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MODIFICATIONS OF OPPOSED ANVIL DEVICES*

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The opposed anvil system for generating ultra-high pressures has been applied to a wide variety of crystal-chemical and mineralogical studies. An enlarged apparatus operated by a 400-ton press, capable of high-pressure studies with ' gram '-sized samples in the usual manner, has been adapted to internal heating and ' hydrothermal techniques ' and also to the mapping of load distribution in wafer samples, using as indicators the changes of electrical resistance at the pressure transitions of metals. An important finding of the latter study is the pressure intensification possible in the centre of sample wafers dependent on their diameter–thickness ratios.

Introduction

In studies of solids where pressure was one of the major variables, a number of experimental systems have been devised to utilise the optimum properties of the materials of construction. The simplest and a very productive system, which is also the one reaching the maximum static pressures, is based on the principle of two opposed anvils first effectively used by Bridgman.[1] In apparatus of this type, high pressures are supported on a small area of the anvils (Fig. 1), and the sample is thin enough to be retained entirely by friction at the edges, thus dispensing with any type of containing cylinder. By appropriate stressing of an inner anvil by shrink fit and tapered supports, pressure two or three times greater than the compressive strength of the anvil materials could be attained. The characteristic distinction of these anvils is the absence of any containing ' cylinder '. With such apparatus, Bridgman claimed to have reached pressures near 200 kb with a ' single stage ' and 425 kb with a ' two stage ' device. He had worked at temperatures usually close to room temperature with a few runs near 300°. Further impetus was given to studies at high temperatures by the interest of petrologists (Griggs & Kennedy[2]) in work on synthesis and phase equilibria in mineralogical systems, following the reports of Coes[3] on the synthesis of several high-pressure phases in piston-cylinder apparatus. Since then the orderly development of this type of apparatus, both to extend the temperature and pressure limits, as well as to calibrate the pressures, has extended the usefulness of opposed anvils greatly.

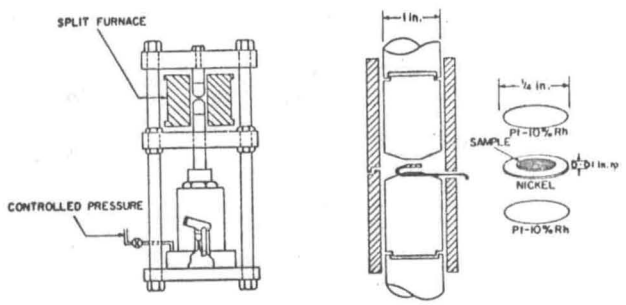


Fig. 1. *Sketch of opposed anvil apparatus with enlarged views of anvil and sample assemblies*

The proportions are for a frame with three 1 in. dia. tie-rods with a 20-ton hydraulic ram as the load unit. For work in the 200 kb region with ¼ in. dia. sample assemblies frames of at least 60 tons capacity are required.

In Fig. 2 is summarised the effective working range of opposed-anvil apparatus for runs of at least 3-h. duration. Greater frequency of breakage is to be expected near the upper limits shown because of critical factors such as alignment and non-uniform sample packing.

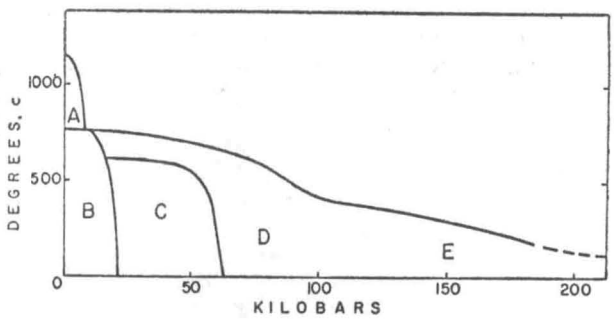


Fig. 2. *Effective combined* P–T *working range of various anvils for runs of over* 3 *h. duration*

In the various portions the following types of anvils are used:
A, polycrystalline alumina; B, Rene' 41; C, 66 HS or Speed Star; D, Tungsten carbides-in-Rene'; and E, Tungsten carbides-in-TK tool steel.

* Contribution No. 61 – 77, College of Mineral Industries, The Pennsylvania State University.

Problems which have been studied in opposed-anvil apparatus, in addition to those of synthesis and phase equilibria, include kinetics of reactions, diffusion, orientation, influence of shearing stresses, crystallisation of glasses or gels. *In situ* measurements of various electrical properties have also been conducted. This broad range of problems is made possible in part by the fact that scaling-up of the size of the apparatus (in this laboratory from 8 to 400 tons) in no way affects the extreme simplicity of operation. The other major advantage which opposed anvil devices have over internally heated piston-and-cylinder apparatus is the accuracy of temperature measurement which is very greatly superior to that in other apparatus. Concomitantly, its greatest limitation is the unattainability of the higher temperatures possible with other apparatus.

Current design of anvils

Materials and shapes

Despite the great interest in high-pressure studies, very little fundamental work has been reported on the design of anvils. The development of this equipment has been based mainly on empirical experience gained through use.* Thus, in the selection of an optimum design of the simple piston, questions raised regarding the ratio of the diameter of the sample face to that of the body, or of diameter of the body to length, or of the angle of the cone, could not be answered by recourse to results of systematic studies.† Rather, a practical sequence of choices was made starting with a minimum sample size (6—10 mg.) determined by the requirements for *X*-ray and optical identification, which should be contained in the $\frac{1}{4}$ in. diameter wafer assembly shown in Fig. 1. An outside diameter of 1 in. was found to be very convenient insofar as centering and supporting on softer Stellite-25 thrust bars. The length of the anvil was determined by convenience and by length of the hot zone of the furnace used to heat the sample assembly. With regard to the cone angle, a broad one close to 180° might be a theoretical choice, but actually angles between 150° and 160° have been found best for most types of work. The larger angles provide enough space to position properly a thermocouple close to the sample. More important, the wider angle between the two anvils practically eliminates the interference with the calculation of pressure on the ' flat ' sample faces which is a very serious consequence of the unknown and variable extrusion of material.

If only from the observation of types of failure of the simple anvils, without being aware of earlier solutions, certain modifications of design would be sure to suggest themselves. In almost every case, simple pistons made of hardenable high temperature steels, 66HS (see appendix), Speed Star, polycrystalline alumina or mullite fail by breaking into three pieces, two being essentially equal halves and the other a small wedge having the sample area ' flat ' as a base (Fig. 3). On the occasions when the anvils do not fail completely, radial cracks will be found starting at the small end of the cone at the edge of the sample flat but very seldom crossing it. Apparently these cracks are caused by peripheral tension failure, and in many cases, occur just before the shear failures which produce the small wedges. Anvils of tungsten carbide fail with considerable shattering and spalling of the conical surface.

Bridgman's first step in improving the performance of anvils was to provide lateral support by compression in a holder, or by a combination of compression and tapered seat as shown in Fig. 4. With such support it has been possible to raise the effective pressure attainable with the special steels from 60 kb to 90—100 kb and with tungsten carbide (6% cobalt) the upper limits are 160—200 kb. Another advance is the graded support developed by Drickamer[4], whereby maximum reinforcement is provided at the region of maximum stress at the end of the cone. In a sense, Drickamer's modifications are intermediate between the simple anvil and the designs

* Prof. Bridgman told one of us (R.R.) that he had chosen his angles, shrinkage and other dimensions in the same empirical manner.

† Some idea of the changes in stress distribution with changes in design have been obtained in this laboratory from studies with simplified two-dimensional photoelastic models of anvils. Thus the influences of cone angle, diameter ratios, and diameter and length ratios have been studied in the stress patterns. The additions of lateral support and then of support to the conical shoulders produce remarkable redistribution of stresses which qualitatively are related to the increase in strength actually observed. More accurate but similar patterns may be obtained using three-dimensional models following a technique used by Stefanko & Tandanand (personal communication). The correlation between complex anvils made of dissimilar materials and the plastic models is not known, but it should be close enough to be instructive.

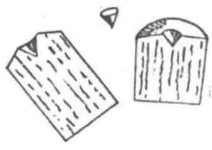


Fig. 3. *Sketch showing the characteristic failure of simple anvils made of 66HS, alumina or mullite*

The Rene' types deform rather than crack, whereas carbide cores crack, deform and splinter very badly when overloaded

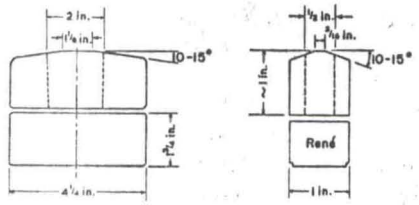


Fig. 4. *Modifications of ' two-stage ' anvils based on Bridgman's design*

The large anvil and flat assembly is the basic one for use in a 400-ton frame. Substitution of carbide cores with $\frac{9}{16} - \frac{5}{8}$ in. sample flats is done for work near 200 kb. The smaller assembly is used in 20 or 50-ton frames

based on extrudable gaskets such as the GE ' belt '. It is obvious that the compound anvils provide further opportunity to combine materials to the greatest advantage. The material of great hardness supports the direct thrust, while a tougher, less brittle material provides lateral support. What the substitution of a suitable polycrystalline diamond body for the carbide would produce is interesting to contemplate.

The use of red-heat tough steels or of high temperature–high strength alloys such as Stellite-25 and Rene' 41 permits work with the anvils at higher temperatures than are possible with the original Bridgman design. An effective two-stage anvil for work in the 100-kb region and 300—400° is made with $\frac{1}{2}$ in. cylindrical tungsten carbide plug force-fitted (1 % interference) into a 1 in. Rene' 41 collar, the end of the plug being finished to a $\frac{3}{16}$ in. circular flat. For use in the 400-ton frame, the safest and most useful all-steel anvil is made with a 2 in. plug of 66HS or similar steel at Rockwell-C hardness force-fitted into a 1° tapered hole in a TK steel holder at Rockwell-C 40—45. Each anvil is then backed with about a 2 in. thick flat of 66HS steel at Rockwell 66. The sample surface is a flat of $1\frac{1}{8}$ or 1 in.

Other materials may be used to work in specific ' *P–T* ' regions beyond those accessible with the anvils described above. Simple pistons of sintered polycrystalline alumina or mullite have been used by us in the range 1000—1200° and 7 kb in studies of the olivine–spinel transition of magnesium germanate. Silicon carbide anvils have been prepared by hot-pressing for use in the same region at higher pressures. Cemented titanium carbide is more resistant to oxidation than cemented tungsten carbide and is substituted for it (in a Rene' collar) for many studies a 600—750° and 35—20 kb. On the other hand, the Rene' alloy has been replaced by tungsten to give greater support to carbide inserts at the highest temperatures.

Size of samples and scale-up

A serious obstacle in laboratory high-pressure research is the restricted amount of sample which can be obtained. Thus in the 20—100 kb range in opposed-anvil apparatus, most of the significant synthesis work reported has been done with thin wafers amounting to 6—15 mg. of sample and a 20-ton ram.

In larger units based on 50, 100 and 400-ton rams, samples of silicates and similar oxides amount to about 40, 110 and 1000 mg. respectively. A typical large sample is $\frac{3}{4}$ in. diameter in a nickel ring $\frac{7}{8}$ in. o.d. and 0·04 in. thick. The significant increase in sample size is obtained at a modest cost of equipment when compared with increases in other types, so that, where studies may be carried out at temperatures up to 500—600°, the anvil apparatus is very convenient for subjecting a ' gram ' size sample to a known temperature, at pressures up to at least 100 kb, and higher with greater ram capacity.

Use of anvils in specialised applications

Shearing stress addition

The major mode of use of opposed anvils has been indicated in Fig. 1. Because of the temperature limitations on the anvils, all methods to increase reaction rates need study. The anvils

are adaptable to studies[5] of the influence of continuous shearing stresses on reactions under pressure in a simple modification of our standard apparatus (Fig. 5). Shearing stresses are applied to the sample wafer by rotating the bottom anvil about its vertical axis back and forth through a maximum of 2° in 15 sec. This oscillating action is maintained mechanically for hours on samples under pressures up to 100 kb and temperatures up to 500° (for lower pressures). In an attempt to do something analogous by Bridgman[1], the same type of action was applied manually in a few alternate strokes each through 60° of arc in about 5 sec. (Drickamer & Larsen[6] and Griggs *et al.*[7] have made use of continuous shearing stresses due to slow rotation in one direction of one anvil against the other.) Under the conditions of our experiments heating due to friction is negligible, a conclusion also arrived at by Bridgman and by Drickamer & Larsen in their respective experiments.

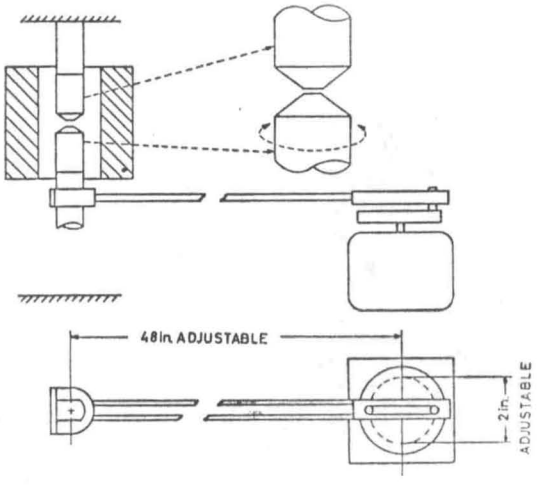


Fig. 5.

Sketch of the essentials of the shear modification of an assembly

The lower thrust bar is rotated back and forth 2° max. in 15 sec. while the sample is under pressure. No bearings or special clamps are required.

Sealed tube samples

One important feature of anvil apparatus is that the sample thickness which can be held by friction between the faces increases with the diameter of the faces. In a 400-ton unit where anvil faces are $\frac{3}{4}$ to $1\frac{1}{8}$ in. diameter, the thickness of sample will be 0·03—0·04 in. in the higher pressure range. However, it is possible to support even thicker samples at lower pressures (10—50 kb) by selecting a stacking of two to six 0·04 in. thick rings or even single rings 0·05—0·06 in. thick. The useful sample volume during such runs is about 0·5 c.c. and yields 1500 mg. of silicates. The distortion of the sample in runs of this type is indicated in Fig. 6 and one sacrifices accuracy of pressure measurement in these samples (see below).

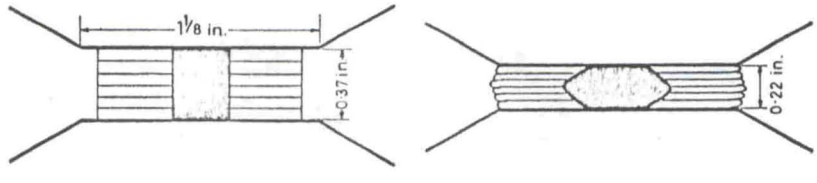


Fig. 6. *Example of distortion of a 'stacked' or thick sample*

The ability to hold thick wafers of silicates makes possible an extension of the hydrothermal techniques into the 50-kb range and higher. In a method being developed by E. Hryckowian in this laboratory, the sample assembly (Fig. 7) consists of a sealed platinum or gold tube containing the water or other volatile liquid and sample, embedded in pyrophyllite or similar medium, all being held in tough metal binding rings of nickel or stainless steel. The anvil–sample assembly is heated in the conventional manner by external heating to temperatures as high as 500°. Thus the *complete* reaction of quartz to coesite is effected easily, made possible at these temperatures only by the presence of water. Hydrous phases such as analcite and phillipsite will remain unchanged at 275° at 10—20 kb but will react completely to jadeite at 450° at the same pressure.

The analcite or phillipsite may also be formed at 225° and 15 kb, starting with a water plus 1 : 1 : 3 mixture (Na_2O : Al_2O_3 : $3SiO_2$). The containment of the very volatile CS_2 also is possible, although sealing into the tubes is more difficult, for the polymerisation reaction (Bridgman[8]) above 42 kb at 100—200°.

Internal heating

Thick wafers also permit a form of resistance heating similar to that used in the belt-type and tetrahedral-ram pressure apparatuses. In this modification (Fig. 8) the cell thickness before compression is 0·125 in., but it will have a lenticular shape after the run with centre thickness 0·08 in. and edge thickness 0·065 in. approximately. It is obvious from the appearance and variable hardness of the wafer that the pressure is greatest in the centre over a flat capsule about $\frac{5}{8}$ in. in diameter and that the outer portion of the wafer provides in effect a graded pressure seal to the edges of the anvil flats. The heating strip is arranged in this space as shown in Fig. 8. With this method it has been possible to contain briefly molten platinum and iron, and on occasion silica, at pressures of the order of 30—60 kb with pyrophyllite wafers as the pressure medium. There appear to be many potentialities for valuable synthesis work with this system, but precise measurement of temperature and pressure is unlikely.

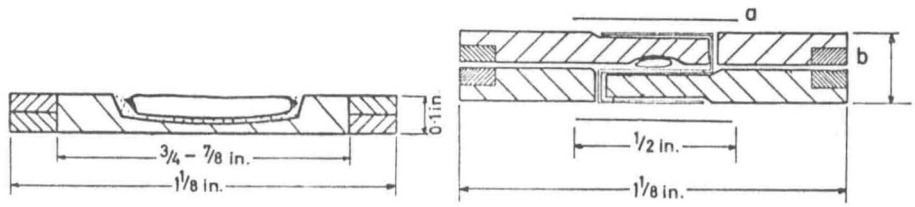


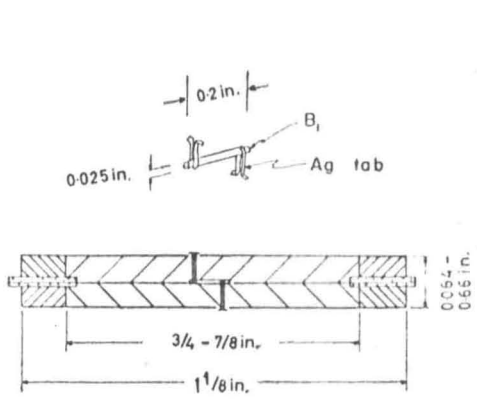
Fig. 7 (left). *Sample assembly for use with sealed tubes for hydrothermal work at opposed-anvil pressures*
Pyrophyllite is used as a pressure medium

Fig. 8 (right) *Sample assembly incorporating a resistance furnace in the form of a strip for use in syntheses at high temperatures and pressures*

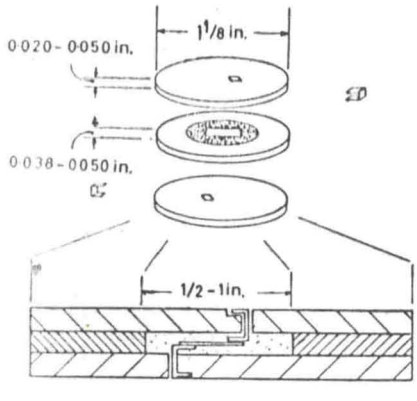
(a) platinum foils for electrical contacts (b) nickel rings enclosing pyrophyllite wafers

Electrical measurements at pressure

Bridgman's work with electrical resistance measurements in the anvil pressure system is well known. In the course of similar work in this laboratory (Myers *et al.*[9]) sample assembly modifications such as those shown in Fig. 9 have been most useful in providing reproducible measurements of changes of resistance under pressure. The major differences with Bridgman's assembly is the use of metal-containing rings instead of pipestone or lavite, and an overall thinner sample. The recognition of the importance of the sample thickness and the accommodation to the radial pressure gradient are the important new features.



(a)



(b)

Fig. 9. *Two sample assemblies used for electrical resistance and calibration studies*

Nature and uniformity of pressure

An extensive study in this laboratory has been made to use various ' fixed points ' in reaction equilibria as well as electrical resistivity measurements to find correlations in results with those obtained in other types of apparatus. In normal use, when the diameter-to-thickness ratio of a sample wafer assembly is about 25 : 1, the pressure distribution has been shown to be uniform. This has been demonstrated[10] in experiments where the ratio of the area of the metal ring to area of sample was varied from about 4 : 1 to 0 : 1 at the equilibrium pressure for the quartz–coesite reaction at 500°. The results showed that, for this wide range of sample distribution the transition pressure was within 0·4 kb of the 20·4 kb average for all cases. With this type of sample, univariant *P–T* equilibrium ' curves ' (Fig. 10) have been obtained for several important solid-state reactions. In some cases, where overlap permitted, these curves were carried down to low pressures where they join the hydrostatic pressure region. Furthermore, Bridgman's synthesis of the waxy ' polymer ' of CS_2 in liquid-pressure apparatus at 42 kb was duplicated by us at the same pressure in the anvil apparatus.

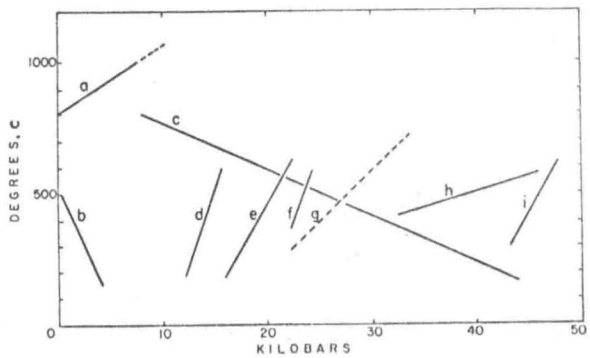


Fig. 10. *Examples of univariant* P–T *curves obtained with our opposed anvil apparatus*

The dashed line is that for the theoretical graphite–diamond equilibrium. In order, they are (a) Mg_2GeO_4 olivine–spinel; (b) PbO litharge–massicot; (c) $ThSiO_4$ thorite–huttonite; (d) PbO_2 I–II; (e) SiO_2 quartz–coesite; (f) B_2O_3 hexagonal–monoclinic; (g) C, graphite–diamond; (h) $HoVO_4$ xenotime–scheelite; (i) BPO_4 cristobalite–quartz

Myers *et al.*[9] found that the pressure distribution changes radically (at temperatures below 200°) as the diameter thickness ratio is reduced. This one factor probably explains most of the variability obtained by some investigators. This behaviour is further modified by changes in the geometry and in the relative hardnesses of the materials of construction of the wafer assembly, and must be taken carefully into account both in experimental procedures and in reporting results which might be applied to calibration.

In Fig. 11 are shown the results of this study of pressure distribution in a relatively thick sample assembly (diameter/thickness ratio about 9). The assembly was identical in each run except for the placement across the diameter at different points of a short length of bismuth wire (0·025 in. dia.) whose I → II transition was used as a pressure indicator (25·4 kb[10]). The figure shows that at the centre of the sample the transition was obtained when the average pressure on the anvil face was only 11·5 kb. However, a calibration wire placed about 1/2 radius out from the centre went through the transition when the average load was 18 kb. The change in stress distribution at the metal–pyrophyllite boundary is probably due to the differences in the flow properties of the materials, causing a break in the continuity of compacted solids at the boundary. The relatively uniform distribution of pressure for a ratio of 14 in. is shown in Fig. 12.

However, if the bismuth wire is placed in the centre, the thickness of the wafer assembly being changed, it is seen from the results summarised in Fig. 12 that as the diameter thickness ratio approaches 16 : 1 the average stress approaches the transition pressure. (Photoelastic models of sample wafers also illustrate the general patterns of stress distribution observed in our direct experiments.)

Temperature measurements

Normally rather little is said about temperature measurements in opposed-anvil experiments because of the simplicity of the setup. This was pointed out by Griggs & Kennedy and has been found to be the general experience of all users of similar equipment. As indicated in Fig. 1, a thermocouple is looped on the shoulder of an anvil with the couple end against the edge of the sample. The assembly of anvils and thermocouple is then enclosed in loose-fitting, thick sleeves of stainless steel or equivalent. The temperature of the sample is taken as the temperature

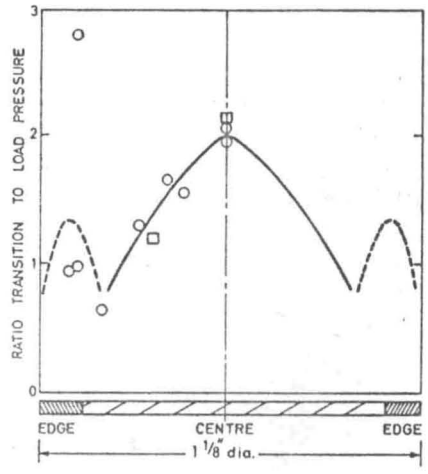


Fig. 11. *Pressure variation in a sample assembly as shown in Fig.* 9a *with the Bi I–II transition of* 25·4 *kb in comparison with the average load pressure for each run*

Circles and squares are for runs at room temperature and 140°, respectively.
Diameter/thickness ratio close to 9

recorded by the thermocouple. Studies have shown that this temperature is only two to three degrees higher than the temperature recorded by a thermocouple embedded and electrically insulated by a thin sample wafer under pressures of at least 15 kb. Automatic control of furnace temperature assures uniformity of sample temperature to within $\pm 5°$ for several days if necessary.

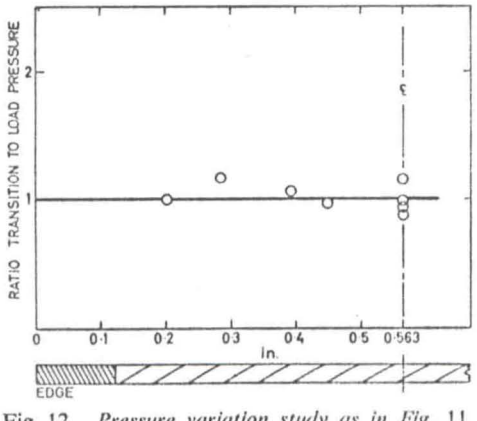


Fig. 12. *Pressure variation study as in Fig.* 11 *but with a diameter/thickness ratio of* 14

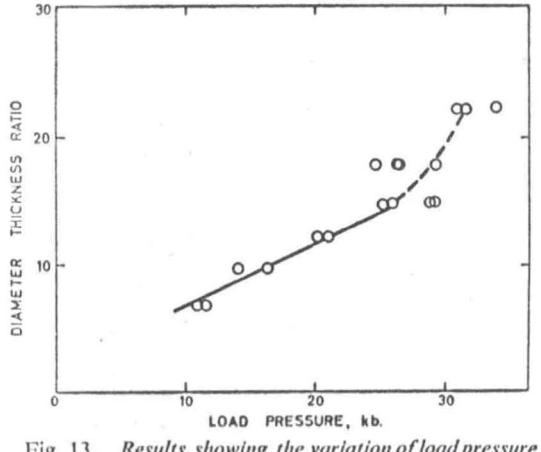


Fig. 13. *Results showing the variation of load pressure with the diameter thickness ratio of an assembly shown in Fig.* 9a *to obtain the Bi I–II transition of a centrally placed sample*

Application

Results of studies made using anvil apparatus have been described elsewhere and will be referred to only briefly here. High-pressure synthesis and equilibrium are represented by studies of silica isotypes,[11] polymorphism of lead oxides,[12] manganous fluoride,[13] boric oxide,[14] titanium dioxide[15] and, more recently, the interesting zinc oxide polymorphism (to the NaCl structure) at pressures over 110 kb.[16] An extensive equilibrium study involving the olivine–spinel transition[17] and its geophysical applications, and a purely crystal chemical study[18] of the pressure-dependence of the ionic size at which a phase transformation occurs in certain rare earth ABO_4 compounds, also attest to the potential of the method in systematic studies involving literally several hundreds of runs each.

Kinetic studies by the present authors[4,19] evaluate effects of pressure, temperature, displacive shearing stresses and even of minute traces of moisture in several solid-state reactions involving amorphous or crystalline compounds. The use of displacive shearing stresses have helped resolve the polymorphic relations in $ThSiO_4$.[20]

Densification of glasses[21] and crystallisation of glasses[22] under pressure have received considerable attention.

Acknowledgment

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APPENDIX

66 HS	Molybdenum high-speed steel, Type 6–5–4–2. AISI-SAE Designation M-2 Source—Bethlehem Steel Co.
Speed Star	Also an M-2 steel Source—Carpenter Steel Co.
TK	Tungsten base—9%, hot work type. AISI-SAE Designation H21 Source—Carpenter Steel Co.
Rene' 41	Also known as Alloy R-41 Vacuum melted, nickel base alloy with high strength in the 650—980° range Source—General Electric; Haynes Stellite
Stellite-25	A cobalt-base alloy with good high-temperature properties Source—Haynes Stellite
Titanium carbide	Nickel cemented titanium carbide in various compositions as Kenntanium, by Kennametal Inc.
Tungsten carbide	Cobalt cemented tungsten carbide in various compositions Source—General Electric; Kennametal
Tungsten	Special shapes made by Metallwerk Plansee, Tirol, Austria