H. T. Hall

APPLICATION OF ULTRAHIGH-PRESSURE HIGH-TEMPERATURE EQUIPMENT TO STUDY OF UO$_2$ REACTIONS

app.

BATTELLE MEMORIAL INSTITUTE

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by

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APPLICATION OF ULTRAHIGH-PRESSURE HIGH-TEMPERATURE
EQUIPMENT TO STUDY OF UO_2 REACTIONS

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Equipment and techniques for high-pressure high-temperature solid-state studies were developed, and some preliminary results for the reaction of uranium oxides with other oxides were obtained.

A new die design has been evolved which appears suitable for any work currently contemplated. The maximum capabilities of this new die are as yet undetermined, but its theoretical pressure limit is in excess of 200,000 atm. The die differs from similar equipment in that internal heating of the sample is employed and maximum pressure and temperature can be maintained simultaneously.

Most of the preliminary work on materials synthesis has been performed at pressures up to 40,000 atm and temperatures to 1000 C. No reactions have been found in the system UO_2 and U_3O_8 with BeO while under pressure. However, a possible reaction between Sc_2O_3 and UO_2 has been detected which was not detected at normal pressure. Sc_2O_3 reacted with U_3O_8 under pressure as it does at ambient pressure.

A new high-pressure high-temperature phase of U_3O_8 has been produced. Preliminary study of the U_3O_8 pressure-temperature phase diagram has been made. The crystal structure of the new U_3O_8 phase has not yet been determined.

BACKGROUND

A significant portion of the understanding of pressure and its effects on material which we have today is directly attributable to the work of Bridgman.[1] This work was concerned both with the development of equipment for high-pressure research and with the use of such equipment to study materials. In general, the bulk of Bridgman's work was conducted in liquid-pressure vessels devised to provide truly hydrostatic compression to 30,000 atm or less at ambient or slightly elevated temperatures. The materials investigated were in large part elements, metallic materials, simple salts, and some organic compounds. The information obtained consisted of compressibility data and measurements of electrical resistivity as a means of determining any transitions that might occur under pressure. The more recent research of Bridgman was concerned with development and use of equipment suitable for pressure research to 100,000 atm and beyond. This work was conducted at ambient or slightly elevated temperatures. Through such research a number of important transition points were thus determined, as well as the effects of pressure on a variety of materials.

The initial pressure research of Bridgman has been currently extended by others in two main areas: (1) determination of the effect of pressure on existing materials, and (2) utilization of pressure combined with temperature as a means of synthesizing new materials.

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(1) References at end.

INTRODUCTION

Synthesis

The early pressure research of Bridgman was extended by others in the synthesis field, notably by Coes[2] of the Norton Company and later by Hall of the General Electric Company[3]. Both devised methods of simultaneously obtaining high temperature and high pressure. This development ultimately culminated in the synthesis of coesite, a dense form of silica and the production of diamond[3] and later Borazon[4]. While diamond itself apparently first was synthesized at moderately elevated temperature and 53,000 atm, by carrying the transformation out at high temperature, the reaction proceeded at much faster rates. The significance of the role of chemical kinetics on the rate of production of new materials under high pressure has been summarized by Hall.[5]

Briefly, it has been shown that for a new material to be produced, both the thermodynamic free energy and the free energy of activation of the rate process must be favorable. For purposes of synthesis, this second factor is quite significant. If the rate criterion is not satisfied, new phases will not be observed even when thermodynamically they would normally exist. Thus, in much of Bridgman's work, the lack of adequate temperature for acceleration of the rate process may have prevented the formation of some possible allotropic modifications.

In view of the importance of temperature with respect to the rate process, Hall invented a device called the "Belt". This apparatus was designed to produce diamonds in a few minutes instead of the many hours first required at moderate temperatures. Because of the importance of industrial diamonds to national defense, the Belt has been classified by the United States Government. Other high-temperature high-pressure devices have quite recently been described.[6]

To illustrate the potential area opened for investigation by combining temperature and pressure, Hall has published an interesting diagram[5] similar to that given in Figure 1. The performance levels of various type die units in this new area are directly compared. For static-pressure measurements, the supported Bridgman-anvil unit exceeds the capabilities of all units and reported values from 250,000 to 500,000 (Russian) atm have been claimed. When heat is applied to such a unit, the strength falls rapidly and for elevated temperatures the internally heated type die is superior. Pressure-temperature research on refractory materials will generally require temperatures in excess of the capabilities of the Bridgman-anvil unit.

In general, it appears feasible to "synthesize" new materials by two means, by transformation from one allotropic modification to another, or, alternatively, by chemical reactions under pressure and temperature. In the latter case new materials may be produced by reacting components which are normally nonreactive, or a chemical reaction may be used to augment production of a new phase. Diamond is an example of the latter in that the direct conversion of graphite to diamond is thermodynamically unfavorable and it is apparently produced by intermediate chemical reaction.[5]

rate-wise

Legend
× Diamond first made
⊗ Diamond commercially made
○ Borazon commercially made

Drickamer optical unit (ambient temperature only)

Belt-type die

New area

Bridgman-anvil-type unit

Tetrahedral anvil die

Belt type die

Right circular-cylinder die

Internally heated die can go to melting point of graphite

Old area

Pressure, 10^3 atm

400
300
200
100
0

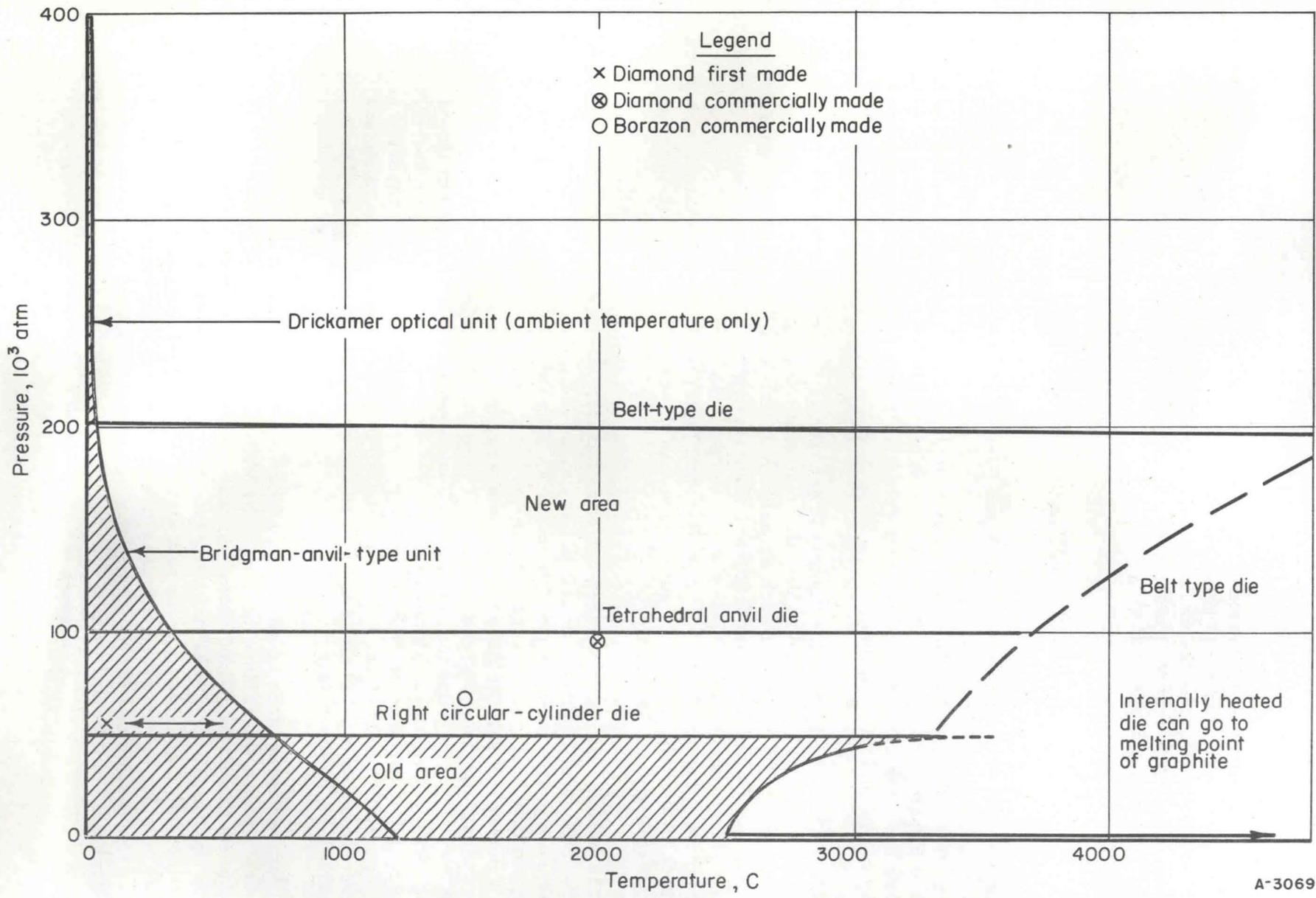0   1000   2000   3000   4000

Temperature, C

A-30690

FIGURE 1. PRESSURE-TEMPERATURE FEASIBILITY DIAGRAM

The availability of both diamond and graphite permitted determinations of the thermodynamic characteristics by which the conditions for diamond synthesis were anticipated. The structural similarity between hexagonal BN and graphite suggested that a cubic modification might exist, even in the absence of any thermodynamic data of the high-pressure phase. In general, however, new materials which may be formed under pressure will not be thermodynamically predictable. To avoid a completely empirical investigation of the "new" area, it appears necessary to develop some criteria for systematic investigation.

High-Pressure Solid-State Research

In addition to synthesis, research has been conducted in a number of areas on the behavior of materials at very high pressure. These include mineralogical research, shock-wave studies, and solid-state studies of the effect of pressure on the energy-band structure of semiconductors. With the exception of mineralogical research, most of this work has been conducted at ambient or only slightly elevated temperature and has not been concerned with synthesis.

The current trend in mineralogical research is to employ a Bridgman-anvil-type unit (described later) modified to provide heat similar to the Griggs and Kennedy[7] "simple squeezer". By use of such apparatus, McDonald[8] explored the quartz-coesite relationships. For higher temperatures, Wentorf used Hall's[9] Belt-type apparatus to study the garnet-hornblende relationship. Coes[10] has described synthesis of several other garnets. The application of simultaneous high pressure and temperature permits duplication in the laboratory of conditions within the earth's crust, making it possible to study mineralogical relationships.

The most promising research activity currently directed toward determining in detail the effects of pressure on solids has arisen from the determination of the effects of pressure on semiconductors and insulators. Physically, pressure has the effect of raising and broadening the electronic energy-band structure. The broadening which occurs generally results in decreasing the energy gap between the valence and the conduction bands, allowing electron transitions to occur. By observing the effect of pressure on the electronic structure of such solids, a better understanding of the effect of pressure will be possible. Theoretical analysis has predicted that all materials will become metallic at sufficiently high pressure.[11] Values have been reported at which solid hydrogen[12] and helium[13] are predicted to transform to metallic phases. Estimated pressures of 5×10^5 and 2×10^7 atm are required to accomplish this for hydrogen and helium, respectively.

Transient pressures of microsecond duration are produced by explosive-shock techniques. Shock waves have been used by Walsh, et al.,[14] to derive the equations of state of metals up to 500,000 atm. In other work, shock waves have been used in an attempt to produce transitions from the insulator to the metallic state.[15] The technique utilizes an explosive to produce a strong shock wave propagating through the solid. The wave velocity is measured and used to compute pressure versus compression in the samples. In this method it is assumed that the material behind the shock wave is in thermodynamic equilibrium. Since the material is subjected to a pulse of pressure of microsecond duration at a relatively low temperature, it appears unlikely that true

equilibrium would be obtained for many materials whose rate process requirements for a transition to proceed would be unfavorable. Thus, although the shock-wave technique is capable of extreme pressure, the higher temperature and longer time under pressure of static-type pressure research should prove more rewarding in producing transformations and reactions.

Direct comparison of the shock technique with static-pressure methods has recently been made by Griggs, et al.[16] Previous shock measurements had indicated a decrease in resistivity of $LiAlH_4$, iodine, and several alkali halides by a factor of 10^6 at pressures up to 280,000 atm. These results were not substantiated by static-pressure measurements of Griggs, et al.,[16] at pressures up to 240×10^3 atm. Since the temperature rise in shock-wave measurements is not known, static-pressure measurements were also extended to reasonable elevated temperatures and again the conversion to metallic conductivity was not detected. The failure of static-pressure measurements to confirm the shock-wave results would strongly support the argument that thermodynamic equilibrium is not obtained in the shock-wave studies.

The use of pressure as a tool to study materials has recently received increased attention in the field of solid-state research. The effect of static pressure in changing electronic structure was noted by Bridgman in early work on black phosphorus.[17] This material, which is ordinarily a semiconductor, exhibited a rapid decrease in resistivity, apparently becoming metallic between 25,000 and 55,000 atm.[18] Keyes[19] in later work concluded that the valence and conduction band of phosphorus should begin to overlap at 25,000 atm at which point it would, of course, be metallic.

Bridgman also found a great decrease in the resistance of tellurium under pressure.[20] This was examined theoretically by Bardeen[21] who considered the pressure dependence of the energy gap to explain the observed behavior. Later Bridgman[22] failed to confirm the tremendous decrease in resistance for tellurium although a decrease was found. At pressures near 32,000 atm tellurium becomes metallic as evidenced by a positive temperature coefficient of resistance. At 44,000 atm a new phase appears, which has a twentyfold decrease in resistance and is certainly metallic.

Later solid-state research has considered the effect of pressure on the Group IV and III-V type semiconductors. Here, however, in the low pressure ranges investigated to date, an increase in energy gap with pressure occurs, resulting in increasing resistance. The effect was observed by Miller and Taylor[23] for intrinsic germanium, by Hall, et al.,[24] for p-n junctions, and more recently by Paul and Brooks[25]. Bardeen and Shockley[26] examined theoretically the effect of pressure in germanium and devised a deformed potential theory for scattering of charge carriers as the explanation of observed behavior. At higher pressures Bridgman[27] observed a maximum in resistance in germanium at 50,000 atm, followed by a decrease to 100,000 atm. Hall[28] has measured the melting point of germanium to 180,000 atm and has reported a linear decrease with pressure from 936 C to 347 C at pressure.

The behavior of the Group III-V semiconductors has been investigated by Keyes[29] and Long[30], the former to 12,000 atm as a function of temperature from -78 to 300 C. As for germanium, in this limited pressure range a decrease in conductivity was observed, indicating an increase in energy gap between valence and conduction band. The behavior of these important materials at higher pressure has not been investigated.

Other types of solid-state research have recently been carried out using measurements other than conductivity. Drickamer[31] has developed apparatus for conducting optical-absorption studies to an estimated 250,000 atm and has described[32] results on a number of materials, for the most part energy-gap measurements in semiconductors. X-ray diffraction has been reported at pressures to 30,000 atm[33] and nuclear magnetic resonance to 10,000 atm[34]. Daniels and Smith[35] have recently determined the pressure derivatives of elastic constants of copper, gold, and silver by internal-friction measurements under pressure to 10,000 atm. In short, it would appear that pressure research in materials has expanded into a considerable portion of solid-state activity. To adequately discuss such work is not possible here; the recent text by Hamann summarizes much of the important work to 1956.[36] The work performed to date indicates that virtually every phase of materials technology either has been or may be investigated with pressure as a new variable.

CURRENT EXPERIMENTAL PROGRAM

The present investigation was undertaken to determine the feasibility of producing new high-temperature materials through use of combined high temperature and high pressure. In general, high-temperature materials are those which exhibit high cohesive energy density and high bond symmetry, and which do not possess transformations in their operational temperature range. Since high temperature and high pressure both tend to produce high bond symmetry and high pressure tends to produce high cohesive energy density (i.e., diamond), it appears feasible that new materials synthesized at extreme pressure and temperature may possess improved high-temperature properties.

Before any investigation of ultrahigh-pressure high-temperature effects on materials could be performed, it was first necessary to develop such equipment. The solutions to problems inherent in this phase of the investigation are discussed first, followed by the proposed program and progress to date on the materials phase of the investigation.

Experimental Work Equipment

At the outset of the investigation it appeared desirable to construct "conventional" equipment pending development of more advanced types. In view of the refractory nature of the materials that were proposed for this investigation, it was obvious that an internally heated die was required. For this reason, the conventional Bridgman-anvil-type unit described later was not deemed satisfactory and a right-circular-cylinder-type die was constructed. Experience gained with this equipment and the desire to achieve higher pressures indicated a more advanced die was required. The following describes details of five dies either proposed or constructed, the last of which holds considerable promise. This unit is tentatively deemed satisfactory for any high-temperature high-pressure work under present contemplation.

Bridgman-Anvil Die

The most commonly utilized solid-state high-pressure high-temperature die design is the Bridgman-anvil type.[37] This unit was modified by Griggs and Kennedy[7] to provide external heating. A simple schematic of the Battelle version of this unit is given in Figure 2 and the general performance region of such a device is that contained in Figure 1. By placing a miniature version of this type unit under 30,000 atm to provide additional support, Bridgman reached the highest pressure yet attained of 425,000 atm.[38] Current Russian work has reported attaining a pressure of 500,000 atm with this unit, apparently without any additional support, however.[39] Basically, the device consists of two abutting surfaces of tungsten carbide. The carbide usually contains between 3 and 6 w/o cobalt binder. For high-temperature use, Cr_3C_2 is substituted since it reportedly has better high-temperature strength than tungsten carbide.[40]

The sample in the form of a thin disk (0.010 in. thick) is placed between the two carbides and the load applied. The friction of the sample material against the carbide prevents pressure "blow-out" and nearly hydrostatic pressure is obtainable. Details of the use of this equipment have been adequately described[22,7], and it should suffice to point out here that the highest static pressures yet attained have been achieved in this type equipment. This occurs even in the absence of the additional support mentioned above. However, since the sample is heated by an external heater, the structural parts are simultaneously subjected to heat and a rapid loss of maximum pressure occurs with increasing temperature. Temperatures of the order of 2000 C required to react refractory materials would render such equipment useless.

Despite the high-temperature limitations, the Bridgman-anvil unit is highly attractive for laboratory use due to its extreme simplicity and low cost. For a large percentage of calibrating work it can also be used to augment the necessarily more complex internally heated high-temperature equipment.

Split Right-Circular-Cylinder Die

Equipment for use at higher temperatures than possible in the Bridgman anvil generally requires use of an internal heater constructed in such a way that the pressure-producing parts are not heated. Dies utilizing pistons which are right-circular cylinders of tungsten carbide have been used by Coes as reported by Roy and Tuttle[41] and also by Hall[6]. Since Hall has described the design and use of the right-circular-cylinder die[6], the only comments that are warranted here are those which are of a supplementary nature.

A modified right-circular-cylinder die design is shown in Figure 3. The main feature of this design lies in the fact that the die itself is split into an upper and lower half to allow powdered iron oxide or other electrical insulation to be applied. This permits resistance heating between the two parts marked by the plus and minus sign. The die itself is composed of an inner tungsten carbide part supported by multiple binding rings of progressively softer steel going from the center. The binding rings have been described by Hall.[6] The sample chamber of the die is contained in the center and an upper and lower piston of tungsten carbide are next to the sample. The bottom carbide piston is completely supported and both the bottom piston and die are supported from beneath by a solid carbide block, which in turn is supported by a large steel support.
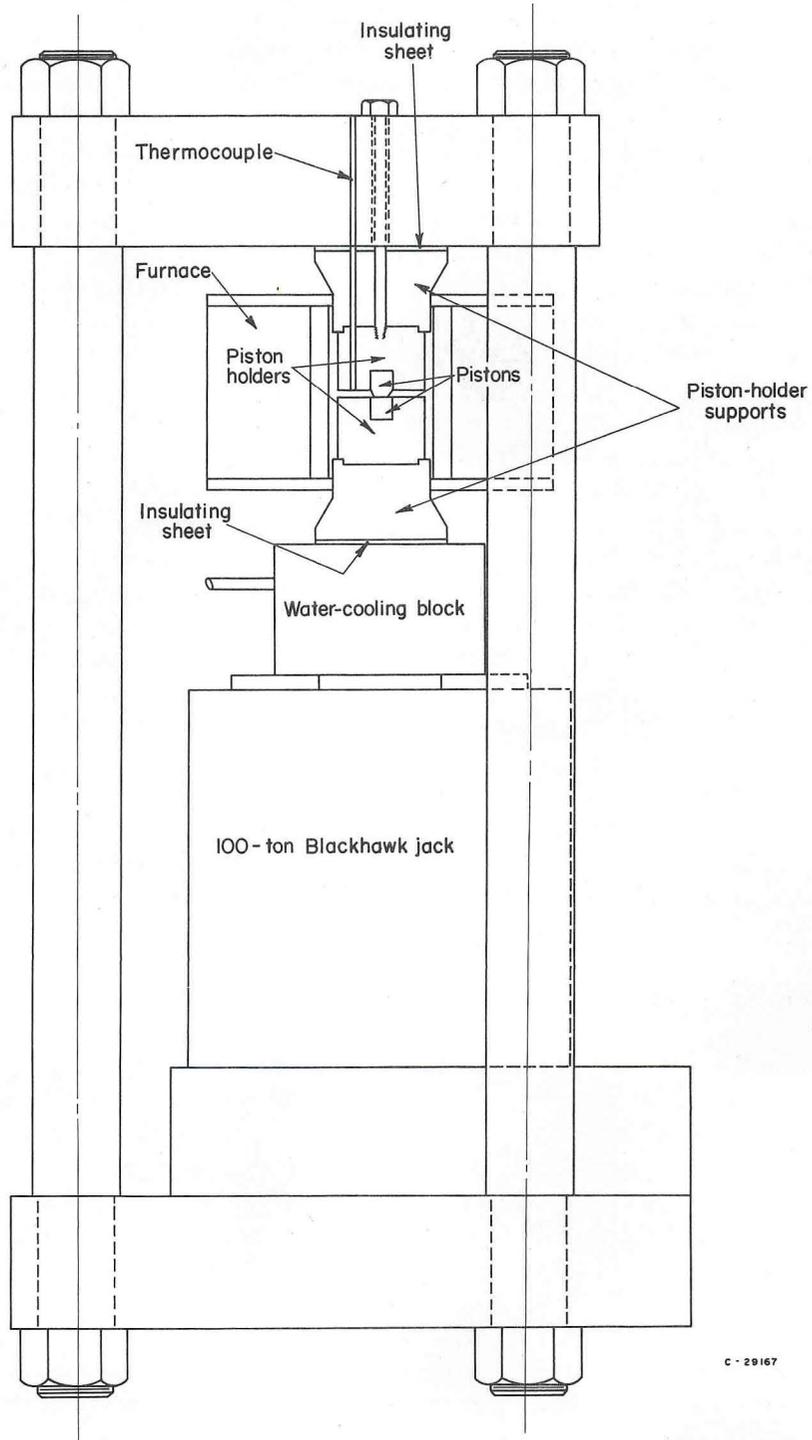
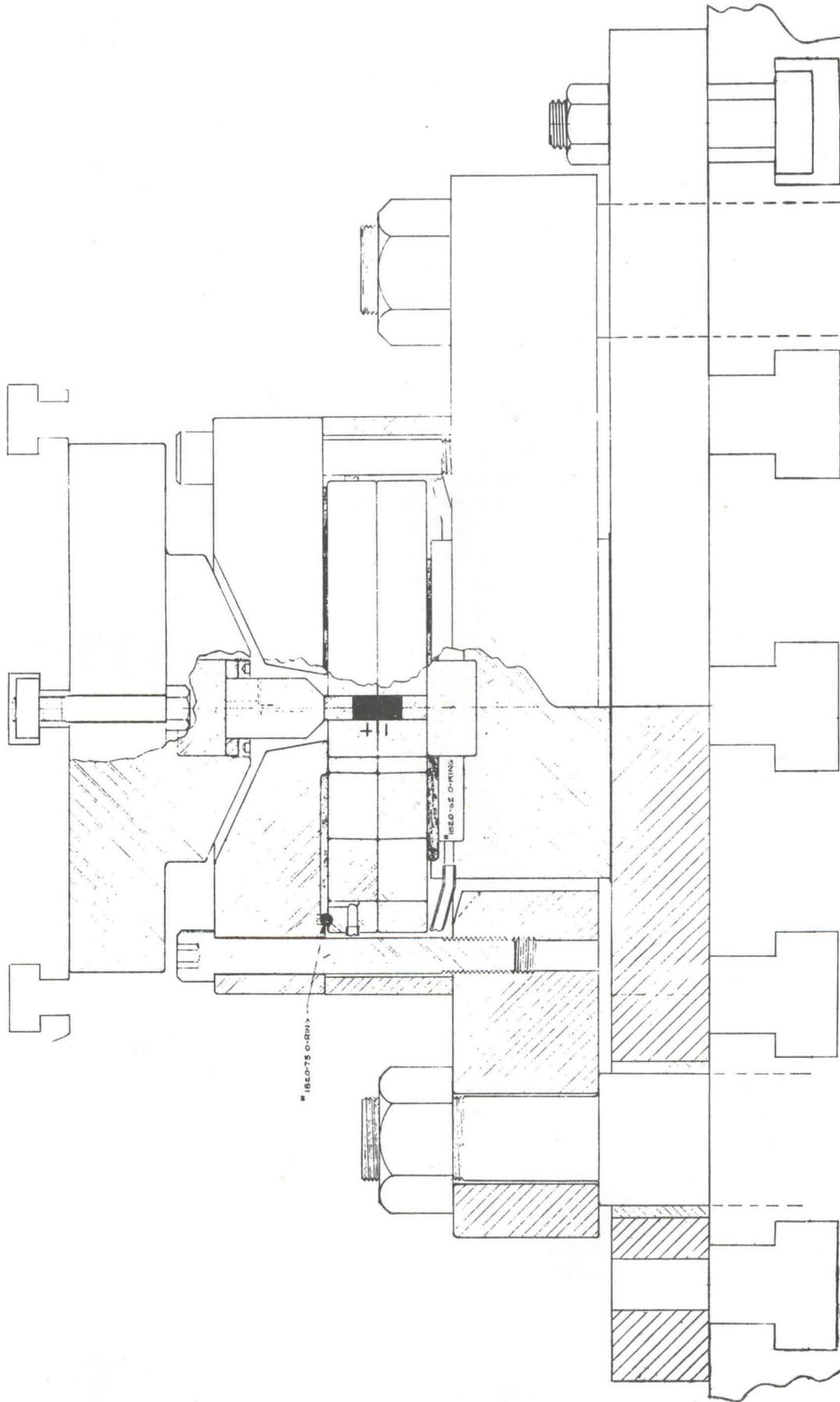FIGURE 2. SCHEMATIC OF BRIDGMAN-ANVIL UNIT

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FIGURE 3. SPLIT RIGHT-CYLINDER DIE

The two die halves are held together by a force pulling downward. This force is transmitted through the large rods shown to a holddown piece which contacts the upper die half at the edge of the carbide. Pressure is applied through a right-circular-cylinder piston just above the sample by the main press force. Thus, a two-force press is warranted for such a split die. Water cooling to maintain the carbides at normal temperature is available on both top and bottom die surfaces as shown.

Since the insulation constitutes a most important phase of the internally heated die design, some detailed comment is warranted. At the suggestion of Dr. Hall[42], a 1-mil raised annular surface was put on each carbide die part as illustrated in Figure 4. The purpose of this ring is to give actual physical separation to the bulk of the upper and lower die halves, permitting plastic insulation to go between. To complete the insulation, a slurry of Fe_2O_3 and alcohol is prepared with which the abutting carbide dies are painted. Since the heating is by low-voltage alternating current, any reasonable insulation value is generally adequate.

In practice, it was found necessary to give careful attention to the dimensions (height and width) and surface finish of the annulus to obtain reliable insulation. Since the die halves were held together by a force of from 30 to 100 tons, roughness on the surface could easily produce a short. To obtain the desired surface finish, the carbide annuli were lapped with fine diamond dust. The dimensions used on each half were a 1-mil height and a 1/4-in. width. Smooth coatings of Fe_2O_3 were found best since agglomerates of oxide have a tendency to produce local stresses in the carbide surfaces and fracture small chips from them. The quality of the insulation is also directly proportional to the amount or thickness of oxide used.

Figure 4 also shows a typical sample container for an internally heated die. An outer 1/2-in.-diameter sleeve of unfired Grade A lava surrounds a 3/8-in.-diameter core of AgCl. The AgCl is drilled out to receive a 1/8-in.-diameter thin-walled platinum tube heater. The sample material is inserted in the platinum tube and lava end caps are placed at each end of the sample. The AgCl insert is used because it transmits pressure more hydrostatically than materials such as lava. However, AgCl alone will allow "blow-out" more easily than lava so the lava jacket is placed on the AgCl. At elevated temperature the AgCl will melt in the vicinity of the heater but, because the die walls are cold, this liquid does not extend to places where leakage can occur, and an actual liquid pressure-transmitting medium can thus be retained. Further details of sample configuration will be discussed in relation to experimental work conducted on materials.

Calibration of the die for pressure is accomplished by use of known transitions from the work of Bridgman. This has been adequately described by Hall[6] and is simply obtained by relating press force to the pressure at which the known transitions occur. A very simple arrangement for calibration has been devised for bismuth, however. To detect the bismuth I and II transitions, which occur at nominally 25,000 atm, a fine bismuth wire is placed in the AgCl and the resistance of the wire is measured as a function of pressure. An initial resistance increase occurs with pressure followed by a decrease of large magnitude at the transition. The bismuth wire is, at room temperature, quite brittle and samples are difficult to prepare. This difficulty is easily overcome by casting molten bismuth down a very fine platinum wire (0.001 in.). The platinum wire is thus coated by a layer of bismuth. Should the brittle bismuth crack the platinum will still provide electrical continuity and its resistance is sufficient to still
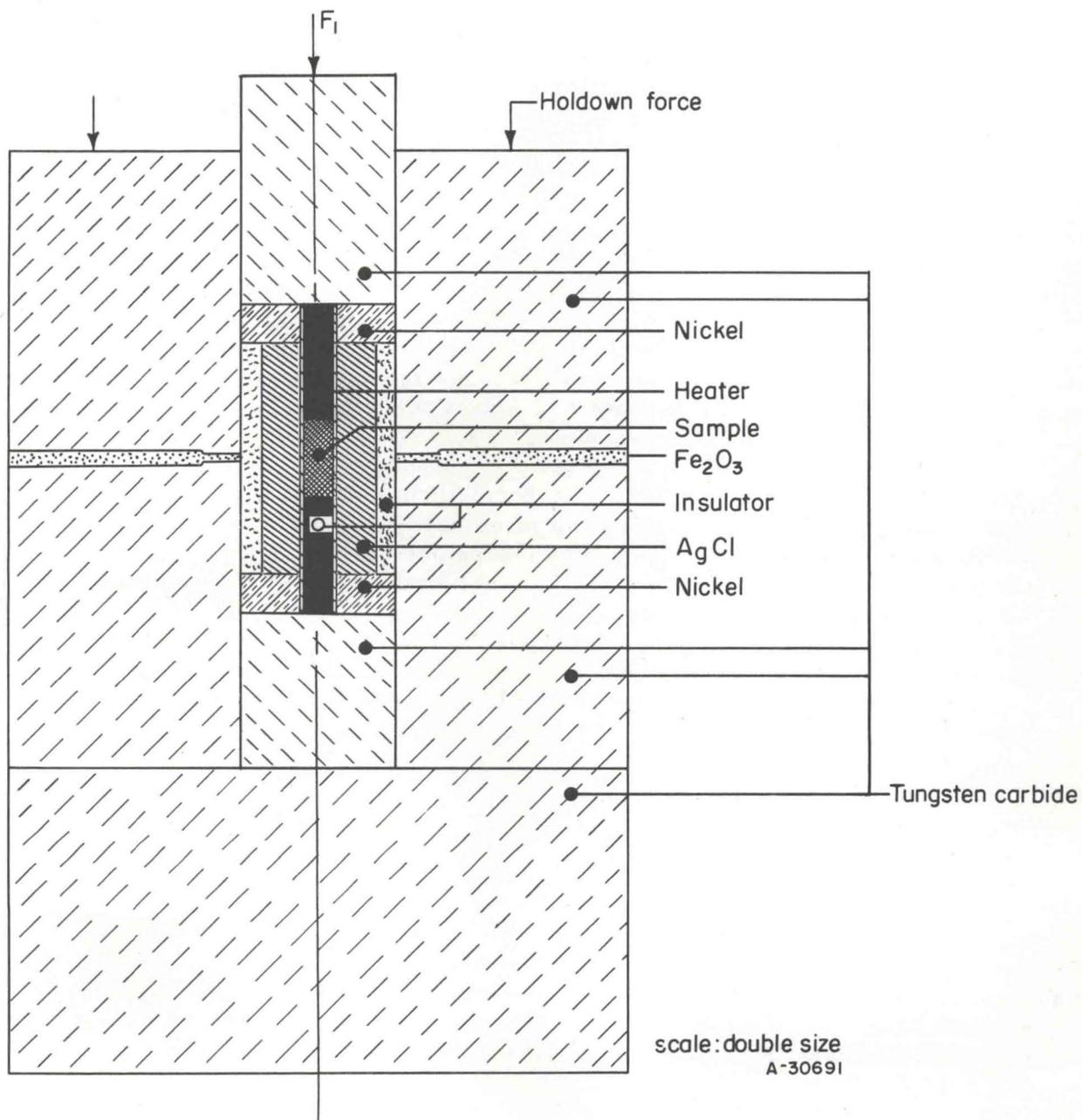
FIGURE 4. SAMPLE CHAMBER OF MODIFIED RIGHT-CIRCULAR-CYLINDER DIE

allow detection of the transition. The bismuth-coated platinum wire is run through a fine hole in the AgCl to each piston face for electrical contact required to determine the transition. With the typical sample described, the calibration indicated that 18 per cent excess force was required to overcome friction in the die.

Temperature calibration was initially accomplished with little or no pressure by inserting a thermocouple into the heater. The heating power was related to the recorded temperature. The assumption was then made that the temperature at pressure was nominally the same as at ambient pressure. Later work indicated that such a calibration was subject to large errors for a variety of reasons and dictated that a thermocouple should be inserted at each run. In the split die this is most suitably accomplished by running the thermocouple between the die halves to the heater.

Two factors combine to make accurate temperature measurement difficult. If temperature calibration is performed without pressure, the application of pressure changes the thermal conductivity of the heater. This is especially true of nonmetallic heaters. As a result, the thermal losses to the heater are increased and the temperatures are lower than expected. Even use of a thermocouple during each run presents uncertainties because of the very large thermal gradients in the heater. In the split die where the heater is 1 inch long, this problem is not too serious, but in dies to be described it constitutes a definite problem. To know the temperature at the sample requires exact placement of the thermocouple.

The split right-circular-cylinder die performed quite satisfactorily within its pressure capabilities. The pressure limit of an unsupported cylinder of tungsten carbide is 700,000 to 900,000 psi. Thus, the unsupported piston at the top of the die would be expected to break at such a value, giving a maximum pressure of nominally 50,000 atm. Friction consumes part of this, further reducing the practical working limit to a somewhat lower value. To eliminate breakage, a still further reduction in pressure is required, and in practice this type unit can be used routinely at 30,000 atm at any reasonable temperature. The 1-in.-long heater length provided somewhat better temperature-gradient characteristics than the shorter heaters to be discussed.

Simple Right-Circular-Cylinder Die

The split right-circular-cylinder die design required the use of a press with two forces available. Because of economic considerations, it became desirable to use a less expensive press unit and a simplified right-circular-cylinder die was devised which utilized the same components as the split-die design. This unit, which is shown in Figure 5, was used for the initial pressure studies on uranium oxides pending development of an advanced die design. The unit is essentially the same unit discussed by Hall[6] except that certain modifications were introduced to facilitate use.

The most serious disadvantage encountered with this die is the insulation of the carbide plug just below the sample. As proposed by Hall, this carbide is wrapped with paper to electrically isolate it from the surrounding die. It in turn contacts the carbide block below, which is also isolated by paper. Experience dictates that paper insulation is in fact difficult to utilize. If the bottom carbide piston is too much undersize, AgCl "blow-out" occurs. If it is oversize, shorting occurs more easily. Substitution of oxide for paper presents essentially the same problem.
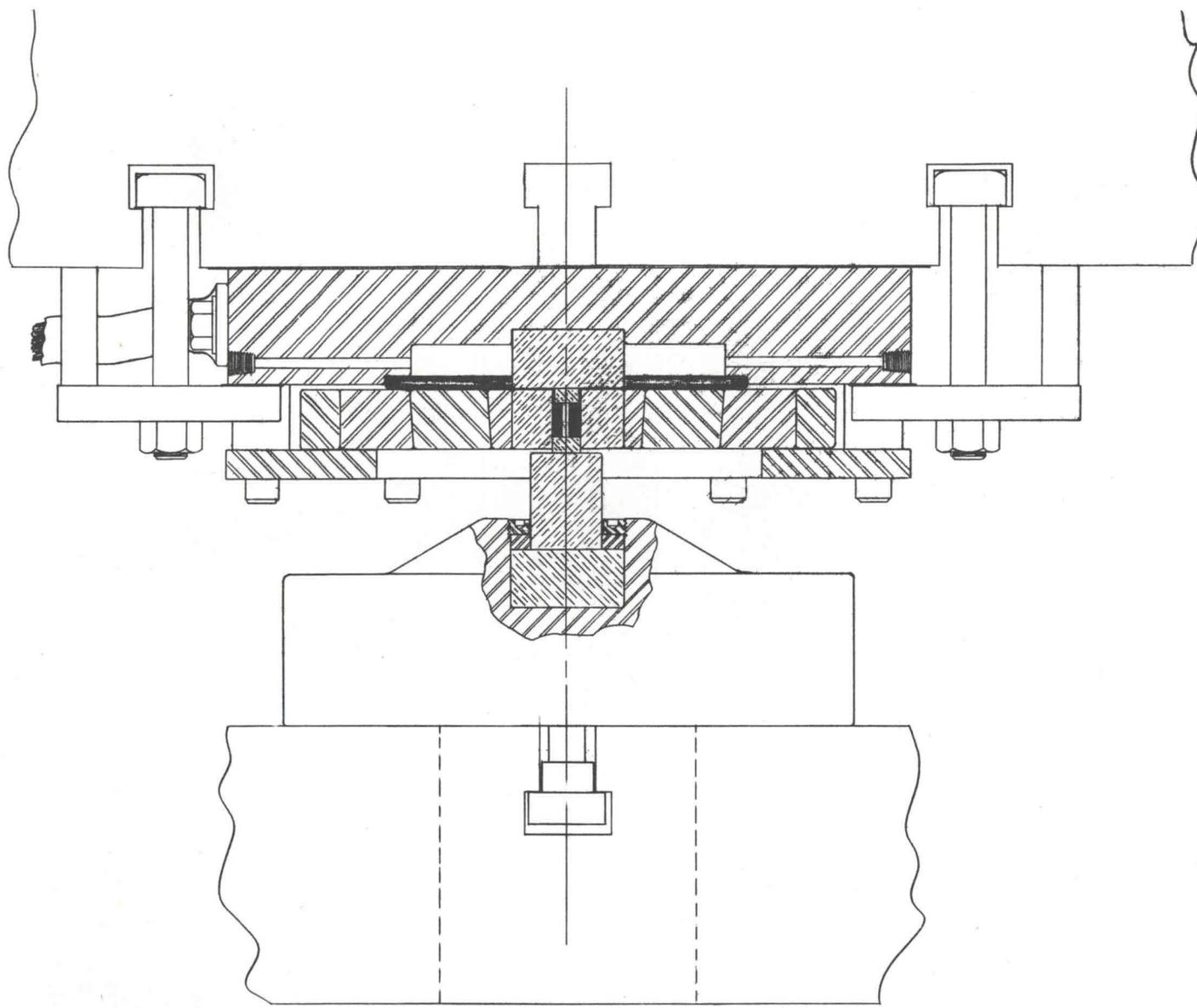
FIGURE 5. SIMPLE RIGHT-CIRCULAR-CYLINDER DIE

For routine use at pressures near 25,000 to 30,000 atm, the bottom carbide plug may be eliminated completely, which in turn affords a longer sample and minimizes temperature-gradient problems. The supporting carbide block is painted with Fe_2O_3-alcohol slurry and the die assembled. The experience gained with this unit in routine use provided the background for the features to be incorporated in a more advanced design.

Temperature and pressure calibration are accomplished in the manner previously described. However, a thermocouple is much more easily inserted into the sample chamber with the bottom plug being removed than in the manner advocated by Hall.[6] The removal of the bottom plug, although simplifying the die operation for routine use, results in increased die breakage near 30,000 atm. Radial cracks at the bottom of the die result at 30,000 atm when the bottom plug is omitted. The same general comment is true of the split-die design. If adequate holddown is not applied radial cracks appear in the region between die halves.

Heated Stepped-Piston Die

The limit of strength of an unsupported right-circular cylinder of tungsten carbide is 700,000 to 900,000 psi or, nominally, 50,000 atm. This imposes an arbitrary limitation in maximum pressure of a right-circular-cylinder die, as previously discussed. To obtain higher pressures than 40,000 atm requires new methods in support of the carbide parts. This was apparently accomplished for the first time by Hall at the General Electric Company, with the Belt apparatus. As mentioned, this apparatus has been classified by the U. S. Government as well as being proprietary information of General Electric. This consideration has necessitated further development of equipment to exceed the right-circular-cylinder capabilities. Hall has advanced two new designs[6] to achieve this. The tetrahedral-anvil die*, recently disclosed, represents a "three-dimensional" approach to the Bridgman-anvil principle of massive support. It has capabilities as indicated in Figure 1 of 100,000 atm at temperatures to 3000 C. It is a "compressible-gasket" die achieving pressure by means identical to the Bridgman anvil.

A second design advanced by Hall is the "stepped-piston" design, the principles of which are shown in Figure 6. To achieve a higher pressure than is possible in a right-circular cylinder, a "geometrical-advantage" principle is employed. The pressure is generated in a narrow annulus region between the piston and die. The area of the annulus is made to be less than the area of the exposed piston cylinder. Thus, the exposed piston may utilize a force up to 700,000 lb times its cross-sectional area. This force, however, generates pressure only in the annulus area which is smaller than the piston top area. This results in pressure intensification.

This experimental design, as given by Hall, did not utilize an internal heater and for this reason was used to obtain pressure alone. Estimates of 200,000 atm as a pressure limit have been suggested.

The principle of the geometrical-advantage type die appeared sufficiently attractive to warrant attention as to how it might be combined with internal heating. Figure 7 illustrates a suggested method as to how this may be accomplished. The piston portion of the die has been split (as Hall did in his model) and a sample chamber placed in the

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*Commercially available from Engineering Supervision Company, 787 United Nations Plaza, New York 17, New York. This unit has just been classified by the U. S. Patent Office.

Clamping force on piston (F_C)

Force pushing piston into cylinder (F_P)

D_L
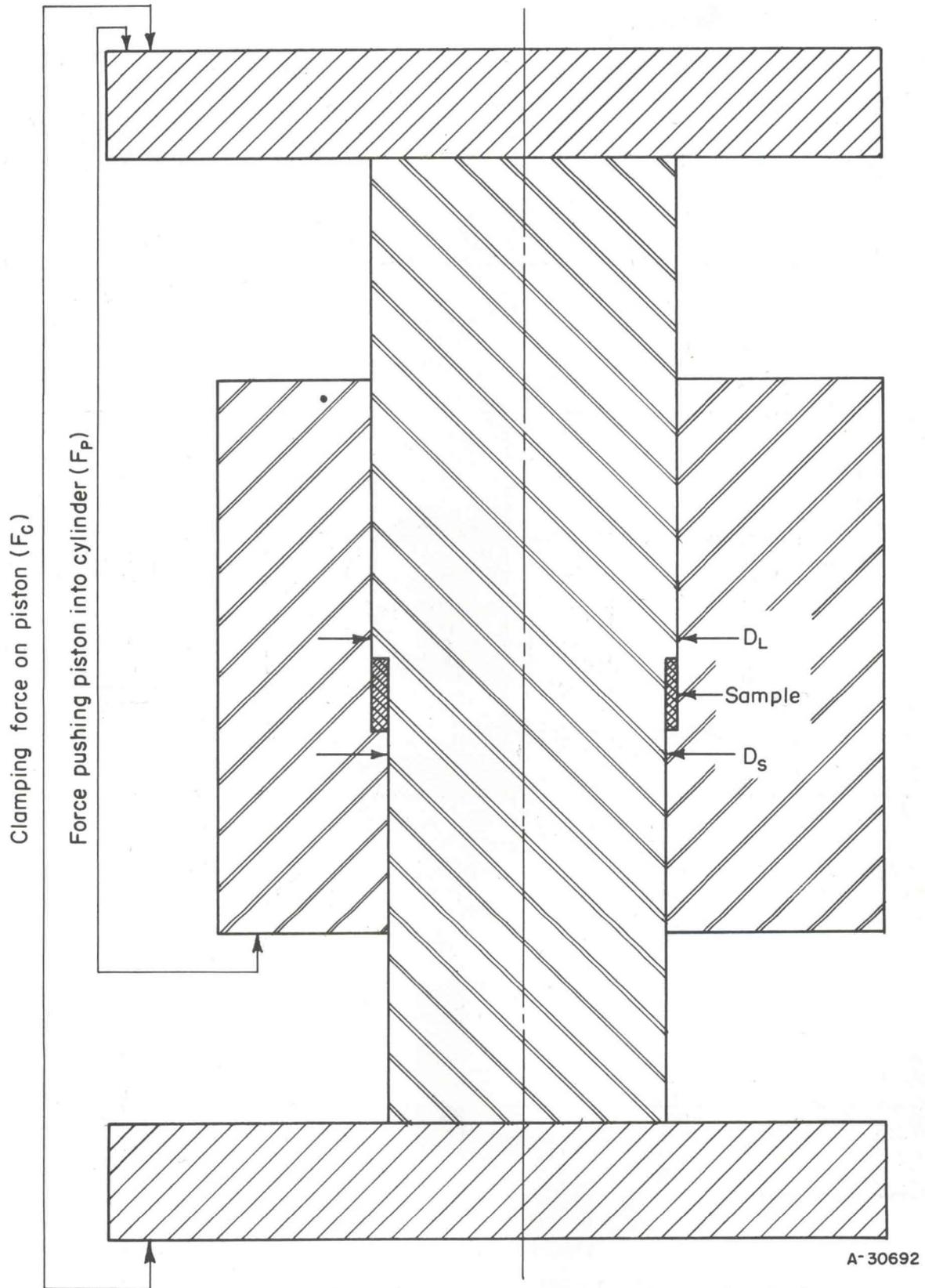
Sample

D_S

A-30692

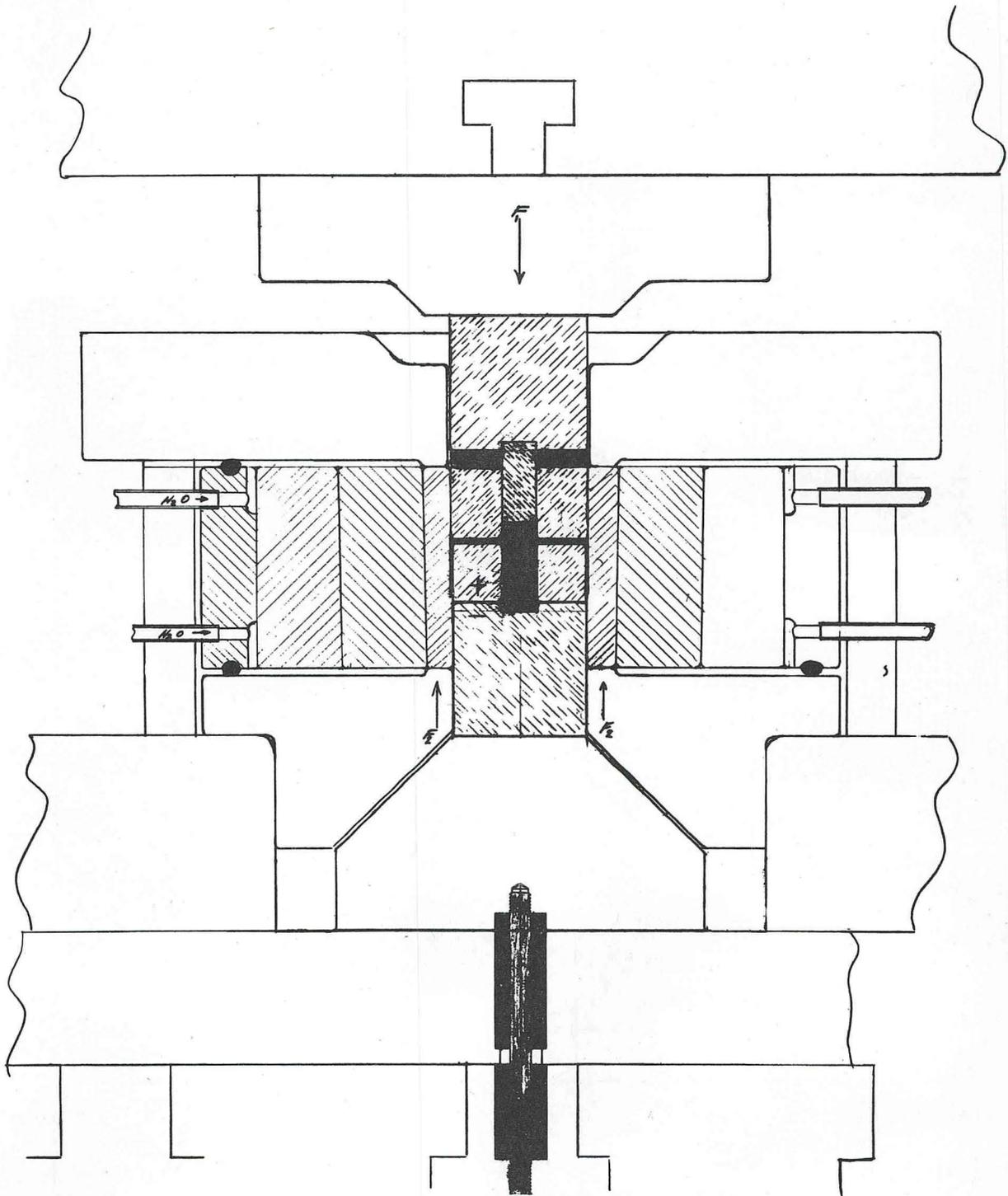FIGURE 6. PRINCIPLE OF THE STEPPED PISTON TYPE DIE

FIGURE 7.   PROPOSED HEATED STEPPED-PISTON DIE

center carbide column. The annulus region is provided with a "bleed-off" into the sample chamber such that the pressure, generated in AgCl in the annulus, may be hydrostatically transmitted to the sample area. A main force F_1 holds the carbide column intact and pressure is generated by a second force F_2 pushing the die upward. An improved method of insulation over that shown in Figure 7 is possible by electrically isolating the completely supported right-circular-cylinder piston just above the sample area, which is blacked in. Although construction of this die design was contemplated, the complexity of such a die, the operational difficulty, and the requirement of a two-force press made a simpler unit mandatory from an economic standpoint.

Vereshchagin et. al

The Girdle   *There is a similar Russian Device Zhur. Tekh. Fiz. 26 874-7 (1956).*

A new die design has been developed and tested which holds considerable promise and appears satisfactory for any work currently contemplated. This unit incorporates the features that an improved die should contain, based on experience gained with the right-circular-cylinder die. These features are:

(1) Ease of insulation

(2) Ease of use of thermocouples

(3) Higher pressures

(4) Minimum of expensive carbide

(5) Fewer parts involving assembly

(6) Water cooling

(7) Self-aligning

(8) Production capabilities.

A mock-up of a die design containing these features was developed which utilized the parts of the existing right-circular-cylinder equipment and satisfied the Bridgman principle of massive support. This unit is shown in Figure 8. It is similar to the Bridgman-anvil unit except that the sample region has been extended in height to allow use of an internal heater. This is accomplished by the use of steel binding rings around the sample area. However, the binding rings extend up the sides of the cone of the pistons as shown. As the pistons are pushed together the wedge effect of the cones forces the die to expand. The geometry operative in the die is shown in Figure 9 which may be used to derive the conditions under which pressure will build. From Figure 9 it may be seen that in the limit, as the cone half angle $\theta \rightarrow 0$ a right-circular-cylinder die results, and as the height $h \rightarrow 0$ the Bridgman anvil results.

For solutions between a right-circular die and the Bridgman anvil, certain restrictions arise if pressure is to be generated. As the pistons each advance an increment Δh the die is required to expand an equivalent Δr. From the drawing, $\Delta r = \Delta h \tan \theta$. For pressure to build in the die, there must be a net volume decrease. Thus, the volume decrease swept out as the pistons advance (disk volume) must be
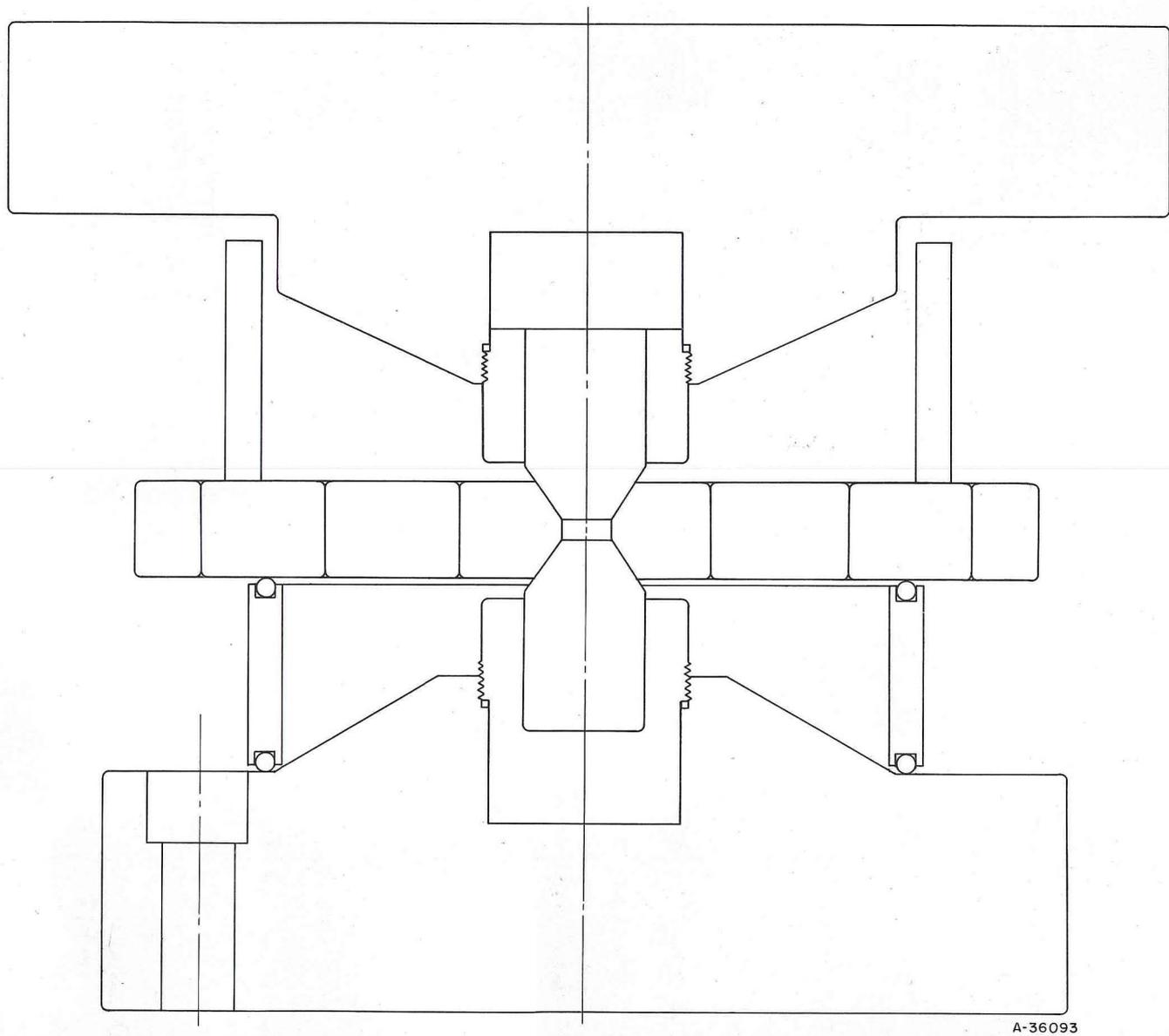
A-36093

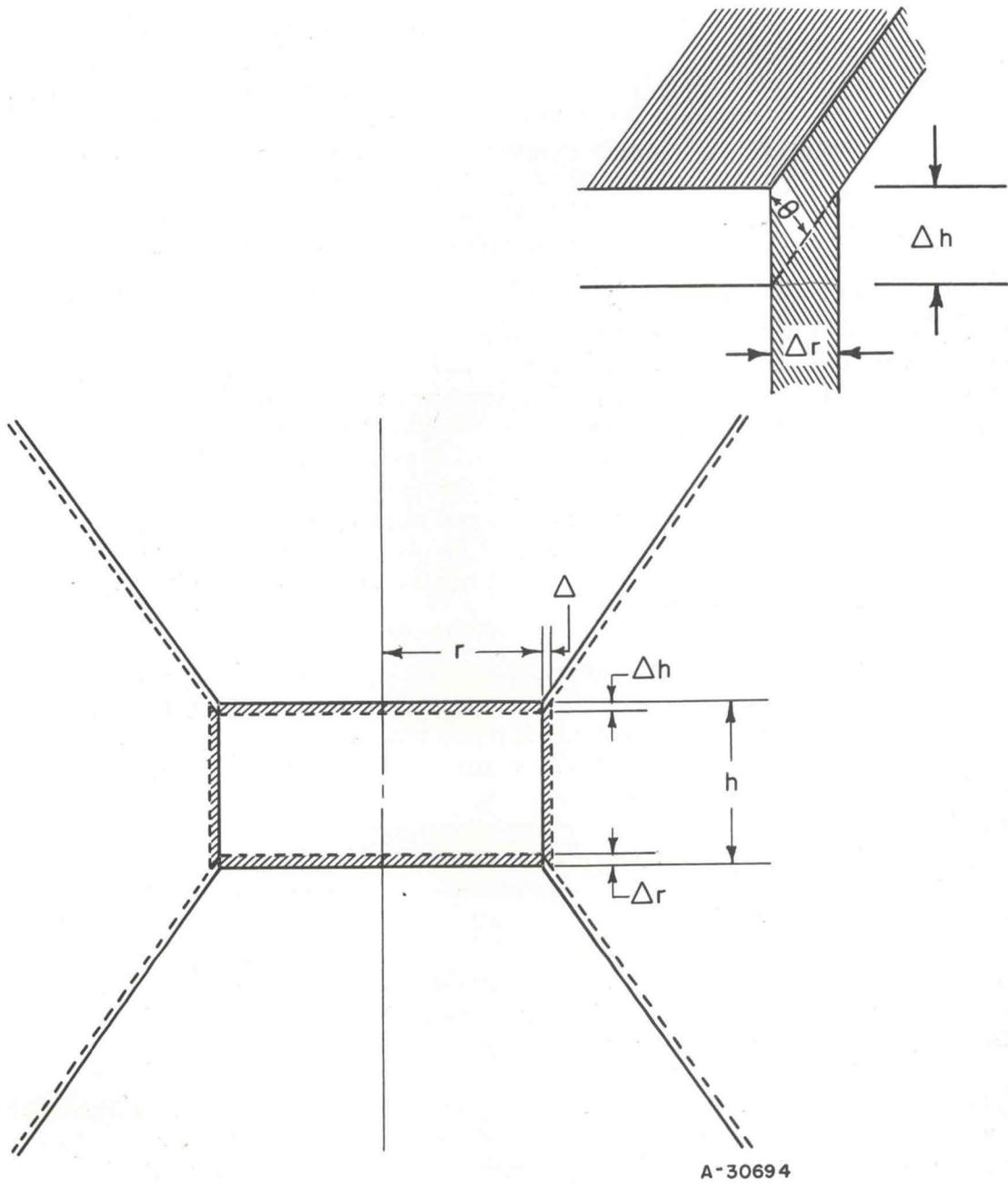FIGURE 8.   THE GIRDLE – A NEW HIGH PRESSURE-HIGH TEMPERATURE DIE DESIGN

FIGURE 9. THE GEOMETRY OPERATIVE IN THE GIRDLE DIE DESIGN

larger than the expansion due to the change in radius (annulus volume). If these volumes are made equal it is found, neglecting second terms, that

$$r = h \tan \theta.$$

To build pressure h must be made smaller than this equal volume value.

Since existing sample materials were 1/2 in. in diameter, it was convenient to use this value. The shear angle for compressive failure of carbide was assumed to be near 45 deg, but use of such an angle required an unnecessarily short sample. For this reason, θ was tentatively set at 35 deg and h was found to be about 0.35 in. In practice, h was made 0.450 in. which was theoretically too large to allow pressure to build. This value was subsequently reduced by grinding to below 0.350 in. before pressure increased.

However, for values near 0.350 in. the internal volume decreases only slowly with piston movement and ultimately a bore height of 0.250 in. was used. As previously discussed, it is desirable because of temperature-gradient problems to have a heating element which is as long as possible. Since the present die is 0.250 in. long (using a sample height of 0.310 in.), additional length could be well utilized. This may easily be accomplished in two ways: the unit may either be scaled up to allow a 1/2-in.-long element or the heating element may be used across the 1/2 in. diameter of the present unit. In practice, however, using a thin-walled platinum tube heating element with direct thermocouple readings, the short heater appears satisfactory as long as the sample is adjacent to the thermocouple.

Prior experience had dictated that the insulation of the die be accomplished as easily and reliably as possible. For this reason, it appeared attractive to have the top surface of the die insulated by painting it and the top carbide with Fe_2O_3. This single surface, in the event of a short, could be easily reinsulated without die disassembly by merely opening the press. The corresponding bottom surface of the die is lubricated and is used to "spread" the die by its wedge advantage.

Water cooling, if needed, may be provided by an O-ring and jacket assembly between die and base as shown in Figure 8. Self-alignment is obtained as a direct result of the cone surfaces. The tungsten carbide insert previously used in the right-circular-cylinder die is replaced by less expensive steel which is also less subject to breakage. Thermocouples are relatively easily brought out of the sample region through the oxide insulation which may, in fact, be quite thick.

A very important feature is inherent in using the binding ring to support both the sample and the carbide pistons, as in Figures 8 and 9. As mentioned, if $h \to 0$, the binding rings are unnecessary and the Bridgman anvil results. With this configuration, if the maximum pressure is exerted, it is found that failure will occur not because of the limited right-circular-cylinder strength of the carbide but because of a radial stress at the periphery of the sample. In practice, this usually occurs at 80,000 to 100,000 atm. Additional pressure may be obtained with the Bridgman anvil by increasing the θ angle to a nearly flat condition and supporting the radial stress by binding rings. Values beyond 200,000 atm have been obtained at Battelle when this modification is performed. In the new die design, however, the multiple binding rings surrounding both the sample and the carbides support this radial stress. In addition, the carbide

pistons pushing down on the die, support the die, thereby preventing the "pinch-off" effect from shearing the die in half. Thus, the binding rings support the carbide and the carbide supports the binding rings.

<u>Die Performance</u>. The ultimate pressure obtainable with this simple die unit has not, as yet, been established. This arises because initial testing was performed for the most part in a small press. Pressures slightly in excess of 60,000 atm have been obtained routinely with 145 tons of applied force. Most recent calibration work has indicated that the barium transition, at 80,000 atm, has been detected during a test to 110,000 atm. A press force of 225 tons was used and no failure of components was experienced during this test. The unsupported portion of the 1-1/4-in.-diameter carbide piston would withstand a load somewhat greater than 400 tons. A linear extrapolation would suggest that a pressure in excess of 150,000 atm is possible with existing geometry, assuming no binding-ring failures. Stress analyses of the binding rings indicate that they should be able to withstand such a load. The supporting parts, however, were taken from a right-circular-cylinder die and the large tonnages necessary to obtain maximum pressure may require a more substantial base than shown in Figure 8.

The performance of the die in use differs markedly from either the right-circular-cylinder or the compressible-gasket type die, such as the tetrahedral anvil or the Bridgman anvil. Since the binding ring is elastic, part of the total force must be used in expanding the die as well as in producing pressure. Thus, if the disk-to-annulus volume ratio, previously discussed, is 1:1, all of the force will be used just to expand the die. However, when the height, h, of the die is shortened to allow pressure to build, an increasing proportion of the total force will be effective in generating pressure. This effect has been termed the die efficiency and is the ratio of the force actually producing pressure to the total force. Thus, the die efficiency may vary from 0 at the 1:1 ratio of disk-to-annulus volume to 100 per cent as h → 0, producing the Bridgman-anvil condition. For comparison purposes, it should be pointed out that the same efficiency factor is operative in all internally related die designs. In the right-circular-cylinder die it involves friction and in the tetrahedral anvil it has the same characteristics as here.

A point of further interest is the total amount of compression $\left(\dfrac{\Delta V}{V}\right)$ theoretically possible in a die. In the right-circular cylinder it is possible, in principle at least, to close the two pistons together. In the tetrahedral anvil a very limited compression is possible, since ultimately all the carbide pistons will abut and further compression will not be possible. For the geometry of Figure 9, a variation in ultimate compression is dependent on the bore height h and, in principle, almost unlimited compression is possible. This factor is of prime importance since materials which exhibit a large compressibility will not build large pressure in dies of limited compression.

The calibration of this die was accomplished using known transitions as discussed previously. The die efficiency factor, however, introduces a greater uncertainty in pressure than exists in right-circular-cylinder dies. Since variations in porosity and voids exist between different samples, a range of internal pressure is produced for a fixed press tonnage. Thus, an uncertainty in pressure arises which requires a special technique to reproducibly attain known pressures. In practice, this may be accomplished by precompressing an oversize sample and then adding 0.010-in.-thick annular

hole vol small compared to Δ vol eliminates this prob.

rings of catlinite to the top and bottom of the sample as makeup volume for the porosity. The excess of the rings is expelled from the die and acts as insulation. This technique shows better reproducibility in obtaining known pressures but the uncertainty is still of the order of plus or minus 2000 atm at 25,000 atm. This error is not cumulative, however, and the same error exists at greater pressures, making a lower percentage error. To obtain the best pressure accuracy, a bismuth transition should be run during each test by use of auxiliary leads into the die.

The friction or pressure hysteresis effect is quite noticeable in this die. For instance, it may be required, due to die efficiency, to apply 50 per cent excess force to produce a known transition. However, after obtaining the transition, the internal pressure may be easily maintained even while reducing the press force, and in practice, when going in the decreasing direction, the bismuth and the thallium transitions at 25,000 and 43,000 atm, respectively, are observed to go at nearly the theoretical value as if the die were 100 per cent efficient. Repeated cycling of a sample to high pressure shows that an increasingly larger force is required to achieve the same pressure. This is because some sample-chamber material is expelled each time to effect a new gasket and reseal the system.

Temperature calibration is accomplished by direct insertion of a thermocouple to the heater, where it may be spot welded if a metallic heater is used. The thermocouple leads are brought out of the die through the iron oxide insulation, between the die and the top piston. This is usually accomplished with ease, but under certain circumstances can give rise to difficulty. Since the oxide insulation is of the order of a few mils thick, even a low voltage can give rise to large voltage gradients. A small leakage current through the insulation will result in large temperatures being generated in the die. This heat is stored in the die. To protect the die, water cooling on the bottom surface has been provided.

It should be re-emphasized, that the die as shown in Figure 8 is a mock-up using existing parts. This was done to effect economy while determining the optimum dimensions and geometry. A larger version with stronger supporting facilities should be capable of the extremes of simultaneous pressure and temperature.

Discussion of Operation of High-Pressure High-Temperature Equipment

Sample Chamber

The early experimental work carried out in the right-circular-cylinder dies indicated that considerable departure from hydrostatic pressure results when certain materials are used in the high pressure portion of the dies. For instance, when unfired Grade A lava (a hydrated aluminum silicate commercially available from the American Lava Corporation) is used as a pressure-transmitting medium, considerable excess force is required to obtain the bismuth transition over that which is required when AgCl is used. Because of this, the typical sample chamber illustrated in Figure 4 was adopted. This has been previously discussed.

When the sample of Figure 4 is heated to high temperature, the AgCl melts. The light emitted from the heater reduces the AgCl, resulting in small single crystals of

silver depositing near the liquid-solid interface of the AgCl. A columnar growth of larger single crystals of AgCl may be grown under pressure at the solid-liquid interface and would be useful as a model system to study crystal growth under pressure. The size of the melted region is obviously related to the heater temperature.

The melting temperature of the platinum heater determines the upper temperature limit of the sample shown in Figure 4. If melting occurs, it is found that the AgCl will generally react with the sample to destroy the test. To achieve higher temperatures a graphite heater may be substituted for the platinum. However, the porosity of the graphite readily allows the AgCl to enter the sample area, where reaction is possible. In one experiment carried out at an estimated 3000 C, the entire center of the sample appeared to melt with the exception, of course, of the graphite heater. Such difficulties may be avoided by use of the graphite heater and lava insulation, omitting the AgCl.

Since the sample, heater, and insulator configuration constitutes a miniature furnace, it is clear that the furnace can cause extreme problems of contamination. For instance, if graphite heaters are required to obtain temperature to 2000 C to study oxide reactions, the oxide will be readily converted to carbides. To prevent this type of reaction from occurring, the use of barriers appears mandatory. In the present work, for instance, BeO has been used as a barrier between the graphite heater and the sample material. The problem of obtaining the optimum heater-sample configuration will generally require different solutions for the variety of materials that may be studied. However, for temperature to 1500 C the use of platinum heaters appears satisfactory.

In order to vary the heater conditions, a variety of heater materials, sizes, and configurations have been devised for specific purposes. Graphite, nickel, and platinum heaters with variable wall thicknesses and diameters from 1/8 to 3/8 in. may be used. The 3/8-in.-diameter graphite heater was used to bring a large volume of the high-pressure region to high temperature for use in the bomb technique, to be described.

Operational Techniques

There are several techniques of operation which may be used during a test. For instance, the temperature may be applied first, followed by pressure. This technique offers the advantage that the pressure is fairly well known. In the alternative, where pressure is raised first and then temperature applied, the temperature increase will further increase pressure through thermal expansion. In general, this is the technique that has been used for the work to be described and the pressure figures represent, therefore, a minimum.

A third special technique which may be used for any die design is called the bomb technique. It may be described by reference to the right-circular-cylinder die of Figure 5, which was used for the experimental bomb work. It will be recalled that the compressive strength of an unsupported right-circular cylinder of carbide is 700,000 to 900,000 psi. In the bomb technique, the length of the right-circular-cylinder piston is selected so that it becomes flush with the top of the die at a pressure just below its crushing strength. In this condition, the piston and all other parts become completely supported and constitute a bomb sealed at high pressure. Further increase in pressure

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then may be generated by raising the internal temperature through use of the massive graphite heaters previously described.

In early work, experimentation was conducted with the bomb technique, but was discontinued. The difficulty of obtaining the exact piston length, and the lack of knowledge of internal pressure and temperature served only to make the new die design more attractive. The use of the bomb technique in the new die design, however, offers even greater extremes of pressures and temperatures.

At the completion of a test it will usually follow that the temperature will be reduced first, followed by a reduction of pressure. This order is obviously required if metastable high-pressure phases are to be retained at ambient pressure and temperature.

Frictional or Pressure Hysteresis –
Temperature Measurement

Previous mention of frictional or pressure hysteresis has been made in regard to the new die design. In practice, frictional or pressure hysteresis has been found to occur in all internally heated die designs and has also been discussed by Hall.[6] For instance, in the right circular cylinder die design about 20 per cent of the force applied to the piston is consumed by friction. When internal heat is applied or the press force is reduced, it is found that the direction of the frictional force reverses. This reversal, where friction may be then used to augment the pressure, offers distinct possibilities in obtaining higher pressures than a die is normally capable of. Thus, if a right-circular-cylinder die has been brought to its maximum pressure and then internal heat is applied, the sample will expand. This expansion tends to force the piston out of the die and may be detected by use of a dial indicator. The reversal of direction of the piston results in the force of friction augmenting the external force and 40 per cent excess pressure may, in principle, be effected by use of such technique.

If pressure has been generated in a die and then the temperature is increased, the pressure will usually increase an undetermined amount. In a right-circular-cylinder die, if the press is shut off and the dial indicator used to measure compressibility is observed, it is found that the internal pressure in the die does not release instantaneously but a relaxation time of the order of minutes is involved. This relaxation time prevents pressure quenching or the instantaneous removal of pressure. Pressure quenching is entirely possible in a Bridgman-anvil unit and it appears possible that pressure quenching may produce structural variations akin to temperature quenching.

The previous discussion has mentioned some uncertainties in knowing the exact pressure obtained through use of various techniques. There remains the uncertainty in temperature measurement to be discussed. At low temperatures the temperature gradients involved are sufficiently small that thermocouples can be used to obtain the temperature. At temperatures in excess of 1000 C, however, gradients become considerable and the relative error in thermocouple readings increases with increasing temperature. At temperatures of the order of 2000 C, only extrapolated calibrations are possible. The uncertainty of temperature is made even more difficult where a plot of temperature versus power required is made. A linear region of fair accuracy is found at lower temperatures, but extremely rapid increases in temperature occur for small increases in power at the higher temperatures. This occurrence tends to make

use of power data unreliable, since large temperature variations result from even small power variations at the higher temperatures. Thus, a thermocouple inserted into the sample or heater region during each experiment is warranted, but even then, because of the gradient problem, some uncertainty will remain.

Materials Research

Purpose

The materials of current interest in the present program are those for very-high-temperature reactor components and, more specifically, reactor fuel materials using uranium dioxide as a base. In addition, the uranium oxide system, together with various oxide additives, represents a unique model system to investigate the effects of pressure on materials. A principal reason why this is so is because considerable study of uranium oxide and uranium oxides with various oxide additives has already been effected at normal pressure with the same general objective as here. This existing background information provides a very convenient reference point for comparison with high-pressure results. To better illustrate why such studies may be of benefit, it appears desirable to digress somewhat into a brief description of the current status of stable nonmetallic nuclear-fuel development.

Uranium dioxide is among the most refractory of uranium compounds and is quite stable in neutral and normal reducing atmospheres. However, in oxidizing atmosphere it oxidizes to U_3O_8, which is a volatile oxide and markedly less refractory than UO_2. To overcome this limitation two alternative research approaches have, in fact, been undertaken. Briefly, the first approach has been to find a compound of uranium oxide with other oxides where the uranium is in the +6 valence state. The alternative to this is to produce a solid solution having the fluorite structure where the uranium could oxidize without, however, suffering a phase transformation.[43] Both approaches have yielded materials of definitely improved performance, but preliminary work on the compounds which have been produced to date has disclosed that they are not as satisfactory as the solid solutions. The same comment is generally true of natural mineral compounds occurring in nature. It is only natural to speculate whether pressure as another degree of freedom to the phase rule might be capable of producing improved high-temperature materials.

Background

From early research work, to "stabilize" uranium oxide it was found, as might be expected, that when relative valence effect and ion size, etc., are favorable, solid solutions are formed, and where unfavorable, compounds tend to form. In some instances, the extreme variation of valence and ion size apparently tends to prohibit any reaction such as between UO_2 and BeO. Since this condition, although oversimplified here, results at normal pressure, it would appear to be a reasonable criterion to facilitate evaluation of reactions at pressure. Thus, it would be required to determine how pressure modifies these relationships determining compound and solid-solution formation. Further, in normally nonreactive systems it is of definite interest to determine if pressure can be used to catalyze reactions to produce new materials.

A program of investigation was undertaken to study the effect of combined high temperature and high pressure on UO_2, U_3O_8, BeO, Sc_2O_3, and La_2O_3. In addition, the study of reaction under pressure between the uranium oxides and the latter oxides was of interest for comparison to the normal pressure behavior of these oxide systems. These objectives have only partially been accomplished because of the necessity of developing equipment and techniques. However, interesting results have been obtained in the preliminary work.

The reactions of some mixed oxides with UO_2 at normal pressure have been discussed by Lang, et al.[44] Lang found no solid-solution or compound formation between UO_2 and BeO from 800 to 1800 C and from 10 to 90 mole per cent BeO. The eutectic was found to occur at 2450 C at 63 mole per cent of BeO. Sc_2O_3 and La_2O_3 reactions with UO_2 were not considered by Lang, but normal-pressure studies just reported at Battelle[43] indicate no reaction between Sc_2O_3 and UO_2 to 1700 C. La_2O_3 was found to form a solid solution with UO_2 to nominally 60 mole per cent La_2O_3 in bodies reacted at 1700 C.

The reactions of U_3O_8 with La_2O_3 and Sc_2O_3 have been reported by Hund and Peetz.[45] A single-phase solid solution with the fluorite structure was found to occur between 33 and 70 mole per cent La_2O_3. A fluorite-structure solid-solution was also detected for U_3O_8 containing 50 mole per cent Sc_2O_3.[45] The lattice parameter of this composition was found to be 5.13 A rather than the 5.23 A value reported by Hund and Peetz. Their value is apparently a misprint in view of their data.

The systems just described embrace behavior ranging from essentially no reaction between BeO and the uranium oxides to that of extensive solid solution for both UO_2 and U_3O_8 with La_2O_3. Sc_2O_3, of intermediate ion size, does not react with UO_2 but reacts to form extensive solid solution with U_3O_8, apparently because the U^{+6} ion is smaller than the U^{+4}. Table 1 shows ion sizes involved.

TABLE 1. COMPARATIVE ION SIZES

Ion	Ionic Radius, A		Compound in Which Extensive Solid Solution Occurs
	Goldschmidt	Pauling	
U^{+4}	1.05	0.97	--
U^{+6}	0.81[a]	--	--
Sc^{+3}	0.83	0.81	U_3O_8
Y^{+3}	1.06	0.93	UO_2 and U_3O_8
La^{+3}	1.22	1.15	UO_2 and U_3O_8
Be^{+2}	0.34	0.31	--
Ca^{+2}	1.06	0.99	UO_2
Mg^{+2}	0.78	0.65	U_3O_8

(a) This value is a calculated value frequently used by Hund and Peetz.[45]

From Table 1, it may be seen that similarity of ion size and valence facilitate the formation of solid solutions. The reaction between U_3O_8 and La_2O_3, however, appears

to be anomalous, because of the extreme difference in ion size. The average ion size of the resulting solid solution, however, is in the correct range of radius ratio for the fluorite structure to be stable. The same general comment is true of the relative valence effect, where the U^{+6} ion is averaged with La^{+3} ion to provide an average tetravalent state nominally required by the fluorite structure. Detailed consideration of these factors has been discussed in BMI-1318[43], previously referred to. The systems discussed in this report form the basis for the normal pressure reactions of oxides of interest here.

Experimental Work on Oxides

The initial study of reactions was performed to determine if pressure could be used to catalyze reactions between oxides which are normally nonreactive. For this type of study, reactions involving Sc_2O_3 with uranium oxide were of particular interest since the scandium ion and valence are such that it represents a marginal case. At normal pressure, Sc_2O_3 apparently does not react with UO_2 but does react with U_3O_8 since the U^{+6} ion is smaller. This marginal characteristic of Sc_2O_3 suggests that pressure might effect reactions in which Sc_2O_3 was involved more easily than for BeO which is nonreactive for both uranium oxides.

Table 2 lists some of the preliminary reactions which have been attempted to date. These early studies provided experience in what constitutes a suitable heater. When a graphite heater was used with AgCl as a pressure-transmitting medium, the molten AgCl permeated the graphite to enter the sample chamber. For this reason, subsequent reactions were carried out with a platinum tube heater. While a graphite heater easily allows temperatures to 3000 C and beyond, the use of platinum restricts temperature to below 1500 C. Because of the experimental uncertainties previously discussed, it is difficult to accurately know the temperature at values beyond 750 C. The difficulty of inserting thermocouples into the right-circular-cylinder die also contributed to temperature uncertainty and the temperature values given in Table 2 represent probable temperatures calibrated by inserting the thermocouple into the heater in the absence of pressure and correlating wattage used against heat obtained.

Substitution of other heater materials introduced other problems. For instance, a nickel heater tube performed satisfactorily with UO_2 but reduced U_3O_8. The same reduction of U_3O_8 occurred when a graphite heater was used. This occurred even when a BeO liner was used between the graphite heater and the U_3O_8-BeO sample, apparently because the liner was crushed. For temperatures to about 1500 C, the platinum tube heater is entirely satisfactory. The graphite heater, when used in conjunction with the BeO liner and an all-lava insulator should permit study of oxides to beyond 2000 C.

Results

Reactions. Analysis of the results of the reaction in Table 2 indicate that under the conditions of pressure and temperature imposed so far, no reaction between UO_2 or U_3O_8 with BeO has been detected. Sc_2O_3 was found to react under pressure with U_3O_8 to yield the same result as normally occur. The reaction under pressure of Sc_2O_3 with UO_2, however, is distinctly interesting since a cubic solid solution with a lattice

TABLE 2. HIGH-PRESSURE HIGH-TEMPERATURE REACTIONS STUDIED

Sample	Composition UO$_x$	RO$_x$	Pressure, 10^3 atm	Temperature, C	Time Hr	Min	Heater Type	Remarks	Parameters (Fluorite Structure), A
2		BeO	40	3000	-	10	Carbon	Fused	
3	UO$_2$		25	500	-	5	Nickel	UO$_2$	$a_0 = 5.47$
8		BeO	35	500	1	--	Platinum tube	BeO	
10	UO$_2$	BeO	25	800	1	--	Platinum tube	UO$_2$ + BeO	$a_0 = 5.47$
11	UO$_2$	BeO	30	1500	1	--	Platinum tube[a]	UO$_2$ + BeO	$a_0 = 5.41$
12	U$_3$O$_8$	BeO	25	500	1	40	Platinum tube	X + BeO	--
15	U$_3$O$_8$	BeO	25	700	1	--	Nickel[b]	UO$_2$ + BeO + NiO	--
17	U$_3$O$_8$	BeO	None	1000	3	45	Vacuum furnace	U$_3$O$_8$ + BeO	--
18	U$_3$O$_8$	BeO	30	650	2	--	Platinum tube	X + UO$_2$[c] + BeO	--
19	UO$_2$	Sc$_2$O$_3$	30	400	-	40	Platinum tube	UO$_2$ + Sc$_2$O$_3$	--
22	UO$_2$	Sc$_2$O$_3$	30	1000	-	30	Platinum tube	UO$_2$ + Sc$_2$O$_3$	$a_0 = 5.47$, $a_0 = 5.42$[d]
24	U$_3$O$_8$		30	R.T.	3	30	Platinum tube	U$_3$O$_8$ + X	--
25	U$_3$O$_8$	Sc$_2$O$_3$	30	500	2	--	Platinum tube	U$_3$O$_8$ + Sc$_2$O$_3$ + solution	$a_0 = 5.08$
29	U$_3$O$_8$	BeO	30	1000	3	45	Platinum tube	U$_3$O$_8$ + BeO	--
30	U$_3$O$_8$	Sc$_2$O$_3$	30	1000	-	30	Platinum tube	Solid solution	$a_0 = 5.13$
31	U$_3$O$_8$		30	400	6	--	Platinum tube	U$_3$O$_8$	--
32	UO$_2$	Sc$_2$O$_3$	30	1000	1	30	Platinum tube	UO$_2$ + Sc$_2$O$_3$ + solution	$a_0 = 5.24$
-4	UO$_2$	Sc$_2$O$_3$	None	1700	2	--	Vacuum furnace	UO$_2$ + Sc$_2$O$_3$	$a_0 = 5.47$, $a_0 = 9.89$
35	U$_3$O$_8$	BeO	30	650	1	--	Platinum tube	U$_3$O$_8$ + BeO	--
36	U$_3$O$_8$	Sc$_2$O$_3$	30	600	2	--	Platinum tube	Only partly reacted	$a_0 = 5.17$, $a_0 = 5.10$
38	U$_3$O$_8$	BeO	30	300	-	5	Platinum tube	U$_3$O$_8$ + BeO + X	--
43	U$_3$O$_8$		25	250	3	30	Platinum tube	U$_3$O$_8$	--
45	U$_3$O$_8$	BeO	25	500	2	--	Carbon[b]	UO$_2$ + X + BeO	$a_0 = 5.47$
71	U$_3$O$_8$	BeO	60	1000	1	--	Platinum tube	X + BeO	--
73	U$_3$O$_8$	BeO	60	1400	1	15	Platinum tube[a]	U$_3$O$_8$ + BeO + UO$_2$	--

(a) Heater burned out.

(b) Heater caused reduction of sample.

(c) UO$_2$ was found there even though the heater appeared to be sound.

(d) The two parameters found here for UO$_2$ are possibly due to oxidation since they were not found in normal pressure work.

parameter of 5.24 A was detected. Since U_3O_8-50 mole per cent Sc_2O_3 gives a parameter of 5.13 A, it appears possible that the 5.24 A lattice parameter represents a reaction between UO_2 and Sc_2O_3. The larger parameter results since the U^{+4} ion is larger than the U^{+6} ion. Further study of this very interesting reaction has been temporarily deferred due to the development work on the new die.

Since pressure should, in general, alter the behavior of phase diagrams, it is also of interest to consider whether pressure is capable of producing changes in solubility, as well as producing new compounds. The reactions which have been investigated to date do not permit any general comment in this regard, as yet. Such studies will require carefully controlled compositions and detailed studies of lattice parameters to determine if metastable excesses of solubility can be retained to ambient pressure.

While the early results are quite interesting, it must be emphasized that the results are, for the most part, inclusive since adequate temperatures to produce complete reactions of refractory oxides have not been attempted in the preliminary work. Temperatures beyond the platinum melting point will, in general, be required, which will require use of the graphite heater and liner technique. This work is currently in process using the new die. It is planned to extend the general range of pressures and temperatures beyond that of Table 2.

U_3O_8 Pressure-Temperature Phase Diagram

During the course of the experimental work to react U_3O_8 with BeO, it was repeatedly found that a new phase occurred. Since the BeO was not affected, direct examination of U_3O_8 alone indicated that it was transforming to a new crystal structure which could be retained at ambient pressure. This material was initially produced in the right-circular-cylinder die. Because of anomalous results due to temperature uncertainty of the die, work was initiated to determine the pressure-temperature phase diagram of U_3O_8 using the Bridgman anvil. This was of direct importance since it is the new gamma phase of U_3O_8 that is the stable phase during attempts to react U_3O_8 with mixed oxides.

Figure 10 illustrates the existence region of the new phase. At room temperature, and at pressures from 10,000 atm and up, only two additional lines are detected in the diffraction pattern of U_3O_8 and these are essentially the same as those produced by the beta modification of U_3O_8.[46] The existence of the beta modification has been confirmed by Hoekstra and Siegel, et al.[47] This beta modification of U_3O_8 is quite closely related by symmetry to the alpha U_3O_8 and has its remaining diffraction reflections superimposed on the latter. For this reason it is difficult to detect. It is not clear whether the observed diffraction lines actually result from the presence of beta U_3O_8 or arise from some transition structure leading to the gamma phase, the third allotropic modification of U_3O_8.

At intermediate temperatures of 200 to 300 C and at pressures near 25,000 atm, the diffraction pattern becomes nearly amorphous. At 16,000 atm and greater and at temperatures from 400 to 600 C, the gamma phase may be reproducibly formed as shown in Figure 10.
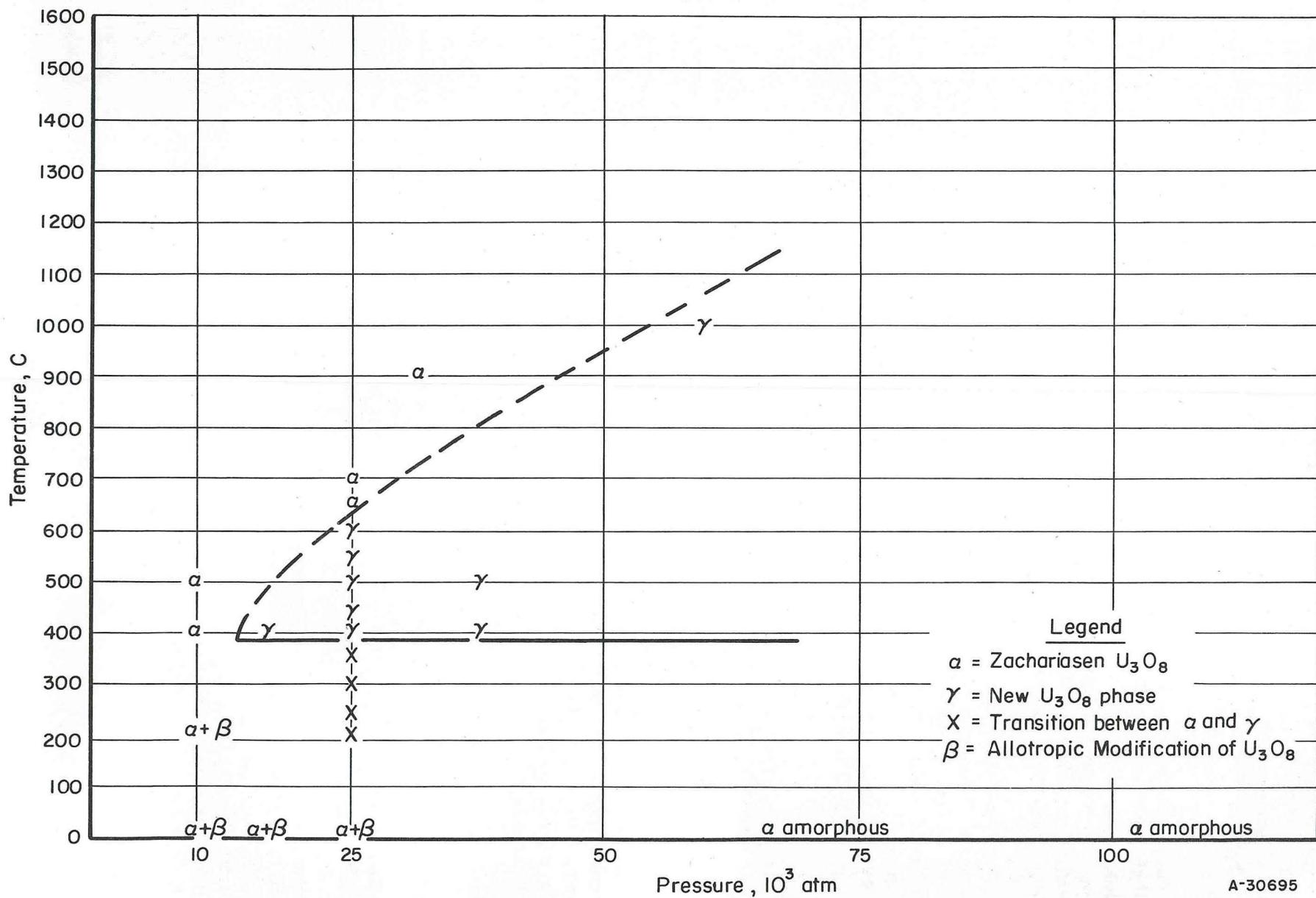
FIGURE 10. TENTATIVE PRESSURE-TEMPERATURE PHASE DIAGRAM FOR U_3O_8

To determine if the gamma phase is sluggish in forming, in the Bridgman sense, the pressure was increased to 100,000 atm at room temperature. The resulting pattern was nearly amorphous, indicating that increasing pressure alone does not produce gamma phase U_3O_8. Work is currently under way in the new die to extend the U_3O_8 pressure and temperature phase diagram.

Early results strongly suggested that the composition of gamma phase was intermediate between U_3O_8 and UO_2 and that pressure tended to produce UO_2 in accord with the Clapeyron relation. Samples of gamma phase produced at 16,000 and at 25,000 atm at 450 C were analyzed by microbalance techniques to determine the uranium-to-oxygen ratio. The results show that it has a composition of $UO_{2.65}$, which is essentially the same as the composition of both alpha and beta U_3O_8.

The crystal structure of the new U_3O_8 phase has not as yet been identified. Preliminary attempts have been made to index the observed X-ray diffraction reflections, without success. The symmetry appears orthorhombic or lower and it would appear that the basal symmetry of the beta modification of U_3O_8 may have been retained, with a collapse of the c-axis dimension. Further work will be necessary to determine if this is the case.

CONCLUSIONS

Although equipment has been developed which is adequate to explore the new high-pressure high-temperature area, much additional work will be required to achieve a significant understanding of the combined effects of high pressure and high temperature on solids. At present there is available only a relatively small background of both experimental and theoretical work by which to proceed on this field. Continued research, however, should greatly increase our understanding and provide a more fundamental basis by which to evaluate the new area and what may be accomplished with it.

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WBW:ims

0 –

.024 Ω
.026 Ω
.0021 Ω

.05
.2
.010

.14
.05
.0070

26
2

(306) Ω

5

– 307 mils –

Bi { I → II   31 ton   24,800.
   { VI → VIII 150 ton   121,000.

Ba 92 ton

= 77,400.

$\frac{121}{24.8} \times 30.5 = 149$ tons

500
300
(200)

$\frac{1}{15} \times 121,000$
8100
129,000 atm

25.0
22.5
1.3
23.

(151
124)
30

(92
74)
18

(29.5
23.8
24)
85.7

.197

5.7 =
29.5

30 .199
151

18 .196
92

Δ trans = 20%
——
trans f

in each case

$2\pi r^2 \Delta h$ disk

$2\pi r \Delta r \cdot h$ ring

$2\Delta r \, h = 2r \, \Delta h$

$\Delta r = \Delta h \tan\theta$
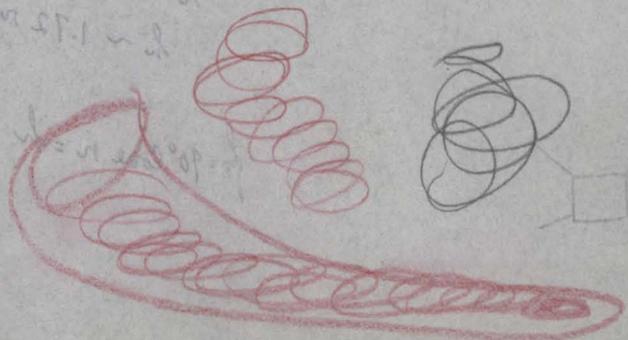
$\Delta h \tan\theta \, h = r \Delta h$ $r = h \tan\theta$

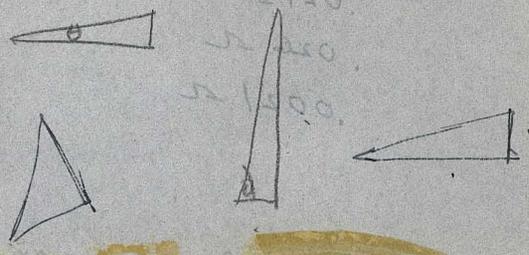$r \tan\theta \, h = r$

$r = \Delta h \tan\theta$

$2\theta = $ angle at apex of the cone

$\tan 15° = .268$

$\tan 30° = .578$
$\tan 18° = .325$
$\tan 45° = 1$
$\tan 17\frac{1}{2}° = .315$
$\tan 35° = .700$

$\frac{27}{}$

$r = h \tan\theta$
$\tan\theta = \frac{r}{h}$

$.5 = .27 h$

$\frac{6}{16}$

$h = $

$.350$

$h \sim$

$r \sim \frac{h}{4}$ $h \sim 4r$ to work

$\frac{3}{27}$
$\frac{5}{}$
$1.35"$

h less than to work

$h \sim 2"$ if $r \sim 1\frac{1}{2}$

if $r \sim \frac{1}{4}$, $h \sim 1"$

works for $h < 1"$

$r = .268 h$
or $D \sim .54 h$
for $30° \angle$ Cone
or $h \sim 1.87$ diam
if $D = \frac{1}{2}"$, $h = .93"$

for $70°$ Cone $h \sim 1.43 r$

for $60°$ Cone
$r = .58 h$
$h \sim 1.72 r \sim .8D$

for $90°$ Cone $r = h$