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NOTES AND NEWS

A VERY HIGH PRESSURE–HIGH TEMPERATURE RESEARCH APPARATUS AND THE SYNTHESIS OF DIAMOND*

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Introduction

The mineralogical significance of research at elevated pressures and temperatures is obvious. As striking also are the implications in the field of special electronic, magnetic and optical materials. The following is a brief report on one aspect of such a program.

A description is given of a research apparatus capable of reproducible* sustained near-hydrostatic pressures to at least 100,000 atmospheres concurrent with temperatures exceeding 3000° C. An experimental example, namely, the synthesis of diamond, also is included.

The Supported Stepped Piston–Cylinder Apparatus

Since operating pressures to 100,000 atmospheres far exceed the maximum strengths of construction materials, existing values must be extended. This can be accomplished by providing auxiliary external support to overstressed components. This principle is generously applied to the apparatus under discussion.

A cross sectional schematic of the pressure apparatus with an exploded view of critical internal components is shown in Fig. 1. Essentially the apparatus consists of two sets of symmetrically opposed stepped cemented carbide pistons,† labeled A, B, and C, and a cylinder assembly consisting of a double bore cemented carbide set, numbered 1 and 2, surrounded by a series of hardened steel bands.‡ The latter are fitted at maximum permissible interference. An outer band of mild steel is included to protect against possible fracture of the hardened steel components. The series of steel prestressing bands and the protection band are labeled 3, 4, 5 and 6. Rigid steel plates, item 7, are used to counter lateral shear tendencies in the carbide cylinder assembly.

Working force can be applied to the piston assembly by a hydraulic press of suitable capacity. Part of the force exerted on piston B is directly applied to the high pressure piston C which in turn bears upon the

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* A reproducibility of 5% at room temperature can be achieved relative to electrical resistance discontinuities as a function of pressure for pure bismuth and barium as reported by P. W. Bridgman (1, 2, 3).

† All cemented carbides used consist of tungsten carbide with 6% cobalt.

‡ All hardened steel used is A.I.S.I. 4340 hardened to RC 52 and triple tempered.

sample volume. The remaining force is exerted (neglecting frictional losses) on the annular volume bearing against the tapered surface of B. The annular space is filled with a compressible pressure transmitting solid, generally pyrophyllite. The compressible segment permits the piston assembly to advance. The high pressure piston can thus compress the sample volume, and at the same time the resulting compressional stress in the annular cavity is transmitted to the exposed wall of the high pressure piston and to the exposed end faces of the high pressure cylinder. The transmitted pressure provides external support to these normally overstressed components, and when properly balanced, no failure occurs.

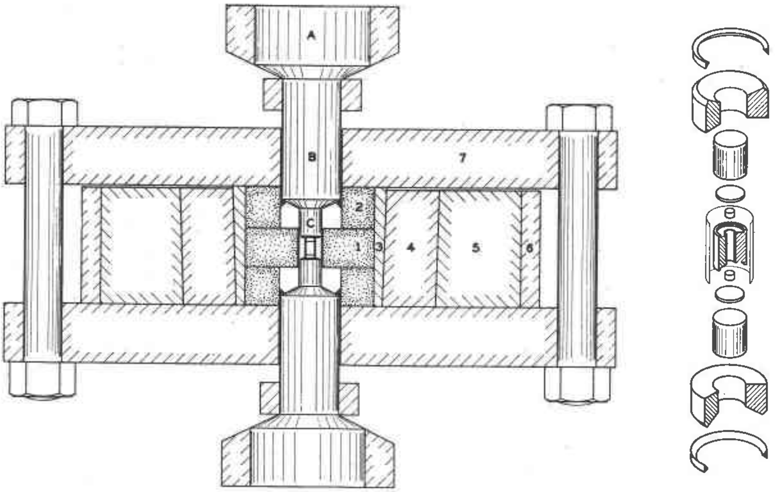

FIG. 1. A cross sectional schematic of the Very High Pressure—High Temperature Apparatus. Also included on the right is an exploded view of critical internal components. For scale, the diameter of the high pressure piston, C, is $\frac{1}{2}$ inch.

The exploded view of internal components of the apparatus shown on the right of Fig. 1 consists of the following from top to bottom: (1) hardened steel seal ring in order to prevent extrusion of pyrophyllite between the piston and cylinder which might cause them to jam. (2) machined pyrophyllite support segment, (3) high pressure carbide piston, (4) metal electrical contact disk used to provide broadest coverage of the 6% cobalt content of the carbide, (5) thin electrical insulation sheath to isolate the high pressure piston from the carbide cylinder bore, (6) metal plugs to compact and contain the sample within the electrical resistance heating tube shown along the axial bore of the pyrophyllite specimen cylinder. The remaining items are symmetrical analogues.

Low voltage electrical power leads are attached to pistons A. Pistons B are insultated from their cyclinder walls by a thin sheet of suitable dielectric material. Temperature measurements are made under specific pressures by means of a thermocouple placed into the sample volume through a small axial bore through a special set of B and C pistons. Calibration data are obtained on the basis of power input for given temperatures for fixed experimental systems. Data can be extrapolated to higher pressures by use of the Simon melting equation (4).

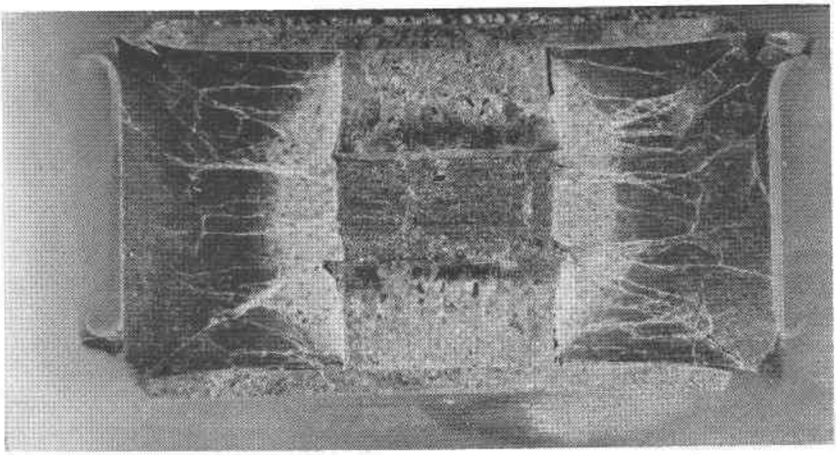

FIG. 2. A cross section of an actual pyrophyllite cylinder containing nickel-carbon-nickel from top to bottom, respectively, which has been stressed to 85,000 atmospheres at approximately 1560° C. for 3 minutes. Note the diamond growth at the top center of the graphite section. Scale is $\frac{1}{2}$ inch for the horizontal width of the cylinder.

DIAMOND SYNTHESIS

Although the first diamond synthesis was achieved by man in 1955 (5), it has been only recently that details on the method have been made available to the public (6, 7). With the proper apparatus, diamond synthesis is remarkably simple.

An appreciable part of our studies in the metal-carbon system have been carried out with pure graphite and nickel at a pressure of 85,000 atmospheres and approximately 1560° C. The elements were chosen on the basis of ready availability. The pressure was chosen because it produced no undue hardships upon the apparatus. Pyrophyllite was used to contain the Ni-C system within the high pressure volume. No contamination of the system has been noticed.

Figure 2 shows an actual cross section of a pyrophyllite cylinder containing a Ni-C system which has been subjected to the above P-T conditions for 3 minutes. The arrangement of items from top to bottom, respectively, are: Ni electrical contact disk, Ni plug, graphite plug, Ni plug and other contact disk. The metal has been etched with HNO_3 to show the recrystallization which has occurred. One diamond can be quite clearly seen protruding from the top center of the graphite section. Others can just barely be detected to the left and above the latter. The color discontinuity at the upper Ni-graphite boundary shows a saturated Ni-carbon area and one of incipient diamond formation. Unfortunately details are not as clear along the lower boundary. *X*-ray diffraction analysis of the Ni at the carbon contact showed no evidence of nickel carbide formation. The white colored area surrounding the Ni-C system graphically illustrates the thermal gradient present during the experiment. The many cracks along the pyrophyllite clearly show the stress distribution upon the specimen. Note that other than initial tolerance adjustments to sample configuration, essentially no deformation has occurred.

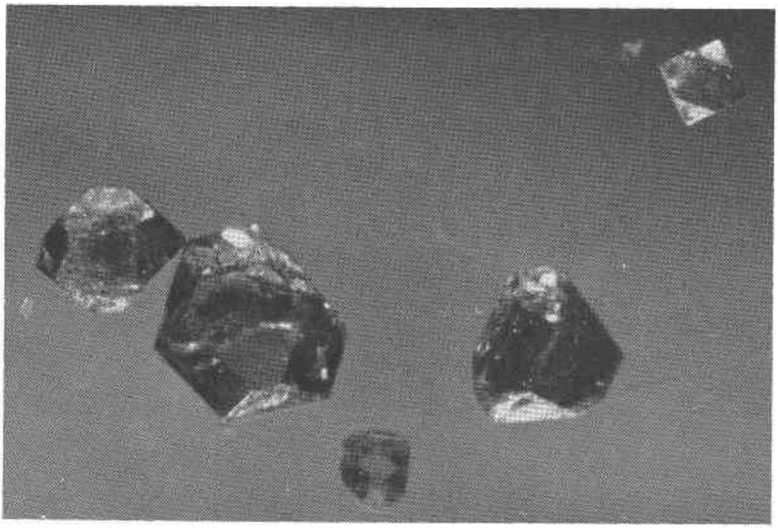

FIG. 3. Yellow diamond crystals grown in nickel under a pressure of 87,000 atmospheres and a temperature of approximately 1560° C. for a period of 5 minutes. Longest dimension of the largest crystal is 0.5 mm.

Figure 3 illustrates several diamond crystals grown in nickel at approximately 87,000 atmospheres and 1560° C. They are colored a bright yellow. Colors have been observed from green to yellow to colorless. The largest dimension observed thus far is 0.8 mm. Crystals are generally well formed giving good optical goniometric reflections. Combination cube-octahedron forms have been most commonly observed thus far, although some octahedra and a few cubes have been found; and dodecahedron faces noted. Twinning according to the spinel law is very common. Although the adamantine luster and typical habit of diamond aided in the initial identification, positive evidence was obtained from single crystal *x*-ray diffraction analysis. A rotation pattern about [001] gave $a_0 = 3.57$ Å, in good agreement with the literature value.

ACKNOWLEDGMENTS

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REFERENCES

1. P. W. BRIDGMAN, *Proc. Am. Acad. Arts Sci*, **81,** 228 (1952).
2. ———, *Proc. Am. Acad. Arts Sci.*, **74,** 438 (1942).
3. ———, The Physics of High Pressure; G. Bell and Sons, Ltd., London (1949).
4. L. SALTER, *Philosophical Mag.*, **45,** 369 (1954).
5. "Man Made Diamonds," General Electric Res. Info Serv., March, 1955.
6. Chem. Engr. News, Nov., 1959.
7. H. P. BOVENKERK, *et al.*, *Nature*, 1094, Oct. 10, 1959.

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IDENTITY OF CALCIUM RINKITE AND GÖTZENITE

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From a lava of the extinct volcano Mt. Shaheru in the Belgian Congo, a triclinic F-bearing Na-Ca-Ti-silicate was described by Sahama and Hytönen (1957 *a*) and named götzenite. It was realized that the mineral was related to calcium rinkite that occurs in the lovchorrite-bearing veins of Mt. Yukspor in Kola Peninsula and which has been briefly reviewed by P. Chirvinsky and I. Borneman-Starynkevich (in Fersman, 1937). The data presented for calcium rinkite were, however, not sufficient for an accurate comparison of the two minerals with each other. For that reason and, further, because of the entire absence of the rare earths, niobium and strontium in the Shaheru mineral, this mineral was distinguished from calcium rinkite.

The unit cell dimensions of götzenite as originally published by Sahama and Hytönen are as follows: $a = 10.93$, $b = 7.32$, $c = 5.74$, $\alpha = 90°$,