MILESTONES IN CRYSTAL GROWTH
THE TRANSFORMATION OF GRAPHITE INTO DIAMOND

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"*And the second row shall be an emerald, a sapphire, and a diamond*." Exodus 28:18

This earliest known reference to diamond assigns emerald, sapphire, diamond and nine additional precious stones to be set in a breast plate to be worn by Aaron, the high priest. Each stone represented one of the twelve tribes of Israel.

Another Old Testament scripture seems to affirm by its imagery that diamond was known by the ancients to be the hardest of substances. Jeremiah 17:1 states: "*The sin of Judah is written with a pen of iron, and with the point of a diamond: It is graven upon the table of their heart, and upon the horns of your altars.*"

It is thought that the earliest diamonds came from India. Centuries later, alchemists seeking to transform ordinary metals into gold also considered transforming common gemstones into more precious types. A scientific discovery presaging the possibility of transforming a common substance into diamond occurred in the year 1792 when Antoine Lavoiser burned diamond in oxygen and obtained carbon dioxide as the only combustion product. He concluded that diamond was comprised of only the element carbon. The common mineral graphite was already known to be carbon.

Thus graphite and diamond were shown to be chemically the same and men began experimenting with ways to transform inexpensive graphite into expensive diamond. If 0.200g of graphite could be transformed into a one carat (0.200g) gem quality diamond, a million fold increase in value would be attained.

C. Cagniard de la Tour seems to have been the first to claim success at making diamond. This claim was made in 1823. From that time until December 16, 1954, when I succeeded in transforming graphite into diamond, the "diamond problem" attracted the interest of many people. Those who pursued the problem included rank scientists including Boyle, Bragg, Bridgman, Crookes, Davey, Despretz, Friedel, Liebig, Ludwig, Moisson, Parsons, Tamman, and Wohler.

British encyclopedias credit J.B. Hannay as the first to make diamond. His diamonds, supposedly made in 1880, are still displayed in the British Museum. Hannay's method employed the use of wrought iron tubes in which lithium metal, bone oil and mineral oil were sealed. The tubes were then heated to redness in a furnace. Some eighty tubes exploded in his experiments. Two survived however, and when cooled and opened were supposedly found to contain three rather large, gem quality diamonds.

Some old school books and encyclopedias credit Henry Moisson as the first to make diamond. He invented the electric arc furnace and used it to synthesize many previously unknown metal carbides and other refractory substances. This success led him to take on the ultimate challenge: the diamond problem.

In the year 1893 Moisson claimed to make diamond by dissolving sugar charcoal in molten iron and rapidly cooling the melt by pouring it into water. He thought that a great pressure would develop on cooling and cause diamond to form. After treating the solidified mass with hydrochloric acid, he reported finding a few

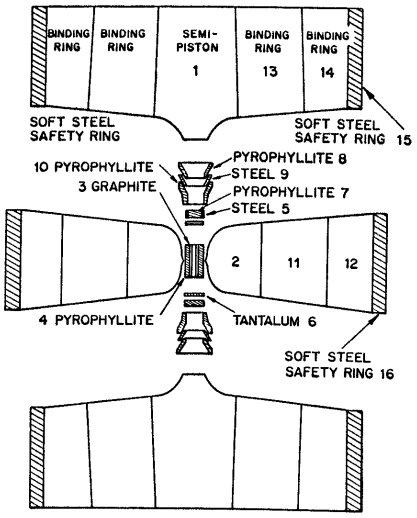

Fig. 1 "Exploded" View of the Belt High Pressure, High Temperature Apparatus

microscopic diamonds in the undissolved residue.

Sir Charles Parsons, who experimented with diamond making from 1882 to about 1922, repeated Moisson's experiments and the experiments of all previous claimants without success. He also performed many ingenious experiments of his own. In 1922, he concluded that neither he nor anyone lese had succeeded in making diamond.

It is worth noting that Parsons was the inventor of the practical steam turbine which rapidly replaced sails as means for ship propulsion in the late 1800's. He amassed a fortune from this enterprise and spent much of it on the diamond problem.

Another noted worker who spent the better part of a lifetime on the problem was Percy. W. Bridgman of Harvard University. He started his work in 1905 and concluded it in 1955. Although he never made diamond, he received the Nobel Prize in 1948 for his prodigious work in the general field of high pressure research. Great secrecy has been companion to most of those who have attacked the diamond problem. In Bridgman's case, David T. Griggs, one of the graduate students who worked with him, stated in a 1954 article: "It was my privilege to work in Bridgman's laboratory during the period when working pressures were increased from 20,000 to 100,000 bars. As each new apparatus was readied for trial, I noticed that Bridgman would become secretive and brusque. During the first run, visitors were not welcome. I subsequently learned that in each case graphite was the first substance tried."

Note that 1 bar = 10 million dynes per square cm = 1.02 kg per square cm = 1 Newton per square m = 100,000 Pascals = 0.987 Atmospheres = 750 Torr = 14.5 pounds per square inch. All of these pressure units have been used at one time or another and have made quite a mess of the published literature. The currently decreed unit is the Pascal (Pa). Chemists have traditionally used atmospheres; geologists, bars.

In 1937, a consortium of companies provided very large financial backing for Bridgman's research on diamond. Work on the project ended in 1942. Diamonds were not made. Bridgman never succeeded in inventing an apparatus that could simultaneously contain a high pressure and a high temperature.

My interest in diamond synthesis began rather early. I had read about the problem as an undergraduate at the University of Utah. Later, while working for a Master's degree, my advisor,

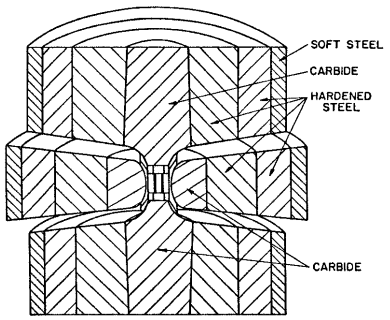

Fig. 2 "Closed" View of the Belt High Pressure, High Temperature Apparatus

G. Victor Beard, encouraged me to conduct experiments concerning the problem, even though my thesis was in an entirely different area. In those days there was no possibility of funding for experimental work on high pressure apparatus, but there was the hope that it might be possible to make diamond without such equipment.

I had been intrigued by a journal article that described the way an ordinary incandescent light bulb had been used to produce sodium metal. The lighted bulb was immersed in a low melting salt solution containing sodium ions. A battery was connected to one terminal of the filament and to an inert electrode in the molten salt. The positive sodium ions passed through the glass and picked up electrons at the surface of the filament to become sodium metal.

I tried, without success to prepare elemental boron using a borate bath and a boron glass "light bulb". And I pondered how to produce carbon ions and pass them through some kind of barrier onto a heated filament. I hoped, of course, that the carbon would deposit as diamond. Several researchers in the last twenty years or so have produced diamond layers up to 100 atoms thick by decomposing methane and other hydrocarbons on heated filaments.

In a different vein, I tried to selectively oxidize graphite with oxidizing acids, believing that regions in the disturbed graphite structure might coalesce into diamond. I also disturbed the graphite lattice by intercalcation with sodium and potassium. Needless to say, I never detected any diamond.

World War II came and I joined the navy. After it was over, I earned a Ph.D. degree with the aid of the GI bill and went to work for General Electric.

In 1951, G.E. Research Laboratory managers called about twenty of their chemists

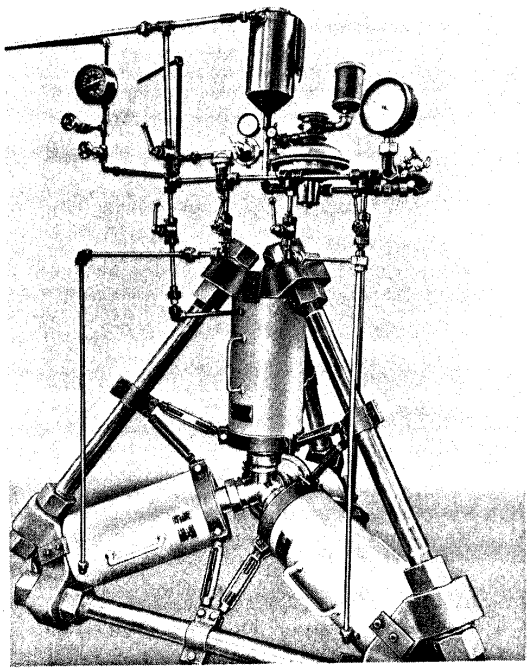

Fig. 4 The First Tetrahedral Press

to a meeting and announced that they were going to tackle the diamond problem. I was elated and ready! Volunteers were called for. I was the only one interested and I got the job.

It was revealed at the meeting that personnel from other disciplines were already at work on some aspects of the problem, such as designing high pressure, high temperature apparatus capable of achieving 35,000 atmospheres and 1000 degrees centigrade. It was anticipated that graphite would convert to diamond under these conditions. Others were working on "non-thermodynamic" approaches to making diamond; believing, for instance, that high pressure might not be necessary. These studies were primarily theoretical.

My assignment related to chemistry. Thermodynamics indicated that high pressure and high temperature would be needed to transform graphite to diamond. But nature and theoretical studies did not give any clues as to how high a pressure or how high a temperature might be needed. Indeed, geologists do now yet know how diamonds were formed in nature.

Since the chemistry of diamond formation was not known, several questions presented themselves: Did diamond (in nature) form directly from graphite, or were other reactants required? Were catalysts needed? Did diamond take a million years or more to form? If the latter were true, man might never be able to demonstrate laboratory diamond synthesis. Could there be several different procedures for making diamond?

For a time, I eagerly pursued these questions. Most notable was my determination that the activation volume of carbon in the transition state was of the order of ten cubic centimeters per mole! Graphite's molar volume is 5.34 cubic centimeters and diamond's 3.42. Thus the pressure that is needed to place graphite in a region where diamond is thermodynamically stable is very detrimental to favorable reaction kinetics. It would take more than a million years to produce diamond this way! If graphite is the starting material, a catalyst is needed. If graphite is not the starting material, several possibilities present themselves. For example, the carbon in carbonates might be replaced by another element such as silicon or sulfur to form silicate or sulfite and diamond. Perhaps copper would, at high temperature, alloy with the tungsten carbide and free the carbon as diamond.

By this point it was apparent that the lack of progress in the invention of high temperature, high pressure equipment was the barrier to really getting hold of the diamond problem. I had no assignment in this area but I began to think of non-conventional means for simultaneously generating high pressure and high temperature. My ideas, however, met with resistance as I found myself intruding on the "turf" of others; a classic problem in industrial R&D. Fortunately, a shop foreman, a machinist, and a manager from another area helped me skirt the roadblocks, and I brought forth the Belt high pressure, high temperature apparatus.

This device advanced into territory far beyond what had been hoped for. It could generate a pressure of 120,00 atmospheres and sustain a temperature of 1800 degrees C for periods of several minutes, in a working volume of about one tenth of a cubic centimeter!

Managers and others were reluctant to accept the Belt and its enormous capabilities. Those charged with the responsibility of developing high pressure apparatus continued to work on unworkable ideas. It took several months for them to become believers. But when they finally did, there was a scramble to get a piece of the action. The vice president for research decreed that "this is big enough for all to share." It is worth noting, however, that U.S. Patent 2,941,248, Belt Apparatus, issued June 21, 1960, bears my name only.

At this writing, about 150 tons of man made industrial diamond, valued at about one billion dollars, has been manufactured in the Belt!

An exploded diagram of the Belt is shown in Fig. 1 and a closed diagram is shown in Fig. 2.

The functions of the various parts are as follows (see Fig. 1): Two conical semi-pistons (1) push into each side of a specially shaped cemented tungsten carbide chamber (2). Pressure is transmitted to the sample contained in a metal or graphite tube (3) by wonderstone (pyrophyllite) (4) a special hydrous aluminum silicate mined in South Africa. The pyrophyllite also serves as thermal and electrical insulation. The sample is heated by passage of an electrical current through the heating tube (3). If the sample is a good electrical conductor, it may be necessary to electrically isolate it from (3) in a container of hexagonal boron nitride or some other high temperature electrical insulator.

Current enter tube (3) through a refractory metal disk such as tantalum (6), which touches steel ring (5), which in turn touches the tip of the semi-piston. Under pressure, these various parts (3, 5, and 6) are forced together and make a good electrical contact. The pyrophyllite disks (7) provide thermal insulation.

As the conical pistons advance, a sandwich gasket of pyrophyllite (8) and (10) and steel (9) compresses that amazingly contains a pressure exceeding a million pounds per square inch!

Interference fit compound binding rings of hardened steel (11) and (12) provide lateral support for the cemented tungsten carbide chamber (2). Lateral support for the cemented tungsten carbide conical semi-pistons is similarly provided by rings (13) and (14). The low carbon steel, dead soft rings (15) and (16) are safety rings provided to absorb the substantial energy released if the binding rings should fail.

The extreme conditions available in the Belt were thought to be more than sufficient to transform graphite into diamond, but experiment proved otherwise. Since the direct transformation would not occur, I attempted hundreds of indirect approaches along the lines previously mentioned. None were successful and I was becoming discouraged. General Electric was considering abandoning the project.

Then, on the wintry morning of December 16, 1954, I broke open a sample cell after removing it from the Belt. It cleaved near the tantalum disk (6 in Fig. 1). Instantly, my hands began to tremble. My heart beat wildly. My knees weakened and no longer gave support. Indescribable emotion overcame me and I had to find a place to sit down.

My eyes had caught the sparkling from dozens of tiny octahedral crystals growing out of the tantalum and I knew that diamond had been made by man!

It took about twenty minutes for me to regain my composure. Then I examined the crystals under a microscope. The largest was 150 micro meters across and contained triangular etch and growth pits such as those that occur on natural diamonds. The crystals scratched sapphire, burned in oxygen to produce carbon dioxide, and had the density and refractive index of natural diamond. A few days later, an x-ray diffraction pattern positively identified the crystals as diamond.

The first successful experiment contained the mineral troilite (FeS) inside a graphite heating tube. The pressure in the Belt was near 70,000 atmospheres (just a little over 1,000,000 pounds per square inch). The temperature was near 1600 degrees C (2912 degrees F). Troilite is associated with the microscopic diamonds found in the Canyon Diablo meteorite. The meteoritic diamonds were probably formed by the transient pressure and temperature generated on impact with the earth. I thought that the FeS might have been a catalyst for graphite-diamond conversion in the meteorite and consequently tried it in my experiment. I repeated this experiment twenty times in the next two weeks varying pressure and temperature to find the pressure-temperature field in which diamond would form. Diamond was produced in twelve of these runs. Diamond always grew on the tantalum end disks. Since troilite is a non-stoichiometric compound, I wondered whether it was FeS, S, or Fe that was important for the catalytic action. I also wondered what role the tantalum played. Experimentation showed that diamonds grew on the tantalum when either FeS or Fe was in the graphite heating tube. But no diamonds were formed when S alone was in the tube. Under the high temperature, high pressure conditions in the graphite tube, sulfur distills from the FeS and passes through the graphite tube into the pyrophyllite, leaving iron behind to alloy with the tantalum. I concluded, therefore, that an alloy of iron and tantalum acted as the catalyst.

A microphotograph of the first diamonds I saw growing out of the tantalum is shown in Fig. 3 (see front cover). Note the unusual interpenetrating twin in the lower right hand corner. The skeletal morphology of the diamonds resulted from very rapid growth at the high

operating temperature. These diamonds grew in just a few seconds, thus evidencing the possibility of economical industrial diamond production. Diamond wheels using this type of diamond proved to be vastly superior to crushed natural diamond grip in the grinding of cemented tungsten carbides. More perfectly formed diamond crystals require growth at a lower temperature and a lower pressure for a longer length of time (a few minutes).

On December 31, 1954, Hugh Woodbury, a company physicist, made diamond under my tutelage using FeS in the graphite heating tube. He thus became the first man to duplicate the diamond synthesis claim of another.

Due to the long history of fraud associated with the diamond problem, company officials carried out "official duplication syntheses" on January 18th and 19th of 1955. I was not allowed to be present. Under the watchful eyes of company officials and attorneys, Hugh Woodbury and Richard Oriani (a company metallurgist) each made three runs in the Belt according to my procedure, using independent sources of graphite and FeS. They succeeded in making diamonds in all six runs.

Management, thus convinced of the authenticity of my synthesis, sent out an impressive press release on February 15, 1955. Within the next two days, most U.S. newspapers carried front page stories reporting that diamonds had been made at the General Electric Research Laboratory in Schenectady, New York.

The lack of recognition I received for this extraordinary dual achievement, the invention of the Belt (U.S. Patent 2,941,248 issued June 1, 1960) and synthesis of the first diamond (U.S. Patent 2,947,608 issued August 2, 1960) was, simply stated, demeaning.

Saddened and hurt, I left General Electric, a company I had admired and aspired to work for since the age of nine.

In August of 1955, I began a new career as director of research and professor of chemistry at Brigham Young University.

I had anticipated building a Belt to continue high pressure research at my new location. But G.E. officials warned that I could not build a belt under any circumstances. So, I had to invent another device. I called this invention the Tetrahedral Press. It was the first of a series of "multi-anvil presses" that I was to invent. I succeeded in obtaining a patent on the Tetrahedral Press (U.S. Patent 2,918,699 issued December 29, 1959) before G.E. obtained a patent on my Belt.

Having thus extricated myself from dependence on the Belt, I was free to pursue a 25-year career in high pressure research at Brigham Young University. A photograph of the first Tetrahedral Press is shown in Fig. 4.

Dr. H. Tracy Hall, age 35 at the time diamonds were made.