**DESIGN, CALIBRATION,
AND CAPABILITIES OF SOLID STATE
PISTON-CYLINDER AND "BELT"
ULTRA HIGH PRESSURE EQUIPMENT**

G. L. KULCINSKI

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By

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G. L. Kulcinski

ABSTRACT

The general design characteristics of "Belt" and "Piston-Cylinder" high pressure-high temperature equipment capable of pressures to 60 kbar and temperatures to 1500 °C are described. The methods of calibrating such equipment by noting resistance changes in cerium, bismuth, thallium, and barium, and volume changes in RbCl and KI, are described in detail. It has been found that for a given load, the pressure on a sample enclosed in a collapsible can filled with a liquid is the same as that determined by noting phase changes in samples inbedded in AgCl sleeves. This result means that calibration curves which have been determined by normal techniques can be used with confidence when using a collapsible can technique for applying hydrostatic pressure. The general capabilities of such equipment are discussed in terms of pre- or postirradiation pressure treatments of materials which are of interest to nuclear metallurgists.

INTRODUCTION

To more fully understand the effect of pressure on the damage induced in neutron irradiated solids, an ex-reactor ultra-high pressure laboratory was established at BNW. This facility is designed to complement information obtained from in-reactor high pressure equipment and to investigate the effects of preirradiation pressure-temperature treatments on materials of interest to nuclear metallurgists. The main purpose of this report is to explain the basic design features, calibration, and general capabilities of the equipment. Future reports will deal more specifically with the various programs currently underway.

SUMMARY AND CONCLUSIONS

Resistance changes in cerium, bismuth, thallium, and barium, as well as volume changes in RbCl and KI, are discussed when employed as calibrants using "Belt" and "Piston-Cylinder" high pressure-high temperature equipment. A collapsible can technique for applying hydrostatic pressure was used, and calibrations of high pressure tooling to 60 kbar and 1500 °C were obtained.

DESIGN CONSIDERATIONS

GENERAL DESCRIPTION

The basic equipment was purchased from PhysMet Corporation which is a

division of ManLabs Inc. of Cambridge, Massachusetts. Figure 1 is a photograph of the working system and its control equipment. There are three distinct units which will be described in more detail below:

- Press (left)
- Pressure and temperature control equipment (center and right)
- Tooling (inside press)

The maximum pressure and temperatures attainable depend upon the type of

tooling used and are listed below:

	<u>Piston Cylinder</u>	<u>Belt</u>
Typical Sample Volume	0.6 in. diam x 1.2 in. long	0.27 in. diam x 0.6 in. long
Maximum Pressure	25 kbar	60 kbar
Maximum Temperature	1200 °C +	1500 °C +

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FIGURE 1. Ultra High Pressure-Temperature Equipment; Press (left), Control Equipment (center and right), Tooling (inside press).

PRESS

The press used to impose loads on the high pressure tooling is a Model 500H, Clifton 500 ton unit. This is a commercial, 4 post hobbing press having free platen dimensions of 11 in. side to side, and 17 in. front to back, with a maximum daylight opening of 16 in. The press is approximately six feet in height and has a main cylinder diameter of 13 in.

The pumping system of the commercial model has been modified to permit very slow and carefully controlled platen advance. The modification uses a low pressure pump to close daylight and a high pressure pump driven by an electric motor through a fluid-drive transmission to apply the load to the sample. The fluid-drive transmission is capable of infinitely variable speeds between 0 and 300 rpm. Previous experiences have shown that the range from 10 to 50 rpm is ideally suited for providing the desired control of the platen advance.

Complete shielding of the press is accomplished by surrounding the tooling with a 1/8 in. sheet metal shield. The shield is provided with three access doors with heavy (3/8 in. thick) plexiglass viewing ports. Shielding for radioactive samples is easily accomplished by stacking lead bricks around the press posts inside the access doors. Since experiments with this equipment involve the use of NaK, a fire extinguisher has been mounted on the back of the press so that it can be operated from outside the press.

CONSOLE

The control center consists of a console and relay rack in which is mounted the controls and instrumentation necessary for pressure and temperature control. The console is removed some four feet from the press area so that additional shielding may be inserted between an operator and the sample if radioactivity levels become too great.

Pressure Control

The pressure on the sample can be varied and controlled automatically or manually. The automatic control is obtained by a Wheelco pressure indicator controller, model 402S-315B. The controller can maintain the load to the sample within 0.1% of the set point over long periods of time. Manual operation can be performed by observing the load on the sample as indicated by a Heise gauge. Pressure can be raised at any desired rate by operating the high pressure pump at various speeds, or lowered by a controller leak valve on the front of the console.

Temperature Control

The samples in the high pressure tooling are heated resistively by means of a small graphite furnace which will be described later. The heating power supply unit consists of an air cooled multitap power transformer capable of 10 kVA (1000 amps at 10 volts) and

associated control equipment. As in the case of pressure control, the temperature may be controlled manually or automatically. Manual operation is accomplished through a motor-driven variable voltage power pack and automatic control through an electrovolt temperature controller. The controller acts through a RI controls solid state SCR Power Pac Model PR-230-100-E-CLA to vary the input into the transformer. All temperature changes can be made directly from the console equipment.

TOOLING

For convenience, each set of tooling will be described separately, namely, Belt and Piston-Cylinder, since their pressure-temperature-sample size characteristics are somewhat different. However, each unit requires the same water cooling arrangements, current leads, and die set as pictured in Figure 1.

Piston-Cylinder (P-C)

Piston and Die Arrangement

Figure 2 is a schematic of this set of tooling showing the major components. The upper picture shows the arrangement of the tooling in the die set and press while the lower schematic shows a magnified view of the tooling. The function of the clamping plates is to maintain proper alignment of the components and good electrical contact between the bottom of the specimen cell and the backing block which contains the current-lead. It also provides a measure of axial support for the die. The die consists of an inner tungsten carbide cylinder with various steel supporting rings shrunk and press-fit

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FIGURE 2. Schematic of Piston-Cylinder Tooling

around it. The tungsten carbide die is 3 in. long with a 1 in. ID and 2 1/2 in. OD. The assembly is equipped with a chamber through which cooling water may be passed. This is necessary at high operating temperatures as the strength of the die materials is considerably reduced above a few hundred degrees centigrade.

The piston is made of tungsten carbide and is 2 1/2 in. long and 0.991 in. in diameter. It is beveled at its leading edge to accommodate a triangular cross section steel ring which prohibits extrusion of the sample. As the load is applied, the ring is forced outward to the wall and extrudes into the gap

between the piston and wall. Such an arrangement is sufficient when compressing solid media but obviously not useful in compressing liquid samples in the chamber.

Specimen Cell

Figure 3 is a schematic of a typical specimen cell equipped with a collapsible can arrangement. Figure 4 is a photograph of such a cell both in assembled and disassembled conditions. The major components of the cell are pointed out in Figure 3, and typical dimensions are as follows:

- Outside diameter of assembly 0.995 in.
- Length of assembly 1.7 in. (2.2 in. with steel closure)
- Outer diameter of tapered can 0.62-0.68 in.
- Inside diameter of can 0.56 in.
- Outside height of assembled can 1.2 in.
- Inside height of assembled can 1.12 in.
- Collapsed outside height of can after pressure application 1 in.

- Collapsed inside height of can after pressure application 0.92 in. (diameter stays roughly the same)
- Thickness of graphite furnace 0.017 in.

It should be pointed out that the volume occupied by the can (1.1 in.³) could be used for other purposes such

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FIGURE 3. Schematic of Sample Cell Assembly for Piston-Cylinder Unit.

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FIGURE 4. Exploded View of Piston-Cylinder Sample Cell Assembly.

as production of high pressure polymorphs or in other cases where the applied pressure need not be truly hydrostatic. The can may be filled with liquids to insure that the pressure to the sample is truly hydrostatic. At low temperatures n-pentane is used; at high temperatures, liquid metals such as Na and NaK are necessary.

The electrical heating circuit is patterned as follows: the current travels from the transformer through the current lead to the bottom backing block. From the backing block it continues through the bottom steel closure to the graphite pad and through the thin graphite furnace. The rest of the circuit extends out of the top pad through the piston to ground of the press. This design offers a maximum of temperature capability with a minimum application of power. As will be seen in the calibration section, temperatures of 1200 °C can be obtained with 6.5 kW of energy input.

The thermocouples are usually chromel-alumel or Pt-Pt 10% Rh, but other types of thermocouples could be used as well.

Belt System

Pistons and Die

This system gets its peculiar name from the design of the die which acts like a circular belt to enclose and contain the sample as the pressure is applied. Figure 5 is a schematic of the unit in the press and also contains an enlarged cross-sectional view of the tooling. In contrast to the Piston-Cylinder arrangement there are two conical pistons acting on the sample. These pistons are thrust into each end

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FIGURE 5. Schematic of Belt Tooling

of a conically shaped tungsten carbide die by the 500-ton press. The pressure is generated by the advancing pistons as they compress the specimen cell and its surrounding gaskets. Unlike the P-C tooling, where an effort is made to prohibit extrusion of the pressure transmitting media, the lavite gasket material is allowed to extrude to its equilibrium thickness in the belt tooling. This extruded gasket not only retains the sample but also provides some measure of support for the pistons.

The pistons themselves are usually made from tungsten carbide with various amounts of cobalt binder. It has been necessary to use 6% Co binder for the

higher pressures (~ 60 kbar), whereas 12% is sufficient below 50 kbars. The latter is somewhat more resilient at lower pressures resulting in a much longer working life. The pistons themselves are supported by shrunk-fit steel binding rings so that the stresses in the pistons are always compressive except at the very highest pressures. This is necessary because the tensile strength of tungsten carbide is much lower than its compressive strength. The face diameter of the piston is 0.5 in.

The die arrangement is similar to the P-C unit in that the tungsten carbide die is supported by shrunk-fit steel binding rings, and provisions are made for water cooling. The difference between the Belt and Piston-Cylinder is mainly the double conical shape of the die necessary to allow piston advance in the Belt System.

Figure 6 shows a sequence of photographs taken while assembling the Belt tooling in the press. First of all, electrical insulation in the form of Teflon or Mica is placed between the bottom backing block and the die set (6a). Next (6b), an aluminum sheet is placed on the bottom backing block, and the bottom piston is placed in position (6c). The aluminum flows easily under load and provides smooth electrical contact between parts of the tooling in addition to serving as convenient electrical contacts. Next, Teflon pads with $1/2$ in. diameter and $1/4$ in. thickness are placed on the piston binding rings, and the bottom gasket and specimen cell are placed on the piston (6d). The pads help to align the die while the rest of the components are assembled. The die

is placed over the sample and upon the pads (6e). Water cooling coils can now be connected. After placing pads on the top of the die and the remaining gasket material in the die chamber, the top piston is put in place. A sheet of aluminum is placed between it and the top backing block, and the assembly is ready for pressure application (6f).

Specimen Cell

Figure 7 is a schematic of a typical specimen cell for the Belt tooling. Figure 8 shows an actual model and an exploded view. The components are pointed out in the figure and typical dimensions are as follows:

- Cell diameter (exclusive of gaskets), 0.497 in., 1 in. long
- Internal can diameter before and after compression, 0.220 in.
- Total inside length of can before compression, 0.570 in.
- Total inside length after compression, 0.470 in.
- Graphite furnace thickness, 0.022 in.

As in the case of the Piston-Cylinder unit, the specimen can volume (0.087 in^3) is useful for other purposes when true hydrostaticity is not required.

Thermocouples can be brought in through the gaskets in many ways. The method shown in Figure 7 brings the thermocouple through the gasket, down through the lava insulation, and through the graphite furnace at the midpoint of the can. The second wire is brought out in a similar manner through the bottom gasket. Of course, the thermocouple must be insulated from the furnace by a lavite or boron nitride plug.

a

c

b

d

e

f

*FIGURE 6. Sequence of Assembly
for Belt Tooling.*

FIGURE 7. Schematic of Sample Cell Assembly for Belt Tooling.

The electrical heating circuit (Figure 5) follows from the transformer through the current lead and bottom backing block to the bottom piston. From the bottom piston the current travels through the steel end pad, graphite pad, and through the furnace and finally, out through the top piston to the ground of the press. Typical temperatures of 1500 °C can be obtained by an input of 2.5-3 kW of power.

CALIBRATION

GENERAL APPROACH

Considerable effort has been exerted by workers in the high pressure field to find suitable ways of relating the actual pressure on the sample to some externally measured quantity. In the simplest case, pressure is the applied force divided by the area upon which

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FIGURE 8. Exploded View of Belt Sample Cell Assembly.

that force acts. However, due to frictional effects, the actual pressures are somewhat lower than the theoretical pressure. In solid state pressure systems such as the P-C and Belt tooling, the currently acceptable method of calibration is to monitor the electrical resistance of elements which undergo phase transitions at rather well defined pressures. The load at which the resistance makes a discontinuous change signifies the start of the transition.

In the pressure range of interest for the PhysMet equipment, the "standards" are as follow: Bismuth, 25.4 kbar; thallium, 37 kbar; barium, 59 kbar.⁽¹⁾ While these three provide adequate coverage for the Belt apparatus, the lowest (Bi) is at the extreme upper limit of the P-C tooling. In order to fill in below 25 kbar, it was necessary to use a secondary standard for calibration, namely the resistance drop in cerium which occurs between 6.5 and 8.5 kbars at room temperature.⁽²⁻⁸⁾ Taking a simple average of the reported values yields a transition pressure of 7.6 kbar which is, in fact, the value measured in the most recent and, in some respects, most accurate experiments.^(7,8) Hence, for this study it will be assumed that at room temperature cerium undergoes its transition from a fcc structure to a more dense fcc structure at 7.6 kbar.

The general technique for resistance change measurements is to surround a wire sample with a soft, electrically insulating material inside of a specimen cell (See Figure 9). In practice it is not possible to measure the resistance of a sample inside a collapsible can such as in Figure 3, so one usually

assumes that the pressure inside the can is the same as that inside the soft insulating material.

A more exact method of measuring the true pressure inside the can would be to monitor the volume change of the specimen assembly as a function of load. When large amounts of the calibrant transform, there will be a sudden volume change at constant load. This volume change can be noted by following the piston movement as a function of load. The chamber walls are assumed relatively incompressible. This measurement is easily made for the P-C tooling, but is almost impossible for the Belt system because of the extrudable gasket technique employed. Therefore, any relationship between the calibration curve determined by electrical resistance and that determined by volumetric changes in the P-C tooling will be assumed to apply in the case of Belt tooling as well.

There are many appropriate materials for such a volumetric calibration with the range 5-20 kbar. Two which are readily obtainable, easy to handle, and which undergo large volume changes are KI and RbCl. The NaCl $\rightarrow$ CsCl type transformation in RbCl was first discovered by P. W. Bridgman⁽⁹⁾ in 1928, who measured the transition pressure of 5.4 kbar at room temperature. Vereshchagin⁽¹⁰⁾ reported lattice parameter measurements at 7.5 kbar, and he estimated the transition to take place at $\sim$ 5 kbar. Several other groups have placed the transition at 5-6 kbars,⁽¹¹⁻¹⁴⁾ but the most accurate and recent work was performed by Pistorius.⁽¹⁵⁾ He found that the transition takes place at 5.3 kbar at 22 °C, and 5.5 kbar at 100 °C.

For these studies the most recent data of Pistorius will be used.

In the case of KI, Bridgman^(9,16) was again the first to observe the NaCl $\rightarrow$ CsCl transition. He reported extreme sluggishness at room temperature and placed the transition between 17.18 and 18.19 kbar.⁽¹⁷⁾ X-ray analysis of the high pressure form recently has been reported,^(13,18,19) and the sluggishness of the room temperature has been confirmed.⁽²⁰⁾ Pistorius⁽²¹⁾ has studied the transition as a function of temperature and found that raising the temperature above 70 °C considerably reduces the sluggishness of the transition. At room temperature he found the transition to be between 17.0 and 17.6 kbar, while at 100 °C it was 17.20 ± 0.05 kbar. Again it appears that the data of Pistorius is most reliable, and it will be used in this paper.

PISTON-CYLINDER TOOLING

Experimental

Material

Bismuth wire was used for the electrical resistance runs. The wire was 0.005 in. in diameter, had a stated purity level of 99.9%, and was obtained from A. D. Mackay, Inc. The cerium metal was obtained from Research Chemicals in the form of 0.007 in.-thick foil with a stated purity level of 99.9%. Both metals were scraped and cleaned of any oxide before the test.

The RbCl was obtained from Fisher Scientific lot R-317. No analysis of impurity levels was given other than

"purified". The KI was crystal reagent from Baker and Adams with less than 0.5% impurities and water. The main impurities were chloride and bromide ions at 0.01% levels.

The compounds were used directly from the bottle and pressed into pellets with a 0.498 in. diameter at 2.9 kbar. The RbCl pellet was 0.638 in. long and weighed 5.1928 g, while the KI pellet was 0.449 in. long and weighed 3.7177 g. The %TD was 95% for RbCl, and 81% for KI.

The pressure transmitting media was n-pentane. This was used in place of the NaK usually used because of the fire hazard. There was no visible reaction between the pellets and pentane after two weeks of contact at one bar.

Specimen Cells

Figure 9 is a schematic of the cells for electrical resistance measurements.

FIGURE 9. Schematic of Calibration Cell used for Both the Piston-Cylinder and Belt Tooling.

The sample in the form of a wire was surrounded by a 0.20 in. diameter cylinder of AgCl. The rest of the cell was grade A lavite or pyrophyllite. Small iron wires were pushed into the holes in the AgCl. Both the sample and iron wires were placed through a hole in a 0.001 in. gold foil and folded over (See Figure 9). This was done to insure electrical contact in case the calibrant wire would break off when being bent.

The calibrating cell for the volume determinations was the same as that pictured in Figure 3.

Auxiliary Equipment

The resistance measurements were recorded on an x-y recorder versus the pressure. The current through the samples came from a bank of wet cell batteries, and in the case of both Cerium and Bismuth, 50 mA currents were used.

The piston advance was measured by a strain gage contacting the piston backing block. The gage was calibrated against a micrometer, and its output

was amplified and fed into one coordinate of the x-y recorder. The accuracy is assumed to be ± 0.001 in.

Results

Resistance

Figure 10 shows the relative resistance of the cerium wire as a function of press load. Three features are apparent from the curve:

- 1) A 33% drop in resistance at the transition.
- 2) A hysteresis of some 57 tons between the forward and reverse transitions.
- 3) A 10 to 12 ton "indifference" span separating the start and finish of the transition.

The reproducibility of the transition is readily apparent from Figure 10, and variation in press pump speed (rate of pressure application) from 25 to 80 rpm seems to have very little discernable affect on the transition. Tables I and II summarize the data resulting from this experiment. The forward transition

TABLE I. Summary of Data for Calibration of Piston-Cylinder Tooling

Calibrant	Transition Pressure, kbars	Calibration Method	Forward transition, Tons			Reverse transition, Tons		
			Start	Finish	Avg.	Start	Finish	Avg.
RbCl	5.5 ⁽¹⁵⁾ (100 °C)	Volume change	53	58	56	20	10	15
			48	59	53	20	10	15
			48	59	53	20	10	15
Ce	7.65 ^(7,8) (22 °C)	Resistance change	63	80	72	19	10	15
			64	78	71	20	8	14
			63	77	70	21	8	15
KI	17.2 ⁽²¹⁾ (100 °C)	Volume change	130	151	141	84	68	76
			130	140	135	89	76	83
Bi	25.4 ⁽¹⁾ (22 °C)	Resistance change	186	203	195	154	134	144
			185	202	193	150	134	142

FIGURE 10. Relative Resistance of Cerium as a Function of Load in the Piston-Cylinder Tooling.

is found to be 71 tons, while the reverse transition is 15 tons.

Figure 11 shows the relative resistance drop of bismuth as a function of press load. The outstanding features of this curve are:

- 1) 80% resistance drop at the transition.
- 2) A hysteresis of some 51 tons between the forward and reverse transitions.
- 3) A 16 to 18 ton region of indifference between the start and end of the transitions.

It should be pointed out that the Bi II→III transition at 27 kbars could have been obtained by application of 5 to 10 tons more load, but the test was stopped at 203 tons when the bottom backing plate cracked under the high stress. Since the tooling was designed only for 20 kbar it was determined that the chance of die breakage at higher loads was much greater than the benefits

FIGURE 11. Relative Resistance of Bismuth as a Function of Load in the Piston-Cylinder Tooling.

of another calibration point. For much that same reason the transition was only obtained twice. Table I lists some of the pertinent data from which a forward transition was determined to take place at 194 tons, and reverse, at 143 tons.

Volume Charge

Figure 12 shows a typical piston displacement load curve on the pellets of RbCl and KI surrounded by n-pentane in the collapsible can in Figure 3. Figure 13 shows a typical can assembly before and after compression. From Figure 12 and Table I it is apparent that the forward RbCl transition takes place at 54 tons, and that for KI, at 138 tons. There is a hysteresis of 40 tons associated with RbCl and 58 tons with KI. The temperature of the runs was $100 \pm 1^\circ\text{C}$, and rough determination of volume changes at the transitions was -11% and -14% for RbCl and KI respectively.

It was found that after the sixth cycle through the transition, the RbCl and KI transitions were quite smeared out, almost to the point of non-detection. Upon unloading the tooling it was found that the stainless steel can had cracked, allowing the pentane to escape. Evidently the loss of the hydrostatic medium reduces the sharpness of the transitions.

Pressure Calibration Curve

Figure 14 relates the sample pressure to the applied load for the P-C device. The most striking features of this curve are that the calibration points for both the volumetric and electrical

FIGURE 12. Typical Load Compression Curve for Rubidium Chloride and Potassium Iodide in a Collapsible Can Arrangement

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FIGURE 13. Typical Collapsible Can Arrangement Before (left) and After (right) a Pressure Run.

FIGURE 14. Pressure Calibration Curve for Piston-Cylinder Tooling.

resistance samples fall on the same curve and are reproducible to within 5% (a quite acceptable accuracy when using equipment of this type). This means that there is very little pressure-loss encountered by using a metal capsule. It also means that calibration curves determined by electrical resistance can be used confidently, even when the sample is in the hydrostatic environment associated with liquid pressure media.

A second feature of Figure 14 is the linearity of the curve, even at higher pressures. If considerable yielding were taking place, it would be bowed away from the theoretical pressure curve.

Finally the double friction values shown in Table II indicate rough agreement with other Piston-Cylinder devices⁽¹⁾. The "region of indifference" mentioned previously is actually a measure of the axial pressure gradients in the cell, i.e., the pressure is

TABLE II. Hysteresis Effects in the Piston-Cylinder Tooling

Calibrant	Temperature, °C	Axial Gradient, kbar	Double Friction Value, kbar
RbCl	100	1.2	4.2
Ce	22	2.4	6.5
KI	100	2.0	8.2
Bi	22	2.3	7.4

greatest on loading just under the piston, and lowest at the bottom of the cell. This axial gradient amounts to 2.3 to 2.4 kbars in the case of a sample encased in AgCl and pyrophyllite, and is only 1.2 to 2.0 kbars in the can assembly at 100 °C. The existence of a hysteresis even in a hydrostatic environment can be attributed to the finite rate of piston advance and to the volume contractions associated with the transitions.

Temperature Calibration Curve

The temperature has been measured as a function of power input, and typical results are shown in Figure 15. The sample assembly used is the same as in Figure 3 except that a pyrophyllite plug was substituted for the collapsible can arrangement.

Considerable difficulty was encountered in the early stages of calibra-

tion due to the fact that pyrophyllite is a hydrate ($\text{Si}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and loses its water of hydration at about 600 °C.⁽²²⁾ This phase change was accompanied by a volume increase of some 6%. If "green" pyrophyllite was used, that is, material which still contains its water of hydration, it was impossible to raise the temperature above 600 °C due to failure of the furnace. It was thought that the volume increase associated with the phase change caused the furnace to separate at its weakest point. This hypothesis is based on the fact that the break in electrical continuity was immediately preceded by an increase in line pressure in the hydraulic system. This increase in pressure could result from the expanded solid pushing against the piston.

It was found that firing the pyrophyllite at 1000 °C in air for 2 hr, or at 850 °C in a vacuum for 18 hr, extended

FIGURE 15. Typical Temperature Calibration Curve for Piston-Cylinder Tooling

the useful life of the furnace to $\sim 1150^\circ\text{C}$. At this point another phase transition takes place, and the mullite phase is formed.⁽²⁵⁾ This transition results in a volume decrease, and the reason for the furnace failure is not known at this time. From post test analysis it was found that the mullite phase was not formed uniformly throughout the inner plug. This non uniform change may have caused buckling of the furnace in localized regions thus causing failure.

From Figure 15 it can be seen that ~ 6.5 kW of power is required to reach $\sim 1200^\circ\text{C}$. From the general slope of the curve it is reasonable to assume that temperatures in excess of 1800°C could be obtained with the 10 kW power supply in the unit.

BELT TOOLING

Experimental

Material

The bismuth wire used was the same as that described previously, and the thallium was obtained from A. D. MacKay, Inc. in the form of 0.062 in. diameter wire. This wire was rolled to 0.040 in. diameter before inserting it in the calibration cell. There was no analysis on the purity of the material.

The barium used for these experiments was obtained from Fisher Scientific Company, and had a stated purity of 99%. Lumps of barium metal were extruded into 0.040 in. diameter wires for this experiment.

All the metals were scraped and cleaned of any oxide material before the final assembly of the cells.

Specimen Cells

A schematic of the specimen cells for this experiment is shown in Figure 9. The technique of insuring electrical contact with Au foil and Fe wire are the same as in the P-C cells. All tests were run at room temperature so that graphite furnaces were not required.

Auxiliary Equipment

The same x-y records, and current supplies used with the P-C tooling were used in these experiments.

Results

Bismuth

Figure 16 is a typical calibration curve for the Belt tooling, and it is similar to the curve in Figure 11 except that the Bi II $\rightarrow$ III transition was obtained above 50 tons. This transition takes place at $27^{(1)}$ kbars, and it is of little value in calibration studies because of its close proximity to the Bi I $\rightarrow$ II transition. Tables III and IV summarize the data obtained and show the following results:

- 1) An 80% drop in resistance at the Bi I $\rightarrow$ II transition.
  - 2) Less than 1.5 kbars region of indifference.
  - 3) A 16 to 17 ton hysteresis between the forward and reverse transitions.
- As stated previously the large drop in resistance corresponds to a pressure of 25.4 kbars.⁽¹⁾

Thallium

Figure 17 shows the relative resistance of thallium as a function of

FIGURE 16. Typical Curve of the Relative Resistance of Bismuth as a Function of Load in the Belt Tooling

TABLE III. Summary of Data for Calibration of Belt Tooling

Calibrant	Transition ⁽¹⁾ Pressure kbar	Forward Transition, Tons			Reverse Transition, Tons		
		Start	Finish	Avg.	Start	Finish	Avg.
Bi	25.4	52	57	55	39	36	38
		48	52	50	34	32	33
		46	49	48	32	31	32
Tl	37	85	88	87	64	59	62
		82	88	85	58	55	57
		82	87	85	56	51	54
Ba	59	133	142	138	98	90	94
		127	134	131	91	83	87
		120	129	125	84	74	79

TABLE IV. Hysteresis Effects In Belt Tooling

Calibrant	Axial Gradient kbar	Hysteresis Tons
Bi	1	17
Tl	2	28
Ba	5	44

FIGURE 17. Typical Curves of the Relative Resistance of Thallium as a Function of Load in the Belt Tooling.

press load, and Table III and IV list the important points of the data. The 30% resistance drop, which corresponds to a sample pressure of 37 kbars,⁽¹⁾ agrees with the data of other authors.⁽²⁵⁾ The region of indifference is 1-2 kbars, and the hysteresis effects are from 25 to 31 tons. These higher values (as compared to bismuth) are to be expected at the increased loads.

Barium

Figure 18 shows that, in contrast to Bi and Tl, barium undergoes a 20% increase in resistance when it transforms at 59 kbars from its low to high pressure form. Table IV shows, as expected, that the indifference region is increased to ~5 kbars, and the hysteresis increased to 44 tons.

Pressure calibration curve

Figure 19 summarizes the calibration data to relate press load to pressure on the sample. Two curves are given, one for the first compression cycle, and one for the third compression cycle. Each has its own usefulness. Unlike the P-C tooling, there is 1-6 kbar difference in the curves depending on what cycle the calibration data is taken. The curve labeled "1st Cycle" is used when there is no attempt to cycle the pressure. For example, when using sample assemblies which contain collapsible can arrangements, it is harmful to cycle the pressure because of can leakage. Hence the tests are performed on the first compression stroke only. The pressure to the sample on the first stroke is always less than if all the

FIGURE 18. Typical Curve of the Relative Resistance of Barium as a Function of Load in the Belt Tooling.

FIGURE 19. Pressure Calibration Curves for the Belt Tooling.

void volume is removed by cycling the pressure.

On the other hand, in experiments where the pressure is to be cycled repeatedly the curve labeled "3rd Cycle" is used. Previous experience shows that, at a given load, very little increase in pressure is gained beyond the third cycle.

While the calibration curve here only applies to the tungsten carbide pistons and die used, calibrations with other pistons and dies of the same nominal dimensions should agree within 5%. The accuracy of the calibration curve in Figure 19 is thought to be $\pm 5\%$ above 25 kbars.

Temperature calibration curve

Figure 20 shows the temperature inside of a Belt specimen cell as a function of power input. The temperature was measured by a Pt-Pt 10% rhodium thermocouple, and the absolute readings were corrected for the effect of pressure on the emf. The cell was at ~ 30 kbars at the time of the test. At this pressure the correction amounts to $+4^\circ\text{C}$ per 100°C of temperature increase. As is noted from Figure 20, roughly 3 kW of power input is required to raise the temperature to 1600°C .

CAPABILITIES

It is not the purpose of this report to enumerate all the studies which may be performed with equipment of this type. Rather a few of the most obvious capabilities will be mentioned while emphasizing that with certain modifications many more studies might be performed.

The large sample volume of the P-C unit makes it especially well suited for:

- The production of macroscopic (100-150 g) quantities of high pressure polymorphs.
- Hot pressing of ceramic materials.
- Compressibility studies.
- High pressure-temperature treatments of steels, nickel-based alloys or refractory metals.

The use of a collapsible can in this tooling allows the samples to be subjected to purely hydrostatic pressures at low temperatures ($<400^\circ\text{C}$) by using organic liquids as pressure transmitting media, or at high temperatures ($\sim 900^\circ\text{C}$) by using a NaK alloy. In addition to using the organics as pressure transmitting media, the effects of

FIGURE 20. Typical Temperatures Calibration Curve for the Belt Tooling.

pressure and temperature on the polymerization of these liquids can also be studied.

The hydrostatic nature of the pressure when using liquids as pressure transmitting media enables one to study solid state properties such as self- and impurity-diffusion as well as the migration and interaction of point defects produced by prior irradiation. It is paramount in such studies to insure that there are few, if any, shear stresses applied to the solid under consideration. Since liquids cannot support shear stress by their definition, they serve this requirement quite well.

The large specimen chamber in the P-C tooling also allows the incorporation of radioactive materials. By this technique one can study the effect of the ionizing radiation emitted from these materials on such phenomena as the rate of polymerization of organic liquids or the formation of color centers in alkali halides. For example, one might include a small cylinder of Co^{60} metal in the capsule with the organic liquid and study the effect of its 1.33 Mev gamma ray on polymerization rates at high pressures and temperatures. One might also include a metal which is a strong beta or alpha emitter to study the effects of charged particle irradiation on polymerization rates, or on color center production.

By the proper instrumentation one can also use differential thermal analysis as a tool to study the melting curves and phase boundaries of materials. Such information can be used to construct pressure-temperature diagrams of many materials.

Practically all of the above capabilities for the P-C tooling are inherent in the Belt tooling except on a much smaller scale (about 1/13 the volume in the P-C tooling). The major exception is that it is very difficult to obtain volumetric data because of the extrudable gasket technique which is employed.

The main advantage of the Belt tooling is the extension of the available pressure range to 60 kbars. This allows the production of many more high pressure polymorphs, such as omega-Zr, cubic BN, metallic InTe, and diamonds, to name just a few.

The can assemblies can also be used to insure hydrostaticity at these higher pressures by using liquid metals as pressure transmitting media. For example, the use of NaK alloys, which are liquid at room temperature and at high pressures, allows one to grow large grain samples of various metals (uranium and plutonium) at high temperatures under extreme pressures. The fact that NaK does not solidify or degrade under these severe conditions insures that the crystals will not be faulted or twinned when increasing or decreasing the temperature and pressure. The extension of these techniques to the growth of single crystals of other materials is indeed a fruitful area of research.

Other techniques that are used to study materials under pressure, such as the measurement of sonic, thermal, and mechanical properties, can be adapted to this equipment at a minimum of cost when the need arises.

In conclusion, the basic design and calibration of two distinct units of

high pressure tooling has been described in detail to 60 kbar and 1500 °C. The outstanding capabilities of each piece of equipment have been enumerated. The use of this equipment, in conjunction with other high pressure cells designed to function in a nuclear reactor and to yield X-rays of materials under pressure⁽²⁴⁾ allows scientists at BNWL to study the effects of pre-, simultaneous, and post-irradiation pressure effects on solid state phenomena in irradiated materials.

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