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Lubrication, gasketing, and precision in multianvil experiments

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Abstract

Lubrication, gasketing, and pressure medium effects on pressure generation and reproducibility were investigated with 35 experiments on the Bi transitions in a multianvil apparatus. The system of integral gasket fins on octahedral pressure media and sliding, cylindrical anvil-driving wedges within a retaining ring, similar to that of Walker et al. (1990), was used for all experiments. Internal friction in this device of ~10% of thrust, the existence of which was previously known from ring-strain hysteresis, has been found to be at the interface between the anvils and their cylindrical driving wedges. This friction is a common property of all MA6/MA8 devices, not just the design employed here. Truncated edge length (TEL) anvil facets of 8 mm on MgO (5% Cr_2O_3) octahedra with epoxy-Al_2O_3 gaskets achieved Bi III → V at 242 ± 6 tons (equivalent to 2.15 ± 0.05 MN, 1 ton force = 2000 lb force = 8.90 kN), in six experiments between 233 and 250 tons with standard deviation of the mean, $\sigma = \pm 2.5\%$. This gasket system gives excellent pressurization efficiency and precision at room temperature and also affords nearly perfect blowout suppression. A procedure for fabricating the pressure medium and gasket fins from castable ceramics in a single operation was developed for high-temperature experiments. Using an MgO-based castable ceramic at room temperature, Bi III → V on 8 mm TEL was found at 266 ± 11 tons (eight experiments, 249–282 tons, $\sigma \pm 4\%$), whereas for 6 mm TEL it was found at 159 ± 6 tons (eight experiments, 149–168 tons, $\sigma \pm 4\%$). The advantages of castable ceramics, in addition to ease of fabrication and rigorous dehydration, include their excellent high-temperature characteristics of thermal insulation, pressure stability, and thermocouple survival. Calibrations on the coesite to stishovite transition at 1200 °C confirm the good performance of these ceramics. Experiments of several days' duration within the melting range have been routinely achieved with this single-substance gasket and pressure medium system.

Introduction

Growing interest in mineralogical research at very high pressures (tens of GPa) on relatively large volumes of material (cubic millimeters) has prompted development of simplified equipment and procedures for multianvil experiments. Walker et al. (1990) reported a cost-effective device based on a system of sliding, split-cylindrical, anvil-driving wedges within a deformable retaining ring. The wedges guide a uniaxial compressive force onto the faces of a standard MA6/MA8 payload, i.e., a cubic cluster of eight separated cubic WC anvils converging on octahedral pressure medium.

The pressurization of samples by such multianvil techniques requires judicious use of lubricating and gasketing materials. Some requirements of the material properties may be contradictory. For instance, for compressive stroke to occur and cause pressurization, sufficient lubrication between sliding stages of the apparatus and sufficient compressibility of gaskets between converging anvils must be available. However, good lubricants and materials of low compressive strength, conducive to these requirements for pressurization, tend to be weak in shear, thereby promoting material extrusion or leakage with diminution of the desired result. Successful experimental design is often therefore an exercise in seeking the proper balance among competing effects.

One way to monitor the efficiency of pressurization and the relative merits of different assemblages of materials is to observe the thrust necessary for particular phase changes to occur. The Bi transitions at room temperature (Lloyd, 1971) and the coesite → stishovite transition at 1200 °C (Yagi and Akimoto, 1976) are convenient references. Repeated observations of these transitions should give some indication of the precision in the pressurization achieved from a specific thrust. The series of observations served as a calibration study of thrust vs. sample pressure for the studies underway in this new laboratory and as an opportunity to explore the effect of changes of lubricants, gaskets, and pressure media upon pressurization in the search for more favorable assemblage of materials. The studies of reproducibility were undertaken to establish the precision of pressurization achieved with the new gasket and pressure medium configurations; these may be of general interest to students of multianvil technique because such studies at other laboratories are somewhat inaccessible.

Experimental methods

A second soft-shell multianvil module similar to the one described by Walker et al. (1990) was built at the University of Cambridge with the following dimensional changes for installation at Lamont-Doherty Observatory. The height and diameter of the split-cylindrical cluster of six wedges were changed from 4.5 in. to 5.5 in. and from 8 in. to 7 in., respectively. The retaining ring was stiffened by increasing the wall thickness of H13 steel from 8 in. id to 7 in. id × 10 in. od and increasing its overall length to 6.5 in. Al plate was substituted for the Tufnol 10G/40 disks at the interface between the base of the wedges and the pressure distribution plates, making it no longer necessary to circulate coolant between the wedges within the ring during experiments at high temperature, although it was still possible to do so. In other respects, the Lamont-Doherty version differs little from the Cambridge prototype, which continues to perform well. (See Fig. 1.)

This module was loaded into a uniaxial hydraulic press of 600-ton capacity normally used for piston-cylinder work (e.g., Agee and Walker, 1988). Oil pressure in the press was read on a 1 kbar Heise Bourdon-tube gauge of 14 in. diameter that was readable without vernier or interpolation in 1-bar increments. Oil pressure was also recorded on a strip chart as a voltage across a bridge circuit in a pressure transducer that was calibrated against the Heise gauge. Press thrust was calculated from the product of the ram oil pressure and the working area of the ram with 16-in. diameter. Ram pressurization was accomplished with an air-driven reciprocating oil pump; the rate of pressurization was manually regulated through trial and error adjustment of a series of two needle valves. Pressurization to achieve all three Bi transitions was usually accomplished in less than 2 h. Depressurization through the same valves usually proceeded two to three times more slowly.

All experiments used the octahedron with integral fin gaskets of Walker et al. (1990) with various substitutions of material for the fins and octahedron. Holes for sample loading were drilled between opposite faces of the octahedron. For the Bi studies, this hole was 1.5 mm in diameter and was stuffed with a 4-mm-long cylinder of 99.999% Bi metal. Excess hole length on either side of the Bi in the middle of the octahedron was filled with Al or Cu electrodes to allow electrical communication between the Bi and the resistance-measuring circuit outside the press. These Al or Cu electrodes contact opposing WC anvils, which become a part of the circuit. Bi resistance was monitored as a voltage drop across the circuit that included two WC cubes, two Al or Cu electrodes, and the Bi cylinder. For a supply voltage of 5 VDC through a 50 Ω resistor, this voltage drop was about 2 mv, about ⅓ of which is attributable to the Bi. Voltage changes were recorded on the same strip chart as the ram oil pressure, and the three Bi transitions at room temperature were easily recognized during pressurization.

For the coesite → stishovite transition at 1200 °C, a hole with a diameter of ⅛ in. was drilled from one face of the octahedron to the other. A tube fabricated from two turns of 0.001 in. Re foil lined this hole and formed the heating element. About 2 mm in the center of this tube was filled with SiO_2 glass powder that had a Pt vs. Pt_{90}/Rh_{10} (type S) thermocouple junction imbedded within it. Excess space within the tube on either side of the SiO_2 powder was filled with crushable Al_2O_3, Al_2O_3 thermocouple ducts, and Zircar Al_2O_3 cement (see Appendix 1). The thermocouple leads were brought out through slits in the ends of the heater tube and run out octahedral fins between WC cubes. Samples were pressurized cold, heated to 1200 °C for 1–2 h, quenched, depressurized in 6–10 h, and examined optically. Complete devitrification was always observed as coarse crystals of low birefringence (coesite), as a mixture of coesite near the heater and finer grained crystals of refractive index >1.70 and high birefringence near the thermocouple (which were identified as stishovite) or as stishovite alone. WC cubes of 1-in. edge of Hertel grade KMY or K05HIP (see Appendix 1) were used in all these experiments; the only cube loss in the whole experimental program (three cubes) occurred as the result of a blowout during a too rapid decompression (100 → 50 kbar in 20 min). At the relatively modest pressures examined in this study (less than 100 kbar), very little anelastic deformation is sustained by the carbide cubes. Thus, the differences between carbide grades that are so obvious in calibrations at more than 150 kbar are not an important factor here.

Substances used for the octahedral pressure medium include the MgO with 5% Cr_2O_3 used by Walker et al. (1990), Cotronics' compound 809, or Aremco's compounds 584, 575, and 645. (Previous experience with compound 511 demonstrated its unsuitability, see Appendix 1). Gaskets as fins on the MgO octahedra were either epoxy-alumina as described by Walker et al. (1990) or compound 575. Gaskets on castable ceramic octahedra were of the same material as the octahedron and were fabricated as an integral cast unit in segmented molds (Fig. 2).

Various lubrication arrangements were tried at the sliding interfaces exhibited in Figure 1. At the A-B interface between the wedges and the ring, a double thickness of 0.004 in. glossy polyester sheet, with PTFE mold-release agent sprayed on the plastic to plastic interface, provided lubrication in all but one experiment. This experiment employed a single layer of the plastic to illustrate the losses experienced to friction on the A-B bore without the double-plastic lubrication. At the A-C interface between the wedges and the cubic anvils, I used pads of fiberglass impregnated with epoxy resin, fiberglass impregnated with silicone resin, Nylon 66 impregnated with molybdenum disulfide, a single thickness of 0.014 in. Mylar polyester, or double thicknesses of 0.007 in. Mylar

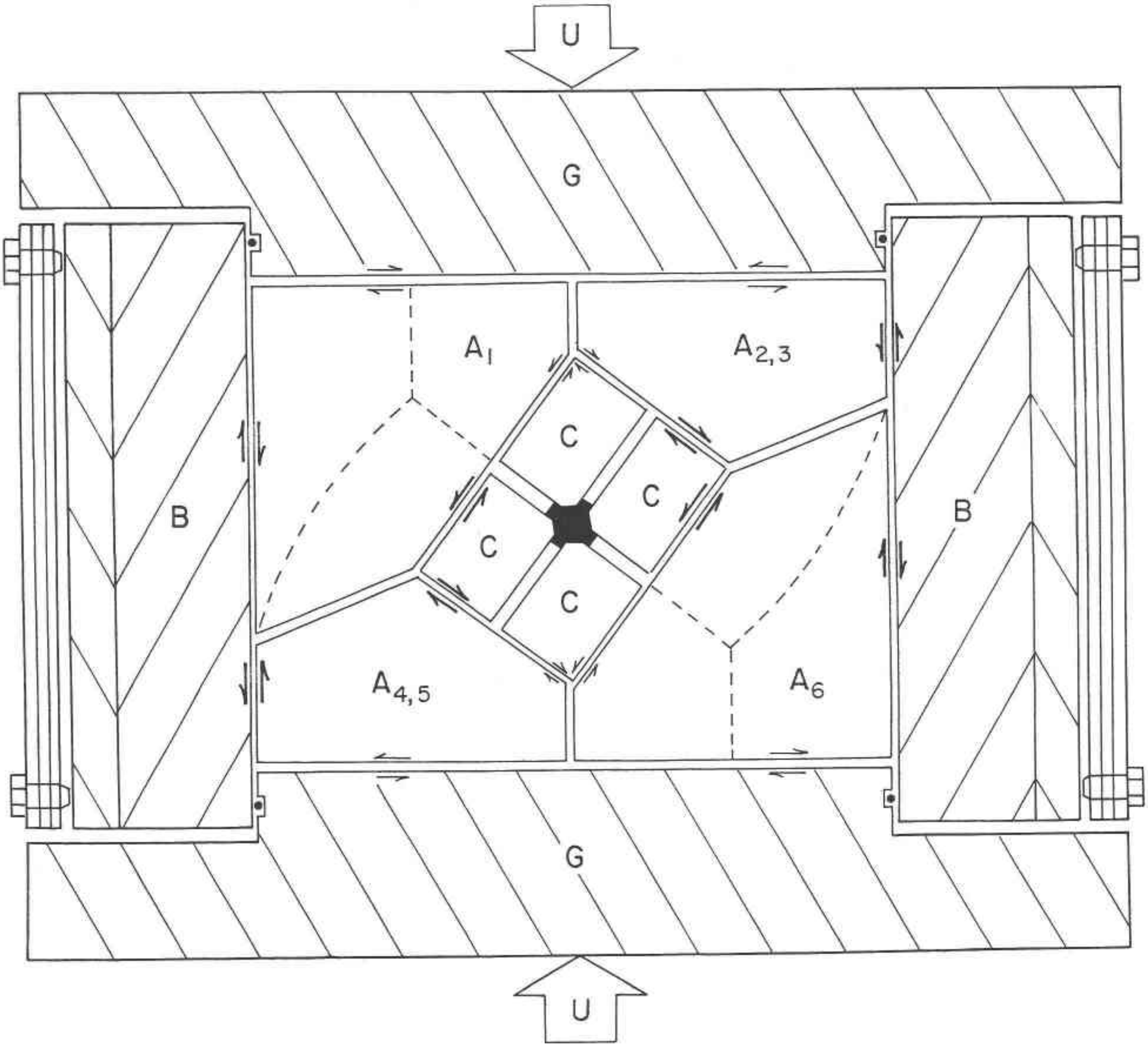

Fig. 1. Axial cross section of cylindrical module used to perform multianvil experiments, closely similar to the unit described in Walker et al. (1990). A_1, A_2, etc. are tool steel, anvil-driving wedges guided by the bore of alloy steel containment ring B. The upper set of wedges, A_1-A_3, and lower set, A_4-A_6, converge on a cluster of eight tungsten carbide cubic anvils, C, when activated by a uniaxial thrust, U, delivered through the aluminum alloy pressure distribution plates, G. The sample resides in the octahedral pressure medium at the convergence point of the WC cubes. The cubes have 1-in. edge dimension. The interfaces that must slide past one another during sample pressurizations are indicated by traction shear couples at sliding interfaces. Friction on these interfaces should be minimized for optimal sample pressurization. A-B and A-G tractions are intrinsic to this design. The A-C friction is shared by all MA6/MA8 devices and appears to be the source of the residual strain hysteresis observed during loading and unloading of ring B once the A-B interface has been lubricated with double-plastic sheet.

with interfacial PTFE spray. Experimental results are given in Table 1.

Discussion of results: lubrication

Inspection of Table 1 and Figure 3 shows a good separation of the forces necessary to observe the Bi transitions for 8-mm truncated edge length (TEL) anvils and for 6-mm TEL. The forces required are reasonably reproducible and are observed to be roughly in the ratio of 1.5/1 for 8 mm/6 mm TEL. However, the expected ratio of forces for achieving some particular pressure is $(8\ \mathrm{mm}/6\ \mathrm{mm})^2 = 1.8$. This discrepancy from the observed value of 1.5 reflects the fact that the forces are not supported entirely by the truncation on the anvils but also by some margin of the anvil flanks through the gaskets.

The control of TEL upon the force required to achieve

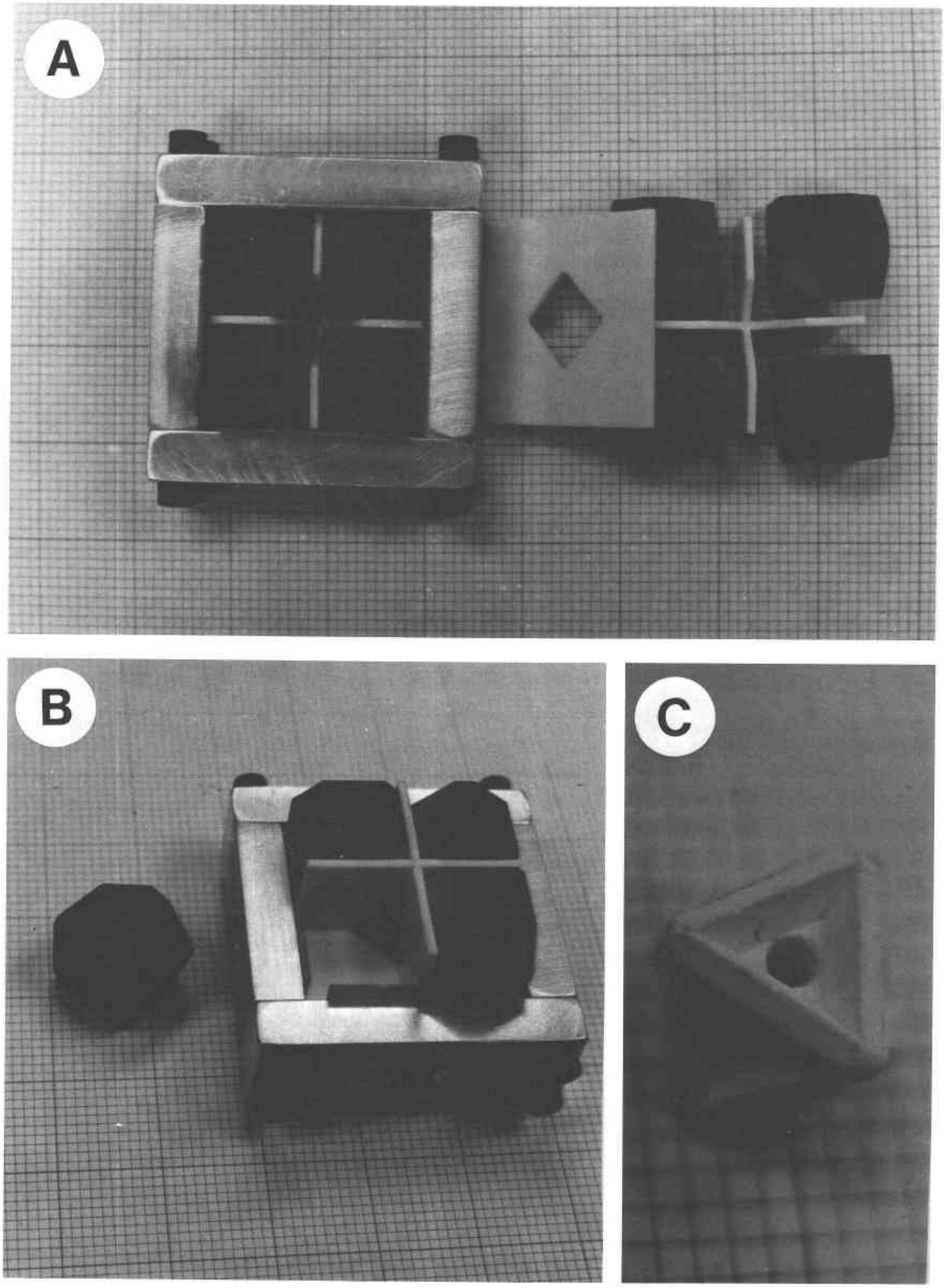

Fig. 2. (A) Partially assembled mold for casting pressure media and gaskets. White teflon sheet provides separation of the dark PVC cubes to form gasket fins. Cubes have various truncations for casting of appropriate TEL dimensions. (B) Mold assembled. Final cube will be inserted after mix is poured into cavity. (C) Finished pressure medium with 6 mm TEL and gasket fins 3 mm wide by 2 mm thick. A hole 0.128 in. in diameter has been drilled after firing at 1000 °C. Grid mesh 0.1 in. in each picture.

TABLE 1. Bi transition results

Experiments for 8 mm truncated edge length anvils

Exper. group	Serial no.	Notes	Pads	Gaskets	Tons: Bi I → II	Tons: Bi II → III	Tons: Bi III → V
MgO (5% Cr_2O_3) pressure medium							
A_1	15	xx	M66	BDH	72	91	233
	12	xx	G10	BDH	73	92	239
	50	xx*	G10	575	73	89	241
	8	xx	G10	0.3 μm	**	**	242
	11	xx	G10	BDH	71	91	**
	5	xx	G10	0.3 μm	82	105	248
	4	xx	G10	BDH	67	92	250
				Summary of A_1	73 ± 5	93 ± 6	242 ± 6
A_2	18	xx	SIL	BDH	100	134	340
	1	X	G10	BDH	84	108	350
584 pressure medium and gasket							
B_1	59	xx*	M14	F T	73	92	258
	23	xx	G10	T	74	92	258
	49	xx*	G10	F T	70	90	273
	51	xx	G10	F T	79	99	282
					74 ± 4	93 ± 4	268 ± 12
B_2	55	xx	M14	H F T	64	80	249
	58	xx*	M14	H F T	67	84	267
	56	xx	M14	H F T	68	82	270
	57	xx	M14	H F T	74	92	277
					68 ± 4	84 ± 5	266 ± 12
				Summary of B_1 and B_2	71 ± 5	89 ± 6	267 ± 11
575 pressure medium and gasket							
C	22	xx	G10		70	86	232
	52	xx	G10	F T	74	90	270
	41	xx*	MM7	F T	71	89	284
					72 ± 2	88 ± 2	262 ± 27
				Summary of A_1, B_1, B_2, and C	72 ± 4	90 ± 6	257 ± 17

Experiments for 6 mm truncated edge length anvils

Exper. group	Serial no.	Notes	Pads	Gaskets	Tons: Bi I → II	Tons: Bi II → III	Tons: Bi III → V
MgO (5% Cr_2O_3) pressure medium							
D_1	20	xx	M66	BDH	52	**	**
	21	xx	G10	575	52	61	155
	53	xx	G10	575T	52	66	176
D_2	17	xx	SIL	BDH	59	82	197
	19	xx	SIL/G10	BDH	60	77	199
584 pressure medium and gasket							
E	30	xx	G10	F	45	52	149
	25	xx	M66		50	61	152
	24	xx	G10		50	60	158
	40	xx*	MM7	F	47	57	160
	42	xx*	MM7	F T	48	58	160
	44	xx	G10	F	47	58	162
	46	xx A*	G10	F T	46	57	163
	47	xx A*	G10	F T	49	60	168
				Summary of E	48 ± 2	58 ± 3	159 ± 6
575 pressure medium and gasket							
F	54	xx	M14	F T	45	52	149
	39	xx	MM7	F T	46	55	176
				Summary of D_1, E, and F	48 ± 2.5	58 ± 4	161 ± 9

Note: xx = Double plastic liner on ring bore at A-B interface. X = Single plastic liner on ring bore at A-B interface. M66 = Pads of Nylon 66, 0.015 in. thick, impregnated with molybdenum disulfide. G10 = Epoxy-impregnated fiberglass pads, 0.016–0.020 in. thick. SIL = Silicone-impregnated fiberglass pads, 0.015 in. thick. M14 = Mylar polyester pads of single thickness, 0.014 in. MM7 = Mylar polyester pads of double thickness of 0.007 in. material. BDH = Coarse, gritty Al_2O_3 in epoxy. 0.3 μm = Buehler polishing Al_2O_3 in epoxy. 575 = Aremco's compound 575 used as gasket fins. F = Gaskets and pressure medium fired at 1000 °C. A = Crushable alumina AN900 core around Bi cylinder. H = 10% Fe_2O_3 added to 584 castable ceramic. T = Teflon tape wrapped on gasket extremities.

* PTFE mold release agent added to A-C interfacial pads.

** Measurement fails or resistance trace uninterpretable.

the Bi transitions is the most obvious (and expected) aspect of the data in Table 1. Another control that is obvious from even the limited amount of data collected is the sensitivity of the results to particular, poor-lubricating substances at the A-B and A-C interfaces. Sections A_2 and D_2 of Table 1 give the results for experiments conducted with MgO (5% Cr_2O_3) pressure media that are relevant to this proposition. Experiment 1 (section A_2)

differs from all other experiments reported in having a single thickness of plastic lining the A-B ring-bore interface instead of a double layer with PTFE mold-release spray between them. Walker et al. (1990) analyzed the hysteresis of strain observed during loading and unloading of the containing ring with the single plastic liner configuration; they concluded that about 30% of thrust was being lost to frictional effects. The hysteresis and presumed loss of thrust to friction decreased but was not entirely eliminated by the use of the double-plastic ring liner configuration. A comparison of the 350 tons force necessary to produce the Bi III → V transition in experiment 1, section A_2, with the mean of the results in section A_1 of 242 tons (for experiments using a double ring liner) confirms in a rough way the conclusion based on ring strain hysteresis: pressurization improvement of ~30% is realized with care in lubrication at the A-B interface.

Insight into possible causes of the residual strain hysteresis over and above that of bore friction may be gained from considering experiment 18 in section A_2 of Table 1 and section D_2 of Table 1. These experiments all employed the double-plastic ring liner but substituted Si-impregnated fiberglass pads for the material at the A-C interface between the wedges and cubes. This silicone-based material was tried because of its substantially higher thermal stability than epoxy-impregnated fiberglass. It can be seen that this choice was not a happy one from the point of view of pressurization efficiency. Evidently, there is as much scope for introducing frictional problems at the A-C interface as there is at the A-B ring bore. Furthermore, friction at the A-C interface is a circumstance common to all MA6/MA8 devices, unlike the friction at the A-B ring bore, which is specific to the split cylinder design of Walker et al. (1990). Thus it is of general interest to become aware of the frictional properties of materials to be used at this interface, silicone fiberglass laminate being a poor choice whatever its benefits of thermal stability may be.

Walker et al.'s (1990) analysis of the strain hysteresis with a double-plastic ring liner suggested that ~10% of thrust was still being lost to friction. They conjectured, if this residual friction were still to be found in the A-B ring bore, that Japanese-style MA6/MA8 devices based on a rigid split sphere, which have no such potentially friction-generating interfaces as A-B or A-G, might show improved pressurization of about 10% when compared with the split, sliding cylinder design if the same configuration of an MgO (5% Cr_2O_3) pressure medium with epoxy-Al_2O_3 gaskets were to be tested. F. R. Boyd (personal communication) recorded the Bi transitions on the Japanese-style MA6/MA8 at the University of Alberta (Edmonton) with an 8 mm TEL pressure medium and gasket assembly fabricated in this lab. His result for Bi III → V (239–242 tons) is indistinguishable from the mean in section A_1, Table 1, although his Bi I → II result (91–94 tons) is significantly higher. Thus it is unlikely that there is significant friction at the A-B ring bore because a device

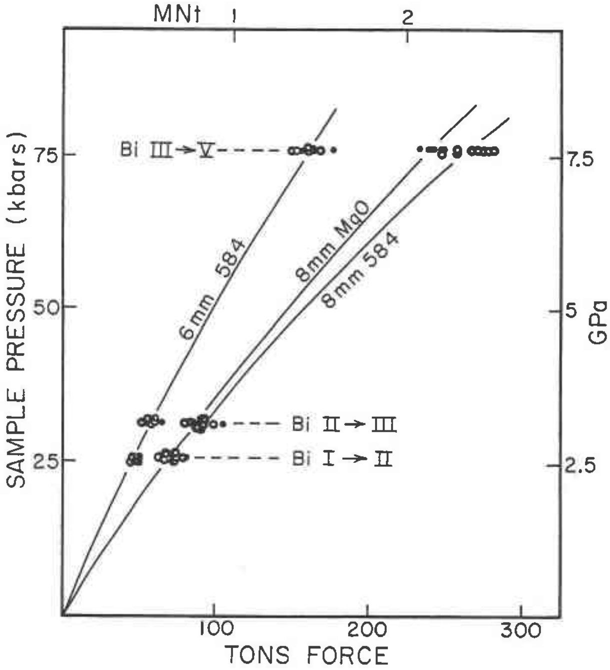

Fig. 3. Bi transition experiments. Clear separation of the forces required to cause transitions to occur is seen as a consequence of change from 6-mm to 8-mm truncated edge length (TEL) on the octahedral facets of the cubic anvils. Open circles are for experiments using Aremco's 584 compound for the pressure medium and gaskets. Filled circles are for experiments using MgO (5% Cr_2O_3) with bonded Al_2O_3 gaskets. Only for 8 mm Bi III → V transitions is there a clear separation of results for the different pressure media. Precision of the pressurization forces required for achieving a transition is typically characterized by a standard deviation ± 4% of the average pressure. Considering that these results were obtained on a series of experiments in which many parameters such as mix composition, gasket character, and A-C interface pads were also changed, it is possible that still higher precision might be obtained when attention is directed toward uniformity of procedure rather than the effects of variations. Nevertheless, the precision realized here is comparable to that quoted from other laboratories.

without such friction does not perform better. The implication of Boyd's result and of the silicone-(non)lubricated experiments 17, 18, and 19 in Table 1 is that nontrivial residual friction resides at the A-C anvil to anvil-driver interface. This will be of interest to those contemplating adoption of one design of MA6/MA8 device over another. Residual bore friction is clearly not a compromising feature of the single ring design with sliding split cylindrical wedges. The residual friction that is present is a common feature of all MA6/MA8 designs; it is easily recognized from strain hysteresis analysis of a ring assembly, but it would be more difficult to recognize in the same way in a split sphere design, even though it must be present.

A more subtle aspect of the data in Table 1 that bears on the question of friction at the A-C interface is the virtual independence of the results from choice of pad materials, other than the silicone-impregnated fiberglass. Epoxy-impregnated fiberglass (key G10), thick single Mylar pads with or without extra PTFE spray (M14), and double-thickness thin Mylar pads with intervening PTFE spray (MM7) gave results that were statistically indistinguishable. The good news is that single thickness (0.014 in.) Mylar is commercially available at about 20% of the cost of epoxy-impregnated fiberglass, and it has better thermal stability. Unfortunately, at press loads of about 400 tons on clusters of 1-in. cubes, the (A-C) interfacial forces are sufficient to cause extrusion of the Mylar from the interface. Thus Mylar is an admirable substitute, which can be used without recalibration, for epoxy-filled fiberglass interfacial pads, but only at modest press loads.

Of the pad materials in Table 1, Nylon 66 filled with molybdenum disulfide (key M66) performs a little better than the other materials in reducing A-C friction. In all three experiments where this material was tested, nearly the lowest forces required to cause the transitions were recorded. This is not altogether a surprise because this material is commercially fabricated expressly for liners and bearings that reduce friction. However, at the compressive forces of these experiments, the material is weak enough in shear to extrude even at modest press loads. As a result, M66 is forced between the wedges that are separated under load. During unloading, the wedges relax on the intruded M66, catching both the pads and the wedges in a grasp that makes disassembling the module extremely awkward. (This is the same problem that plagues Mylar at press loads above 400 tons with 1-in. cubes.) For this reason, further experiment with M66 was abandoned, although inquiries were made (without success) for a product composed of fiberglass-reinforced polyester sheet filled with molybdenum disulfide.

Discussion of results: gasketing and precision

The picture that emerges is one in which pressurization of specimens can be strongly influenced by TEL selection and by mistakes in the selection of lubricating substances at various interfaces between stages in the apparatus. In subsequent discussion, we ignore the data in sections A_2 and D_2 of Table 1 and the distinctions between pads at the A-C interface. The residual information in Table 1 is a compilation of results by type of pressure medium and gasket employed, investigations at 8 mm TEL being slightly more extensive than at 6 mm TEL. Each general letter category (A, B, etc.) in Table 1 gives the result for a particular pressure medium and gasket combination. The multiple entries reflect on the precision of pressurization to be expected from the different combinations.

Section A (Table 1) gives results obtained at Lamont for the combination of 8 mm TEL MgO (5% Cr_2O_3) octahedra with epoxy-Al_2O_3 gasket fins described in Walker et al. (1990). It is clear that there is some variation associated with these transition force measurements. The averages of the transition forces required for the Lamont-based results in Table 1 (A) are lower than the force for the single comparable Cambridge experiment reported by Walker et al. (1990). However, the Lamont range includes the Cambridge result comfortably within 2 sd of the mean. Attention to the standard deviation of replicate analyses should give an estimate of experimental precision. The standard deviations for each of the 8 mm TEL Bi transitions for MgO in Table 1 (A) is ± 5–6 tons; on the face of it, precision increases with pressure. For the Bi III → V transition, the standard deviation of the force for six measurements has diminished to $\pm 2.5\%$ of the average. This is respectable precision. Variation of Al_2O_3 grain size or binder (BDH in epoxy, 0.3 μm in epoxy, or 575—a castable Al_2O_3 ceramic) does not appear to change this result.

Given this performance characteristic, the ease of preparation compared to some alternatives, and the virtual absence of blowouts, one might hesitate before seeking additional pressure medium, gasketing systems. However, the high-temperature performance of this combination leaves significant room for improvement. The epoxy base to the Al_2O_3-powder gaskets loses strength at high temperature, so excessive pumping is required to maintain pressure at high temperature. This circumstance and the accompanying extrusion of the gaskets and leakage of the pressure medium has unfortunate consequences for thermocouple survival rates. MgO, even with 5% Cr_2O_3, is also a relatively poor thermal insulator at high temperature, leading to high power consumptions and unnecessary carbide and apparatus heating. Furthermore, the epoxy base for the fins precludes a rigorous firing procedure to dehydrate the MgO once the assembly is fabricated. To remedy these problems, fabrication of pressure media and integral gaskets as a uniform ceramic in a single casting operation was explored. Aremco's 584 potting compound was most extensively tested, although Aremco 511, 575, and 645 and Cotronics 809 were also investigated. The fabrication procedure is extraordinarily simple if appropriate molds are available: mix, pour, set, release from mold, and bake. No particular pains were taken over mixing procedures or setting times and temperatures. Firing at 1000 °C for 2 h is also recommended as this improves the machinability of the product through the introduction of ~15% porosity. Firing is done prior to drilling holes through the octahedra for samples and heaters and slicing slits for running thermocouple leads. Firing is absolutely essential for high-temperature experiments. Without firing, evolution of binder residues leads to blowout upon heating a sample almost every time. Of course, such firing can also be done with sample assembly in place within the gasket and pressure medium assembly to insure optimal dehydration.

Composite gasket and pressure media of compound 584 were tested for both 8 mm and 6 mm TEL. For Bi I → II and Bi II → III, the forces required at 8 mm TEL are not statistically distinguishable from those found for MgO/5% Cr_2O_3, with the same standard deviations. Too few MgO measurements were taken at 6 mm TEL to make a statistically significant comparison, although no discrepancies in forces required for the Bi transitions at 6 mm TEL appear for the different pressure medium and gasket combinations tested.

Unlike the case for 8 mm TEL MgO combinations, the 584 pressure medium and gasket measurements do not exhibit a constant standard deviation with measuring pressure; they show an increase in standard deviation that remains a roughly constant percentage of the average value (~4%). Also for 8 mm TEL Bi III → V determinations, it is clear that 584 requires more force than MgO. Recalling that at 6 mm TEL there was no such obvious increase of the force required for Bi III → V for 584 compared to MgO combinations suggests that the departure at 8 mm TEL may be a function of the higher thrust necessary. Alternatively, the anomalously decreasing percentage of the standard deviation of the MgO measurements with pressure may indicate an unrecognized problem with the 8 mm TEL measurements for MgO. Although it is very difficult to imagine that highly reproducible results should be problematic, the 8 mm TEL results for Bi III → V in MgO are anomalously well clustered compared with all the other data combinations, including Bi I → II and Bi II → III in MgO. Most of the data sets collectively show a standard deviation that is ~4% of the average value. In any case, this lower precision is well within the ranges quoted by other laboratories (e.g., Ohtani et al., 1982).

Another interesting feature of the data for the ceramic pressure medium and gasket combinations is the apparent lack of sensitivity to the details of the constitution of the ceramic. For instance, the limited data presently available for compound 575 do not show any striking deviations from the results for compound 584 at room temperature. This is somewhat surprising in that 575 is nearly pure Al_2O_3, whereas 584 has hefty admixtures of SiO_2 and MgO. Perhaps even more surprising is a comparison of sections B_1 and B_2 of Table 1. Section B_1 is for regular 584, whereas B_2 is for 584 with 10% Fe_2O_3 powder added to the mix. No statistical difference is seen between the results of these two ceramics. Evidently, vigilance over the proportions of ingredients and the process control in pressure medium fabrication are not key factors in achieving ~4% reproducibility.

The high-temperature performance of the castable ceramic gaskets greatly improves upon the epoxy-Al_2O_3 combination. The latter typically dissipate 10–30% of the applied thrust by extrusion and gasket flattening when the sample is first heated. This thrust loss is unrecoverable without further pumping. By contrast, the 584 gaskets rarely lose more than 3% of the applied thrust when heated. This small loss is rapidly made up as the press heats. Evidently 584 is a tight gasket at high temperature. The mechanical stability inherent in this tightness is probably a key feature of our almost-perfect thermocouple survival record with these gaskets. The thermal insulation properties of 584 are such that about 340 watts are required for our Re heaters to produce internal temperatures of

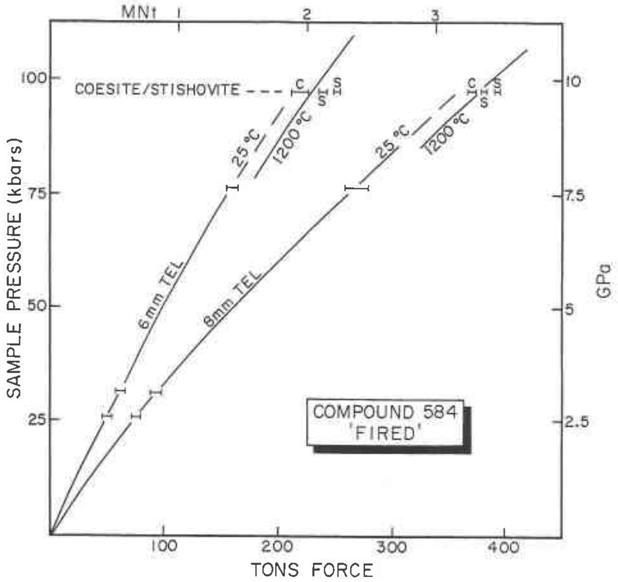

Fig. 4. Performance of Aremco's compound 584 on the Bi transitions at room temperature and for the coesite-stishovite transition at 1200 °C. The error bars on the Bi transitions are 1σ bounds on the variations observed in multiple experiments. The error bars (upon individual experiments) for the six C-S experiments reflect the increase in ram pressure experienced during heating of the experiment with a closed hydraulic system. The C or S designation corresponds to the SiO_2 polymorph recovered at the thermocouple junction even though C may have been recovered at the heater margins.

1200 °C in an 8 mm TEL assembly. By contrast, MgO (5% Cr_2O_3) pressure media absorb about 700 watts to reach this temperature. These mechanical stability and thermal insulation characteristics make experiments of several days' duration with stable *P, T* routinely achievable.

A further indication of the satisfactory performance of this material at high temperature is given by the data in Table 2 and Figure 4 for the coesite → stishovite transition at 1200 °C. The forces required to cause pressuri-

Table 2. Coesite and stishovite results at 1200 °C in castable ceramic assemblies

Serial no.	Pads	Tons	Result: 1200 °C (on heater wall)
	6 mm TEL compound 584		
65 C/S-1	G10	212 → 226	coesite
66 C/S-2	M14	236 → 243	stishovite (coesite)
67 C/S-3	M14	248 → 252	stishovite (coesite)
	8 mm TEL compound 584		
70 C/S-5	G10	366 → 374	coesite
72 C/S-7	G10	379 → 385	stishovite (coesite)
71 C/S-6	G10	390 → 394	stishovite
	8 mm TEL compound 575		
74 C/S-9	G10	416 → 418	coesite
	8 mm TEL compound 645		
75 C/S-10	G10	392 → 397	coesite
	8 mm TEL compound 809		
85 C/S-12	G10	383 → 386	stishovite (coesite)

zation at 1200 °C are only minimally larger than for 25 °C. This provides additional evidence of the tightness of the 584 gaskets. The entry for C/S-9 indicates however that too much gasket stiffness can be counterproductive. Experiment C/S-9 employed the stronger pure Al_2O_3 castable ceramic compound 575 for the gasket and pressure medium combinations. At a force well in excess of that required for the recovery of nothing but stishovite in compound 584, the stiffer 575 yielded only coesite, indicating reduced pressurization efficiency with gaskets that are too strong. Experiment C/S-10 using silica-based compound 645 illustrates a similar result.

Experiment C/S-12 in Table 2 gives the result for Cotronics compound 809, which is MgO based. Its performance is comparable to Aremco's MgO-based 584. It differs in having a coarser grain size for the MgO nuggets, a lower price, and superior mechanical cohesiveness both before and after firing. Compound 584 occassionally gives difficulty in curing properly without sufficient silicone grease in the mold, a problem never experienced with compound 809. However, the superior bonding of 809 particles to one another is paralleled by an extraordinarily tenacious bonding to the mold even with silicone grease, with the result that it is somewhat less convenient to cycle through the casting procedure when the effort to separate and clean the molds is considered.

Both MgO-based ceramics alone have a useful temperature limit of about 1600 °C, when they begin to melt. This limit has been sucessfully extended past 2000 °C by insulating the ceramic from the Re heating tube with a ZrO_2 sleeve. Initial drilling of the heater hole at $\frac{5}{32}$ in. leaves an oversize cavity that is coated with Cotronics zirconia cement compound 904. Once this paste has been cured and fired, the heater cavity can be redrilled to finished diameter of $\frac{1}{8}$ in., leaving a ZrO_2 liner to protect the pressure medium from partial melting.

Conclusions

In summary, the use of castable ceramic pressure medium and gasket combinations has much to recommend it, especially for experiments at elevated temperatures. Attention to the lubrication between all the sliding interfaces in MA6/MA8 devices is desirable.

Acknowledgments

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Appendix 1. Materials and suppliers

Alumina cement—Bulletin ZPI-306. Zircar Corporation, 110 North Main St., Florida, New York 10921; U.S.A.

Tungsten carbide—Both KMY and KO5HIP nominally 5% cobalt binder. KMY is mixed grain size, whereas KO5HIP is nominally micrograin size. Hertel AG, Postfach 1751, D-8510 Fürth, Germany

MgO–5% Cr_2O_3—Tiles of mixed grain size pressed and sintered to 20% porosity were sawn into octahedra. Supplied by Mr. Alan Hardstaff, G.R. Stein Central Research Laboratory, Sandy Lane, Worksop, Nottinghamshire S80 3EU, U.K.

Castable ceramics—Proprietary formulations by the suppliers.

Aremco Products Inc., P.O. Box 429, Ossining, New York 10562-0429, U.S.A.

Compound 584	MgO based
Compound 575	Al_2O_3 based
Compound 645	SiO_2 based
Compound 511	Zircon-MgO based

Cotronics Corp., 3379 Shore Parkway, Brooklyn, New York 11235, U.S.A.

Compound 809	MgO based
Compound 904	ZrO_2 cement

Semisintered tube and rod:

Alumina—grade AN900, Norton Co., Worcester, Massachusetts 01606, U.S.A.

Magnesia—grade HP, Ozark Tech. Ceramics, 402 Ware St., Webb City, Missouri 64870, U.S.A.

Thermocouple junction tubing: 99.8% alumina, two-hole and four-hole 0.015 in. id, 0.060 in. od. Bolt Technical Ceramics, Box 718, Conroe, Texas 77305-0718, U.S.A.

Thermocouple lead ducts: mullite, single bore, 0.030 × 0.015 in., Coors Porcelain, 600 9th St., Golden, Colorado 80401, U.S.A.

Epoxy-filled fiberglass laminate: G10 grade mfg. by Westinghouse, 0.016 in. thick, and Polyester sheet: 0.004, 0.007, and 0.014 in. thick Mylar, Ain Plastics, Box 151, Mt. Vernon, New York 10550, U.S.A.

MDS-filled Nylon 66: 0.015–0.020 in. thick strip, McMaster-Carr, Box 440, New Brunswick, New Jersey 08903, U.S.A.

Re strip: 0.001 in. sheet for rolling heater tubes, Sandvik Rhenium Alloys, Box 245, Elyria, Ohio 44036, U.S.A.