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APPARATUS FOR PHASE TRANSFORMATION STUDIES AT HIGH PRESSURES AND TEMPERATURES

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The apparatus described consists essentially of Bridgman anvils which compress a pressure cell containing an internal heating element. The construction and operation of the pressure cell are described in detail. Besides housing a stable heating system, it functions as a pressure intensifier, so that the pressure on the sample is about 60 kb higher than the mean pressure across the anvils. The pressure on the sample is given by the mean press load divided by anvil area, plus an additional term representing the pressure difference between that at the centre of the anvils and the mean pressure. This latter term must be obtained by a separate calibration upon a known phase transition. Problems of calibration are briefly discussed. The apparatus is capable of developing pressures on a sample exceeding 200 kb, simultaneously with temperatures of about 1000 °C. This *P*, *T* range makes it very useful for studying phase transformations. A large number of new transformations have been discovered with this apparatus.

BRIDGMAN (1952) employed a pair of opposed tungsten carbide anvils supported by steel rings (fig. 1) to determine the resistances of many materials to 100 kb. The effectiveness of Bridgman anvils for generating very high sustained pressures has since been demonstrated by many workers. For example, HARRIS *et al.* (1961) have claimed pressures of 400 kb by this method. Attempts have also been made to combine some form of heating system with the Bridgman anvils, so that measurements can be made over a wide range of temperatures and pressures. The simplest method of doing this is to surround the anvils with a furnace (e.g. the "squeezer" of GRIGGS and KENNEDY, 1956). Although many valuable results have been obtained using the simple squeezer, the pressures developed are severely limited by the weakening effect of high temperature upon the anvils and supports.

Ideally, the most effective means of developing high pressures and temperatures simultaneously would be to insert some kind of heater between the faces of the anvils. Because of the small thickness of the pressure cell which can be confined between the anvil faces (usually $\leq 0.010''$) this has been a difficult undertaking. By using large anvils, a greater thickness of sample can be confined, e.g. DACHILLE and ROY (1962). Thus BUNDY (1964) succeeded in synthesizing diamonds using anvils of 2 inch O.D. and 0.8 inch face diameter. More recently RINGWOOD and MAJOR (1966a) synthesized diamonds using anvils of 1 inch O.D. and 0.5 inch face diameter. These experiments, however, have not achieved pressures much in excess of 70 kb.

This paper describes the further development of an internal heating system with which it has been possible to subject samples to sustained pressures above 200 kb simultaneously with temperatures of about 1000 °C. A large number of new phase transformations has been discovered with this apparatus.

The Bridgman anvils and support blocks as used in the present apparatus are shown in figs 1 and 2. For pressures below 140 kb, the anvils are preferably made of Kennametal K-68, K-96 or Carbolloy 883. Use of these softer grades of tungsten carbide results in long life. These anvils deform excessively at pressures above 150 kb, and for higher pressures, harder grades of tungsten carbide—e.g. Kennametal K-11 and Carbolloy 999 are used. The lives of these grades are comparatively short, particularly above 200 kb. The anvils are ground with an appropriate taper on the outer diameter—e.g. 0.010 to 0.015 inches per inch, and forced into support rings with an interference of 1 to 1.5 percent on the diameter. Support rings are of hardened Bethlehem Omega or Assab 8407 tool steels. Fig. 1 shows a 1 inch O.D. anvil with one support ring (Rockwell C 48) whilst fig. 2 shows a 1.5 inch O.D. anvil with two support rings (Rockwell C 49 and 43). The 1.5 inch anvil assembly is capable of developing a significantly higher pressure than the 1 inch anvil. Diameters of the faces of all anvils are 0.5 inch and the tapers ground on the ends are 8 degrees for softer grades and 5 degrees for harder grades.

The development of a workable pressure cell containing an internal heater posed a number of problems. Thus, the cell must be stable, i.e. it must not blow out when under high pressure. The deformation of the heater when under pressure must be minimised to prevent non-uniform heating and hot spots. At the same time it must be possible to maintain a stable high temperature within a very small volume in close proximity to highly conductive anvils. The cell must also permit easy recovery of sufficient sample after a run, so that optical and X-ray studies may be carried out. Finally, in order to obtain the highest pressures, it was desirable to design the cell as a pressure intensifier, so that pressure on the sample in the centre was much higher than the mean pressure across the anvils.

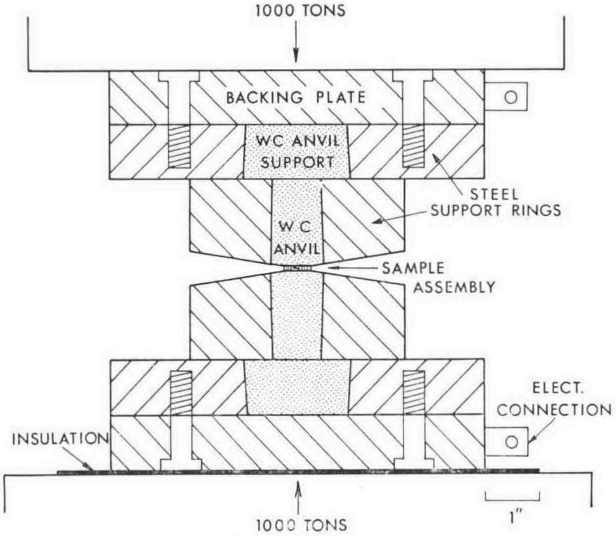

Fig. 1. Bridgman Anvil assembly with 1 inch diameter anvils and single support rings.

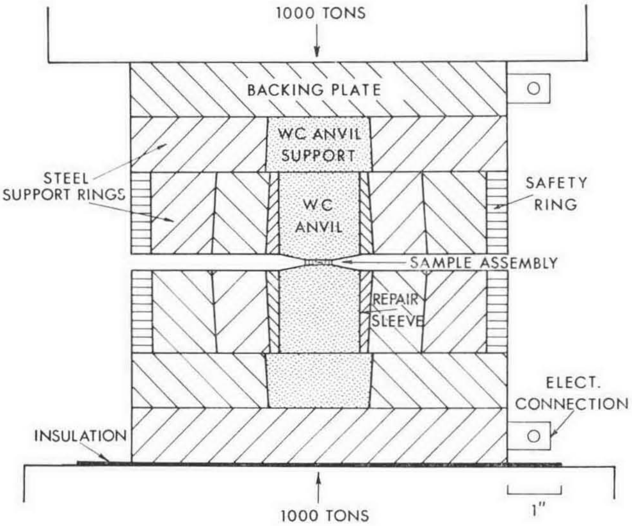

Fig. 2. Bridgman Anvil assembly with 1.5 inch diameter anvils and compound support rings.

The cell shown in fig. 3 illustrates a practicable solution to these problems. It consists basically of three sets of concentric rings. The outer ring, coated with rouge, is entirely of pyrophyllite and is 0.005 inch thicker than the inner rings, so that when the anvils are brought together the outer ring comes into contact first and supplies an initial confining pressure to the inner rings. The intermediate rings consist of two pyrophillite rings on the top and bottom, and between them, a ring of dense sintered aluminium oxide, e.g. Degussit A123. The central group of discs, containing the heater and sample are more complex and are shown in detail in fig. 3 (bottom). The top and bottom discs are of mica, which contributes towards a slight required initial compressibility for the cell and also supplies thermal and electrical insulation, without displaying excessive horizontal spreading under pressure. Next to the mica discs are two sintered, dense aluminium oxide discs. The physical properties of these discs are critical to the successful operation of the apparatus. They must not be too dense, otherwise they crack and spread under pressure, tearing the heater apart. If they are not dense enough, they flow excessively and again result in excessive deformation of the heating elements. A fine grained sintered alumina rod (Degussit A123) with a density of 3.5 to 3.7 g/cm^3 has been used successfully. Between the Al_2O_3 discs is a pair of discs of reagent grade aluminium oxide powder, cold pressed at 30 kb. These separate the dense alundum discs from the heating elements and facilitate easy removal of the heating elements plus sample after a run.

The heater is made of strips of nickel foil 0.002 inch diameter, with 0.005 inch nickel electrodes at each end. This encloses the sample which is prepressed at 30000 atm to a thickness of 0.003–0.005 inch. Separating the sample from the heater are strips of 0.0002 inch gold foil. These protect the sample from contamination by the nickel heaters, and also serve as an indicator of

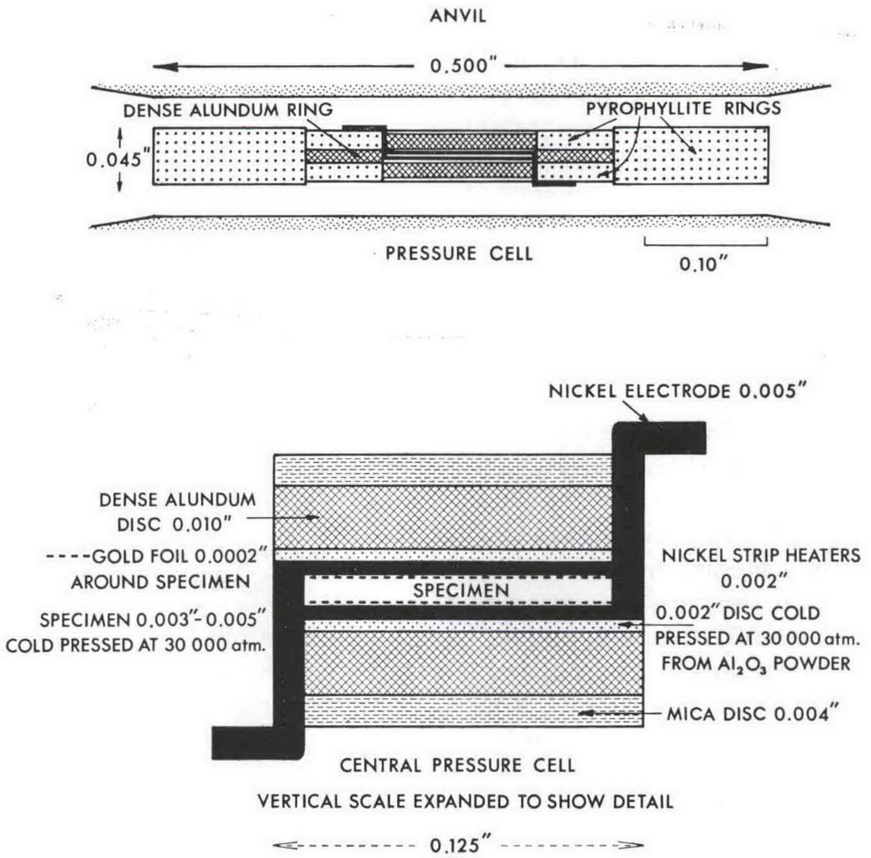

Fig. 3. Top: Section of pressure cell and internal heater used with Bridgman Anvils. Bottom: Expanded section of central region of pressure cell.

temperature distribution within the furnace. Where the furnace becomes hot (≈ 1000 °C) the gold diffuses into the surface layer of the nickel. However in cooler regions the gold remains unaffected. Accordingly, it is possible to select sample from regions of the furnace which have been strongly heated and to reject unheated material. Although the gold diffuses into the nickel in hot regions of the furnace, it continues to prevent contamination of the charge by nickel. This can be demonstrated by accurately measuring the refractive indices of phases—e.g. clinoenstatite ($MgSiO_3$) which have been synthesized in the apparatus and which would reveal the entry of less than 2 percent of nickel oxide or by precise measurements of lattice parameters of synthesized phases, e.g. Fe_2SiO_4, Co_2SiO_4 spinels, which would reveal the entry of less than 1 percent of NiO. The only occasions where nickel contamination was observed were in runs on hydrous oxide mixtures, rich in water, which were overheated. It is impossible, however, to use the nickel heaters with highly oxidised phases, e.g. Fe_2O_3 or $MgFe_2O_4$. In such runs, clear evidence of reaction of nickel with sample is seen. (No such evidence however was seen during runs on $NaFe^{III}SiO_4$ glass.) Other metals—e.g. gold, tantalum, platinum, iron, have been used as heaters in place of nickel, but were inferior. What is needed is a relatively inert metal which work-hardens strongly without becoming brittle during deformation. Iridium or platinum 60 rhodium 40 would probably be suitable substitutes.

In carrying out a run, the anvils and assembled pressure cell are carefully aligned using appropriate jigs, and pressure is applied *slowly* (to prevent blowout) by a suitable hydraulic press. When the desired load has been applied to the anvils, the nickel strips are slowly heated by an electric current. The power supply consists of a 240 volt variable transformer supplying a 20 to 1 stepdown transformer. A power input of 15 to 20 watts is maintained for 3 to 5 minutes in most runs. With higher power inputs, the nickel strips become difficult to remove from the surrounding ceramic components. There is also an increased risk of developing a hot spot and melting the nickel. With lower power input, the temperature may not be sufficient to activate the desired phase transformation. Runs may be carried out for much longer periods, but most transformations proceed to completion in 3–5 minutes under the above conditions. (Reaction rates in the present apparatus are observed to be very much faster than in piston-cylinder and belt types of high pressure apparatus.) After a run, the sample is quenched under pressure by terminating the power supply. The assembly is allowed to cool for 15 minutes under an air blast, then pressure is reduced and the sample assembly removed. The nickel furnace plus included sample is recovered, and the sample is removed. This latter operation is best performed under a low-power binocular microscope. The quantity recovered is usually ample for refractive index determination, and X-ray powder diffraction studies.

Much has been written about the problems of pressure calibration in Bridgman anvils and in other types of apparatus (e.g. GIARDINI and LLOYD, 1963). In the present design, the pressure cell acts as a kind of pressure intensifier, the central alumina discs constituting an inner pair of pistons which compress the sample into the alumina ring or die (fig. 3). This configuration greatly increases the pressures which can be attained. Whereas the mean pressure acting across the pistons is accurately known from their areas and the press load, the difference between the mean pressure and the pressure at the centre of the anvils must be obtained by calibration. It is desirable to base this calibration upon a phase transition which occurs at similar temperatures to those developed during normal use of the apparatus. Use of the "standard" Ba, Bi, Pb transitions is not desirable since they are determined at room temperature, and the operation of the heater in the very small volume of the pressure cell probably has a substantial effect on pressure distribution. Unfortunately, it is difficult to find a suitable series of phase transitions for use as reference points.

The present practice is to determine the mean pressure at which the coesite-stishovite transition occurs in the apparatus. This is obtained by a series of closely spaced runs on a sample of moistened (2% H_2O) quartz. With new pistons, the transition occurs at a press load of 42 ± 3 tons (mean pressure across anvils 33 kb). With older pistons which have become dished, the load for the transition may be as high as 47 tons (37 kb). The coesite-stishovite transition has been determined by STISHOV (1963) using the "standard" Bi, Tl, Ba calibration points. The pressures assigned to these transitions have since been revised substantially downwards by JEFFERY *et al.* (1966) and these new values are clearly preferable to the old. Using the new values for the "standard" transitions Stishov's pressure for the coesite-stishovite transition is 95 kb at 1000 °C. This is the value which is assigned to the coesite-stishovite transition in the present apparatus. *Accordingly, because of the pressure intensification effect within the pressure cell, the pressure on the sample at the coesite-stishovite transition is about 60 kb greater than the mean pressure across the anvil faces.* It is assumed that this pressure gradient is maintained at higher pressures. Since the shear strength of most materials increases with pressure, it does not appear likely that this gradient will be any smaller at higher pressures. It will be possible to check this when a series of reference transitions at higher pressures are finally available. The pressure in an experiment is thus given by two terms:

(i) the mean pressure across the anvil faces, and
(ii) the difference between the mean pressure and the pressure at the centre of the anvils, which is determined by calibration.

This method of calibration is far from ideal. But the problem is not unique to the present apparatus. Pressures quoted for the present method are probably not inferior to those quoted for belt-type apparatus in common use. Thus, the major term in the pressure is accurately known, being calculated from the press load and face area of anvils. The calibration applies only to the pressure differential discussed above (approx. 60 kb). Even if this is wrong by 30 percent at a pressure of 250 kb, the error in total pressure is only 7 percent. In contrast, the pressures quoted for other types of apparatus, e.g. the high compression belt, are completely dependent upon "standard" calibration points, which in the light of the recent experiments of JEFFERY *et al.* (1966) are almost certainly seriously wrong above 100 kb. The pressure distribution on the sample between the nickel strips in the present apparatus is surprisingly uniform. This is shown from the reproducible and sharply defined results obtained on the coesite-stishovite transition. It is also apparent from current investigations of the olivine-spinel transition in the system Mg_2SiO_4-Fe_2SiO_4. Runs within the two phase region yield spinels with clearly resolved back reflexion lines. From the measured dependence of "d" spacings of spinels with pressure in this system (unpublished results) it is estimated that the pressure variation across the sample was smaller than ± 3 kb.

The temperature of the sample during a run is known only within rather broad limits. These are obtained by comparing the transformation behaviour of a large number of substances, e.g. $MgSiO_3$ glass, Ni_2SiO_4, Fe_2SiO_4, Co_2SiO_4, $MgGeO_3$, $MnGeO_3$, in a simple externally heated squeezer where temperature is accurately known, with their behaviour in the present apparatus. From properties such as minimum devitrification temperature, minimum transformation temperature and crystal size, it is possible to establish that the temperature within the sample in a typical run with 15–20 watt power input is within the range 1000 °C ± 200 °C. This is supported by studies of the conditions under which gold will diffuse into the nickel during arun.

This may appear to represent a gross source of uncertainty but it is actually of small consequence. Consider a typical solid-solid transformation with a gradient dP/dT of 20 bars/°C. At 200 kb, an error of 200 °C in the temperature of the sample amounts to ± 4 kb or 2 percent of total pressure. This error is much smaller than other possible sources of error. It must be emphasized that in the present apparatus, temperature is not employed as an independent variable. Its sole role is to activate the desired transformation so that it proceeds to completion within a period of about 2 minutes. Because of the high reaction rates in the present apparatus the temperature needed to cause a wide variety of solid-solid transformations to proceed to completion are substantially smaller than in apparatus of the piston-cylinder type, where conditions are initially more hydrostatic.

The maximum pressures developed by the apparatus are limited by deformation of the anvils (mainly dishing) and by eventual catastrophic failure. With the simple anvils (fig. 1) mean pressures of 200 kb across the anvil faces are obtainable, implying a nominal pressure of about 260 kb at the centre. The compound anvils (fig. 2) have been used to a mean pressure of 250 kb implying a nominal central pressure of about 310 kb. It is probable, however, that these estimated pressures are somewhat high because of elastic deformation of the anvils under load, which increases the effective surface area (HARRIS *et al.*, 1961).

About 400 experimental runs at pressures above 100 kb have been carried out in this laboratory, and a large number of new phase transformations discovered in minerals and compounds of geophysical and geochemical significance, e.g. RINGWOOD and MAJOR (1966b, c; 1967), RINGWOOD (1967). The simplicity and cheapness of the apparatus make it a most useful tool in searching for new high pressure transformations and for synthesizing high pressure phases so that their properties can be measured. With careful work, systematic investigations of phase equilibria at high pressure can be carried out with a precision in absolute pressure of about 10 percent between 100 and 200 kb. When suitable calibration points finally become available in the pressure range 100–300 kb, it will be possible to improve this precision.

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