much of the last year's effort has been spent in solving these problems of the growth of optical quality perfectly shaped diamond single crystals, either cubes or cubo-octahedron.

We have examined some 125 different chemistries for diamond synthesis and made some 600 batches of diamonds during the last year. We have found quite a few different chemistries that grow diamonds sharply more optically perfect than those currently marketed by General Electric, the Japanese, or the De Beers Syndicate. Among the mixes which seem to work well are those that involve invar to which 0.01 aluminum have been added. This seems to be just about the right amount of aluminum to scavenge the oxygen and not scavenge the nitrogen. Systems containing ferrocyanide and mixes containing calcium carbide also grow superior stones. In addition, we have found that mixes containing 12% metallic silicon gives results sharply better than straight invar mixes. Mixes made of 50% 304 series stainless powder added to 50% invar powder appear to make stones of higher quality than those made of straight invar. Again, we gauge the quality by the percent of stones that have metallic inclusions and the percent of stones that have white veils of carbon dioxide bubbles.

The quality of the carbon used is also of extreme importance. We early noted that only high purity carbon could be successfully used and this should be coarsely crystalline to present the minimum possible area for surface absorption of nitrogen and oxygen. There is a great deal about carbon chemistry that remains black magic to us. Spontaneous nucleation of diamonds takes place in some grades of carbon and in other grades growth takes place only on introduced sub micron seeds. We note that if the carbon used is exceedingly fine grained and has a very high surface energy, the graphite-diamond equilibrium boundary seems to be a bit displaced toward the low side, probably owing to surface energy of the very fine carbon. We also note that the resistance of our runs steadily drops as a function of time owing to the recrystallization of carbon even though we start with fairly coarse graphitized carbon. Almost certainly we have not investigated a sufficiently large spectrum of carbons to have identified the best one for the growth of diamond.

THE PREPARATION OF BONDED POLYCRYSTALLINE DIAMOND

We report here some 48 experiments on the bonding together of small diamonds to make a large polycrystalline mass. The cutting efficiency of each of our stones has been tested and is reported. Our results on our best formulation are almost within the data scatter of the results on a single crystal of diamond.

The diamond crystals used for bonding in these experiments were synthesized at this laboratory from a mixture of graphite and invar metal powders at 56-58 kb and at about 1350^{o}C. Synthesized diamond crystals range in size between 20 mesh and 80 mesh. Under a binocular microscope, synthetic crystals are transparent, yellow in color, and some crystals have opaque inclusions of invar metal.

All crystals were shaken in a paint shaker with 1/4" stainless steel balls for 4 hours. Only 30% of the crystal remained over 60 mesh size. Presumably the weaker crystals were broken up. This coarse fraction of -40 ∿ + 60 mesh was presumed to be the strongest fraction of the synthesized diamond crystals and only this fraction, after magnetic sorting by a strong hand magnet, was used as the starting material for bonding.

A fraction of the -40 ∿ + 60 mesh diamond crystals was then crushed by the use of a Spex mixer mill for ∿ 20 minutes. After 20 minutes all crystals had been crushed to under 325 mesh size. The crushed diamond powder was cleaned in hot aqua-regio, washed, filtered on a paper, and dried.

The diamond powder was mixed with additives in the desired proportions. The mixture was loaded into a metal capsule, nickel was used in most runs, and a thin titanium disc was placed at the top as a nitrogen and oxygen getter. The capsule with a lid lightly pressed in was placed in a vacuum oven kept at 200°C for longer than 30 minutes. This process was not taken for runs prior to Run 25. Then, the oven was filled with nitrogen gas, the capsule was quickly removed from the oven and put in a plastic glove bag filled with nitrogen.

The capsule was kept under vacuum again at room temperature for about 1 minute, then nitrogen gas was flushed into the glove bag. The lid of the capsule was hammered to a tight fit with the capsule in the nitrogen atmosphere. The capsule was considered to be mechanically sealed. It was hoped by doing this that most oxygen was stripped off and only nitrogen was present inside the capsule.

As soon as the capsule was sealed, a furnace cell was assembled as shown in Fig. 1 and the cell was placed in the vacuum oven at 200°C for longer than 1 hour. Before starting a high-pressure run, nitrogen gas was flushed into the vacuum oven and the cell was quickly set in the high-pressure vessel. Prior to Run 25, the cell was dried at 200°C in room atmosphere.

The pressures stated in this report are the nominal pressures on the piston calculated from the applied oil pressure. The temperature was measured with W3Re-W25Re thermocouples. No correction for the pressure effect on the emf of thermocouple were made. Runs were held at the desired temperatures and pressures for circa one hour, then the temperature was slowly decreased.

After a run the bottom end of the capsule was machined off to expose a part of the sample. Then, the capsule was immersed in hot aqua-regia for 1 $\sim$ 4 minutes to dissolve metal film on the surface of the bonded diamond.

The exposed surface of diamond compact was examined first under a 40 X binocular microscope to see the structure, and by X-ray diffraction to determine the crystalline phases. Then, the diamond compact was tested for hardness.

TESTING PROCEDURE

We elected to test the quality of our diamond bond by determining the cutting efficiency of the stone when pressed against a silicon carbide wheel. Thus we purchased 10 silicon carbide wheels from the Simonds company of Philadelphia. The wheels were approximately 7" in outer diameter and 1" in thickness, the designation was GC120-I-V9 grain size was fine, the grade was soft, the bond type was vitrified. We purchased a 1 carat perfect octahedron of natural diamond and calibrated our wheels by machining away part of each wheel with our natural diamond and recording the ratio of the weight losses of the silicon carbide to weight loss of the diamond. After a series of cuts on all 10 of the wheels the total wheel weight loss was 350.2 grams and the total weight loss of our diamond single crystal was .00095 grams with little variation among the wheels indicating they were all essentially uniform hardness. The diamond tool was cleaned prior to each weighing by immersing in a beaker of trichloroethelyne and then subjecting it to ultrasonic sound waves for 5 minutes. It was then air dried and weighed. The total wheel weight loss divided by the total diamond tool weight loss was circa 370,000:1 which gives us the cutting efficiency of this particular single crystal on these particular wheels.

We also determined the cutting efficiency of a number of other products. Among our products tested was the polycrystalline mass of diamond used as a machine tool in Russia and made in Vereschagin's high pressure institute. Its cutting efficiency was 47,000:1, a little more than 10% of that of a natural stone. We also examined the cutting efficiency of a fragment of Tracy Hall's recently produced megadiamond which was supplied to us. This tool wore away so fast, the tool was gone before we had achieved any detectable weight loss of the silicon carbide wheel, therefore, we set its cutting efficiency under these test conditions at zero. We have also examined the cutting efficiency of two polycrystalline masses of bonded diamonds supplied us by Kennametal Corp. One of these showed a cutting efficiency of circa 2,000:1 and the other showed a cutting efficiency of 580:1.

All cuts were made in essentially identical fashion. Our polycrystalline masses as well as a single crystal of diamond were jigged in a standard wheel dressing apparatus. Five to seven passes were made, each cut was approximately .010 to .015" deep.

It is perfectly certain that the results we report here both for the Russian polycrystalline mass as well as our own polycrystalline mass of a diamond are not optimal. Diamond has circa 3-4 times the thermal conductivity of copper and it is very difficult to get the point of a large single crystal of diamond hot as heat is conducted away into the holder. However, in the case of polycrystalline masses, dozens of metal film between bonded particle of the diamond greatly reduces the thermal conductivity of the mass. These tools were observed to become visibly red hot during the course of cutting. This assuredly would promote the plucking out of fine diamond particles and perhaps even graphitization of fine diamond. We did not attempt to water cool any of the tool as this would have interfered with determining the weight loss of our silicon carbide wheel. Thus, all the cutting efficiencies of our polycrystalline stones reported in this paper can be presumed to be minimal. With proper water cooling etc., higher efficiencies should be obtainable. We do, however, believe that our tests are relative as all tests were made in the same fashion. Further, in some of our tests we had not completely removed all of the metal capsules surrounding the polycrystalline diamond mass and some metal wear is included in weight loss ratio. Thus, we conclude that with more carefully controlled preparation and testing techniques our reported wear ratio would increase and that our stones are actually better than we report here.

RESULTS

1. Bonding by Elements which form Carbide Compounds Reacting with Diamond

Such elements as B, Si, Ti, W, Zr, V, Ta and Hf react with diamond to form hard carbide compounds. When they react with diamond crystals, they may bond with diamond crystals and form hard polycrystalline diamond mass. We have not studied extensively the bonding properties of these elements. The results shown in Table 1 show that these elements are not very promising binders.

TABLE 1

Run No.	P(Kb)	T(^{o}C)	Duration (min)	Wearing Ratio
A. 90% diamond (-325 mesh) + 10% silicon				
14	48	1200	60	770
17	53	1300	60	980, 540, 975
20	56	1300	60	not tested
B. 60% diamond + 40% W_2C + 10% Cr				
15	48	1200	60	0.1
C. 90% diamond + 10% boron				
16	53	1300	60	not tested

Runs prior to #16 were made in stainless steel capsules, and runs after #17 in nickel capsules. Untested samples were weakly bonded as determined by microscopic examination.

2. Bonding by Interstitital Growth of Diamond

A mixture of graphite (ultra-pure, -325 mesh flakes) and invar metal powder was mixed with diamond in such a proportion that the mixture filled interstices of diamond crystals. Under a diamond-growth condition of pressure and temperature, graphite transformed to diamond on the diamond crystals and the diamond crystals interlocked with each other to form strong polycrystalline stone. This method turned out to be very promising. Results of runs are shown in Table 2.

TABLE 2

Run No.	Starting Material		P(Kb)	T(^{o}C)	t (min)	Wearing ratio	Remarks
18	Di (40-60 mesh) Graphite Invar	10.0 2.1 0.9	55 →56	1340 1340	30 60	46,000 28,000	- -
23	"		56	1400	60	65,000	-
27	Di (100-200 mesh) Graphite Invar	10.0 2.4 0.6	56	1400	60	-	Ta capsule Graphite remained
21	Di (200-325 mesh) Graphite Invar	10.0 2.1 0.9	56	1340	60	145,000 59,000	-
24	Di (200-325 mesh) Graphite	10.0 2.0	56 →56	1340 1400	30 30	32,000	Graphite remained in the center
25	Di (200-325 mesh) Titanium Graphite	10.0 1.0 2.0	56	1400	90	-	Graphite remained
31	Di (-325 mesh) Graphite Invar	10.0 2.1 0.9	58	1400	60	138,000	tr. graphite
36	"		58	1450	60	-	Ta capsule Graphite remained
33	"		56	1400	60	-	Fired pyrophyllite capsule. Graphite remained.
35	Di (-32 [illegible] Graphite	10.0 3.0	58	1400	60	154,000	Co disc on the top
38	"		58	1400	90	42,000	Co disc on the top

TABLE 2 (continued)

Run No.	Starting Material		P(Kb)	T(^{o}C)	t(min)	Wearing ratio	Remarks
22	Di (ultrafine) Graphite Invar	10.0 2.1 0.9	56	1340	60	-	Graphite remained
32	Di (ultrafine) Graphite Invar	10.0 1.4 0.6	56	1400	60	40,000	tr. graphite
39	Di (ultrafine) Di (1μ) Graphite	10.0 1.0 1.0	58	1400	65	-	Graphite remained
34	Diamond (1μ) Graphite Invar	10.0 2.1 0.9	57	1400	60	-	Graphite remained

Runs were made in Ni-capsules otherwise mentioned.

Untested samples are weakly bonded.

Ultrafine diamond powders were made by 20-minute grinding in a Spex mixer mill.

Grains are much finer than 325 mesh size.

Effect of Temperature - Because of possibe large errors (by a factor of 2 or 3) in the results of hardness testing, the effect of temperature on the hardness cannot be clearly demonstrated (Table 3).

Table 3

Effect of Temperature

Run No	18	23
P(Kb)	56	56
T(^{o}C)	1340	1400
Wearing ratio	46,000 28,000	65,000

The eutectic temperature between diamond and nickel (used for capsules) at 56 kb is about 1390^{o}C. The polycrystalline diamond of Run 23 made at a temperature above the eutectic temperature is never weaker than the stone of Run 18 made at a temperature below the eutectic temperature. It is reasonable to expect that stronger bonding is favored by higher temperatures.

Effect of Grain Size - It appears that moderately fine powders (-200 or -325 mesh) of diamond bond most strongly. When the grain size of diamond is too fine, complete conversion of interstitial graphite to diamond was not attained (Table 4)

Table 4

Effect of Grain Size

Run No.	23	21	31	22	34
Grain Size	40 ∿ 60 mesh	-200	-325	ultrafine	1μ
Wearing Ratio	65,000	145,000 59,000	138,000	-	-

All runs in Table 4 were made in Ni-capsules at 56 kb, 1400°C for 60 minutes. Run 31 contains trace amount of graphite and Runs 22 and 34 contain significant amount of graphite. Samples of Runs 22 and 34 are weakly bonded. I suspect that oxygen attached on the surface of very fine diamond powder suppresses the graphite-to-diamond transition, or that the diffusion of carbon from graphite to diamond through molten metal is slow or prohibited in fine diamond aggregates because their interstices are small.

Total conversion of graphite to diamond may be attained at higher pressures and temperatures, but such conditions may be practically unfavorable. Nearly total conversion was attained when the amount of graphite was reduced (Run 32). The wearing ratio (40,000) was not so high as the stones made from coarser diamond powders (Runs 21 and 31). It was therefore concluded that ultrafine diamond powders are not favorable for bonding.

Effect of the Amount of Metal - Because Ni-capsule eutectically melts and the molten metal diffuses into interstices of diamond crystals, the amount of metal is not well controlled. It is expected that the amount of metal (mainly nickel and iron) in a bonded diamond compact is slightly higher than that added in the starting material. The stone of Run 24 with no metal in the starting mixture was analysed under the electron microprobe analyser and found to contain about 2% (± 50%)nickel.

Because of poor reproducibility of the testing results, we cannot safely deduce any conclusions from the present results shown in Tables 5 and 6. I suspect that reducing the amount of metal below 7% level does not bring fruitful results for the cutting ability of stones.

Table 5. Effect of the amount of metal

Run No.	31	35	38
Starting Material			
Di (-325 mesh)	10.0	10.0	10.0
Graphite	2.1	3.0	3.0
Invar	0.9	0.0	0.0
Wearing ratio	138,000	154,000	42,000

All runs at 58 kb and 1400°C

Table 6. Effect of the amount of metal

Run No.	21	24
Starting Material		
Di (200-325 mesh)	10.0	10.0
Graphite	2.1	2.0
Invar	0.9	0.0
Wearing ratio	145,000	32,000
	59,000	

Run 21 at 56 kb, 1340°C for 60 min., and Run 24 at 56 kb, 1340°C for 30 min., then at 58 kb, 1400°C for 30 min.

Effect of Capsule Material - Three kinds of capsules were used (Table 7)

Table 7 Effect of Capsule Material

Run No.	31	36	33
Capsule	Ni	Ta	Fire pyrophyllite
Wearing ratio	138,000	-	-

The starting material of all runs in Table 7 is the same (see Table 2). In Run 31, a trace of graphite remained but the sample is strongly bonded. In Run 35, a significant amount of graphite remained. In Run 33, more amount of graphite remained. Both stones of 36 and 33 are weakly bonded.

Both capsules of Runs 31 and 36 were sealed in N_2-atmosphere. Nickel apparently diffused from the capsule into the diamond-graphite mixture, mixed with invar and helped the catalytic effect. The amount of invar in Run 36 in a tantalum capsule seems not to be enough to achieve total conversion of graphite to diamond.

The pyrophyllite capsule of Run 33 is not sealed. It is not certain if possible presence of H_2O in fired pyrophyllite and oxygen in the unsealed capsule prevented total conversion of graphite in Run 33. The amount of graphite reamined in Run 33 is significantly larger than that in Run 36. Therefore, I feel that unsealed pyrophyllite capsules are not favorable for bonding diamond crystals.

3. Diamond-diamond bonding

When extremely fine diamond powders are heated in a Ni-capsule with titanium or aluminum as a getter of nitrogen under diamond-stable conditions, they sinter to a fairly hard polycrystalline mass. The sintered fine-grain (1μ) diamond is not superior (the wearing ratio

= 10,000 $\sim$ 50,000) to the best stones of polycrystalline diamond bonded by interstitial growth of diamond from graphite (their wearing ratio = 150,000). However, it is much harder than any carbide compounds (the wearing ratio of WC < 1). Therefore, if strong, coarse diamond crystals are bonded with each other by the sinterable ultrafine diamond crystals, the bonded stone is expected to be quite strong. This method seems to be one of the best methods to bond diamond crystals (Table 8).

Table 8

Run No.	Starting Material		P(Kb)	T(^{o}C)	t(min)	Wearing Ratio	Remarks
28	Diamond (1μ)		56	1400	60	17,000	Ni capsule
26	Diamond (1μ)		56	1400	70	32,000 13,000	Co disc on top Ta capsule
40	Diamond (1μ)		58	1450	60	46,000	Co powder on the top Ta capsule
37	Di (40-60 mesh) Di (1μ)	2 1	56	1400	75	254,000 281,000	Ni capsule
41	Di (200-325 mesh) Di (1μ)	10 3	58	1400	60	not yet tested	Ni capsule
47	Di (20-40 mesh)[1] Di (1μ)	2 1	58	1400	60	227,000 327,000	Ni capsule
48	Di (40-60 mesh)[2] Di (3-5μ)	2 1	58	1400	70	370,000	Ni capsule

[1] Only gem quality diamond crystals were hand-picked and used for the starting material

[2] Smoky grains, irregular shape grains and non-diamond grans were hand separated out from the starting material

1) The effect of capsule material is not clear. The wearing ratios for Runs 28 and 26 are not significantly different.

2) The effect of temperature is significant. A stone made at 1450°C (Run 40) seems to be harder than a stone made at 1400°C (Run 26).

3) Polycrystalline diamond of 3-5μ size (Run 46) is definitely stronger than that of 1μ size (Run 26).

4) Coarse grain diamond crystals can be bonded by ultra-fine diamond matrix. Under the present experimental conditions, the coarse grain diamond crystals grow in place of interstitial ultra-fine diamond. Under a binocular microscope, stones show a mosaic texture of coarse grain diamond, though a small amount of ultra-fine diamond remains interstitially.

5) Mosaic textured polycrystalline diamond made from a mixture of coarse grain diamond and ultra-fine diamond is nearly comparable in hardness to ~~with~~ a single crystal of natural diamond. The strength seems to be dependent on the quality of coarse grain diamond used in the starting material. Diamond crystals of 200-325 mesh are all irregular in shape and are fragments of crushed diamond. A stone made of such diamond (Run 41) is rather weak. Diamond crystals of 40-60 mesh are mostly idiomorphic (cube-octahedron) crystals. Crystals used for Run 37 contain a small amount of impurities and irregular-shape diamond. Impurities and irregular-shaped diamond are discarded for the starting material of Run 48. This treatment apparently improved the hardness of stones (from 280,000 to 370,000).

6) The stone of Run 47 was recovered broken horizontally. It seems that 20-40 mesh size crystals are too coarse to make a homogeneous stone of the present size.

7) It is very difficult to homogeneously mix coarse grains with ultra-fine grains. To obtain a homogeneous mixture and compact packing of coarse grains, we shook the mixture added with acetone in an ultrasonic cleaner and let acetone dry during shaking. We still found heterogeneous distribution of coarse crystals in ultra-fine matrix. This heterogenuity is a main cause of the poor reproducibility of testing results for the stone of Run 47.

8) There must be an optimum grain size to obtain the hardest stone. Diamond crystals finer than 60 mesh are mostly fractured fragments and non-idiomorphic. If we can obtain idiomorphic gem-quality diamond of sizes finer than 100 mesh, we can probably synthesize stronger stones with good reproducibility, because mixing is easier. The effect of grain size should be studied in the future.

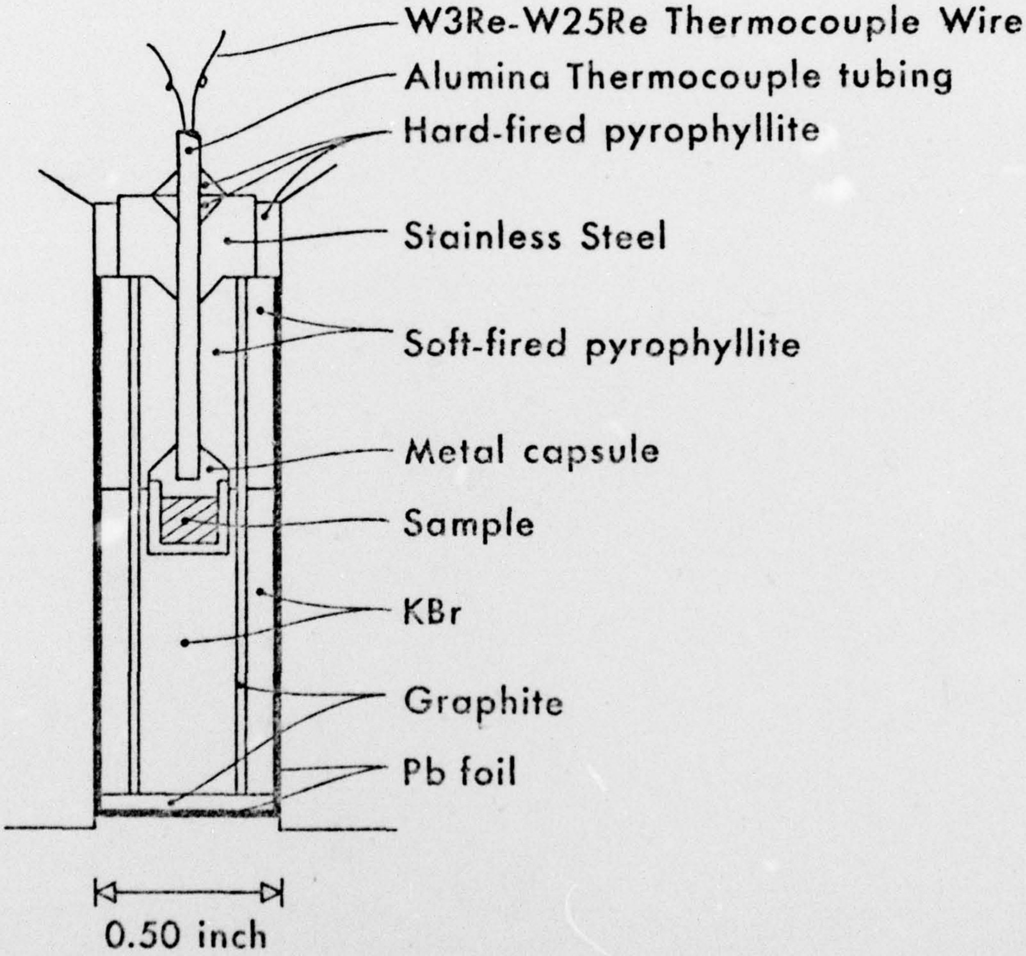
9) It is not clear whether 3-5μ diamond is superior to 1μ diamond as bonding matrix, though polycrystalline diamond of 3-5μ size is significantly harder than that of 1μ size.

10) When polycrystalline diamond is fractured, fracture takes place through coarse-grain diamond crystals and not along the grain boundaries (Run 47). Thus, bonding is strong. The strength of polycrystalline diamond therefore depends on the strength of coarse-grain diamond crystals.

SUMMARY AND CONCLUSION

It is perfectly clear that our 40 odd runs casually looking at a number of the many parameters of the bonding of diamond crystal have not remotely exhausted the topic. However, we were delighted to find that a substantial number of the polycrystalline masses were sharply superior to the Russian stone submitted to us. We believe that our best result obtained on Run 37, if properly tested with proper coolant, would cut equivalent to that of a natural octahedron of diamond.

A careful examination of these run results shows a number of inconsistencies. We believe that this quick screening of methods of attacking the problem show extremely promising results and extremely promising directions for further investigation.



W3Re-W25Re Thermocouple Wire
Alumina Thermocouple tubing
Hard-fired pyrophyllite
Stainless Steel
Soft-fired pyrophyllite
Metal capsule
Sample
KBr
Graphite
Pb foil
0.50 inch