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Device for Ultra-High-Pressure High-Temperature Research*

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A new device has been developed for materials research at high pressures and high temperatures. The unit may be described as an extension of the Bridgman "anvil," modified to permit internal heating. The principle of "massive support" is retained with pressure being achieved through the elasticity of multiple binding rings, rather than through the "compressible" gasket effect. The unit has been calibrated to pressures beyond 100 000 atm with temperature to 2000°C. The operational characteristics of the device and problems associated with high-pressure high-temperature research are discussed.

INTRODUCTION

A SIGNIFICANT portion of the present understanding of pressure and its effects on materials is attributable to the work of Bridgman.[1] The major portion of this research was conducted at ambient or slightly elevated temperature in devices designed to provide truly hydrostatic pressures. The more recent research of Bridgman was concerned with the development and use of equipment to 100 000 atm and beyond.[2]

Recent research in high pressure has been directed, in part, toward obtaining high pressure simultaneously with high temperatures. Elevated temperatures generally are required to provide needed activation energy for reactions to proceed. The significance of pressure and temperature on reaction rates has been discussed by Hall.[3]

Various investigators,[4] especially Coes, as reported by Roy and Tuttle,[5] Hall,[6,7] and Griggs and Kennedy[8] have described high-pressure high-temperature equipment. Griggs and Kennedy have modified the "anvil" concept of Bridgman[2] to include use of an external heater. This provides an advantage, in that the temperatures and pressures are known better than they are with the internally heated designs. However, the use of an external heater introduces serious pressure and temperature limitations since the elevated temperatures reduce the strength of the components.

The internally heated die designs which have been described to date are generally of two types: the piston and cylinder type, and the "compressible gasket" type such as Hall's tetrahedral anvil.[6] The former has the advantage of unlimited compression and is capable of nearly 50 000 atm. The latter is a three-dimensional version of the Bridgman anvil and represents a solution to the formidable problem of combining the extremes of high pressure with high temperature. The present die design, like the tetrahedral anvil, is also an attempt to achieve higher pressures and temperatures than are possible in the piston and cylinder type devices.

APPARATUS

A schematic of the present high-pressure equipment is given in Fig. 1. The unit, called the "girdle" may be described as a modification of the Bridgman anvil. Conventionally, the Bridgman anvil consists of two abutting truncated cones of tungsten carbide. The sample, in the form of a very thin disk, is placed between the carbide surfaces. Friction prevents the expulsion of the sample as the pressure, generated between the carbides, is increased. Samples which do not have suitable frictional properties may be surrounded by a compressible ring gasket, such as Bridg-

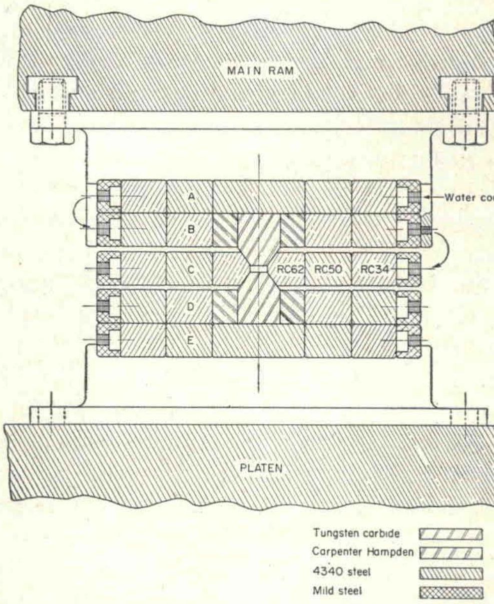

Fig. 1. The "girdle" ultra-high-pressure die.

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[*] Work performed under an AEC contract.

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[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81** (1952).

[3] H. T. Hall, paper in Proceedings of the Stanford Symposium on High Temperature, Stanford Research Institute, Menlo Park, California (1956).

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[5] R. Roy and O. F. Tuttle, *Physics and Chemistry of the Earth* (Pergamon Press, London, 1956), vol. 1, pp. 138–180.

[6] H. T. Hall, Rev. Sci. Instr. **29**, 267 (1958).

[7] H. T. Hall, paper presented at Symposium on High-Temperature Technology, Stanford Research Institute, Menlo Park, California (1959).

[8] D. T. Griggs, and G. C. Kennedy, Am. J. Sci. **254**, 722 (1956).

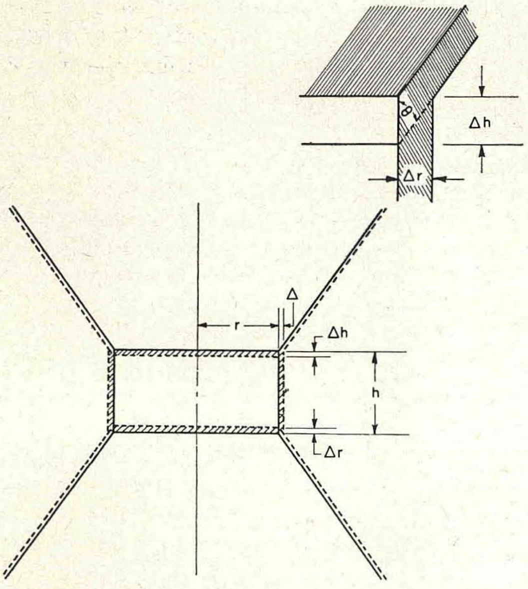

FIG. 2. The geometry operative in the girdle die design.

man's "pipestone," to prevent "blowout" or expulsion of the sample.

The present apparatus uses a principle of elastic distortion rather than the compressible gasket to obtain compression. In order to increase the sample height and to allow use of an internal heater, the auxiliary binding ring[9] "C" is placed around the periphery of the sample region. The binding ring also extends up the sides of the conical pistons, thus supporting a large portion of the radial stress in the pistons. Further support of the radial stress in the pistons is afforded by additional binding rings A, B, D, and E. As the conical pistons are forced into the conical recess of the central binding ring, the wedge effect of the cones forces the die to expand. The geometry operative in the die is shown in Fig. 2, which may be used to derive the conditions under which pressure may be generated.

From Fig. 2 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. In the latter case, the binding ring is superfluous. For solutions between the right circular cylinder 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 forced to expand an amount Δr. From the figure $\Delta r = \Delta h \tan\theta$. To build pressure in the die, there must be a net volume decrease. Thus, the volume swept out by the piston advance (disk volume) must be greater than the volume expansion due to the change in radius. If these volumes are made equal, it is found, neglecting second-order terms, that $r = h \tan\theta$. To build pressure, h must be made smaller than the equal volume value. The internal bore diameter of the prototype was made $\frac{1}{2}$ in. to conform to existing sample dimensions. The shear angle for compressive failure of carbide was assumed to be near 45°, but the use of such an angle for θ imposed a severe restriction on sample height. For this reason, θ was set at 35° and h was found to be 0.35 in. However, for h near 0.35 in. the internal volume decreases very slowly with piston displacement, and ultimately the bore height gradually was reduced by grinding to 0.25 in.

The use of the conical carbide pistons in conjunction with the central binding ring results in the mutual support of both the pistons and the binding rings. Under normal conditions, pressure would tend to split the hardened steel (Rockwell C65) die insert in the central binding ring. This is prevented by virtue of the large compressive force exerted by the taper of the carbide acting on the steel. Thus the binding ring supports the radial stress of the carbides, and the carbide prevents the "pinch-off" effect from occurring in the die.

Typical high-pressure sample configurations, consisting of the specimen, heater, and pressure transmitting medium (which is also the thermal insulator) have been described by Hall.[5] Conduction through the heater is accomplished by impressing a voltage between the pistons. This is made possible by applying oxide insulation between the die (central binding ring) and the piston and electrically isolating the bottom portion of the unit from the press. This insulation increases the effective bore height h and in practice the actual sample height used is 0.35 in.

Experience obtained with other high-pressure equipment dictated the incorporation of certain features in the present design. For example, insulation difficulties which may be encountered require only simple remedies which do not involve disassembly of the apparatus or experiment. In the event of a short, the removal and reinsulation of only the top piston is required in the present design. Again, since the oxide insulation is a semiconductor, sustained heating in the high-pressure region will ultimately raise the temperature of the insulation. This lowers the resistivity of the insulation resulting in the possibility of an eventual short. Dielectric breakdown of the insulation, which directly shorts the high current transformer, results in an "explosion" sufficient to damage the apparatus. Water cooling of each binding ring is utilized in the present design to minimize these difficulties.

PERFORMANCE

The ultimate pressure obtainable with the "girdle" unit has not been established. Calibration to date has given the bismuth, thallium, and barium transitions of Bridgman[2]; pressures of 100 000 atm with varying temperatures have been used routinely. With the die dimensions used, a press force of 225 tons is required to produce 100 000 atm. The "unsupported" position of the piston

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[9] The binding rings have been described by Hall, reference 6.

should withstand an ultimate load of 350 to 450 tons, suggesting that 200 000 atm are possible with existing geometry. The theoretical pressure limit occurs when the geometry is varied to the Bridgman anvil condition. Pressures of 280 000 atm have been obtained with the conventional Bridgman anvil device using $\frac{3}{16}$-in. carbide surfaces when the multiple binding rings are used to support the radial stress.

Preliminary analysis of the stresses produced on the top surface of the steel insert have been made using miniature strain-gauge indicators. The results show that tensile stresses of the order of 10 000 psi are produced adjacent to the carbide piston. This surprisingly low result can be explained by assuming that the large frictional forces between the carbide and the steel insert are subtractive to the tensile stresses produced by the die expansion. The outside diameter of this steel insert also indicated only nominal (4000 psi) stresses which were compressive.

The use of a slightly oversized sample, 0.35 in. in height, generally results in the extrusion of a small amount of material between the top piston and the die. This "compressible gasket" has a tendency to produce localized stresses which shortens the life of the top piston. However, the excess can be removed after precompaction to obtain more even stress distribution, allowing longer piston life and possible higher pressures.

An alternative technique has been employed in which a uniform thickness, pre-machined compressible gasket is used in lieu of the oxide powder insulation. Its use requires a 0.40-in. sample height and permits the "girdle" apparatus to function as a combined compressible gasket and elastic distortion apparatus.

The major limitations of the internally heated ultrahigh pressure devices are (a) temperature uncertainty, (b) contamination, (c) gas release, and (d) pressure uncertainty. For purposes of obtaining transformations occurring over broad ranges of temperature, the uncertainty of temperature is relatively minor. In more precise investigations, uncertainty of temperature, together with possible gas release, constitute a major problem.

Temperature usually is measured by inserting thermocouples through the gasket or oxide insulation to the heater. In practice this is difficult to accomplish reliably since the pressure in the gasket or insulation tends to "pinch off" the thermocouple leads. In addition, the thermocouple leads increase the probability of shorting across the insulation. For devices such as the "tetrahedral anvil" it would appear feasible to utilize the two pistons not employed in heating as contacts for the internal thermocouple, thus eliminating the necessity of bringing leads through the insulation.

The existence of large temperature gradients further augments the temperature uncertainty, even when thermocouples are successfully inserted into the apparatus. The use of metallic heaters such as platinum results in very large gradients. Emphasis was placed, in early work with the present apparatus, on use of a $\frac{1}{8}$-in. diam thin-walled platinum heater 0.35 in. in height. Jackets of BeO, an electrical insulator with high thermal conductivity, have been employed to smooth out such gradients. Graphite heaters, which have high thermal conductivity and a negative temperature coefficient of resistance, automatically tend to eliminate temperature gradients. They are, however, restricted in use to conditions which are thermodynamically compatible with the system under investigation. Further improvement in the temperature-gradient problem appears possible by employing heaters with a more favorable length-to-diameter ratio. This may be accomplished with existing ultra-high-pressure apparatus designs by either scaling up the size of the unit or reducing the heater diameter.

The prototype of the "girdle" apparatus was designed to utilize available components from existing piston and cylinder type apparatus. By varying the pistons and central die insert of the binding rings, it is possible to change from the "girdle" configuration to either a "Bridgman anvil" or a simple piston and a cylinder apparatus. This simple interchangeability also should facilitate geometrical and dimensional variation of the "girdle" configuration.

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