Static ultrahigh pressures above 500 kilobars

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A two-stage apparatus for ultrahigh pressures has been developed. It consists of a pair of Bridgman anvils in a Bundy-type high compression belt. A normal working pressure for this arrangement is 160 kilobars in the outside belt, which gives around 700 kilobars between both Bridgman anvils or only 500 kilobars if we consider Drickamer's new calibration values. A new calibration point is proposed: ZnS maximum of resistance at 640 or 480 kilobars. The apparatus is capable of reaching pressures far above the last known calibration point of ZnS at 550 or 415 kilobars in a new scale. Attempts to convert graphite to metallic carbon without heating have not been successful.

INTRODUCTION

The industrial world has been fascinated by static ultrahigh pressures for 20 years or so. Scientists have investigated new behaviors of matter at pressures always higher. The scientific literature mentions new semiconductor properties, new metallic phases, new plastic and flowing abilities of materials.

Very exciting objectives have been proposed, like metallic hydrogen (with a tremendously highly concentrated reserve of energy), metallic ammonia, metallic carbon (maybe harder than diamond), and so on. More down-to-earth objectives have been reached. The synthesis of diamond and cubic boron nitride around 55 kilobars has proved the realistic aspect and the industrial importance of some of these objectives.[1]

Our purpose was the development of an apparatus for the range above 500 kilobars. A combination of known techniques permits us to draw near the megabar.

APPARATUS

The Bridgman anvils principle is always an interesting approach for very high static pressures. If the anvils can be strengthened by some support and if the flow mechanism of the sample can be restricted, pressures up to 500 kilobars may be reached.[2]

The high-compression belt is another interesting approach.[3] Bundy's apparatus can reach high temperatures at 200 kilobars thanks to a higher sample volume than Bridgman's or Drickamer's anvils. A multistage combination is a well-known idea too.[4]

Our final choice is a two-stage apparatus. The outside stage may be considered as a high-compression belt which reaches 200 kilobars. The first realisation we have made can be seen in Fig. 1. The second stage consists of a pair of pistons like Bridgman anvils, but with an hydrostatic environment of about 180 kilobars and considerable distance between both anvils relative to anvil size (Fig. 2). The first-stage pressure enables us to use very hard cemented tungsten carbide (less than 2% cobalt) for the second-stage anvils and to give them a plastic flow ability without breakage. Like every Bridgman anvil, the nose of our pistons tends to make a cavity which delimits the very high pressure region but with a considerable pressure gradient perpendicularly to the anvil axis. The useful volume for the sample must stay confined in the central part of the cavity during compression.

CALIBRATION

The first stage can be easily calibrated by classical bismuth, barium, and lead transitions, in the presence of the second stage, of course. The typical arrangement that can be seen in Fig. 3 gives calibration points of bismuth and barium together. The second-stage calibration can be obtained by the same arrangement (Fig. 3). At M we place the sample for electrical resistance examination. Both electrical circuits, through barium and through M are, of course, different with only one common point: the upper anvil.

Calibration values generally accepted in the 1960's are called "old scale" in Table I.[5] New values proposed by Drickamer[6] are called "new scale." It must be perfectly understood that all calibration points mentioned here have no absolute meaning; discussion of their real value is always open. This situation will persist for some time.

Plotting pressure values vs load, it appears that the first stage exhibits a perfect linear relationship (Fig. 4); the

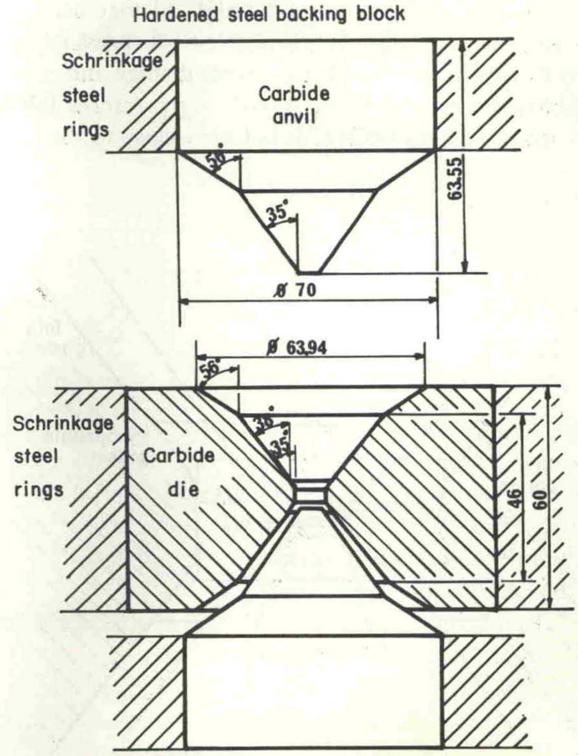

FIG. 1. First-stage assembly. All sizes in mm.

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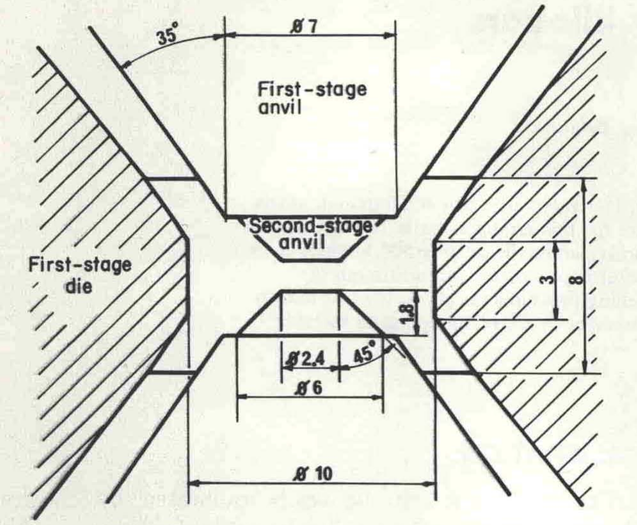

FIG. 2. Second-stage assembly in first-stage apparatus. All sizes in mm.

same is true for the second stage below 250 kilobars. Most of the calibration points (at least six experiments for each transition except for Ca) fall between both lines drawn in Fig. 4.

Relative to the old scale, there is a sharp increase in dependence on load above 250 kilobars. If we assume that this fact must be incorrect and that the relationship cannot be better than linear, a new completely linear scale may be proposed (see last column of Table I and "second-stage extrapolation" in Fig. 4). Even this assumption seems optimistic at the higher pressures.

The most efficient experiment in calibration is obtained by the arrangement shown in Fig. 3 with ZnS in place of M. So, the first stage exhibits four transitions (Bi 25, Ba 59, Bi 89, Ba 141), and the second stage gives three calibration points (ZnS 245, ZnS 550, ZnS 640 old scale), all together in the same experiment (Fig. 5). Hysteresis of pressure with respect to load is very low for the second stage and most of the calibration points during decreasing pressures fall between the same lines on Fig. 4, but very close to the upper line.

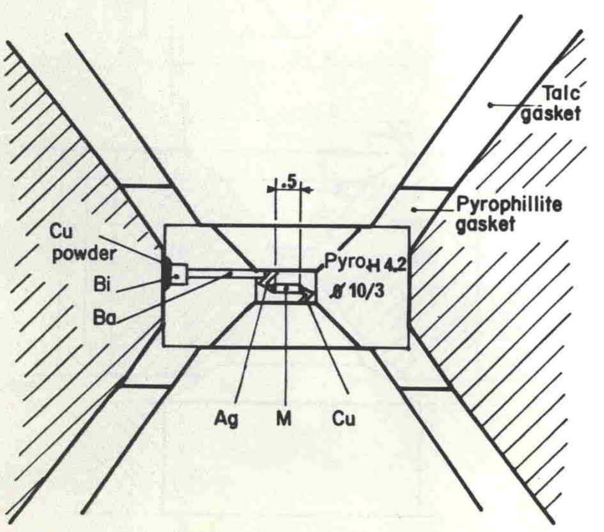

FIG. 3. Calibration cell for both stages. All sizes in mm.

TABLE I. Calibration points.

Stage	Calibration material	Old scale (kilobars)	New scale (kilobars)	Linear extrapolation from old scale below 250 (kilobars)
First and second	Bismuth	25		25
	Barium	59		59
	Bismuth	89	74	89
	Barium	141	120	141
	Lead	161	130	161
Second	Rubidium	193	148	193
	Zinc sulfide	245		245
	Calcium	365	245	310
	Rubidium	425	305	330
	Zinc sulfide	550	415	380

Zinc sulfide exhibits a weak maximum of resistance at 550 kilobars (old scale)[5] and a second one that we locate, by extrapolation, around 640 kilobars. Five experiments with good continuous electrical contact during loading and unloading have been successful up to the first maximum of resistance, and in three of them we reached the second maximum of resistance, which appears as a reversal although very weak (see, e.g., Fig. 5). We propose this second maximum of resistance as a new calibration point.

LIMIT OF APPARATUS

Above 250 kilobars, small second-stage anvils have to be replaced after each cycle because of some cracks and of their distorted shape (cavity in the nose). Speaking in the old scale, it seems that no major difficulties have to be expected below 700 kilobars (see working load in Fig. 4), i.e., below 155 kilobars near the die.

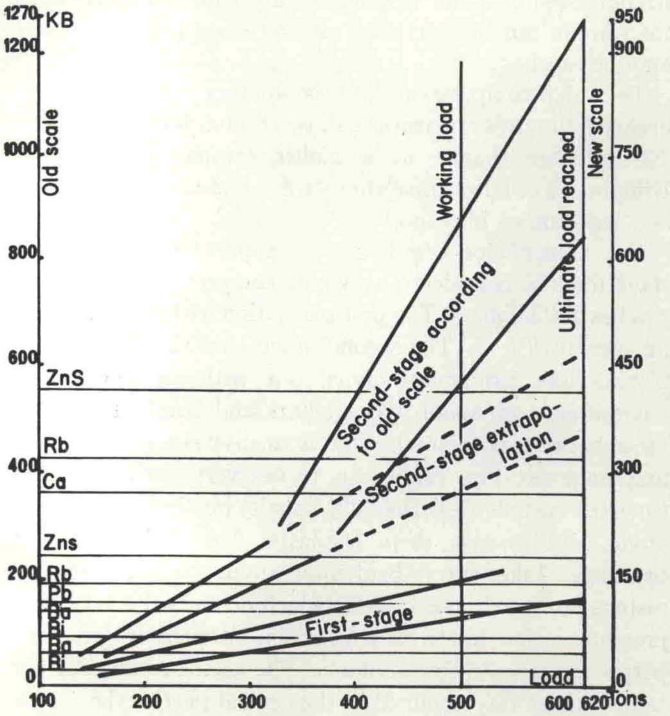

FIG. 4. Calibration diagram. Pressure vs load.

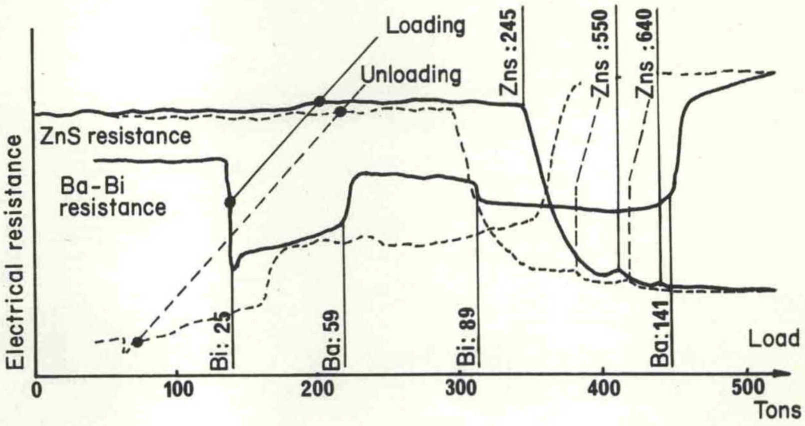

FIG. 5. Typical calibration run. Resistance vs load.

Catastrophic breakage of the first stage may happen in the range above 700 kilobars. The maximum pressure we have reached is between 830 and 1270 kilobars on the old scale (see Fig. 4), i.e., about 620 to 950 kilobars in Drickamer's new scale, or between 470 and 620 kilobars in linear extrapolation of old scale calibration points below 250 kilobars.

Without any doubt, improvements can be expected with new efforts for the near future and the megabar will be reached soon if we have not attained it in this work.

CARBON ABOVE 500 KILOBARS

The temptation to synthesize metallic carbon has been very high and graphite has been submitted to pressures up to the actual limit of the apparatus.

The metallic state was never seen, even in the most promising experiments, i.e., pyrolytic graphite oriented with its *c*-axis along the anvil axis. Generally, the electrical resistance of graphite increases between 120 and 500 kilobars (old scale) but things go back to their initial state during decreasing pressure. This is in agreement with observations of Bundy.[3,7] Heating would be necessary to stabilize the kind of hexagonal diamond obtained. Conversion of graphite to metallic carbon probably needs heating too for an appreciable rate of transformation.

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