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January 31, 1977

Dear Tracy,

Attached are my remarks and slides I planned for the ceremonies in San Diego on March 22. Your comments are welcome. I hope mine will mesh with your preceding presentation properly. Twelve or thirteen minutes time allowance doesn't give much room for elaboration.

Again congratulations on receiving this well earned award. We are looking forward to seeing you there. We expect to be flying in from Honolulu as we will be visiting our Hawaii based son in March. We leave here February 25.

Sincerely,

Herb

In case you want to reach me in Hawaii, the address is:

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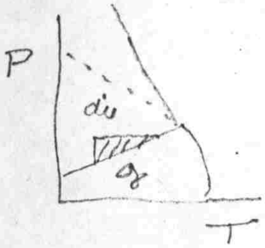
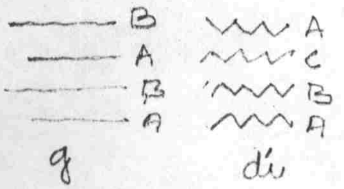
Copy for Tracy Hall

THE GROWTH AND PROPERTIES OF DIAMOND

H M Strong



My remarks are directed to the shaded portion of the temperature-pressure phase diagram of carbon. This is the pressure temperature region that was available for experimentation in early 1954. Here reproducible diamond synthesis was accomplished later in the same year. Here also are the conditions for synthesizing industrial abrasive diamond.



In the early experiments on diamond synthesis, the first disappointment was the finding that at the available pressures and temperatures, graphite would not transform to diamond, no matter how hard, hot or prolonged the squeeze applied. Initially, it didn't seem that graphite should have been much inconvenienced to pucker its flat hexagonal carbon nets a little and then reorder its layer stacking a bit. The The applied pressure favored this readjustment since the volume of diamond is but 2/3rds that of graphite. Evidently graphite crystals would have to be taken apart and reassembled more to our liking.

Sources of Free CARBON
I Decomposition
CARBIDES, CARBONATES,
ORGANIC COMPOUNDS
II Solutions
a) ALKALI CARBIDES,
CARBONATES, SOME
SALTS, OXIDES
b) HYDROUS SILICATE
MINERALS
c) FERROUS METALS & ALLOYS

Some hints about this came from the real world of one atmosphere. For example, certain carbon compounds can, by appropriate chemistry, be persuaded to release free carbon. Also, there are solvents which can take carbon from one place and put it down in another with the help of a temperature gradient or by electrolysis, if the carbon is ionized. All of these reactions yield graphite at one atmosphere, but under a pressure thermodynamically agreeable to diamond, carbon is definitely obligated to form diamond when turned loose, or so it seemed. But carbon had not heard about this so it followed its predilection to form graphite in all cases, save two. The reaction of nickel releasing lithium from lithium carbide produced a product that gave an elusive hint of diamond in the form of weak x-ray diamond diffraction lines, but diamond crystals were not seen.

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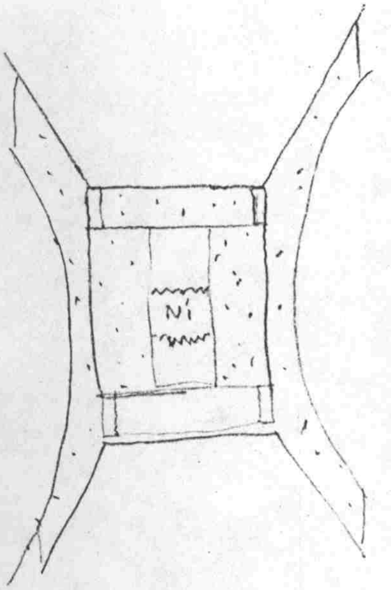
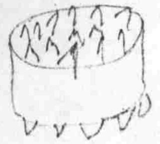
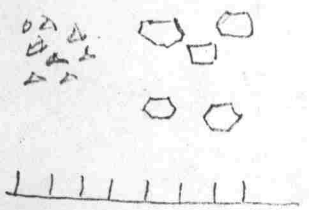
The reaction between graphite and molten iron under pressure gave a momentous and exceptional result because seeable, feelable crystals formed having the capability of scratching everything in sight. Very convincing. But the interval between the first synthesis and its proof of reproducibility had its full share of suspense for the experimenters.

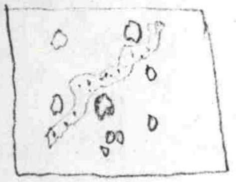


The experiment is quite simple. Alternating pieces of graphite and any ferrous metal, or many of their alloys, are stacked in the pressure cell. A current is passed through the pressurized stack to heat it to about 1400°C whereupon the metal graphite system melts together at the interfaces forming diamond spontaneously and rapidly beneath a thin film of molten metal. This picture of a nickel piece with the lumpy surfaces shows the diamonds collected at the interfaces beneath a thin skin of nickel. A little acid soon brings the newly born crystals out into the light of day. They may look like some of these, their sizes ranging from a few microns to 1 mm, just right for abrasive use. Their sizes, color and shapes are controlled by the pressure, temperature, time, and nature of the solvent-catalysts employed to bring about the reaction. A wide range of crystal characteristics is thus available.



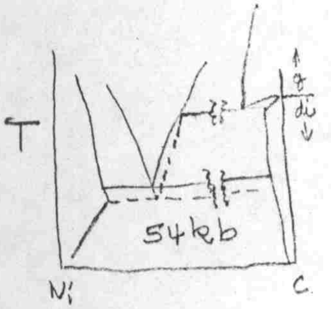


The term catalyst associated with solvent is appropriate because the ferrous metals and many of their alloys are unique among solvents in ability to yield diamond from dissolved graphite. Curiously, copper which is neither solvent nor catalyst becomes a catalyst and an extremely weak solvent with the addition of about 2% nickel. Diamonds form surprisingly easily in the 2% nickel alloy. Electrolysis experiments indicate that carbon may be a positive ion in liquid ferrous metal solutions, unlike most other solutions of carbon wherein the carbon is either neutral or negative. The formation of positive carbon ions may be a precondition for diamond formation.

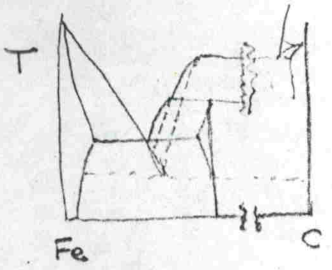


g from Ni + Ni_3C

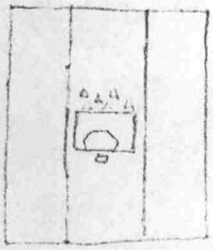
Solid ferrous metals are not diamond catalysts. All carbon precipitating from solid metal becomes graphitic. Likewise, the metal carbides, iron carbide, nickel carbide, etc. may be decomposed under pressure by heating, but the separating carbon is always graphite.

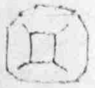


Diamond forms in two component systems, carbon and ferrous metal. Their binary phase diagrams for one atmosphere are well known. Under pressures near 55 kbars, the diagrams are similar, but melting temperatures are higher and compositions altered slightly. Also, the melting eutectics reflect the presence of two phases of carbon. In the nickel carbon system at 54 kb, the nickel graphite eutectic lies a little below the nickel diamond eutectic and at a bit higher carbon concentration because graphite is now the unstable phase. The small solubility difference is where the drive to form diamond is ultimately felt. Diamond may be formed right at the graphite nickel eutectic, but the crystals are black, of poor crystal quality and lacking the usual nickel skin. Diamonds are normally formed well above the diamond eutectic. A complication develops because nickel is slightly soluble in graphite. Graphite in this system is then slightly more stable in respect to diamond than pure graphite. This lowers the diamond stable temperature at 54kb by about 12° degrees.



In the iron-carbon system at 57 kb, stable iron carbide introduces a third eutectic, iron-iron carbide which lies above those of diamond and graphite. At temperatures below the carbide eutectic, iron consumes both diamond and graphite forming iron carbide. Diamonds form only at temperatures above the carbide decomposition temperature.





TYPE IIA 1ct Di

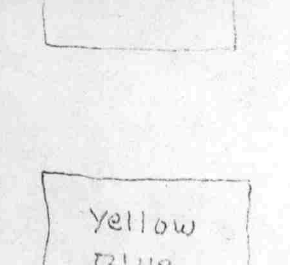
So far in this talk only small diamonds have been made. Why not large ones? The principal factor limiting growth in the system described is the large volume shrinkage occurring when graphite becomes diamond. The apparatus does not closely follow this volume decrease, hence the pressure falls reducing the drive for diamond growth to zero. This problem is solved by using diamond as a carbon source in the pressure cell. Small abrasive diamonds are used as the nutrient carbon which is dissolved in a pool of molten ferrous metal at a high temperature and allowed to swim down to a cooler zone where the solution becomes supersaturated with carbon that precipitates out on a seed diamond. Through careful control of the supersaturation rate, a nice gem quality crystal can be grown to 6 to 7 mm size in about a week.

Cut Gem

Yellow
Blue
Colorless

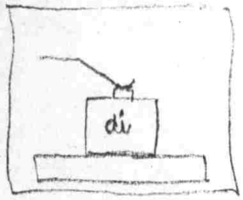
9 one ct, di's

These make nice expensive gems. Strange that such a bit of thermodynamically unstable matter should have become the symbol of ever enduring love. These crystals afford the opportunity to study diamond properties in terms of controlled additions of impurities, particularly substitutional boron acceptor atoms and substitutional nitrogen donor atoms. Pure diamond is colorless and, except for weak carbon bands at 4 microns, it is transparent from the band gap at 2250 A to at least 1 mm. Nitrogen and boron introduce characteristic visible and infrared absorption bands which impart yellow and blue colorations respectively. Boron doped diamond is a p-type semiconductor, but with nitrogen the donor level is 4 ev deep and no room temperature conduction is observed.



The extremely rigid, light atom lattice of diamond imparts some unusual properties to diamond: exceptionally high Debye temperature, low specific heat, remarkably high thermal conductivity and thermal diffusivity, and lastly great strength. Impurities do detract from these properties some, but diamond remains extreme in its properties.

Diamond's great strength and transparency has led to its wide use for anvils in miniature pressure devices capable of generating nearly 1 megabar pressures.



Heat sink
di

Its transparency and high thermal conductivity find use for high power laser beam windows. Its high thermal conductivity is much required in electronics for keeping tiny power diodes cool. There are many other uses for diamond.

Bob Wentorf will next tell you about synthesizing diamond's next of kin, cubic boron nitride, or borazon, and how this and diamond are being used.