Sintered Diamond Process

In 1955, Tracy Hall assumed the position of Research Director and Professor of Chemistry at Brigham Young University. Company secrecy and a secrecy order from the U., S. Department of Commerce made it necessary for Hall to invent a new apparatus in order to continue his high pressure work. He invented the multi-anvil press — first, tetrahedral; then, the hexahedral (cubic) press, which has greatly facilitated the sintered diamond process. The fascinating story of the "Belt", the original diamond synthesis and development of the multi-anvil press was told briefly by Hall in his Chemical Pioneer Award address (2). All commercial and most of the high pressure apparatus used for research for 50 KB or above has closely patterned either Hall's Belt or the Multi-Anvil press principles. In April 1966 Megadiamond Corporation was formed to do research and development on diamond and other high pressure, high temperature processes. Figure I is a photograph of the Megadiamond T cubic press used in the sintering process.

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In 1958 Hall discussed the desirability and possibility of a synthetic carbonado product of sintered diamond powder (3). From experiments conducted since that time, he has delineated the practical temperature and pressure limits for bonding of pure diamond powder (4) and for bonding combinations of diamond powder with other materials. Figure 2 illustrates the diamond sintering regions for pure diamond powder.

Line 1 is a graphical representation of the Berman-Simon equation (5) for carbon diamond - carbon graphite equilibrium. Above line 1, diamond is the stable form of carbon; below line 1, graphite is the stable form of carbon. Line 3 indicates a somewhat arbitrary lower temperature limit for obtaining usable sintered diamond product.

As the sintering temperature decreases approaching line 3, the required time for sintering increases. Decreasing the temperature also lowers the rate at which diamond converts to graphite. For a specific heating time there is a region bounded by lines 1 and 3 in which sintering occurs at a faster rate than the diamond to graphite conversion. In this region diamond powder can be sintered to usable product, even though the temperature-pressure condition for sintering is below the thermodynamic equilibrium line. Line 2 delineates this region for a specific sintering time of 30 minutes. A longer time decreases the area between lines 1 and 2, whereas a shorter time increases the area. For each heating time line 2 is unique.

At a given pressure sintering is more rapid as the temperature approaches line 2; consequently the shortest sintering-time is possible at the highest pressure. Only a few seconds are required to obtain good sintering at 85 KB (50 KB is equivalent to about 750,000 psi.). Operating above line 2 and to the right of line 3 gives sintered diamond product with negligible conversion of diamond to non-diamond carbon. It is also possible to form strong sintered product below line 2; however, there is a partial conversion of diamond to non-diamond carbon. Above line 2 the product color is light white to grey. Below Line 2 the product is black.

Sintered diamond product properties can be modified and in some respects improved by the addition of minute and sometimes fairly large amounts of additives to diamond powder before sintering. These additives have Included transition metals, refractory metals, and non-metals. For each additive a modified region of operation exists of the same general form as shown for pure diamond powder in Figure 2.

In preparation of the synthetic carbonado a cubic press is preferred. When the anvils are withdrawn, the undeformed sample drops free. With the belt-type apparatus elaborate precautions must be taken to prevent fracturing of the product because of the uniaxial stress distribution in the die of the Belt. Stromberg and Stephens discuss this problem of sample breakage in their work on sintered diamond (6). By using an intermediate indium can between two tantalum cans they were able to prevent sample fracture in their "girdle" apparatus, which is a modified Belt.

In the Megadiamond process, diamond powder usually in the micron range (0-25 u) is packed into a graphite or refractory metal heater. This assembly is placed within a cubic pyrophillite sample cell. Electrical energy is carried from the anvils of the press through steel current rings and refractory metal end tabs. The assembly is pressed to the desired pressure; the temperature is increased to the region 2400°K for a specified time, then cooled at pressure. Pressure is released after 10 or more seconds and the Megadiamond is removed from the sample cell. Variations in composition, pressure, temperature, and time are made to optimize the properties.

Properties of Megadiamond

Form and Size. One of the advantages of the Megadiamond process for sintered diamond is that the product reproduces the mold faithfully except for a small amount of shrinkage. Cylinders as large as 0.5 inches diameter by 0.5 inches in thickness weighing approximately 20 carats have been produced. Small cylinders have been produced as small as 0.012 inches in diameter and 0.020 Inches in length. Discs 0.26 inches in diameter and 0.015 inches in thickness can be produced. The tapered hole characteristic of wire drawing dies has been formed in cylindrical pieces as small as 0.5 carat and as large as 8 carats. Straight hole diameter has been produced as small as 0.005 inches and as large as 0.125 inches. Other shapes such as cubes, wedges, conical points have also been formed. These are summarized in Table 1. If the mold is well-polished, a similar surface will be reproduced on the Megadiamond.

Comparison of Properties. Like carbonado, Megadiamond has some porosity with density ranging between 3.1 and 3.48 g/cc. Table II shows a comparison of properties of Megadiamond with some other hard materials. In hardness it compares well with natural diamond and carbonado. Transverse rupture strength is quite good, exceeding that of single crystal natural diamond. The poly-crystalline nature of Megadiamond with random orientation of the crystallites makes it isotropic on a macroscopic scale and the absence of cleavage planes gives improved toughness and ability to withstand mechanical shock. The compressive strength of Megadiamond approaches that of the stronger grades of tungsten carbide.

For the wire drawing industry single crystal diamond is ideal for hardness, surface polish, and resistance to wear. When the hole diameter exceeds 0.04 inches, diamond cannot compete with tungsten carbide in most cases because of strength and cost factors. Because of strength, formability, and resistance to wear, Megadiamond may be expected to compete favorably with tungsten carbide in die applications. The rate of wear of Megadiamond was two to three per cent of the wear of natural diamond in the soft vector under identical load conditions. In comparisons of grinding wheel dressing the best Megadiamond had a weight loss rate equivalent to that for a single point natural diamond dresser and also for a carbonado dresser.

Megadiamond can withstand 1200°C heating for at least one hour in vacuum. At 800°C in air it will oxidize and the sintered product will disintegrate. It has excellent resistance to thermal shock and can be plunged red-hot into cold water without spalling or fracture. Thermal conductivity of one Megadiamond sample has been found to exceed that of copper at 20°C.

The electrical properties of Megadiamond can be varied over a wide range. Resistance has been measured at less than I ohm cm and more than a mega ohm cm for some samples. Both n- and p-type semiconductor behavior has been exhibited in different samples.

Those who work in the materials field know that numbers on material properties must be fixed with caution, because they are so dependent upon history of preparation, crystal size, orientation, surface defects, and a myriad of other conditions which affect the particular test. In the final analysis, the criteria of acceptability is how the material performs on the job; that is, an industrial performance test will determine a material's acceptability.

Applications of Megadiamond

Megadiamond is presently being used or tested as grinding wheel dressers, wire drawing dies, metal cutting tools, large grit, sputtering target for vacuum diamond coating, lapping gages, small grinding wheels, small styll, bearings, and high pressure nozzles. Electronic properties of Megadiamond are also being exploited. These are the more obvious and conventional possible applications. Creative exploitation of the properties of Megadiamond should bring new applications not now conceived.

The Megadiamond process makes it possible to utilize the large existing and potential supply of diamond powder of particle sizes smaller than the useful sizes for abrasive use. Both synthetic and natural powders may be used.

The superior wear characteristic of Megadiamond has been Utilized In distance stops for precision machinery where a work piece is to be ground or lapped to very close tolerances. The stops provide a simple means of precisely controlling stock removal. For example, in the manufacture of semiconductor devices, wafers of silicon and other materials go through several stages of lapping in which dimensions must be controlled to close tolerances. Megadiamond stops prevent the lapping from proceeding beyond the desired thickness. Conductive Megadiamond on a metal lap can be used in connection with an electrical system to indicate to the operator the completion of the lapping. Large wear-stop areas can be provided by Megadiamond for relatively small cost as compared to the same flat area for single crystal diamond. Table 111 shows comparative wear rates.

Nozzles for high pressure water jet cutting have been made of Megadiamond. In a test at water pressures above 35,000 psi, tungsten carbide nozzles were disintegrating in not more than six hours. A Megadiamond nozzle In the same service shows no wear after much longer service. The test is continuing.

Table IV shows tests of Megadiamond used in cutting tests and compared with single crystal diamond and tungsten carbide tools. As yet, Megadiamond does not lap to as fine a cutting edge as single crystal diamond. However, this quality is improving as we optimize particle size distribution and other process variables.

Conclusion

Sintered diamond products show promise of filling a need in industry for moldable diamond shapes with the toughness of carbonado. In the industrial diamond use, natural diamond mining and in synthetic diamond manufacture, micron-size particles are recovered so that abundant supplies are available. As larger particles of diamond are crushed and cleaned, the particles should become more pure and perfect in crystal form because cleavage and crushing occurs at the weaker boundaries.

The sintered polycrystalline Megadiamond can be preshaped into many forms depending on the application desired. This characteristic opens up an entirely new capability in the manufacture of diamond tools. Points, wedges, fiat plates, pierced parts, and rollers are all formable in a large variety of sizes. Rather than selecting a natural diamond, which approximates the desired shape, and working it for a specific tool, It will become possible to form the Megadiamond to specifications. This development may well prove to be more important in industrial diamond technology than the original synthesis of diamond from graphite.

I sold this new business opportunity to Mega on April 11, 1969 in exchange for a 2% royalty to be paid on all the sintered diamond products that Mega would sell in the future. Mega now had a product to sell that GE did not have! By the end of the year Mega had made and sold $1602.00 worth of sintered diamond, a small but prescient look into the company's future. Mega sold more than $10 million worth of PCD material in 1987.

Word of Mega's new product spread rapidly and created a great deal of interest. On September 24, 1970 Mega held a formal press conference at its office and plant, 275 West-2230 North, Provo, Utah. The news was published around the world. Dr. Harvey Fletcher, former Director of Research of the Bell Telephone Laboratory called the achievement "one of far reaching significance." Utah's governor, Calvin L. Rampton, issued the following statement: "The creation of a multi-carat diamond by man is, without question, a technological breakthrough of the highest order. We are justly proud that this event has been achieved in Utah . . . Utah salutes Dr. Tracy Hall and Megadiamond Corporation." GE, no doubt spurred on by Mega's success, worked overtime to get into this new business. GE finally entered the market in 1972, about 3 years after Mega.

It is worth noting, before passing on that General Electric never challenged the manufacture of the Ni/Mn catalyst diamond grit as infringing any of their patents. The three of us, in retrospect should not have worried so much.

Smith International Incorporated (SII) acquired Mega on February 12, 1985 and changed its name to SII Megadiamond or Smith-Megadiamond as previously indicated.

With this bit of historical background behind us, let’s turn to the subject of High Pressure/High Temperature equipment suitable for the production of diamond. My Belt (U.S. Patent No. 2,941,248 June 21, 1960) is perfectly satisfactory for the mass production of industrial diamond products. However, my Cubic Press is better.

In the production of grit or PCD's, the pressure-temperature-time cycle is important. Perhaps the most critical factor is the falling off of pressure with time due primarily to the transformation of pyrophyllite to coesite and the transformation of graphite into diamond, coesite and diamond both occupy more volume than there precursors. Consequently the pressing members of the Belt and the Cubic Press must provide some type of follow through to maintain the desired pressure. In the Belt, only two members are pressing forward to maintain the pressure. In the Cubic press there are six anvils pressing forward to maintain the pressure. Consequently, experience indicates what one might expect, the Cubic press is four times as effective at maintaining or increasing pressure as is the Belt.

The great importance of this shows up in the “dwell-time" or “soaking time"; required to make the desired product. In United States patent practice the patent must indicate the "preferred embodiment" (the optimum conditions (pressure, temperature, and time, etc. to make the best product). GE's primary patent for making PCD's give an optimum time of 60 minutes for the dwell time. This long time is required to let the pyrophyllite and other ingredients make the proper mechanical adjustments in the pyrophyllite and other cell ingredients to maintain uniform pressure throughout the material being pressurized. In the cubic press, a dwell time of only 3 minutes is required for the dwell time in making PCD's. This is because of the fast pressure follow-through created by the six moving anvils which quickly reduces pressure gradients within the cell.

In connection with pressure follow-through and adjustment, the use of a salt (NaCl) liner inside of the pyrophyllite cell helps reduce pressure gradients within the cell. The use of NaCl is absolutely necessary for the Belt but it also improves the effectiveness of the Cubic Press.

Pyrophyllite cells give off various undesirable substances during the process of making diamond from graphite or in making PCD's. Also, graphite itself is a harbinger of various gases absorbed from the air. In the case of converting very fine diamond powders into PCD's, the diamond powders used have previously absorbed various gases from the air or have acquired impurities in the wet methods employed for their size classifications. All of these impurities degrade the quality of the products. Consequently, "getters" of very reactive metals such as thin sheets of zirconium and titanium are placed within the salt liners to react and remove deleterious products from the cell environment.

All of the PCD's manufactured by GE and DeBeers have flat surfaces; i.e., the thin diamond surface is bonded to a flat surface of tungsten carbide. Only Smith Megadiamond makes PCD s with curved surfaces. The attached brochure entitled "Megadiamond: The Competitive Edge" shows some of the conical, spherical, and saddle-shaped tools that have been manufactured. One of my son's, David, is indicated as the person to telephone for more information. None of the Hall's, Tracy Sr., Tracy Jr, or David are associated with SSI Megadiamond at this time.

David R. Hall is now the president and chief executive officer of Novatek, 85 West Center Street, Suite 100, Provo, Utah 84601, and telephone (801) 374-6000. David was formerly Vice President of Mega and the prime mover in the invention and development of enhanced diamond products (multi-layered surfaces) and in the development of diamond bits that can withstand impact. Also attached to this report is an article reprinted from Design News of January 5, 1987 which shows the efficiency of diamond hammer bits in rock drilling. Note that the diamond drilling bits drilled six times the footage of carbide bits. Smith-Mega currently manufactures such bits up to 12 inches in diameter. David's new company is engaged in the development of advanced, computer controlled drilling equipment that can effectively utilize the advanced diamond technology that is now available.

Tracy Jr. is a private inventor currently working on the design of very large scale high pressure machines. His office is in Orem, Utah, a city that adjoins Provo on the north.

The phenomenal performance of enhanced PCD s has opened many new avenues for their use. Diamond need no longer be considered a specialty material. It is relatively cheap in light of its dramatic properties. It is finding use in bearings of all types to operate in a very gritty, dirty environment. The use of down-hole motors for rock drilling which utilize diamond thrust bearings are a significant new development and have become a major money maker for Smith-Mega. Attention is now being given to the use of PCD in clutches and brakes, possibly for automotive use.

Possibly, the most significant use of diamond for the near future is the drilling of very deep holes to tap the thermal energy of the earth. When holes drilled into the earth become deep, a major expense of the drilling is pulling up the string of pipe to which the drill bit is attached in order to replace the worn out bit. Hammer bits drill faster and as shown in the attached Design News reprint drill six times the footage of carbide. Hot, dry rock is everywhere below the surface at depths that could probably be economically drilled in the not to distant future to provide absolutely environmentally safe energy to everyone upon the face of this earth.