

Final Report

HIGH TEMPERATURE STUDIES

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ABSTRACT

An apparatus for subjecting up to 10 cubic centimeters of material to pressures of 15,000 atmospheres at temperatures as high as 10,000°C has been developed and described. The apparatus is relatively simple in its design and could readily be scaled-up by a factor of 25 in volume, if desired. Temperatures of 10,000°C can usually be maintained for periods of 5 to 15 seconds, but in some instances have been maintained for as long as one minute.

With this new apparatus, a survey of the effects of very high temperature has been made on several carbide, boride, nitride, phosphide, oxide, sulfide, and some miscellaneous systems. One material produced under these high-temperature, moderate pressure conditions may have immediate practical use. This material is fused silicon carbide. The compressive strength of this material is 30 times as great as that of ordinary hot-pressed SiC. This high strength silicon carbide may be useful as a cutting tool material.

Some of the oxide systems of chromium and manganese exhibited rather high compressive strengths following high temperature treatment. This was true also for ZrB₂ and TiB₂. Some of the metallic oxides produced under high temperature conditions formed semi-conducting materials and might be of further interest with respect to their electrical properties.

Some, systems were studied at 94,500 atmospheres at relatively high temperatures in the Tetrahedral Anvil Apparatus. Two definite new materials were produced under these conditions. One of these is a face-centered cubic BP with $a = 4.54 \text{ \AA}$. The other material is BS with a diamond cubic structure and $a = 4.33 \text{ \AA}$. Results of microscopic and X-ray examination on many of the systems studied are given.

The research reported here may be regarded as a survey--the results of which point to the desirability of studying the more interesting systems in greater detail.

APPARATUS

This project was undertaken with two objectives in mind, The first objective was to attempt to construct apparatus that would make it possible to subject materials in a condensed phase to temperatures as high as 10,000°C. Once this objective was achieved the second objective could be undertaken. The second objective was to subject various materials to these high temperatures to see what effects might be produced. At the time this project began, there were four general means for obtaining high temperatures: (1) exploding wires by high voltage discharge (at which time reported temperatures of about 20,000°C had been obtained). (2) use of shock waves (approximately 50,000°C). (3) electric arcs. (4) solar furnaces. Since early 1956 there has been considerable success in increasing the temperatures that can be obtained by each of these means.

The first two methods listed above are, of course, not steady state. The temperatures obtained are obtained only for a very brief period. The temperatures obtained in electric arcs have been restricted to gases and are not applicable to condensed phases. Although solar furnaces can be used with condensed phases, the maximum temperatures obtainable cannot exceed the temperature of the sun's surface (approximately 5,000°C). Since the inception of this project there has been a great deal of interest in utilizing extremely high temperatures to produce new materials. There is a particular interest in producing materials that will withstand high temperatures and at the same time possess great strength. The modus operandi has been, "things resistant to heat must be born of heat". However, to this investigator's way of

thinking, it would be unlikely that such materials could be produced by reactions in the gaseous phase. It seemed important to design equipment whereby materials could be subjected to very high temperatures and maintained in the condensed phase (solid or liquid state).

Previous experience with the "Belt" ultra-high-pressure, high-temperature apparatus which I had designed and used to synthesize diamonds at the General Electric Company, convinced me that it should be possible to construct apparatus in which temperatures as high as 10,000°C could be achieved in a condensed phase¹. Because of commercial implications and a Department of Commerce secrecy order on the "Belt" apparatus, it was not possible to use this device at Brigham Young University. However, during the course of this high temperature contract, research was underway with a National Science Foundation Grant² to devise alternate means for obtaining pressures of the order of 100,000 atmospheres., simultaneously with high temperatures. This research resulted in the development of the Tetrahedral Anvil Apparatus³. Consequently, towards the end of this contract, some experiments were performed at pressures near 100, 000 atmospheres simultaneously with high temperatures.

One fascinating hope, not realized in this research, was that at very high temperature, within a condensed phase, a process might take place similar to some newly discovered processes that take place at very high pressures; i.e., valence electrons might be forced to occupy empty orbitals closer to the nucleus. When a substance is heated at low pressure, a temperature is eventually reached (approximately 7,000°C) where ionization begins to take place. If the condensed material being heated is confined to constant volume, ionizations of electrons (electron escape) cannot take place in the usual sense. As an alternative to ionization, sufficiently high temperature could conceivably drive the electrons to occupy unfilled orbitals. New chemical compounds might be formed under such conditions and might be "captured" for study at normal room temperature and pressure by rapid thermal quenching. Although, as mentioned, this hope was not realized during the course of this investigation. A search for such an effect still seems to be worth pursuing.

Several devices were built and tested before a satisfactory apparatus was obtained that could be routinely used to subject materials to high temperatures. The first device used is shown in Figs. 1 and 2 (Figures are to be found at end of this report.) This device has been described in a previous publication⁴. High temperature is generated in the apparatus of Fig. 1 by electrical resistance heating of an element (the centrally located rod of Fig. 2.) properly insulated and confined by the "bomb". The bomb served to confine the material being heated so that it remained in a condensed phase in spite of the high temperatures achieved. During operation, the thermal insulation immediately surrounding the heating element becomes molten. The zone of molten material grades off radially into solid material with the radial temperature gradient that is established. Chemical reactions are carried out in the high temperature zone simply by placing the reactants inside the heating element - the heating element being a hollow tube. In some instances the reactants may be electrically conducting and the heating tube may not be necessary. Temperatures of at least 10,000°C may be obtained in the apparatus of Fig. 1. A typical assembly consisting of a pyrophyllite cell, SiC-C heating element, and carbon end cones is shown cut open in Fig. 3 after a 15 second run at 3000 watts power input (approximately 10,000°C). The white area surrounding the dark, 1/8 inch diameter C-SiC heating rod shows how far the molten zone extended into the surrounding pyrophyllite. It also indicates a rather large region of temperature uniformity. The heating element will, of course, be liquid at the higher operating temperatures. The heat loss at the ends of the bomb along the axis will be such as to provide a thermal gradient from the central regions of the bomb toward the ends so that material will also grade from molten to solid here and in this wise eliminate the usual container problem. In this bomb, the material is confined by tightening the nuts on the tension bolts of Fig. 1. The pressure exerted upon the material within the tomb by this technique is small. Indeed it is insufficient to close up any voids initially present, so it is important to have good fitting components in order that materials within the bomb might remain as condensed systems when they become molten at the high temperature.

In the first bombs constructed the heating element was a carbon rod and the thermal insulation was a readily machinable stony material known as pyrophyllite. Pyrophyllite is a naturally occurring,

¹ H. T. Hall, Rev. Sci. Instr., 31, 125-131 (1960). Note: This article first appeared as G.E. Research Laboratory Report # RL-1064, March, 1954. This article had rigidly limited distribution within the General Electric Company.

² N.S.F. Grant G-2749

³ H. T. Hall, Rev. Sci. Instr., 29, 267-275 (1958).

⁴ H. T. Hall, B. Brown, B. Nelson and L. A. Compton, J. Phys. Chem, 62, 346 (1958).

extremely fine grained hydrous aluminum silicate that, when confined, melts to a glass-like substance at a temperature around 1500°C. In order to estimate temperature, the bomb of Fig. 1 was modified by splitting the confining cylinder in a plane perpendicular to the axis of the heating element. A platinum, platinum-rhodium thermocouple was then brought in between thin sheets of insulation between the two sections of the cylinder. Occasionally these leads would be blown out as pressure developed within the bomb. However, they would remain in place often enough that a temperature calibration such as that shown in Fig. 4 could be obtained. The platinum, platinum-10% rhodium thermocouple operated satisfactorily to the neighborhood of 1700°C where it melted and was no longer useful. An additional point on the plot of power input in watts versus temperature was obtained by finding the power necessary to melt a small tungsten wire adjacent to the graphite heating tube.

With a carbon rod heater and pyrophyllite insulator it was found possible to obtain extrapolated temperatures of the order of 6,000°C for periods of 15 seconds. For periods of the order of minutes it was possible to obtain temperatures of the order of 4,000°. The maximum temperature obtainable with carbon heaters was limited by intrusion of molten pyrophyllite material across the carbon heating element. This intrusion, which seems to be a combination mechanical and chemical effect, results in interruption of the electric current and, therefore, limits the temperature obtainable. Substitution of thermal insulation material for the pyrophyllite immediately surrounding the carbon rod was attempted in order to eliminate or minimize this current cut-off effect. Alumina, porcelain, silica, and glass were tried. Alumina and porcelain were no better than the pyrophyllite. Silica was inferior. Pyrex glass, however, seemed to increase the temperature that could be obtained before cut-off occurred. A pyrex glass sheath of approximately 1/32-inch wall thickness immediately surrounding a 1/8-inch diameter carbon rod allowed extrapolated temperatures as high as 15,000° to be obtained for periods as long as 15 seconds. Some attempts were made to substitute compressed refractory powders for the pyrophyllite thermal insulation for use with various heating elements. This was without success. In the first place, it was difficult to obtain a dense compact mass free of minute voids. Of course, on heating such material vaporization would take place into the voids, and a condensed phase would not be maintained. Secondly, it soon became apparent that when operating at 10,000° it matters little whether the refractory being used melts at 1500° or 2500°. In view of this, most of the experiments utilizing this and subsequent apparatuses were conducted with pyrophyllite as the refractory element. The principal advantage of pyrophyllite over other materials is that it can be readily machined to any shape.

In attempting to reach even higher temperatures than those obtained with graphite or carbon heating elements, it seemed desirable to experiment with some high melting metallic materials such as tungsten and molybdenum in place of carbon. This was advisable because there seemed to be some chemical reaction between the carbon and the pyrophyllite, and this chemical reaction may have been partly responsible for the cut-off phenomena. Because of the much higher thermal conductivity of these metals over that of carbon it was found that much larger wattages were required to obtain a given temperature with these substances. All other conditions of geometrical arrangement, and so forth, remained the same. (A new temperature calibration must be obtained for each change in materials or geometrical dimensions and arrangements.) With molybdenum and tungsten, the cut-off phenomenon was observed again. As before, the highest temperatures were obtained when the heating element was sheathed with pyrex glass. With this arrangement, temperatures of 10,000° were maintained for about 15 seconds before cut-off. There seemed to be no evidence of chemical reaction between the metal and the pyrophyllite. Cut-off seemed to be caused by the molten metal withdrawing into a ball and by the molten refractory material flowing into the space from which the metal withdrew. The forming of this ball of metal seemed to be due to two effects: (1) An actual electrical "pinch-off" due to the high current flowing through the metal, and (2) an attempt by the metal to reduce its surface area because of the large difference in surface energy between the metal and the molten pyrophyllite.

At this point in experiments with the bomb, it seemed that this cut-off phenomenon might be eliminated if the heating element were composed of some material that, when molten, would possess cohesive forces more like that of the ceramic insulator and also if the electrical resistance of this element were a factor of 100 or so higher than that of tungsten. The higher resistance would require much lower current to obtain the same wattage within the element and hence the electrical current "pinch-off" effect would be reduced. The materials experimented with in this connection were in general semi-conductors such as silicon carbide, copper oxide and sulfide, elemental silicon and so forth. Through these experiments a heating element was found in which it was not possible to produce cut-off at the maximum power inputs available (20 kilowatts). This heating element is composed of an approximately 50-50, by volume, mixture

of fine silicon carbide and graphite powders. When about 100 volts is impressed across a 1/8-inch diameter by 1-1/2 inch length of silicon carbide-graphite mixture, sufficient electrical conduction occurs to heat the rod and melt the pyrophyllite in the immediate vicinity of the rod. At this point the silicon carbide-graphite mixture diffuses into the pyrophyllite, and the pyrophyllite likewise diffuses into the silicon carbide-graphite mixture. However, the resultant mixture continues to be electrically conducting and a cut-off of the electric current does not occur. Initially, a power input of about 3000 watts corresponds to a temperature of 10,000°C. However, there is considerable diffusion of the material throughout the pyrophyllite and within a few minutes the entire mass becomes liquid to within 1/8 inch of the wall of the steel containing cylinder as is shown in Fig. 5. Inspection indicates that the hottest region of the pyrophyllite is still somewhere near the central axis in spite of the diffusion. Tungsten wires inserted at various places throughout the pyrophyllite, to obtain some indication as to possible temperature gradients within the mass, merely indicate that the temperature is above the melting point of tungsten everywhere that the material is fluid (with a power input of 3000 watts). The pressure developed inside these bombs with silicon carbide-carbon powder heaters at estimated temperatures of 10,000° seems to be appreciable. Some alloy steel cylinders designed to withstand pressures in the neighborhood of 10,000 atmospheres have exploded and hot material from the core has escaped with considerable violence - molten material, in some instances, having completely "ringed" the wall of an 8 foot diameter test-pit. Fig. 6 shows some of the material scraped from the wall.

It is not always desirable in attempts to obtain the very highest temperatures, to have a uniform temperature gradient along the length of the heating element. It is possible to make the thermal gradient along the element from the center outward "barrel-shaped" by increasing the amount of heat flow out the ends. This can be accomplished by placing materials at the end which have high thermal conductivity or by increasing the geometrical size of the endpieces so that more heat is conducted. "Carbon" and graphite are the most useful materials to use for end pieces. "Carbon" has a much lower thermal and electrical conductivity than graphite. By judicious use of these two materials in the internal components of the bomb, the temperature gradient from the middle of the heating element to the ends can be easily varied.

As an aside, on the silicon carbide powder, graphite powder mixture that will not pinch or cut-off the current at the highest power inputs available to us, it may be that this simple system might be of value as a thermo-nuclear device in which pulsed currents of millions of amperes are sent through a bomb similar to that of Fig. 1.

Having successfully obtained a device capable of producing estimated temperatures of 10,000°C it became very desirable to have a better way of measuring or estimating such temperatures. At this point in the research, some equipment was borrowed from the Electrical Engineering Department and preliminary experiments were conducted on the use of thermal-noise power as a measure of temperature. However, it soon became apparent that measurement of temperature within the high-temperature bomb by such means would become a research project in itself that would consume much more time than was available. It was decided, therefore, that, for the present, temperatures obtained from extrapolations of power input versus temperature would be used as a basis for estimating temperature.

Experiments with the high-temperature bomb of Fig. 1 soon indicated that it would not be possible to maintain a condensed phase at high-temperature in this device. Gases released during operation at high temperature had sufficient pressure to push back the pyrophyllite and other materials within the bomb leaving large cavities occupied by gas. Obviously, the way to suppress this would be to redesign the bomb so that moderate pressures could be applied to the contents before the temperature was introduced. Furthermore, the plain steel bomb proved to have insufficient strength under some conditions. Also, the chore of tightening the nuts on the six tension bolts to effectively close the bombs was a deterrent to completing very many experiments in a given period of time. An improved bomb eventually evolved that, in reality, was a moderate pressure, high-temperature apparatus. Hydraulic presses to operate these devices were constructed from government surplus landing gear taken from large bombers. This improved device utilized a cemented tungsten carbide cylinder liner surrounded by compound binding rings to prevent the explosive rupture previously encountered. A diagram of the device is shown in Fig. 7. As can be observed from this figure, the original simple steel cylinder has been replaced by a compound cylinder consisting of a carbide liner, shim, tapered, interference fit binding rings and a safety ring. This compound ring assembly provides much greater strength than can be obtained with a single cylinder⁵.

⁵ H. T. Hall, Rev. Sci. Instr. 29, 267-275 (1958). (Design information on compound rings is found in this reference.)

The largest diameter of the pistons of Fig. 7 is 1/32 inch smaller than the inside, diameter of the carbide liner so that electrical heating current can be brought in through these pistons to heat the sample without shorting through the sleeve, Pressure is generated by forcing the pistons together with a hydraulic press. As the pistons are forced together pyrophyllite (lava) squeezes a short distance into the small annular space between the major diameter of the pistons and the liner. In use, the cylindrical surface of the lava must be given a coat of molybdenum di-sulfide powder. Otherwise, after completion of a run, it will not be possible to push the pyrophyllite assembly from the liner. The small diameter portion of the piston tends to keep the piston and liner coaxial as pressure is applied thus preventing shorting of the piston to the liner. Experience with similar simple piston and cylinder devices⁶ indicates that the pressure within the sample space is approximately 90% of the calculated pressure obtained by dividing the press load by the cross-sectional area of the cylindrical hole in the carbide liner. The device of Fig. 7 proved very successful and was the one used to conduct most of the investigations carried out under this contract.

Thermocouples were initially inserted in this device by running the wires through the narrow annulus between the piston and the cylinder. However, difficulty was encountered in that the extruding pyrophyllite pinched off the thermocouple wires. This problem was eventually solved by admitting a 1/32 inch diameter, sheathed thermocouple into the central sample region through a tight fitting axial hole through one of the pistons and carbon end disk. With this arrangement, the thermocouple would stay in place even when the pressure inside the bomb was as high as 15,000 atmospheres. Three sizes of graphite-heater sample tubes were used in work with the apparatus of Fig. 7. Dimensions of these are given below together with other dimensions of the cell assembly:

Lava cylinder: 3-3/4 inch long x 1 inch outside diameter.

Carbon end disks: 3/8 inch long x 3/4 inch diameter.

All graphite sample heater tubes: 2 inch long.

Small graphite sample heater tube: - 3/16 inch I.D. x 1/4 inch O.D.

Medium graphite sample heater tube: - 9/32 inch I.D. x 3/8 inch O. D.

Large graphite sample heater tube: - 5/16 inch I. D. x 7/16 inch O. D.

Small graphite disks used to plug ends of sample heater tubes are 1/8 inch thick.

Temperature was estimated for each of the small, medium and large assemblies used in the apparatus of Fig. 7 in the same manner as indicated in Fig. 4.

In the initial work with the high temperature bomb of Fig. 7, the pistons and the liner were constructed of tungsten carbide. The pistons had a very short life. They would continually break at the step. New pistons were obtained wherein the step was made very rounding, but the problem still persisted. Finally, the pistons were constructed of an air-hardening die steel. After a very few runs these pistons would deform into a barrel-shape; but, because of the increased toughness of the steel over that of the tungsten carbide, no difficulty was experienced with breakage at the step. By keeping a dozen pairs of pistons on hand it was possible to set up a grinding schedule to grind the barrel-shaped pistons back into shape so that experiments could be performed at a suitable rate.

As finally evolved, this apparatus proved to be very useful in the moderate pressure range for subjecting large quantities of material (large quantities compared to the quantities of material that can be subjected to pressures of 100,000 atmospheres in currently available ultra-high-pressure apparatus) to very high temperatures.

Of the several apparatus designs tried, only one other will be mentioned. This was a "bomb" in which a 1/8 inch diameter tungsten rod was used as the heating element. One end of the rod was attached to a hydraulic ram. When sufficient current was passed through the rod to melt it, the hydraulic ram would feed in additional rod. It was hoped that this procedure would prevent the pinch-off effect for a sufficient length of time to develop very high temperatures. Pinch-off did occur, however, and this apparatus was abandoned.

Towards the end of the project, many of the systems that seemed of interest from work performed. in the device of Fig. 7 were subjected to pressure in the vicinity of 100,000 atmospheres at somewhat lower temperatures in the Tetrahedral Anvil Device developed under a National Science Foundation Grant.

⁶ H. T. Hall, Rev. Sci. Instr. 29, 267-275 (1958).

EXPERIMENTAL RESULTS ON CHEMICAL SYSTEMS

During the initial work aimed at finding an electrically conducting material that would not cut off, it appeared that silicon carbide might have been melted in some of the experiments. Since at one atmosphere pressure silicon carbide does not melt but sublimes, this observation warranted further investigation. Consequently, some of the early work with chemical systems centered on silicon carbide. In some of these experiments, green silicon carbide powder of 600 mesh size was tamped into the sample space of a cell assembly such as that shown in Fig. 7. At a pressure of 15,000 atmospheres the voltage across the cell as a function of amperes through the cell appears as is shown in Fig. 8. The dog leg in the curve may be an indication of the melting point. The temperature at this point is in the neighborhood of 3200°C. Several samples were heated to a maximum temperature in one of the regions marked by the numerals 1, 2, 3, 4, and 5 along the curve as shown. The temperature was increased to the maximum during a period of approximately 4 minutes and held at the maximum temperature for about 1 minute, at 1, 2, and 3. At 4 and 5 the maximum temperature was held for about 5 seconds only. In the region 5, estimated temperatures are in the 10,000°C range. After holding at the maximum temperature the electrical power was abruptly disconnected thus quenching the sample. (Cooling time is just a few seconds.) The silicon carbide sample was then removed and a fractured surface was examined under the microscope. The silicon carbide quenched from region 1 is compact and gray in color. Material quenched from region 2 and 3 is more compact than that quenched from region 1 and is lighter in color. Material quenched from region 4 has a higher metallic sheen than those quenched from lower temperatures. Material quenched from region 5 shows varying degrees of decomposition into elemental silicon and graphite.

The main evidence indicating that silicon carbide has been melted comes from the fact that some samples quenched from temperature above that of region 3 have shown smaller grain size upon x-ray examination than the grain size originally present in the starting material. On the other hand, silicon carbide held at temperatures in the neighborhood of region 1 for a period of time, shows, after quenching, larger grain size than was present in the original starting material. Several silicon carbide samples quenched from region 2 were fashioned into cylinders of approximately 1/4 inch diameter and 5/16 inch long, by grinding with a diamond wheel. These samples were then subjected to compressive tests. About a half dozen specimens failed in the neighborhood of 300, 000 p.s.i. load. However, one specimen withstood 693,000 p.s.i. before failure and another failed at 575, 000 p.s.i. Ordinary commercial hot pressed silicon carbide has a compressive strength in the neighborhood of 20,000 p.s.i. Two of the above specimens, therefore, showed a phenomenal increase in compressive strength over commercial material of a factor of about 30. Some fused silicon carbide specimens were fashioned into lathe cutting tools (see Fig. 9) and given qualitative tests in comparison with some standard cemented tungsten carbide cutting tools. In these tests the silicon carbide tools seemed to keep a better edge than the tungsten carbide tools and also seemed to be less fragile with respect to breaking under interrupted cutting conditions. There is certainly a future for this material in cutting and possibly in drilling applications.

Considerable difficulty was experienced in obtaining silicon carbide pieces greater than 1/4 inch in length. On cooling and releasing pressure, the silicon carbide would almost invariably break into discs. This breakup is thought to be caused by longitudinal expansion of the pyrophyllite on release of pressure. Apparently, the forces developed in this expansion are great enough to stretch the solid silicon carbide sample beyond its ultimate tensile strength. Therefore, instead of obtaining a long sample of silicon carbide many short discs are obtained. Some experiments were conducted at low pressure to see what effect this would have on sample break-up. It was found that a reduction of the pressure from 15,000 to the neighborhood of 8500 atmospheres would partially eliminate this problem. At this pressure it was still possible to obtain silicon carbide with the same strength characteristics as that obtained at 15,000 atmospheres. A type of "bomb" in which pressure is applied symmetrically, perpendicular to the axis of the sample rather than parallel to the axis would probably eliminate this problem. Such a bomb was constructed in which tapered wedges moved towards a central axis as they were forced into a set of tapered binding rings. A gasket was formed in spaces between the wedges (in a fashion analogous to that occurring in the Tetrahedral Anvil Apparatus) and as this gasket compressed, a pyrophyllite cylinder and sample was also compressed. While this device also seemed to help the break-up problem, there were mechanical problems in its operation. Perfection of this device was not accomplished due to the press of time to complete other phases of the project.

Because of the success in obtaining silicon carbide specimens with very high compressive strengths, some work was conducted on subjecting B_4C to temperatures between 3000 and 7000°C, and

also mixtures of $B_4C + SiC$ to these conditions under moderate pressures. The specimens thus obtained did not have strengths any higher than those that have been obtained in ordinary hot pressing of these materials.

In addition to some of the early experiments on silicon carbide, some experiments were directed towards the possibility of producing cubic material similar to diamond in structure and hardness. In these experiments the following materials in the atomic and molecular proportions indicated were thoroughly mixed together as fine powders and then heated at temperatures in the 5000 to 10,000°C range and quenched: BN:C, BN:Si, BN:SiC, SiC:C. The nominal pressure in these experiments was 15,000 atmospheres. These materials were also mixed with nickel powder which, it was hoped, might act as a solvent for the production of some new compounds from these combinations. There was no indication of the formation of any new materials in these tests.

Leo Brewer, John Margrave and others have recently shown the unexpected existence of lower oxides of various metals in the gas phase at very high temperature. This raises the question as to the possibility of producing these lower metallic oxides in the solid phase by some quenching technique. Some attempts were made to do this by heating mixtures of fine metal powders and metal oxide powders to various temperatures between, 3000° and 10,000° followed by quenching. The systems studied were: $Al_2O_3:Al$, $Al_2O_3:4Al$, $Al_2O_3:Mo$, $Al_2O_3:Fe$, $Al_2O_3:Sn$, $Al_2O_3:Cr$. The formation of lower oxides in these experiments was not detected. However, some rather good mechanical compacts were obtained in some instances. (See comments appearing later under examination of high temperature runs on oxide systems.) The pressure used here again was nominally 15,000 atmospheres.

As work progressed, with the high-temperature, moderate pressure apparatus, there would be periods when the high temperature could be achieved without any problems. Then there would follow long periods when extreme difficulty with cut-off or burn-out would be encountered. During one period it was necessary to make 55 separate high-temperature runs to obtain 2 silicon carbide specimens satisfactory for compressive tests. When such troubles were experienced, a great deal of effort was put into cell design (mainly geometrical modifications) aimed at alleviating the cut-off problem. Of various cell arrangements, the one depicted in Fig. 7 with graphite end discs seems to be more satisfactory from the standpoint of current cut-off. Graphite is a much better thermal conductor than carbon and gives a barrel-shaped current distribution along the length of the heater sample tube. The reason for the cycles of cut-off troubles was never tracked down. It may be possible that certain batches of pyrophyllite, pyrophyllite being a natural material, may have different properties than other batches and might be responsible for these problems.

Some definite new materials resulted from this work. Boron and phosphorus powders in equal atomic proportions form a new material. This new material is black in color, is soft and is a fine-grained solid as obtained in the experiments. It is a moderately good electrical conductor. X-ray diffraction shows the new BP to be face centered cubic with $a=4.54\text{\AA}$. It has been produced at 94,500 atmospheres at a temperature near 2500°C. The material can also be prepared by reacting B_4C and P. At 10,000 atmospheres, cubic material is not formed. Instead, a very complex x-ray diffraction pattern is obtained for the low-pressure, high-temperature product.

Equal atomic proportions of boron and sulfur at 94,500 atmospheres and 1850°C gives a new BS of diamond cubic structure with $a = 4.33\text{\AA}$. The product obtained consists of a mass of soft, silvery-gray, elongated polycrystals with a very high electrical resistance.

Carbon and sulfur appear to react over a very wide range of proportions at very high temperatures and pressures of 10,000 - 100,000 atmospheres. X-ray examination yields an enormous number of diffraction lines.

Rhenium oxide and metal in the proportions $Re_2O_7 + 10Re$ yields a brilliant, scarlet solid (apparently ReO) at 10,000 atmospheres and high temperature of simple cubic structure with $a=3.74\text{\AA}$.

Rhenium and carbon in equal atomic proportions form a hexagonal close packed structure with $a=2.795$ and $c= 4.467\text{\AA}$. This is very close to the Re structure ($a=2.765$, $c=4.470$) except that a has been expanded about 1% by entrance of carbon into the lattice. The product was formed at 10,000 atmospheres and temperatures of 2700°C.

There follows a list of most of the materials subjected to high-temperature, moderate pressure conditions and also to high-pressure, high-temperature conditions arranged in order of increasing temperatures. The sample heater tube size is indicated by: Small S, Medium M, and Large L, (dimensions previously given). Run identification is given because these samples are being kept on file at Brigham Young University, since they may be of additional interest to others as well as to ourselves.

Nominal Pressure (Atm.)	Max. Temp. Attained (°C)	Sleeve Size: Small, Medium, Large	Run Identification	Comments
TiC (26 runs)				
7200	1600	S	3/4-13-59HEC	
3000	2000	L	3/4-25-59WCP	
9000	2600	M	3/5-2-59WCP	
6000	2900	S	1/4-18-59WCP	
3000	2900	S	4/4-18-59WCP	
6000	3000	S	5/4-3-59WCP	
9000	3000	S	2/4-13-59HEC	
3000	3000 watt	L	1/4-25-59WCP	Special heater arrangement
15000	3300	L	2/4-15-59WCP	
7800	3500	M	1/4-21-59HEC	
9000	3700	L	1/4-13-59HEC	
18000	4000	S	2/4-3-59WCP	
3000	4600	S	3/4-18-59WCP	
18000	5000	M	2/5-9-59WCP	Special heater arrangement
21000	5100	S	4/4-3-59WCP	
3000	5500	L	4/4-25-59WCP	
21000	5600	S	3/4-3-59WCP	
15000	6000	S	1/4-3-59WCP	
6000	6000	L	5/4-25-59WCP	
18000	6100	M	4/5-2-59WCP	
6000		S	2/4-18-59WCP	"flashed" to burnout
6000		L	6/4-25-59WCP	"flashed" to burnout
18000		M	1/5-2-59WCP	Special heater
18000		M	2/5-2-59WCP	Special heater
18000		M	1/5-9-59WCP	Special heater
18000		M	3/5-9-59WCP	Special heater

In the lower temperature range of the above titanium carbide runs there was some sintering of the carbide but the bond formed was very weak. In the high temperature range there was apparent melting and recrystallization of the TiC. The resultant material is bonded together very poorly. The appearance of this material is very similar to the appearance of zirconium carbide subjected to the same treatment.

SiC + B4C (50-50% by weight)
(13 runs)

9000	2400	S	1/3-25-59GEB	
9000	2900	L	1/4-22-59GEB	
9000	3300	L	1/4-14-59GEB	
9000	3300	L	2/4-22-59GEB	
9000	3600	L	2/4-14-59GEB	
9000	3700	L	3/4-14-59GEB	
9000	4100	L	2/4-1-59GEB	
9000	4900	S	1/4-1-59GEB	
9000	5000	S	2/3-30-59GEB	
9000	5500	S	3/3-25-59GEB	
9000	6600	S	1/3-25-59GEB	
9000	23000	S	2/3-25-59GEB	"Flashed" (exploding wire)

Nominal Pressure (Atm.)	Max. Temp. Attained (°C)	Sleeve Size: Small, Medium, Large	Run Identification	technique.) Comments
7800	"flashed"	L	3/4-1-59GEB	Apparatus exploded

Rather well sintered compacts of the mixture $B_4C + SiC(1:1 \text{ wt. } \%)$ are obtained at temperatures as low as 2000°C. Samples prepared at the higher temperatures are about the same in appearance as those prepared in the neighborhood of 2000° but at the higher temperatures the graphite sleeve seems to "weld" to the sample.

These runs were made with the hope of obtaining some additional samples suitable for compression tests but none were obtained.

ZrC (10, runs)

9000	2600	M	3/4-21-59HEC
9000	2900	S	6/6-10-59MAR
18000	2900	S	1/6-11-59MAR
15000	4200	S	4/6-10-59MAR
9000	5000	S	5/6-10-59MAR
15000	6600	S	1/6-10-59MAR
18000	6600	S	2/6-11-59MAR
18000	6600	S	3/6-11-59MAR
15000	6700	S	2/6-10-59MAR
15000	6800	S	3/6-10-59MAR

At 3000°C there is a slight sintering of the zirconium carbide powder. At the high temperatures achieved in the above runs there is an apparent melting, with decomposition, so that the resultant product obtained on rapid cooling consists of angular grains approximately 1/2 millimeter across separated by flakes of graphite surrounding each grain. The grains are not very strong and can be readily crushed under a spatula. At temperatures near 5000° there is an apparent melting and re-crystallization on cooling without noticeable decomposition. The re-crystallized grains are much larger than the powder grains used in the starting material. They are a dark, silvery-gray in color and are bonded together only weakly.

B + Pred. 1:1
atomic percent
(7 runs)

12000	900	S	1/4-23-59GEB
12000	1300	S	3/4-22-59GEB
6000	1400	L	4/4-23-59GEB
12000	1800	L	3/4-23-59GEB
12000	1900	S	2/4-23-59GEB
6000	3300	S	1/5-1-59GEB
12000	6000	S	2/5-1-59GEB

At temperatures of 1800°C and above, a silvery, black, hard polycrystalline material was produced. The agglomerate is quite strong. The graphite sleeve is "welded" to the polycrystalline agglomerate. This material is not noticeably attacked by boiling hydrochloric acid or aqua regia. The material is easily worn away by a silicon carbide grinding wheel. It is a good electrical conductor. The product is probably BP which has recently been prepared by other procedures. At the higher temperatures an occasional spherical ball of this hard black material, was found within a matrix of pyrophyllite. Immediately surrounding the spherical ball was a layer of graphite. It is possible that the graphite sleeve may be entering into the reaction taking place in these experiments. We hope to gain further information concerning this system by means of x-ray diffraction.

BN + Pred. 1:1
at % (3 runs)

9600	2500	S	2/5-7-59GEB
12000	2800	S	1/5-7-59GEB
12000	5500	S	1/5-6-59GEB

Nominal Pressure (Atm.)	Max. Temp. Attained (°C)	Sleeve Size: Small, Medium, Large	Run Identification	Comments
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There appeared to be no reaction between the boron nitride and the red phosphorus in the above experiments. However, the red phosphorus was converted to black phosphorus in each run.

B₄C + Pred.

(4 runs)

9000	2900	S	2/5-20-59GEB
9000	4700	S	1/5-20-59GEB
9000	6700	S	2/5-16-59WCP
9000	7000	S	1/5-16-59WCP

In the run at 2900°C there was a segregation of the material. The red phosphorus was converted to black phosphorus. There are, however, some shiny black and dull black intermixed regions. Both regions are very hard. The shiny region is a very good electrical conductor while the dull region is semi-conducting. At the higher temperature there also seems to have been a segregation of materials but the shiny and dull-black regions noted in the lowest temperature run are not observed at the higher temperature. The red phosphorus, again, was converted to black phosphorus.

Al + Pred. 1:1

at. %

(2 runs)

15000	1600	M	1/6-9-59HEC
15000	3000	M	2/6-9-59HEC

A grayish, soft, non-adherent powder was observed in the above run aluminum and red phosphorus powders.

Al₂O₃ (5 runs)

2400	2500	L	6/5-16-59WCP
2400	3300	L	5/5-16-59WCP
4200	6000	S	3/5-16-59WCP
9000	7000	S	1/6-15-59HEC
4800		L	4/5-16-59WCP

This material was fused into a white, polycrystalline. very strong mass under all range of temperatures used in the above experiments.

MnO₂ + Mn, 1:1

mole (5 runs)

18000	1500	S	3/6-12-59MAR
18000	1600	S	1/6-12-59MAR
18000	1700	L	4/6-12-59MAR
9000	2600	S	4/6-11-59MAR
18000	3300	S	2/6-12-59MAR

At the lower temperatures a sintered, black, fine, polycrystalline mass was observed. The material is fairly soft and is readily scratched by a sharp steel point. At the higher temperatures the same black material formed at the lower temperature was present, but seemed to be more dense and somewhat stronger. At the higher temperatures there was also a small amount of fine grain, green materials, formed. At the higher temperature a low melting "glass", light yellow brown in color, formed inside and outside of the graphite tube by mixing with the pyrophyllite. This low melting glass readily caused "cut-off" and limited the maximum temperature that could be obtained in these runs to a rather low value.

MnO₂ + Mn (1:1

mole) + 8 weight

% cobalt binder (3

runs)

18000	1600	S	1/6-16-59MAR
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Nominal Pressure (Atm.)	Max. Temp. Attained (°C)	Sleeve Size: Small, Medium, Large	Run Identification	Comments
18000	2400	L	2/6-15-59MAR	
18000		L	3/6-15-59MAR	short circuit

These runs were made to determine if cobalt would bind the sintered mass together and give it increased strength. However, the cobalt was not miscible with the material and segregated from it forming a spherical ball.

Fe₂O₃ (4 runs)

9000	625	L	2/6-18-59MAR
18000	670	L	4/6-18-59MAR
9000	1300	S	2/6-17-59MAR
9000	1700	L	3/6-17-59MAR

Cut-off problems with ferric oxide occurred at a rather low temperature. In the run at 1700° a shiny black, weakly magnetic, coherent, strong solid was obtained. This material is not scratched by a hard steel point but is easily worn away by a silicon carbide grinding wheel. The material crystallized in long needles growing radially from a central axis. These needles form a strong coherent mass.

Fe₂O₃ + Fe, 1:1 mole (6 runs)

9000	1600	S	3/6-16-59MAR	
18000	1600	S	4/6-16-59MAR	
	1600	S	1/6-19-59MAR	wedge-type bomb
9000	2500	S	2/6-16-59MAR	
18000	2600	S	1/6-15-59MAR	
		S	2/6-19-59MAR	wedge-type bomb shorted

It is difficult to obtain a very high temperature with the above mixture because of cut-off problems. In the runs near 2500° a black, strong, hard, slightly magnetic material is obtained. Embedded in this material are spherules of iron which are surrounded by a thin layer of graphite flakes. The black material is difficult to dissolve in boiling hydrochloric acid or aqua regia.

Fe₃O₄ (2 runs)

9000	570	L	1/6-18-59MAR
18000	705	L	3/6-18-59MAR

A high temperature was not obtained in the above runs because of cut-off problems.

Fe₃O₄ + Fe, 1:1 mole (1 run)

9000	1500	S	1/6-17-59MAR
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The material resulting from the above run was similar in appearance to that obtained with a mixture of Fe₂O₃ + Fe.

There follow 92 runs in which materials were subjected to moderate pressures (about 6,000 - 20,000 atmospheres) at rather high temperatures - 1500° - 10,000°C. Standard x-ray diffraction films were prepared on the starting materials subjected to high pressure, high-temperature prior to their being subjected to these conditions. Those materials that by visual examination indicated x-ray studies might be useful were then subjected to x-ray diffraction. These results are given later. Microscopic examination was made of all of these samples and observations concerning these examinations are given. Electrical resistance of a sample was measured by clamping the sample in one clip of an ohmmeter and then touching a pointed steel probe connected to the other ohmmeter lead to the sample surface. Such a measurement, of course, is only a qualitative indication as to whether the material is an insulator, semi-conductor or metallic conductor. All these samples were run in graphite heater tubes unless otherwise indicated.

A. Oxide Systems.

Run # 1/6-22-59 MAR tapered bomb Fe₂O₃ + Fe

Pressure about 8000 atmospheres. Maximum temperature about 2900°C. (very rough estimate)

Reaction occurred. Shiny, black, polycrystals (small) intergrown--occasionally a ball of metal. Electrical resistance about 30 ohms.

Hardness:-Does not scratch glass. Seems to be only one solid phase present.

Run # 2/6-22-59 MAR same as above

Pressure about 8000 atmospheres. Maximum temperature about 1800°C (very rough estimate).

Product dull black, mottled, If crystalline, crystals are very tiny. Seems to be a faint metallic network throughout mass. Electrical resistance about 4 ohms.

Hardness: Does not scratch glass. Material is slightly magnetic.

Run # 1/6-25-59 MAR tapered bomb $\text{Fe}_2\text{O}_3 + \text{Fe}$

Pressure about 5000 atmospheres. Maximum temperature about 1500°C. (Very rough estimate).

Mottled appearance—same as #2/6-22-59 MAR, due apparently to separation of two phases. Darker colored phase has electrical resistance of about 1000 times greater than lighter phase. Overall appearance is dull black. Lighter colored phase electrical resistance about 4 ohms.

Run # 6/6-24-59 MAR $(\text{MnO}_2 + \text{Mn}) + 25 \text{ wt } \% \text{ Ni binder}$

Pressure about 2400 atmospheres. Maximum temperature about 940°C.

Reaction occurred and a rather strong cermet was obtained. There are two definite solid phases present and a fine metallic network. Matrix is dark gray with an imbedded light metallic appearing gray phase. This cermet does not scratch glass. It is quite shock resistant. Qualitatively as good as cemented tungsten carbides. Individual grains in the material are quite large. The matrix has a very low electrical resistance (< 1 ohm). The light, gray metallic appearing phase has a medium electrical resistance (about 2000 ohm). This material warrants further study in regard to mechanical properties. Material is magnetic.

Run # 3/6-22-59 MAR $(\text{MnO}_2 + \text{Mn}) + 25 \text{ wt } \% \text{ Ni binder}$

Pressure about 900 atmospheres. Maximum temperature about 900°C.

Characteristics same as above. One compressive test was run. Failure occurred at 375,000 p.s.i.

Run # 2/6-25-59 MAR tapered bomb MnO_2

Pressure about 8000 atmospheres. Maximum temperature about 950°C.

A dense, dark gray material formed. It is hard (scratches glass) and is fine-grained. Resistance is about 20 megohm. In another section of the specimen there were two phases present and the grains were larger. Light metallic gray particles present in a darker matrix had a point electrical resistance of about 10,000 ohms. Material is brittle but strong. Material is weakly magnetic.

Run # 9/6-24-59 MAR tapered experimental bomb $(\text{MnO}_2 + \text{Mn}) + 25 \text{ wt } \% \text{ Ni binder}$

Pressure about 8000 atmospheres. Maximum temperature about 940°C. (Rough estimate).

Material is very similar to # 6/6-24-59 MAR.

Run # 1/6-26-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$

Pressure about 8000 atmospheres. Maximum temperature about 1050°C. (Rough estimate).

Reaction occurred. Black, hard substance formed (scratched glass readily). Fine-grained in some sections-coarse in others. Two phases are present. Electrical resistance of one is

about 1 ohm. Electrical resistance of the other is about 5,000 ohm. Material is non-magnetic.

Run # 2/6-26-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$
Pressure about 8000 atmospheres. Maximum temperature about 1050°C. (Rough estimate).

Material more uniformly fine-grained than above run. Under the microscope there seems to be a few tiny dark particles and a greater number of larger metallic gray particles in a dark gray matrix. The material is fairly tough and very hard. Electrical resistance is about 20 megohms.

Run # 1/6-29-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$ experimental tapered bomb.
Pressure about 4000 atmospheres. Maximum temperature about 1000°C. (rough estimate).

Characteristics similar to # 2/6-26-59 MAR. A few point contacts could be found where the electrical resistance was about 10 ohms. but most contacts gave a resistance greater than, 20 megohms.

Run # 1/7-1-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$
Pressure about 18,000 atmospheres. Maximum temperature about 2500°C.
Material characteristics same as # 1/6-29-59 MAR except it is more glossy in appearance.

Run # 2/7-1-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$ Troubles- abandoned.

Run # 3/7-1-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$ in nickel heating tube.
Pressure about 18,000 atmospheres. Maximum temperature about 1100°C.
Characteristics of the material same as previous run.

Run # 4/7-1-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$ in nickel heating tube.
Pressure about 9000 atmospheres, Maximum temperature about 1050°C.
Material obtained has characteristics similar to that of the previous run.

Run # 5/7-1-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$
Pressure about 9000 atmospheres. Maximum temperature about 1500°C.
Characteristics similar to above materials. However, material is more glossy in appearance and also more homogeneous in appearance. This may have resulted from the fact that the maximum temperature was held for 35 minutes in this run whereas in the above runs the maximum temperature was maintained for a period of 1 to 3 minutes only. In this run, a silvery, metallic film was deposited on the outside, cylindrical surface of the sample.

Run # 1/7-2-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$
Pressure about 9000 atmospheres. Maximum temperature about 1625°C held for 35 minutes.
Characteristics of material after run are very similar to run # 5/7-1-59.

Run # 2/7-2-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$
Pressure about 3000 atmospheres. Maximum temperature about 1500°C.
Material obtained similar to that of above runs.

The main material formed in all of the above runs is undoubtedly CrO.

Run # 1/7-21-59 MAR $\text{Cr}_2\text{O}_3 + \text{Cr}$
Pressure about 12,000 atmospheres. Maximum temperature about 1450°C.
Material same as that obtained in previous runs.

- Run # 2/6-29-59 MAR Cr_2O_3
 Pressure about 8000 atmospheres. Maximum temperature about 1500°C.
 A coherent, very fine-grained, dull black (with slight tinge of green) solid formed. This solid forms a green powder when pulverized. It is very hard and readily scratches glass. It seems to be almost as hard as carboloy grade 883 (cemented WC 6% Co binder). Electrical resistance is greater than 20 megohms. One specimen, subjected to compressive test, failed at about 50,000 p.s.i. I believe, however, that the inherent strength is much greater than this. The material is just, slightly magnetic (attracted by a magnet.)
- Run # 3/6-29-59 MAR Cr_2O_3
 Pressure about 18,000 atmospheres. Maximum temperature about 1600°C.
 Material obtained has same characteristics of that of run # 2/6-29-59 MAR.
- Run # 1/7-3-59 MAR Cr_2O_3
 Pressure about 9000 atmospheres. Maximum temperature about 975°C.
 Material obtained has same characteristics as above.
- Run # 1/7-13-59 HEC NiO
 Pressure about 9000 atmospheres. Maximum temperature about 2600°C.
 Nickel sheath formed near the graphite heating tube. Central regions consist of black, fine-grained solid which can be scratched by a steel needle. Electrical resistance of this material is greater than 20 megohms. It is somewhat magnetic.
- Run # 4/7-14-59 HEC ZnO
 Pressure about 9000 atmospheres. Maximum temperature about 2800°C.
 The oxide seems to have fused. It is white with a tinge of gray. It can be scratched with a needle point. Electrical resistance is about 3000 ohms. (point contact).
- Run # 5/7-14-59 HEC CaO
 Pressure about 9000 atmospheres. Maximum temperature about 6500°C.
 Material fused but properties unchanged. Did not react with carbon heater. Some CaO did escape through carbon heater and react with pyrophyllite, however.
- Run # 1/6-30-59 MAR $\text{MoO}_3 + 2\text{Mo}$
 Pressure about 18,000 atmospheres. Maximum temperature about 7000°C.
 The graphite heater seems to have entered into the reaction and reduced MoO_3 to Mo metal.
- Run # 2/6-30-59 MAR $\text{MoO}_3 + 2\text{Mo}$
 Pressure about 18,000 atmospheres. Maximum temperature about 2500°C.
 Graphite again entered into reaction reducing MoO_3 .
- Run # 1/7-15-59 HEC $\text{Al}_2\text{O}_3 + \text{Al}$
 Pressure about 9000 atmospheres. Maximum temperature about 2500°C.
 There seems to have been no reaction to form AlO but, rather, a network of Aluminum metal surrounding small crystals of Al_2O_3 seems to have formed. The material is coherent and quite strong.
- Run # 2/7-16-59 HEC $2\text{Re}_2\text{O}_7 + 10\text{Re}$
 Pressure about 9000 atmospheres. Maximum temperature about 2650°C.
 Some brilliant red ReO_3 made. Most of sample seems to be original ingredients. Any reaction was slight. Material can be readily scratched with a needle point.

Summary Statement on Above Oxide Systems

Among the oxide systems studied, the following would seem to be of further interest because of their electrical properties. ZnO, (Cr₂O₃ + Cr), (MnO₂ + Mn + 25 wt % Ni), (Fe₂O₃ + Fe).

The following appear to warrant attention because of their mechanical properties. Cr₂O₃, (MnO₂ + Mn + 25 wt % Ni), and (Cr₂O₃ + Cr).

B. Sulfide Systems

- Run # 1/7-27-59 MAR W + S powders tapered bomb
 Pressure about 8000 atmospheres. Maximum temperature about 1500°C.
 A gray-black, coherent body was produced. The material is rather soft and leaves a black streak on paper. Electrical resistance 2-100 ohms.
- Run # 1/7-28-59 MAR W + S powders.
 Pressure about 12,000 atmospheres Maximum temperature about 3500°C.
 Material produced is similar to #1/7-27-59 MAR.
- Run # 1/7-30-59 MAR W + S powders.
 Pressure about 15,000 atmospheres Maximum temperature about 6400°C.
 Material produced is similar to #1/7-27-59 MAR.
- Run # 3/7-31-59 MAR W + S powders.
 Pressure about 15,000 atmospheres.
 Experimental difficulties—run abandoned.
- Run # 4/7-31-59 MAR W + S powders.
 Pressure about 15,000 atmospheres Maximum temperature about 3500°C.
 Carbon sleeve not used. Heating accomplished by passing current through a tungsten wire imbedded in the sample. Material produced is similar to run # 1/7-27-59 MAR.
- Run # 1/8-3-59 MAR W + S powders.
 Pressure about 18,000 atmospheres Maximum temperature about 4300°C. Material produced is similar to run # 1/7-27-59 MAR.
- Run # 2/8-3-59 MAR W + S powders.
 Pressure about 24,000 atmospheres.
 Broke pistons—run abandoned.
- Run # 1/8-6-59 MAR W + S powders.
 Pressure about 15,000 atmospheres Maximum temperature about 4600°C.
 Material produced is similar to run # 1/7-27-59 MAR except crystals of WS are much larger and have grown radially from the centerline of the cylindrical sample.
- Run # 2/8-6-59 MAR W + S powders.
 Pressure about 15,000 atmospheres Maximum temperature about 3500°C.
 Tungsten strip heater used in place of graphite sleeve. Material produced is similar to that of run # 1/7-27-59 MAR.
- Run # 4/7-30-59 MAR Ta + S powders.
 Pressure about 12,000 atmospheres Maximum temperature about 4500°C.
 A hard (scratches glass), silvery, polycrystalline, coherent, product was obtained.
 Electrical resistance about 1 ohms.
- Run # 3/7-30-59 MAR Mo + S powders
 Pressure about 12,000 atmospheres Maximum temperature about 6700°C.
 Silvery, needle-like polycrystalline, coherent product obtained. The product can be scratched with a dissecting needle. Electrical resistance is less than 1 ohm.

- Run # 2/7-31-59 MAR Zn + S powders.
 Pressure about 12,000 atmospheres Maximum temperature about 4100°C.
 Lustrous, polycrystalline, faintly brownish mass obtained. It can be scratched with a needle. Its electrical resistance is greater than 20 megohms.
- Run # 1/7-31-59 MAR Co + S powders.
 Pressure about 12,000 atmospheres. Maximum temperature about 1650°C.
 Golden, fine-grained, coherent, polycrystalline, brittle product obtained. Material is hard but will not scratch glass. Electrical resistance is about .2 ohm.
- Run # 3/7-27-59 MAR Fe + S powders.
 Pressure about 1200 atmospheres.
 A golden, brittle, polycrystalline substance was obtained. Its electrical resistance is about 1 ohm. It is ferromagnetic.
- Run # 2/7-28-59 MAR Mn + S powders.
 Pressure about 9000 atmospheres. Maximum temperature about 1100°C.
 Dark gray, coherent, polycrystalline solid obtained. Material is weakly magnetic. It is readily scratched with dissecting needle. Electrical resistance is about 100 ohm.
- Run # 1/7-29-59 MAR Mn + S powders.
 Pressure about 9000 atmospheres. Maximum temperature about 1200°C.
 Product similar to above run.
- Run # 2/7-30-59 MAR Mn + S powders
 Pressure about 12,000 atmospheres Maximum temperature about 5600°C.
 Product similar to above but electrical resistance is 1000-10,000 ohms. In the hottest sample region there was considerable reaction of the MnS with the pyrophyllite.
- Run # 1/7-23-59 MAR Cr + S powders.
 Pressure about 12,000 atmospheres Maximum temperature about 4600°C.
 Silvery, brittle, polycrystalline, fine-grained product obtained. It is weakly magnetic. Electrical resistance is about 1 ohm. Material can be scratched with a needle point.
- Run # 3/7-23-59 MAR Cr + S powders.
 Pressure about 18,000 atmospheres Maximum temperature about 7000°C.
 High temperature was held for about 1 minute. Graphite heater, CrS and pyrophyllite all intermixed and reacted. Graphite dissolved in pyrophyllite and re-precipitated as large flakes in cooler regions. Products formed unknown.
- Run # 4/8-7-59 MAR Si + S powders.
 Pressure about 12,000 atmospheres. Maximum temperature about 2100°C.
 Most of the material obtained has the appearance and properties of silicon. A small amount of golden material that may be SiS was obtained as was also a small amount of silvery material that may be SiS₂. The electrical resistance of these two materials was greater than 20 megohms.
- Run # 3/8-6-59 MAR C + 2S powders.
 Pressure about 9000 atmospheres. Maximum temperature about 3000°C.
 The sulfur and carbon reacted to form a fairly soft solid. The material may be similar to solid CS₂ produced by P. W. Bridgman from liquid CS₂. Its electrical resistance is about .5 ohm. Pyrophyllite mixed with product.
- Run # 4/8-6-59 MAR C + 2S powders.
 Pressure about 6000 atmospheres. Maximum temperature about 1300°C.

Product similar as above.

- Run # 5/8-6-59 MAR C + 2S powders.
Pressure about 6000 atmospheres. Maximum temperature about 370°C.
Seems to have been no reaction or only slight reaction.
- Run # 1/8-7-59 MAR C + 2S powders.
Pressure about 6000 atmospheres. Maximum temperature about 800°C.
Material formed is similar to run # 3/8-6-59 MAR.
- Run # 2/8-7-59 MAR C + S powders.
Pressure about 6000 atmospheres. Maximum temperature about 800°C.
Product is similar in appearance to run # 3/8-6-59. However, its electrical resistance is about 50 ohm.
- Run # 3/8-7-59 MAR C + S powders.
Pressure about 6000 atmospheres. Maximum temperature about 3500°C.
Appearance of product is similar to run # 3/8-6-59 MAR. Electrical resistance is about .2 ohm.
- Run # 1/8-11-59 MAR B + S powders.
Pressure about 12,000 atmospheres. Maximum temperature about 5500°C.
The graphite (heater tube), boron, sulfur and pyrophyllite intermixed and reacted giving a very heterogeneous product. There were small particles present that would scratch glass.
- Run # 2/8-11-59 MAR B + S powders.
Pressure about 12,000 atmospheres. Maximum temperature about 3300°C.
Product same as above.

C. Carbide Systems.

- Run # 3/7-16-59 HEC WC powder
Pressure about 9000 atmospheres. Maximum temperature about 7500°C.
Material bonded together to form a strong compact mass.
- Run # 4/6-24-59 HEC TaC powder.
Pressure about 9000 atmospheres. Maximum temperature about 3000°C.
Material bonded together to form a compact mass. Color is still golden.
- Run # 5/6-24-59 HEC TaC powder.
Pressure about 9000 atmospheres. Maximum temperature about 2700°C.
Product same as above.
- Run # 8/6-24-59 HEC TaC powder.
Pressure about 9000 atmospheres. Maximum temperature about 3500°C.
Product same as above.
- Run # 3/7-10-59 HEC Mo₂C powder.
Pressure about 9000 atmospheres. Maximum temperature about 5700°C.
Product is silvery color. It definitely melted in hottest region and formed a very shiny, metallic body. Crystals are large.
- Run # 4/7-10-59 HEC Mo₂C powder.
Pressure about 9000 atmospheres. "Flashed" to maximum temperature of 6600° C. for 3 seconds only.
Product is pearly gray, very fine-grained and very strong.

- Run # 1/7-10-59 HEC NbC powder.
Pressure about 9000 atmospheres. Maximum temperature about 5300°C.
Material fused in hottest region--sintered in cooler areas. Product is fine-grained. Color is brown.
- Run # 2/7-10-59 HEC NbC powder.
Pressure about 9000 atmospheres. Maximum temperature about 5400°C.
Product same as above.
- Run # 1/6-24-59 HEC ZrC powder.
Pressure about 9000 atmospheres. Maximum temperature about 2700°C.
Material partially sintered. Appearance same as original powder.
- Run # 2/6-24-59 HEC ZrC powder.
Pressure about 9000 atmospheres. Maximum temperature about 2700°C.
Product same as above.
- Run # 3/7-14-59 HEC ZrC powder.
Pressure about 9000 atmospheres. Maximum temperature about 6600°C.
In the hottest sample region the ZrC seems to have melted and decomposed, recrystallizing in large grayish, friable crystals with large graphite flakes at the grain boundaries.
- Run # 2/7-14-59 HEC B4C powder.
Pressure about 9000 atmospheres. Maximum temperature about 4600°C.
Sample melted in hottest region forming compact, dark gray, metallic appearing mass.
Electrical resistance varies from 5 to 1000 ohms.
- Run # 1/7 -17 -59 HEC B4C powder.
Pressure about 9000 atmospheres. Maximum temperature about 4500°C.
Product same as above.

D. Miscellaneous Systems.

- Run # 1/7-10-59 HEC ZrB₂ powder.
Pressure about 9000 atmospheres. Maximum temperature about 9000°C.
Sample melted in hottest region. Material is silvery in color. (Original powder was dull gray.) It seems almost as hard as tungsten carbide. Electrical resistance is less than .1 ohm. Material is very metallic in appearance. Material is weakly ferromagnetic.
- Run # 2/7-10-59 HEC ZrB₂ powder.
Pressure about 9000 atmospheres. Maximum temperature about 6500°C.
Product is similar to above. A compressive test on a 1/8" diameter by 1/8" long specimen was run. Failure occurred at 300,000 p.s.i.
- Run # 3/7-10-59 HEC ZrB₂ powder.
Pressure about 9000 atmospheres. Maximum temperature about 8500°C.
Product is similar to above. In one spot, ZrB₂, flowed through the graphite heater tube into molten lava surrounding the tube and solidified to form a large globule. Simultaneously, molten lava (pyrophyllite) flowed inside the heater tube to replace the escaping ZrB₂
- Run # 2/7-15-59 HEC ZrB₂ powder.
Pressure about 9000 atmospheres. Maximum temperature about 7700°.
Material did not fuse.

- Run # 1/7-16-59 HEC ZrB₂ powder.
Pressure about 7000 atmospheres. Maximum temperature about 6000°C.
Product similar to run # 1/7-10-59 HEC.
- Run # 2/7-18-59 HEC ZrB₂ powder.
Pressure about 6000 atmospheres. Maximum temperature about 10,000°C. for 35 seconds.
The graphite heating tube dissolved in the molten ZrB₂ and upon cooling precipitated out as graphite flakes between large grains of ZrB₂. (The latter may still contain some carbon.) The large ZrB₂ crystals can be readily crushed but they are hard enough to scratch glass.
- Run # 2/7-13-59 HEC TiB₂ powder.
Pressure about 9000 atmospheres. Maximum temperature about 6400°C.
Product is very similar to ZrB₂ in appearance. Original powder was brownish. In daylight the product has a bright silvery appearance but in artificial light the material has a gold cast. In the hottest zone, lava, graphite, and TiB₂ all mixed and apparently reacted. At least three phases appear to have separated on cooling--all different in properties from the starting materials. Electrical resistance of fused material is less than .1 ohm.
- Run # 3/7-15-59 HEC TiB₂ powder.
Pressure about 7000 atmospheres. Maximum temperature about 2300°C.
Material compacted but did not fuse.
- Run # 4/7-13-59 HEC TiB₂ powder.
Pressure about 6000 atmospheres. Maximum temperature about 4100°C.
Product similar to # 2/7-13-59 HEC.
- Run # 1/7-14-59 HEC TiB₂ powder.
Pressure about 6000 atmospheres. Maximum temperature about 7000°C.
Product similar to run # 2/7-13-59 HEC. One piece .207" diameter by 3/8" long was subjected to compressive test. Failure occurred at 417,000 p.s.i. load.
- Run # 3/7-15-59 HEC TiB₂ powder.
Pressure about 9000 atmospheres. Maximum temperature about 7000°C.
Product similar to run # 2/7-13-59 HEC. One piece .228" diameter by 3/8" long was subjected to compressive test. Failure occurred at 540,000 p.s.i. load.
- Run # 1/8-12-59 MAR TiN powder.
Pressure about 12,000 atmospheres Maximum temperature about 2700°C.
Brown powder fused to gold colored solid in hottest region. Electrical resistance of this material is less than .1 ohm. Material is not as hard as WC.
- Run # 1/7-22-59 MAR MoSi₂ powder
Pressure about 12,000 atmospheres Maximum temperature about 1800°C. A silvery gray, compact product was obtained. It is ground away quite readily with a SiC wheel. Electrical resistance is less than .1 ohm.
- Run # 2/7-22-59 MAR MoSi₂ powder
Pressure about 18,000 atmospheres Maximum temperature about 3200°C.
Product same as above.
- Run # 4/7-22-59 MAR MoSi₂ powder
Pressure about 18,000 atmospheres Maximum temperature about 4600°C.
Product similar to above.

Run # 2/7-21-59 MAR Zirklor powder (a proprietary, high temperature Zirconium chloride).
Pressure about 12,000 atmospheres Maximum temperature about 1000°C.
Material decomposed.

Run # 3/7-21-59 MAR Zirklor
Pressure about 12,000 atmospheres Maximum temperature about 5700°C.
Zirklor, graphite and pyrophyllite have intermixed and reacted.

Run # 4/7-21-59 MAR Zirklor
Pressure about 12,000 atmospheres Maximum temperature about 1400°C.
There was some decomposition yielding Zr metal. Most of the material was soft, dull black and is waxy or pasty. It is an electrical insulator. A tiny amount of red material formed on the surface of the Zirklor next to the graphite tube.

The following runs were made in the Tetrahedral Anvil high-pressure, high temperature apparatus. (See Rev. Sci. Instr. 29, #4, pp. 267-275, April 1958, for a description of this device.) Anvil size is $\frac{3}{4}$ inch (length of triangle leg on face). All runs were made at a pressure of 94,500 atmospheres.

Temperature at the mid-point of the heater tube is estimated from the measured power input to the graphite heater tube from a graph of power input as a function of temperature as indicated by a Pt-Pt 10% Rh thermocouple up to the couple's useful working limit of about 1750°C. These calibration measurements were made at 95,000 atmospheres with pyrophyllite inside the graphite heater tube. Similar runs with SiC inside the graphite heater tube (the thermal conductivity of SiC is at least an order of magnitude greater than that of pyrophyllite) given the same curve. In these experiments and those that follow, the tetrahedron is made of lava and the current tabs are made of tantalum metal.

Materials subjected to high pressure simultaneously with high temperatures are listed below together with comments made upon microscopic examination of the product obtained.

As in previous work at the lower pressures, several minutes time is taken to reach the maximum temperature in a given run. The highest temperature achieved is held for several minutes in the lower range of temperatures. At intermediate temperatures, the temperature is maintained for shorter periods of time and at the highest temperatures achieved, the temperature is maintained for only a few seconds, as a general rule.

Pressure is always applied before temperature. After heating, heating power is abruptly terminated to quench the sample. This is followed by reduction of pressure to one atmosphere.

A. Oxides at 94,500 atmospheres:

Run # 2/9-11-59 HEC ZnO powder
Maximum temperature 2250°C.
Graphite dissolved in the molten ZnO and precipitated out as large flakes with the ZnO body on cooling. This is interesting because the temperature and pressure are such that diamond is thermodynamically stable over graphite. Despite this, dissolved carbon precipitates as graphite rather than diamond. The author has observed this phenomena previously in other non-metallic substances in which carbon is soluble at high pressure and temperature. The ZnO starting material was snow white in color. The product obtained was very definitely yellow.

Run # 1/8-25-59 HEC Fe₂O₃ powder
Maximum temperature 1400°C.
Product is black in color. It is not very hard. It is a good electrical conductor.

Run # 2/8-25-59 HEC Fe₃O₄ powder
Maximum temperature 1875°C.
Product is black and is quite hard. It is a poor electrical conductor. There are some small patches of green material scattered throughout the black material.

Run # 3/9-8-59 HEC Fe₂O₃ + Fe Powder

Maximum temperature 2075°C.
Product is black, glassy, hard, brittle, and a poor electrical conductor.

Run # 3/9-9-59 HEC Fe_2O_3 + Fe Powder

Maximum temperature 2275°C.
Product is black, shiny, hard, brittle and semi-conductor.

Run # 3/9-11-59 HEC MnO_2 powder

Maximum temperature 1775°C.
Product is heterogeneous green and black, non-conducting, relatively soft solid.

Run # 2/9-9-59 HEC MnO_2 + Mn powders

Maximum temperature 1950°C.
Product consists of large, shiny, black polycrystals plus a lighter colored, fine-grained matrix that seems to consist of two phases—one lighter in color than the other. The darker crystals grew in a compact mass near both ends of the cylindrical sample. In this region individual crystals were elongated with their axis parallel to the sides of the cylinders. A few isolated large black crystals also grew in the central region of the lighter colored mass. Polycrystals are somewhat waxy. Not all the Mn metal reacted. Some of it melted into spherules. Products' electrical resistance is greater than 20 megohms. Material is magnetic.

Run # 1/9-9-59 HEC MnO_2 + Mn + 25% Ni Powders

Maximum temperature 2000°C.
Product had large black and lighter colored fine-grained crystals as above. The nickel did not cement the mass together but melted into a mass by itself. A few tiny diamonds were formed.

Run # 4/9-8-59 HEC Cr_2O_3 + Cr powders

Maximum temperature 2250°C.
Product is dark black and is easily pulverized. Some of the Cr did not react. The product is magnetic. Its electrical resistance is in the range of 5-500 ohm.

Run # 1/8-10-59 HEC Al_2O_3 powder

Maximum temperature 1680°C.
Powder slightly sintered.

Run # 1/9-11-59 HEC Al_2O_3 powder

Maximum temperature 2400°C.
Material sintered into a compact, hard, white mass.

Run # 1/9-10-59 HEC Al_2O_3 + Al powders

Maximum temperature 1935°C.
Product is a white powder. No aluminum metal is visible. Material is a non-electrical conductor.

Run # 2/9-10-59 HEC Al_2O_3 + Al powders

Maximum temperature 2500°C.
Product is same as above but contains graphite crystals.

B. Sulfides at 94,500 atmospheres.

Run # 2/8-26-59 HEC W + S powders

Maximum temperature 1775°C.
Explosion—Sample lost.

- Run # 4/8-26-59 HEC W + S powders
Maximum temperature 2350°C.
Shiny, black, soft, elongated, electrically conducting crystals grew radially from central axis of sample.
- Run # 2/8-27-59 HEC Ta + S powders
Maximum temperature 2650°C.
Product has a silvery, metallic appearance. It is quite soft and is a good electrical conductor.
- Run # 1/8-27-59 HEC Ta + S powders
Maximum temperature 2700°C.
Explosion—Sample lost.
- Run # 2/9-8-59 HEC Sn + S powders
Maximum temperature 2180°C.
Product is black, lustrous, soft, elongated crystals growing radially from cylinder axis. Electrical resistance is about 500 ohm.
- Run # 3/8-27-59 HEC Zn + S powders
Maximum temperature 2200°C.
Product is polycrystalline, rather large-grained, soft, non-conducting white solid.
- Run # 1/9-8-59 HEC Mo + S powders
Maximum temperature 2750°C.
Product is very hard, gray colored, metallic appearing solid. Electrical resistance is low.
- Run # 5/9-9-59 HEC Co + S powders
Maximum temperature 2650°C.
Product is a golden, brittle, electrically conducting polycrystalline mass.
- Run # 4/8-27-59 HEC Fe + S powders
Maximum temperature 2160°C.
Product is polycrystalline mass that can readily be broken apart. Large, shiny black crystals grow near the ends. (The end regions are cooler than the middle section of the cylindrical sample.) Fine-grained dull black crystals are found in the mid section. Electrical resistance is 2 to 5 ohms.
- Run # 1/8-28-59 HEC Mn + S powders
Maximum temperature 2375°C.
Product is black, soft and non-conducting (electrically).
- Run # 1/9-4-59 HEC Cr + S powders
Maximum temperature 2375°C.
Product is fine-grained, lustrous black, fairly hard and has an electrical resistance of 2-500 ohms.
- Run # 1/9-2-59 HEC Si + S powders
Maximum temperature 2200°C.
Product consists of black, large rather soft polycrystals. Material is non-electrical conductor.
- Run # 2/9-4-59 HEC C + 2S powders
Maximum temperature 2800°C.
Product is soft, waxy, black solid. Electrical resistance is about 500 ohms.

- Run # 1/9-3-59 HEC C + S powders
Maximum temperature 2800°C.
Product same as above but resistance is about 20 ohm.
- Run # 5/9-8-59 HEC B + S powders
Maximum temperature 1850°C.
Product is a mass of soft silvery-gray, elongated polycrystals. Electrical resistance is about 1 megohm. This is a new material. Its structure is diamond cubic with $a = 4.33 \text{ \AA}$.
- C. Carbide Systems at 94,500 atmospheres
- Run # 6/8-25-59 HEC ReC powder.
Maximum temperature 2250°C.
Product slightly sintered. Material is relatively soft. Electrical resistance is less than .1 ohm.
- Run # 5/8-25-59 HEC WC powder.
Maximum temperature 2750°C.
Product is well sintered, strong, grayish solid with an electrical resistance of less than .1 ohm.
- Run # 2/7-23-59 HEC TaC powder
Maximum temperature 2200°C.
Product is well sintered, strong, gold colored, fine-grained solid with an electrical resistance less than .1 ohm.
- Run # 5/8-7-59 HEC TaC powder
Maximum temperature 1525°C.
Product same as above.
- Run # 3/8-25-59 HEC Mo₂C powder.
Maximum temperature 2800°C.
Product consists of large silvery crystals. Electrical resistance is less than .1 ohm.
- Run # 2/8-24-59 HEC NbC powder.
Maximum temperature 1675°C.
Explosion—Some samples remained. It has a metallic gray-gold luster, is very hard and has an electrical resistance of less than .1 ohm.
- Run # 1/8-24-59 HEC ZrC powder
Maximum temperature 1450°C.
Material weakly sintered.
- Run # 3/8-7-59 HEC SiC powder
Maximum temperature 2150°C.
Material sintered into gray-green solid.
- Run # 3/8-26-59 HEC B₄C powder
Maximum temperature 1575°C.
Product is black, very hard, well sintered mass with an electrical resistivity of about 5000 ohms.
- D. Miscellaneous Materials
- Run # 1/7-18-59 HEC ZrB₂ powder
Maximum temperature 2150°C.

Product has a steel-gray, fine-grained metallic appearance. Electrical resistance is less than .1 ohm.

- Run # 1/7-20-59 HEC ZrB_2 powder
 Maximum temperature 1100°C.
 Explosion—lost sample.
- Run # 1/7-21-59 HEC ZrB_2 powder
 Maximum temperature 1950°C.
 Product same as # 1/7-18-59 HEC.
- Run # 2/7 21-59 HEC ZrB_2 powder
 Maximum temperature 1450°C.
 Explosion—lost sample.
- Run # 3/7-22-59 HEC ZrB_2 powder
 Maximum temperature 2050°C.
 Product appears same as run # 1/7-18-59 HEC
- Run # 6/8-7-59 HEC TiB_2 powder
 Maximum temperature 1800°C.
 Product is hard, silvery, metallic solid. Electrical resistance is less than .1 ohm.
- Run # 4/9-11-59 HEC Al + P (red) powder
 Maximum temperature 2750°C.
 Explosion—lost sample.
- Run # 1/9-12-59 HEC Al + P (red) powder
 Maximum temperature 2500°C.
 Product is fine, light gray powder. Its electrical resistance is greater than 20 megohms. It burns in air when ignited.
- Run # 1/8-5-59 HEC B + P (red) powders
 Maximum temperature 2500°C.
 Product is black, soft, fine-grained solid. Electrical resistance is 5 ohm. X-ray analysis shows product to be a new, well-defined face centered cubic material with $a = 4.54 \text{ \AA}$.
- Run # 2/8-5-59 HEC BN + P (red) powders
 Maximum temperature 2075°C.
 Product is mixture of soft black and soft white crystals. Electrical resistance ranges from 50 to 10,000 ohms.
- Run # 4/8-25-59 HEC B_4C + P (red) powders.
 Maximum temperature 2500°C.
 Product consists of large, lustrous, black polycrystals with graphite flakes at the grain boundaries. The large crystals are very hard. Electrical resistance is about 10 ohms.
- Run # 2/8-12-59 HEC TiN powder
 Maximum temperature 1600°C.
 Product is hard, dense, gold colored metallic material.
- Run # 1/8-26-59 HEC TiN powder
 Maximum temperature 2300°C.
 Product similar to above but grains are larger and a small amount of a grayish second phase is present. This phase appears to have precipitated on cooling.

Run # 4/9-9-59 HEC Zirklor
 Maximum temperature 1900°C.
 Material decomposed, apparently giving off chlorine which passed through the graphite tube into the pyrophyllite. The material remaining is a soft, whitish-brown powder. It is non-conducting electrically.

Run # 6/9-9-59 HEC MoSi₂ powder.
 Maximum temperature 2650°C.
 Product is metallic silvery gray in color. It is fine-grained and hard. Its electrical resistance is .2 ohm.

Standard X-ray photographs using the Debye-Scherrer powder method with the film in the Straumanis position were made on preceding samples for which visual observation indicated that this might be worthwhile. The photographs have been compared with similar photographs of the starting material before it was subjected to high-pressure, high-temperature conditions. The results of this comparison have been divided into three categories as follows:

Category I. Samples for which no significant change was indicated by a comparison of the "before" and "after" X-ray photographs.

Category II. Samples for which no variation was indicated in crystal structure, but the particle size and orientation of crystallites after the run differed from that of the starting materials, indicating that recrystallization had probably taken place.

Category III. Samples in which a significant change took place after high-pressure, high-temperature treatment. Each individual sample will be described in these cases.

Category I. (No change) runs are listed below:

TaC	Run # 8/6-24-59
TaC	Run # 2/7-23-59
NbC	Run # 2/8-24-59
NbC	Run # 1/7-10-59
B ₄ C	Run # 2/7-14-59
NiO	Run # 2/12-29-59
NiO	Run # 1/7-13-59
Fe ₂ O ₃	Run # 1/9-25-59
Fe ₃ O ₄	Run # 2/8-25-59
Cr ₂ O ₃ + Cr	Run # 4/9-9-59
Al ₂ O ₃ + Al	Run # 1/7-15-59
Al + P	Run # 1/9-12-59

Category II. runs are listed below with some comments on the probable change in crystallite sizes after a run compared to the size before the run. Some shifts in lattice parameter are also noted. Starred systems warrant additional X-ray study.

*Re + C	Run # 3/7-16-59	lattice parameter a increased by about 1%.
Re + C	Run # 6/8-25-59	lattice parameter a shifted about 1.0% with excessive line broadening.
WC	Run # 5/8-25-59	larger crystallites.
WC	Run # 5/7-10-59	larger crystallites.
TaC	Run # 5/8-7-59	excessive line broadening.
Mo ₂ C	Run # 3/8-25-59	much larger crystallites.
ZrC	Run # 3/6-10-59	much larger crystallites.

ZrC	Run # 3/7-14-59	line broadening.
TiC	Run # 1/12-29-59	smaller crystallites.
SiC	Run # 3/8-7-59	crystallites much smaller.
B ₄ C	Run # 3/8-26-59	some line broadening.
ZrB ₂	Run # 2/7-11-59	line broadening.
ZrB ₂	Run # 3/7-11-59	line broadening.
ZrB ₂	Run # 1/7-18-59	lines excessively broad $\Delta d/d$. approximately .5%
ZrB ₂	Run # 3/7-15-59	line broadening.
TiB ₂	Run # 6/8-7-59	smaller crystallites, line broadening
MoSi ₂	Run # 4/7-22-59	larger crystallites, high orientation.
MoSi ₂	Run # 2/7-22-59	smaller crystallites, some line broadening.
MoSi ₂	Run # 6/9-9-59	larger crystallites, some line broadening.
MoSi ₂	Run # 4/7-22-59	smaller crystallites.
TiN	Run # 1/8-26-59	line broadening.
Si + S	Run # 2/9-2-59	smaller crystallites.
Al ₂ O ₃	Run # 1/8-10-59	larger crystallites.
Al ₂ O ₃	Run # 1/9-11-59	much larger crystallites.

Category III. Runs and comments follow: Starred systems warrant additional X-ray study. Items doubly starred seem of more interest than those that are singly starred.

*Re ₂ O ₇ + 10Re	Run # 2/7-16-59	Black product gave multiplicity of low density lines plus all standard lines. Red product gives well defined simple cubic pattern with a $= 3.74\text{\AA}$
*W + S	Run # 4/8-26-59	Tungsten structure weak, set of other lines of low symmetry is present.
Ta + S	Run # 2/8-27-59	Tantalum structure disappeared. Multiplicity of lines. Excessive line broadening.
Mo + S	Run # 8/9-8-59	Original structures disappeared. Amorphous type pattern.
Sn + S	Run # 2/9-8-59	Multiplicity of lines at low angles. Amorphous type pattern.
ZnO	Run # 2/9-11-59	Slight distortion of crystal structure amounting to about .0013%. Some lines sharp, some broad.
**Zn + S	Run # 3/8-27-59	Sphalerite formed.
**NiO	Run 3/12-29-59	Change to Ni structure but with expanded lattice of about 1%. Excessive line broadening with $\Delta d/d$ approximately .4%.
*NiO	Run 1/7-13-59	Change to Ni structure but with expanded but with expanded structure of about .5%. Some line broadening but less than $\Delta d/d =$.1%
Note:	In the above NiO specimens, it appears that the graphite heater-sample tube has reduced the NiO to metallic nickel.	
Ni + B	Run # 1/12-22-59	Multiplicity of lines. Complex pattern.

${}^{\circ}\text{Co} + \text{S}$	Run # 5/9-9-59	Some new lines, large crystallites. Old lines present with some new lines. Troilite formed.
${}^{\circ}\text{Fe} + \text{S}$	Run # 4/8-27-59	
${}^{\circ}\text{Fe}_3\text{O}_4 + \text{Fe}$	Run #3/9-9-59	Original pattern disappeared. Wustite formed.
${}^{\circ}\text{Fe}_2\text{O}_3 + \text{Fe}$	Run # 3/9-8-59	Same as Run # 3/9-9-59
MnO_2	Run 3/9-11-59	Multiplicity of faint lines.
$\text{MnO}_2 + \text{Mn}$	Run 2/9-9-59	Three of four new lines. Large crystal size.
$\text{MnO}_2 + \text{Mn} +$ 25 wt.% Ni	Run 1/9-9-59	Same as $\text{MnO}_2 + \text{Mn}$.
${}^{\circ}\text{Mn} + \text{S}$	Run # 1/8-28-59	Alabandite formed.
${}^{\circ}\text{Cr} + \text{S}$	Run # 1/9-4-59	CrS of known structure formed.
${}^{\circ}\text{P} + \text{B}_4\text{C}$	Run # 4/8-25-59	Two new structures seem to be super-imposed. One is f.c.c. BP below.
${}^{\circ}\text{P} + \text{B}$	Run # 3/4 23-59	New material formed f.c.c. with $a = 4.54\text{\AA}$
${}^{\circ}\text{P} + \text{B}$	Run # 1/8-5-59	New material formed f.c.c. with $a = 4.54\text{\AA}$
${}^{\circ}\text{P} + \text{BN}$	Run # 2/8-5-59	Graphite, phosphorus and BN lines present in addition to some very definite new lines.
${}^{\circ}\text{Al}_2\text{O}_3 + \text{Al}$	Run # 1/9-10-59	Three or four new lines plus all old lines.
${}^{\circ}\text{Al}_2\text{O}_3 + \text{Al}$	Run # 2/9-10-59	Same as above.
${}^{\circ}\text{C} + 2\text{S}$	Run # 2/9-4-59	Graphite lines plus multiple amorphous-type lines.
${}^{\circ}\text{C} + \text{S}$	Run # 1/9-3-59	Enormous number of lines.
${}^{\circ}\text{B} + \text{S}$	Run # 5/9-8-59	New material. Diamond cubic structure $a = 4.33\text{\AA}$.
Zirklor	Run # 4/9-9-59	A multiplicity of faint lines.

In the above X-ray examinations, broad lines indicate lattice distortions or the presence of small crystallites less than .1 micron diameter. Smooth lines indicate no distortion or relatively small crystallites of 1-5 microns diameter. A "spotty" pattern indicates crystallite size greater than 20 microns.

In conclusion, this research has developed a moderate pressure, high-temperature device that makes it possible to obtain temperatures at least as high as 10,000°C. in condensed systems for short periods of time, i.e., periods of several seconds.

With this new tool a survey has been made of several carbide, boride, nitride, phosphide, oxide, sulfide, and some miscellaneous systems to determine the effects of such high temperature on them. The systems that showed changes that may be of interest to other investigators have been listed. A new boron phosphide and boron sulfide are of particular interest. One material produced under these high temperature conditions may have immediate practical use. This is the fused silicon carbide which possesses a 30-fold superior property of compressive strength over that of ordinary hot-pressed silicon carbide, and which may well hold promise as a cutting tool material.

Personnel, other than the principal investigator, associated with this project part of the time during the contract term were:

Dr. Billings Brown, Department of Chemical Engineering
 Dr. Lane A. Compton, Department of Physics
 Mr. F. K. Nielsen, Department of Physics
 Dr. J. Dean Barnett, Department of Physics
 Mr. Herbert E. Christensen, Physics student
 Mr. Mark A. Rasmussen, Physics student
 Mr. George E. Bone, Physics student

Mr. William C. Powell, Physics student
Mr. Bruce R. Nelson, Chemical Engineering student
Mr. N. Ross Gordon, Chemical Engineering student
Mr. D. Clifton Carlson, Chemistry student.

Their invaluable assistance is gratefully acknowledged. Thanks is due also to Mr. Fred Childs and his associates of the B.Y.U. Science Instrument Shop for their efforts in the construction of the many experimental components and devices utilized during the course of this research.

Respectfully submitted,
H. Tracy Hall

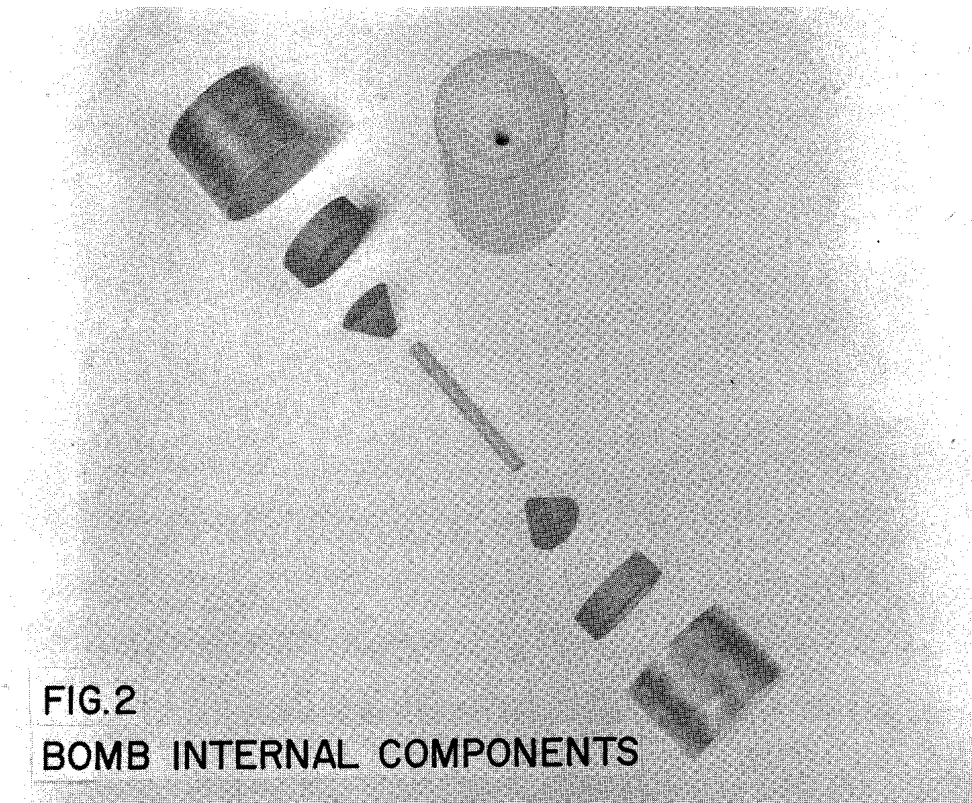
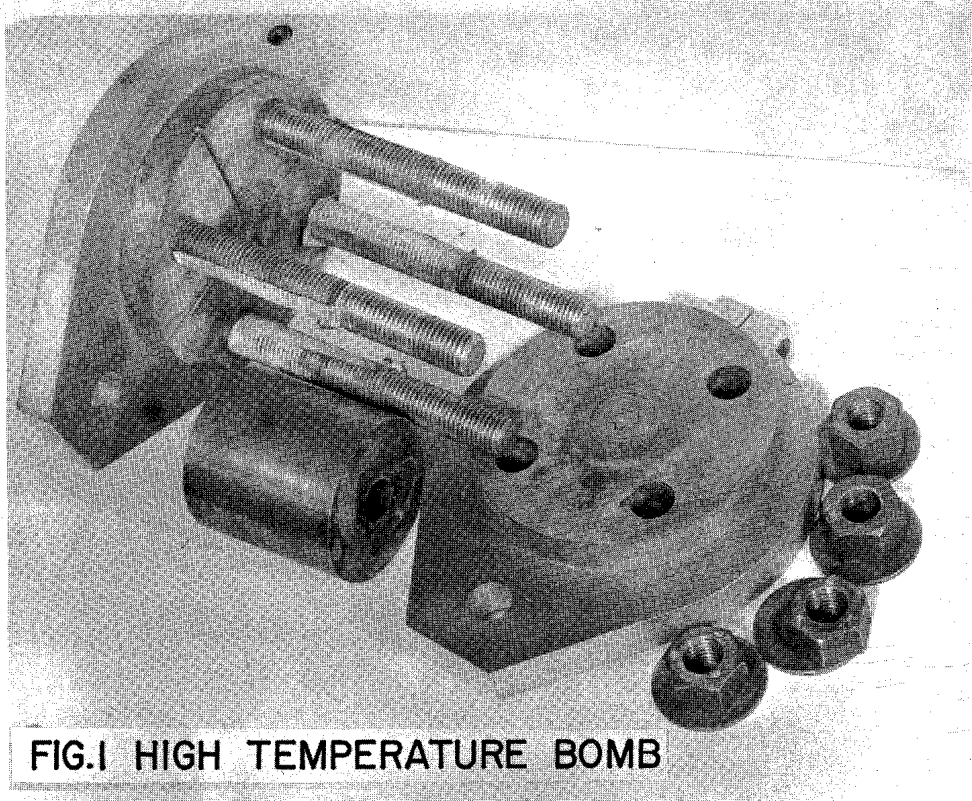


FIG. 4 TYPICAL TEMPERATURE CALIBRATION

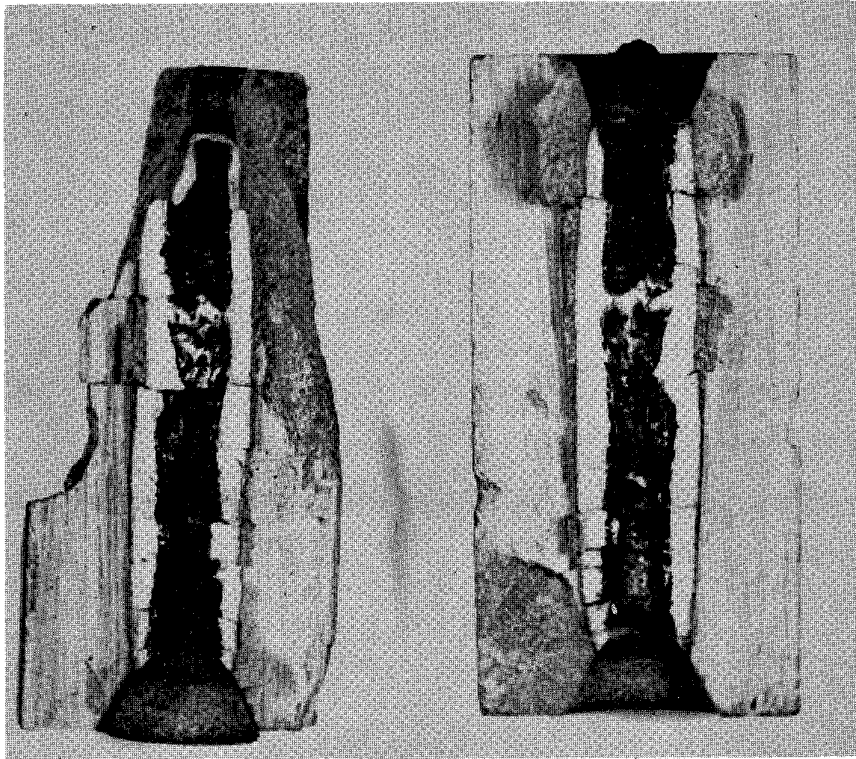
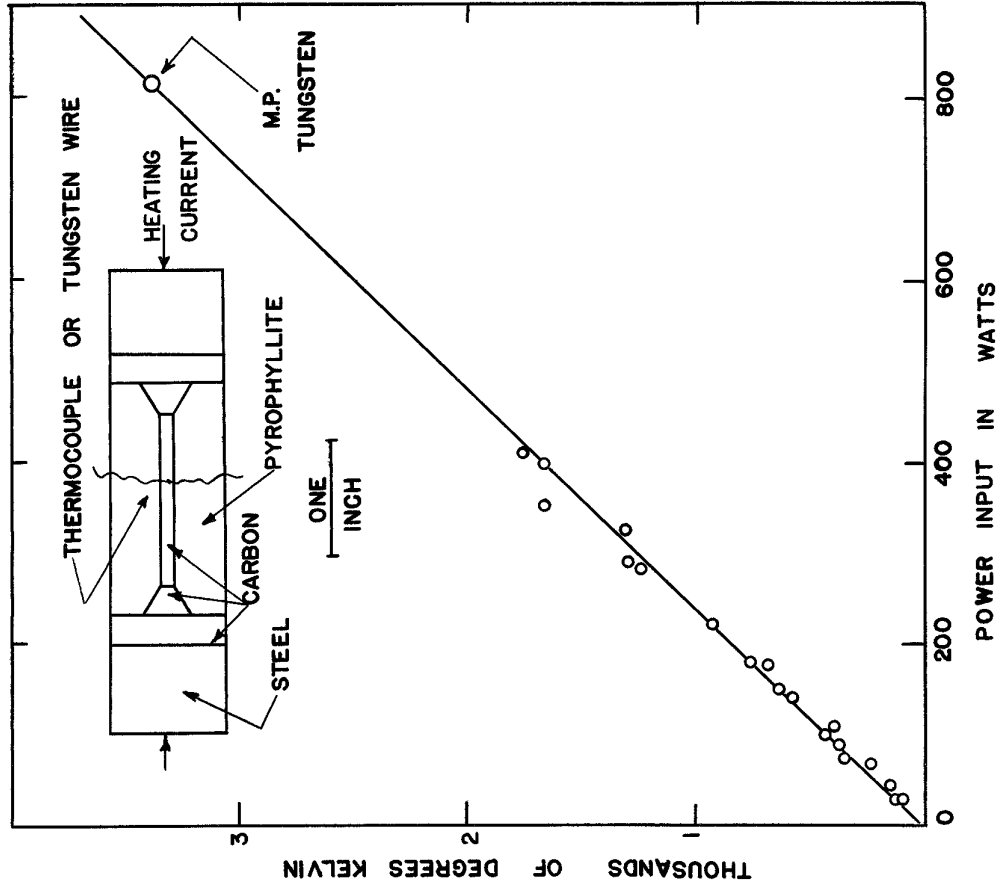


FIG. 3 PYROPHYLITE ASSEMBLY (SiC HEATER)
AFTER 15 SECONDS AT 3000 WATTS
(APPROXIMATELY 10,000°C)

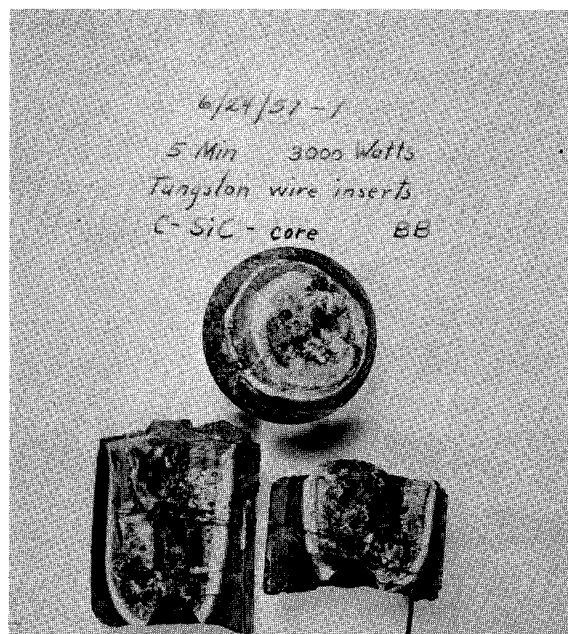


FIG. 5. PYROPHYLLITE ASSEMBLY (SiC-C HEATER) AFTER 5 MINUTES AT 3,000 WATTS (INITIAL TEMPERATURE APPROXIMATELY 10,000°C)

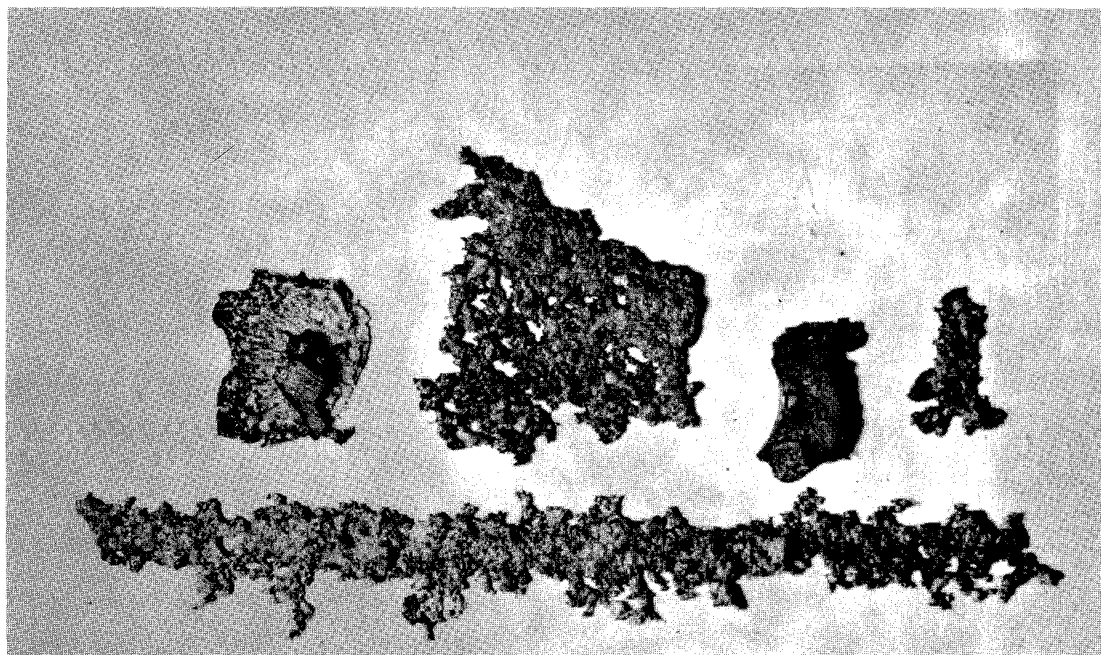


FIG. 6. MOLTEN MATERIAL TAKEN FROM TEST-PIT WALL AFTER BOMB EXPLOSION.

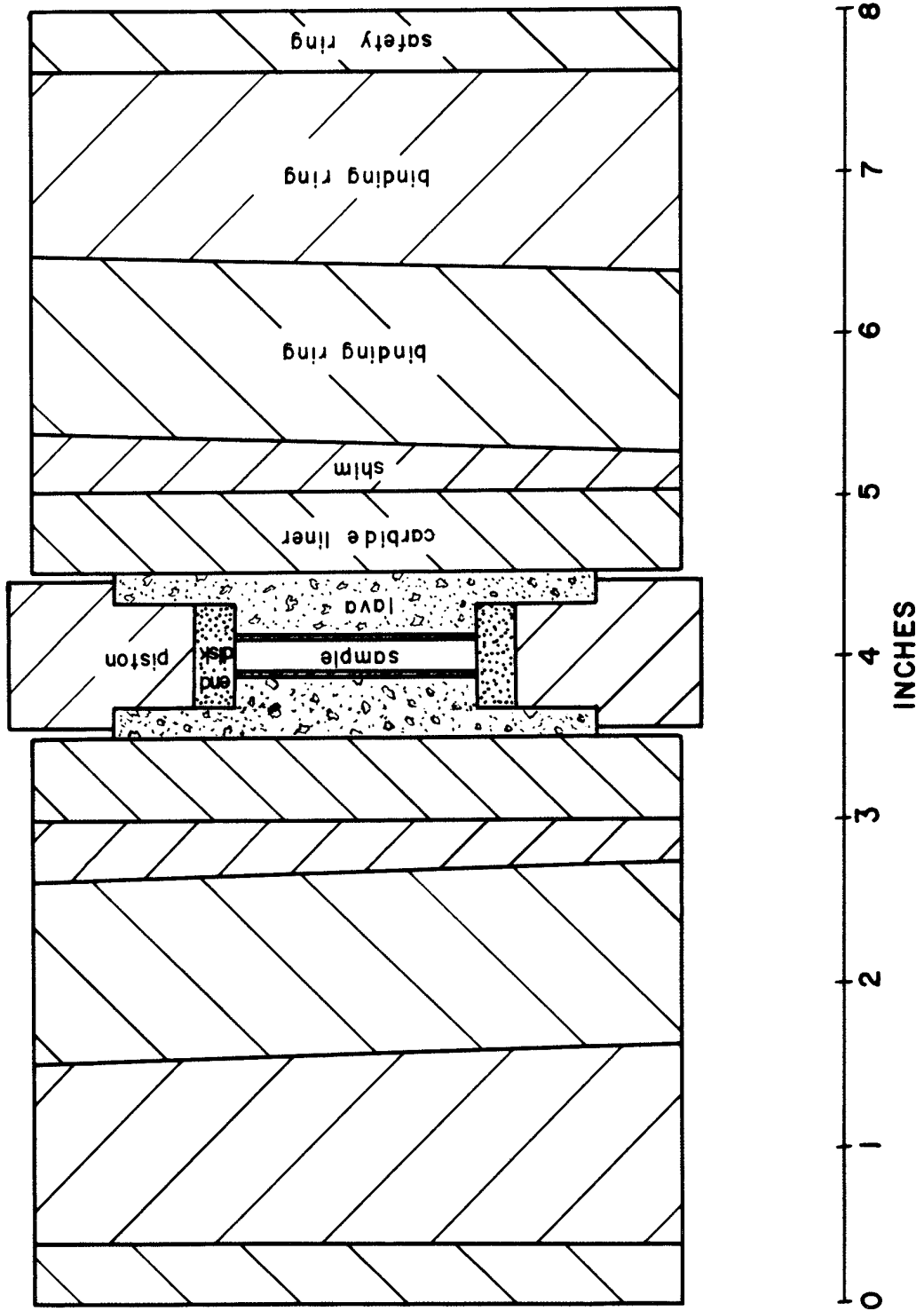


FIG. 7 HIGH TEMPERATURE BOMB

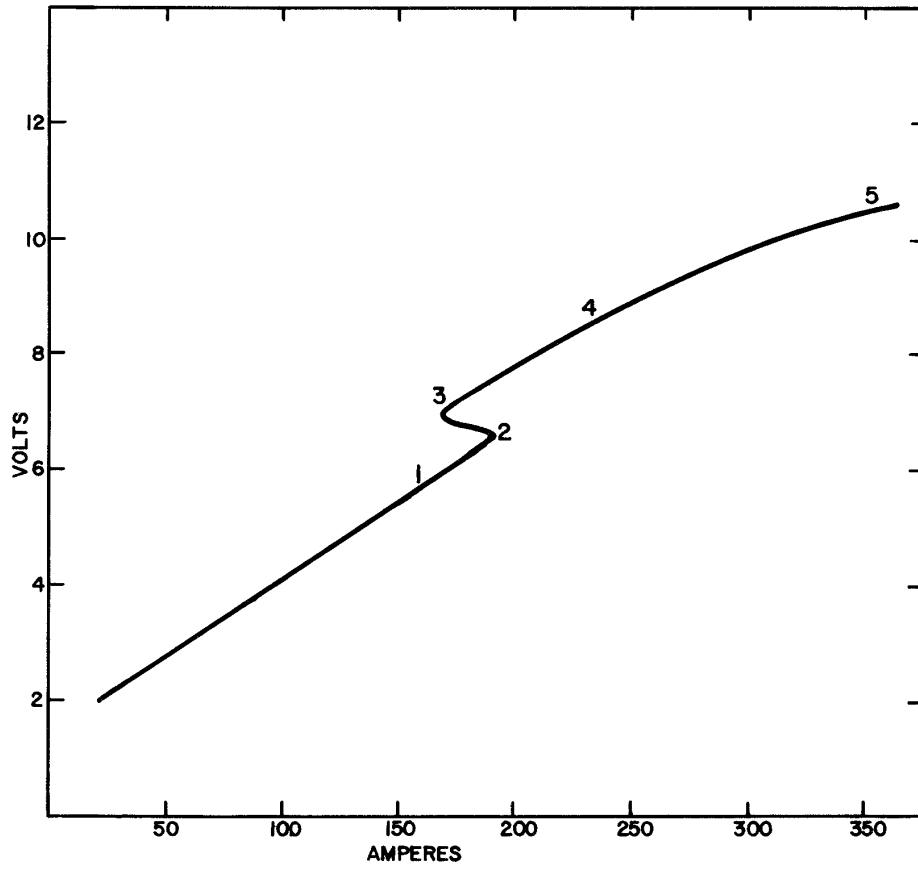


FIG. 8 TYPICAL VOLTAGE-CURRENT CURVE for SiC POWDER in GRAPHITE HEATING TUBE

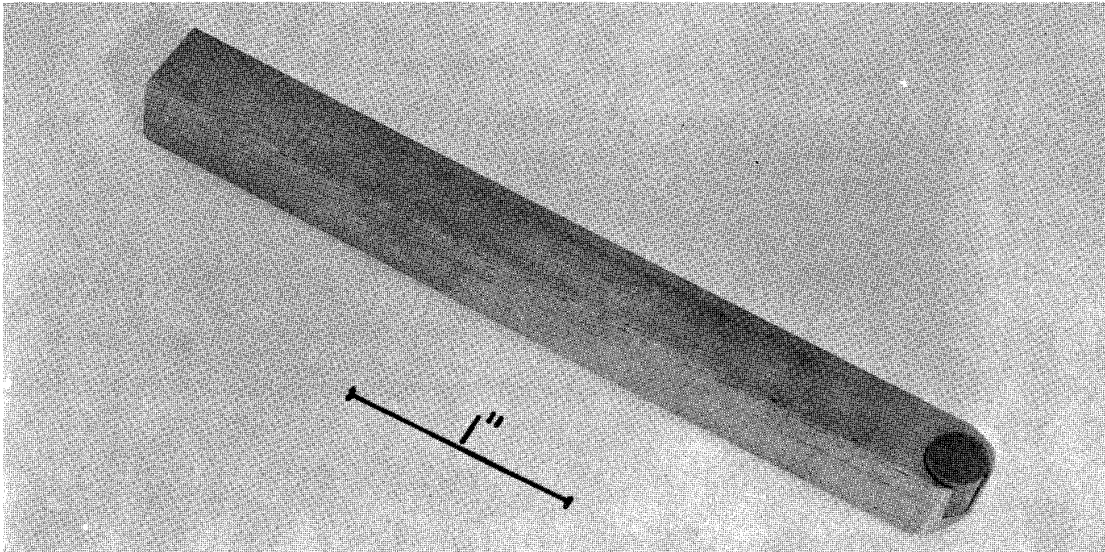


FIG. 9 EXPERIMENTAL SiC CUTTING TOOL

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