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Description and Calibration of a Modified Girdle High-Pressure, High-Temperature Apparatus

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Sample pressures to about 140 kilobars have been obtained in a modified girdle high-pressure, high-temperature device. The modified girdle incorporates some features from other compressible-gasket high-pressure devices. Among the unusual features of the girdle apparatus is the use of steel rather than tungsten carbide in the die. The apparatus, its calibration, and performance are described. Problems arising in connection with calibration are discussed. As a test of the pressure-temperature capability of the modified girdle, stishovite, the new high-pressure rutile-type SiO_2 modification was synthesized at about 120 kilobars and 1200 C.

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Description and Calibration of a Modified Girdle High-Pressure, High-Temperature Apparatus

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The high-pressure, high-temperature devices capable of the highest pressures have generally been of the compressible-gasket variety. Among such devices are the Strong (1)[1] apparatus, the Hall (2) belt, and the Daniels (3) apparatus. The Wilson (4) girdle featured elastic strain in the die and binding rings to obtain high pressure. However, an altervative technique was mentioned in the girdle paper, in which compressible gaskets were used in lieu of the oxide-powder insulation.

With the use of special gaskets based in part on the gaskets used by Strong, Hall, and Daniels, it has been possible to obtain pressures to about 140 kilobars (kb) [revised pressure scale (5)] in the girdle. This is probably near the upper pressure limit attainable in present-day high-pressure high-temperature devices.

Interest in obtaining pressures in this range has been aroused by the announcement (6) by the Russian scientist, Stishov, of the synthesis of a rutile-type modification of SiO_2 at a reported pressure of 160,000 atm and temperature over 1200 C. Sample pressures and temperatures higher than required for stishovite synthesis have been obtained in the girdle apparatus. At about 120 kb and 1200 C, stishovite crystals large enough for detailed optical analysis were produced (7). Sample temperature was estimated on the basis of curves of heater wattage versus thermocouple readings taken at lower pressures. For pressure calibration, the Kennedy (5) and Drickamer (8) values for transition points in the resistivity of bismuth, barium, and iron were used. Assuming that Stishov used the Bridgam value of 80,000 atm for the barium transition in estimating pressure, his figure of 160,000 atm should be revised downward to about 120 kb on the revised scale.

The modified girdle apparatus is described in this paper. An engineering feature of interest in the girdle is the use of steel rather than tungsten carbide in the supporting die. The possible effects of a steel die and the new gaskets in obtaining high pressures are discussed. Problems connected with pressure calibration of high-pressure, high-temperature devices are also discussed.

DESCRIPTION OF APPARTUS

Several high-pressure, high-temperature devices, the Strong apparatus (1), the girdle (4), and the Daniels device (3) are similar in many respects. They all make use of opposing tungsten-carbide pistons and a supporting die. The apparatus to be described, a modified girdle, also incorporates features from the aforementioned devices, as will probably any apparatus in which high pressure is obtained by massive support of tungsten-carbide pistons in a matching die.

The piston-die-binding ring assembly in the modified girdle was essentially the same as previously described (4). Truncated-cone pistons and a die insert were supported in compression by hardened steel binding rings, using tapered interference fits. The truncated-cone portion of the opposing pistons has a 35-deg cone angle and 1/2-in. piston face; the die had a 35-deg cone angle, 1/2-in. bore diameter and 1/4-in. bore height. Tungsten carbide with 6 percent cobalt binder was used for the pistons. The die was made of Carpenter Hampden steel hardened to Rockwell C 60-63.

The modifications of the girdle, resulting in increased efficiency and higher ultimate sample pressure, were in the specimen cell and gasket configuration. A schematic of the specimen cell and gaskets used in synthesizing stishovite is shown in Fig.1. The incorporation of features from other devices is apparent from the figure. For instance, the concept of a sandwich gasket, two pyrophyllite cones with a steel cone between them, is borrowed from the belt apparatus (2). The steel filler disk is similar to Daniels' decompression cap (3). However, fillers of various types to vary the height of the pyrophyllite cylinder and sample had been used in the girdle for some time prior to the announcement of the Daniels' device. A more important contribution based on Daniels' use of plastic gaskets, was the use of polyethylene films between the metal surfaces and the pyrophyllite gaskets.

The films consisted of 0.004-in. polyethylene sheets, precut and joined at the edges by pressure and heat to form cones.

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[1] Numbers in parentheses designate References at end of paper.

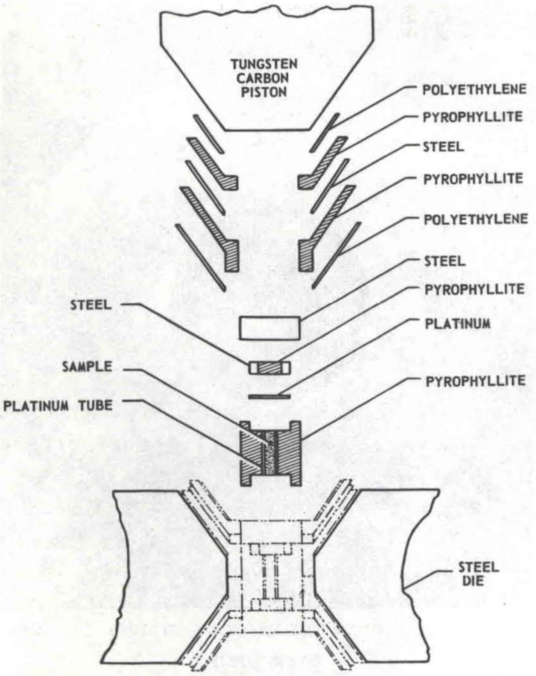

Fig. 1 Schematic of specimen cell and gasket assembly in the revised girdle apparatus

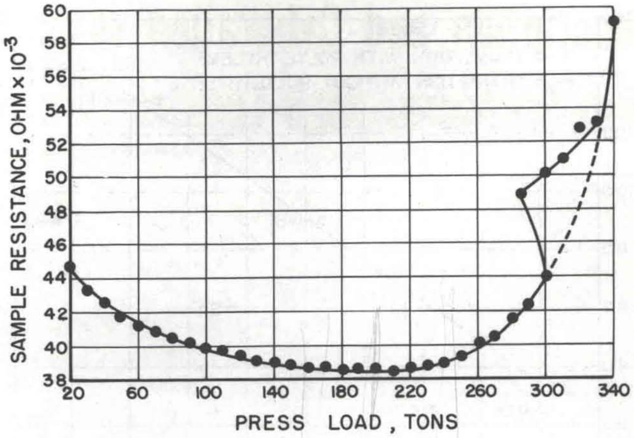

Fig. 2 Resistance of iron to 340 tons' press load in the revised girdle

In synthesizing stishovite, a 1/16-in-id platinum tube with 0.005-in. wall thickness was used both as container and heater. Electrical contact was made on either end to the piston via a 0.005-in. platinum disk, a steel washer with pyrophyllite insert, and a steel disk as shown in Fig.1. The heater requirements for this synthesis were 675 amp and 0.92 volt. The press load was 300 tons.

It has not been possible as yet to measure sample temperatures at the highest pressures obtainable in the girdle since the thermocouples fail. Approximate sample temperatures are based on wattage-versus-temperature curves obtained at pressures from 25 kb. For research purposes, it is desirable to know the sample temperature at pressure. Some modifications of methods for bringing out thermocouples, which have been successful in a belt apparatus, are being tried in the girdle.

PERFORMANCE

The pressure capability of high-pressure, high-temperature devices is generally determined by the detection of discontinuities at transition pressures in the electrical resistance of metals such as barium and bismuth. Several new transition points have recently been discovered by Drickamer (8). Conbined pressure and temperature capability can be determined roughly by synthesis of materials such as coesite, diamond, and stishovite.

For electrical resistance measurements in the modified girdle, a cylinder of silver chloride enclosing an axial metal wire was substituted for the platinum tube in Fig.1. The load was applied to the press through a hydraulic ram, the line pressure of which was controlled by hand pumping. In this way there was no surge in the piston advance in case of blowout.

Resistance-versus-pressure curves were plotted for bismuth, barium, and iron. The curve for iron is shown in Fig.2. Drickamer has placed the beginning of the rise in resistance of iron at 133 kb. It is evident from the curve in Fig.2 that there was some smearing of the transition point possibly due to difference in pressure along the length of the wire. There was also in the axial sample a decrease in resistance due to shortening of the sample, which offset in part the resistivity increase at the transition pressure.

The break in the curve in Fig.2 donotes a partial blowout with some drop in press load as indicated. The sample resistance generally increased slightly after a blowout probably because of a poor contact. However, on reapplying the load the resistance would come back to a point on a continuation of the curve as shown in the figure. Calibration runs with barium and bismuth proceed normally without blowout.

The calibration curve for the modified girdle is shown in Fig.3. The Drickamer values of 133 kb for iron and 144 kb for barium are used. The uncertainty range for the bismuth I-II, lower barium, and bismuth VI-VIII transitions is derived from different points in several runs. For the iron and upper barium, smearing of the type shown in Fig.2 was present in all runs. The uncertainty

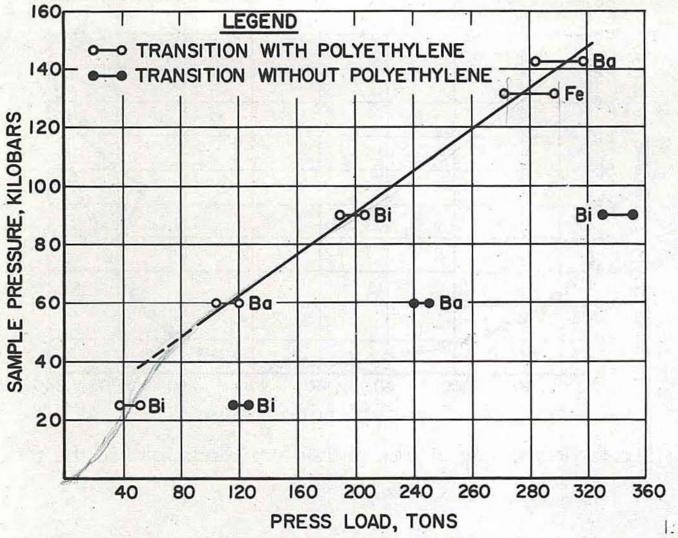

Fig. 3 Pressure calibration of girdle with and without polyethylene films

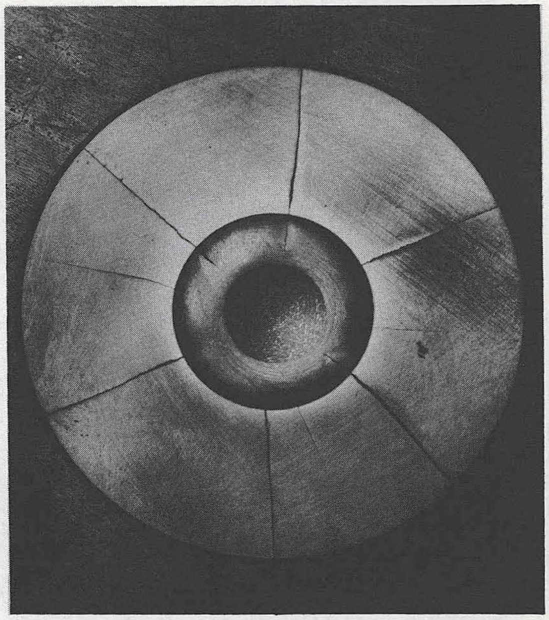

Fig. 4 Girdle die after two runs to over 300 tons press load

range is indicative of the smearing as well as some variation in different runs. For comparison, transition points in the girdle without the polyethylene films are shown in Fig.3.

Failure in the modified girdle generally occurred after cracking of the die accompanied by blowout and a drop in press load of 80 to 100 tons. Even after such a large pressure drop, it was sometimes possible to pump back up to the original press load. However, in a calibration run, the sample resistance was either considerably increased or was shorted out after a large pressure drop, and could not be used to determine the sample pressure. It has been possible to obtain interpretable resistance readings to about 340 tons press load. This has not been high enough to complete with certainty either the iron or barium transition, both of which require some superpressure to complete the conversion. Because failure occured before the conversion was completed, the usual sharp reverse transition on unloading was not observed.

A peculiar feature of the modified girdle was that the tungsten-carbide pistons did not fail. The pistons have never been replaced. Die failure was initiated by radial cracks. Fig.4 shows a die after two runs to over 300 tons. The cracks have not yet penetrated into the bore where the high pressure occurs.

No more than two runs over 300 tons were made with any one die. A 300-ton load expanded the bore of the die from 0.500 in. to approxi-
? mately 0.500 in. For a second run, an enlarged pyrophyllite cylinder with diameter to fit the bore was used. Several runs to 220 tons, i.e., sample pressure about 90 kb, could be made after one run to 300 tons. The press load required for the bismuth VI-VIII transition was about the same in an expanded die and a new die.

There is little information on the life of the dies at pressures under the maximum obtainable pressure since all of the dies to date have eventually been used at over 300 tons. In one die six runs were made at 220 tons before the die was taken to higher pressure.

DISCUSSION

Hall (9) has discussed the functions of the compressible gasket in a high-pressure apparatus. The gasket must yield to the moving pistons. However, it must also confine the material being compressed. The yield to the moving pistons in the girdle was greatly increased by the use of polyethlyene films as the comparison in Fig.3 shows. At the same time, the use of the sandwich gasket helped prevent blowout.

The third gasket function, that of support, was furnished by the large area of contact via gaskets between the pistons and the dies. To avoid piston failure, the cross section of the pistons outside of the support area should be as large as possible, compatible with reasonable efficiency in transmitting pressure to the sample. In the girdle, the cross section of the exposed portions of the pistons is about 1 in. in diameter. With 300 tons press load, the loading on the unsupported piston area is about 800,000 psi, which is

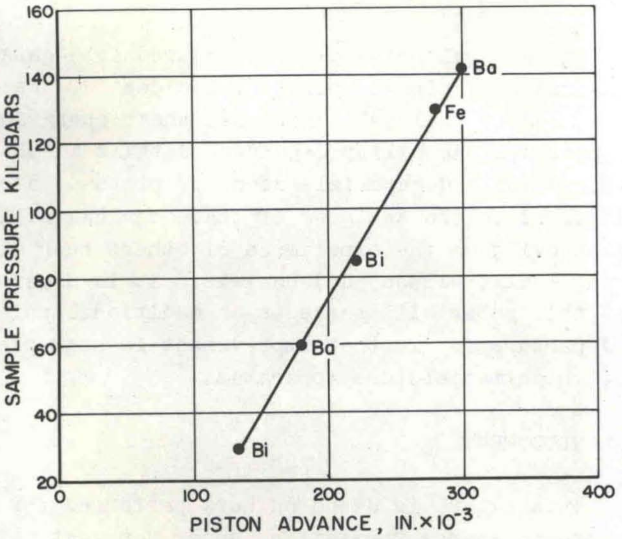

Fig. 5 Piston advance versus sample pressure in revised girdle

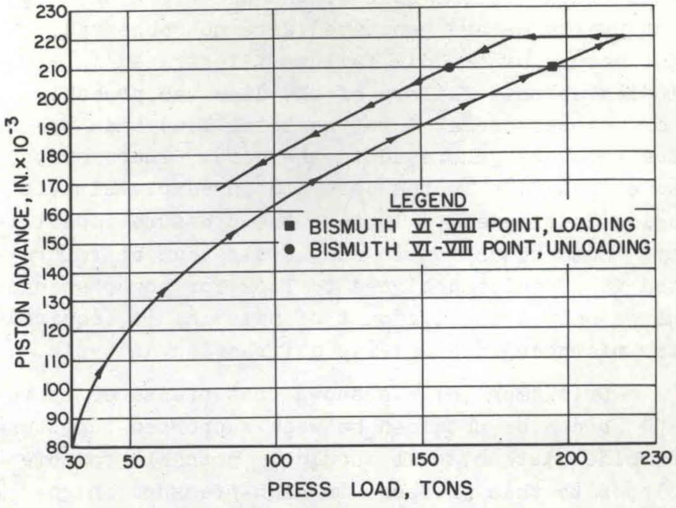

Fig. 6 Piston advance to the bismuth VI-VIII transition point on loading and unloading cycles

approximately the compressive strength of the tungsten carbide.

not so

The girdle is unique in the use of a steel die to obtain very high sample pressure. In the original concept of the girdle (4), which featured the principle of elastic support and which did not normally use gaskets, the height-to-diameter ratio in the bore was adjusted so that a piston advance and lateral bore expansion decreased the volume of the bore. A steel die was used rather than tungsten carbide because the former would allow more lateral expansion and piston advance with consequent decrease in the bore volume and pressure build-up in the specimen cell.

In practice it was found that in order to squeeze out the pores in the pyrophyllite cylinder and the sample, it was necessary to make the cylinder height oversize. In this case, some of the pyrophyllite was extruded out between the piston and dies. As stated in the original paper (4), an alternative technique was also employed in which a gasket was used in lieu of the oxide-powder insulation permitting the girdle apparatus to function as a combined compressible-gasket and elastic-distortion apparatus.

When the girdle was used as a compressible-gasket device, the original reason for the use of a steel die was invalidated, at least in part. However, the use of a steel die was continued because it appeared from present knowledge that sample pressures as high or higher than those in devices with tungsten-carbide dies could be generated.

The steel die expands both elastically and plastically. The expandable steel die and the small height-to-diameter ratio of the bore may still be important in the performance of the girdle. The piston advance and sample pressure are related as shown in Fig.5. Piston advance is facilitated by expansion of the die with probable resulting increase in sample pressure as long as the height-to-diameter ratio is kept low enough. Admittedly, anything approaching exact analysis of pressure transmission in a compressible-gasket device is nearly impossible. The possible advantages of an expandable steel die and a short bore over other die designs and materials will have to be decided by more experiments.

The hysteresis phenomenon found in calibration tests on loading and unloading is well known. Fig. 6 shows the relationship between piston travel and the bismuth VI-VIII transition point on loading and unloading. The load was applied beyond the transition point. Even though the polyethylene films must act as a lubricant during the piston advance, the load was reduced 40 tons before there was perceptible piston motion on unloading. It is interesting to note that the transition occured at the same piston spacing during the loading and unloading cycles. The hanging up of the pistons on unloading and the dependence of sample pressure on piston advance indicated that sample pressure was probably not affected by small blowouts in which the press load dropped by 10 to 20 tons. The larger blowouts which sometimes occurred at press loads of 280 to 300 tons were probably related to die cracking rather than to the lubricating property of the polyethylene films.

Even after the highest loading, chipping and fine cracks in the bore of the die where the highest pressures are generated were not observed. The nature of the die failure illustrated in Fig.4 indicates that failure of the dies was probably more closely related to the total load than to the pressure generated in the bore. Therefore, some reduction in the bore and in sample size is being considered to improve the pressure capability. Some reduction in sample size can be tolerated in a device designed to look for phase changes since only a small amount of material is required for microscopic and x-ray diffraction analysis.

Drickamer (8) has shown that pressures up to 450 kb can be obtained between supported tungsten-carbide pistons. It should be possible to come closer to this pressure in high-pressure, high-temperature devices.

The discovery of new transition points by Drickamer was timely for the calibration of high-pressure, high-temperature devices. However, there is a large pressure difference between the bismuth VI-VIII and iron transition point as seen in Fig.3. This pressure range is at the limit of present capability of high-pressure, high-temperature devices. It has not been possible to obtain complete conversion of iron and the upper barium in the girdle apparatus. It is evident that more transition points are needed in this range to calibrate high-pressure, high-temperature devices. One likely possibility for a transition in this range would be titanium. Titanium and zirconium both undergo phase transformations at elevated temperature from alpha hexagonal to beta body-centered-cubic modification. Bridgam (10) reported a pressure transition in zirconium at 80,000 atm. This was probably the alpha-beta transformation since beta is the denser phase. He did not detect any transition in titanium to 100,000 atm, or probably about 80 kb on the "volumetric" scale. It seems likely that titanium will transform at higher pressures and possibly in the range of interest between 90 and 130 kb. Hafnium and yttrium, which are hexagonal close packed initially with nearly the same c/a ratio as in titanium and zirconium, also might undergo pressure transitions in the 90 to 130-kb range.

For calibration at high pressure and temperature, phase boundaries in materials such as coesite, diamond, stishovite, chromium vanadate, aluminum arsenate and others which have high-pressure modifications, may be used to determine the pressure and temperature range in which a device is operating for a given press load and heater wattage. Along these lines, an attempt has been made to extend the calcite-aragonite phase boundary into the high-pressure, high-temperature range (11).

CONCLUSION

The general principles of compressible-gasket, high-pressure, high-temperature devices have been enunciated by Hall (9). However, their operation and pressure capability depend on details in the construction and materials used for pistons, dies and gaskets. The designer of these devices will lean heavily on the experience of others such as Strong, Hall, Wilson, and Daniels. It is hoped that this paper will serve as an additional point of departure for further improvement in high-pressure, high-temperature apparatus.

ACKNOWLEDGMENT

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