Externally heated cold-seal pressure vessels for use to 1200° C at 1000 bars

By D. W. Williams

Department of Earth Sciences, University of Leeds, Leeds 2

Summary. Apparatus using cold-seal pressure vessels of molybdenum–0·5 %-titanium alloy, where each vessel is protected from oxidation by an argon gas jacket, is described. At 1000 bars pressure these vessels can be used for long runs at temperatures up to 1200° C, an increase of approximately 300° C over the range of conventional Stellite vessels. The possible use of other alloys to extend the range of this type of apparatus further is briefly discussed; pure tungsten has been shown to be too brittle.

FOR the experimental study at high pressures and elevated temperatures of silicate and other systems involving volatile components, two types of equipment are in use: the externally heated cold-seal vessel (Tuttle, 1949), and several types of internally heated vessel (e.g. Yoder, 1950). The former, often called the 'Tuttle bomb' or 'test-tube bomb', consists of a thick-walled blind tube of a high-temperature alloy, capable of withstanding the operating pressure when the vessel is held in a furnace at the required temperature. An internally heated vessel is a thick-walled steel cylinder, with removable closures at each end, and has a furnace inside the vessel under full operating pressure. An external water-jacket holds the bulk of the vessel wall at room temperature, whatever the furnace temperature, thus enabling full operating pressure to be used up to the temperature limit of the furnace materials. The low initial and running costs of the cold-seal apparatus, together with its simplicity and safety in use, when compared to internally heated apparatus, have made it the more widely used in geological work. Internally heated vessels are normally used for work only at pressure–temperature conditions beyond the range of cold-seal vessels.

The working range of externally heated vessels is limited by the temperature-dependent long-term rupture strength of the vessel material. The vessels described here are made of a molybdenum–titanium alloy, which retains a high rupture strength to higher temperatures than previously used alloys. This extends the working range of the cold-seal type of equipment by roughly 300° C at 1000 bars. This extension enables, for example, the melting and crystallization behaviour of basic igneous rocks and related systems to be studied at up to 1500 bars water pressure in cold-seal vessels, in the same way as granitic materials have been previously studied (e.g. Tuttle and Bowen, 1958). Hitherto, nearly all work above 1000° C in the presence of volatile components has had to be done in internally heated vessels.

Materials for cold-seal vessels

The first cold-seal vessels (Tuttle, 1949) were made of a cobalt-based alloy, Stellite (Haynes Alloy no. 25), and had an external to internal diameter ratio of 4:1. More recently, similar vessels have been made of a nickel-based alloy, René 41, with a wall diameter ratio of 5:1 (Luth and Tuttle, 1963). These latter have greatly extended the working range of the apparatus, runs at pressures up to 10 000 bars being possible with them. However, the strengths of both Stellite and René fall off rapidly at temperatures above 800° C, restricting the useful working range of both these vessels to temperatures below 1000° C for long runs at 1000 bars (fig. 2).

Recent research and development of the so-called 'refractory metals' (molybdenum, tungsten, tantalum, etc.) and their alloys for high temperature structural use, particularly for turbine and space-vehicle applications, has shown that several of them retain high strengths at temperatures well above 1000° C. Some of the molybdenum alloys and pure tungsten appear very promising in the temperature range 1000° C to 1300° C (Cross and Simmons, 1954; Weinberg, 1963). It was, therefore, decided to try to use cold-seal vessels made of these materials for work above 1000° C. Initially vessels of pure tungsten were tried, but proved too brittle and unreliable. During 1963, however, vessels made of a molybdenum–0·5 %-titanium alloy (one of the strongest of the molybdenum alloys at these temperatures) were first used, and since then have given many hundred hours of satisfactory service.

All the refractory metals and their alloys oxidize in air at high temperatures, and no protective coating system with the required long life and reliability is at present available (Miller and Cox, 1961; Pentecost, 1963). Therefore, vessels of these materials must be protected from oxidation by an inert atmosphere, in this case argon. Since water, the pressure medium normally used in cold-seal vessels, would also react with these metals at high temperatures, an inert pressure medium is required, and again argon is the most convenient.

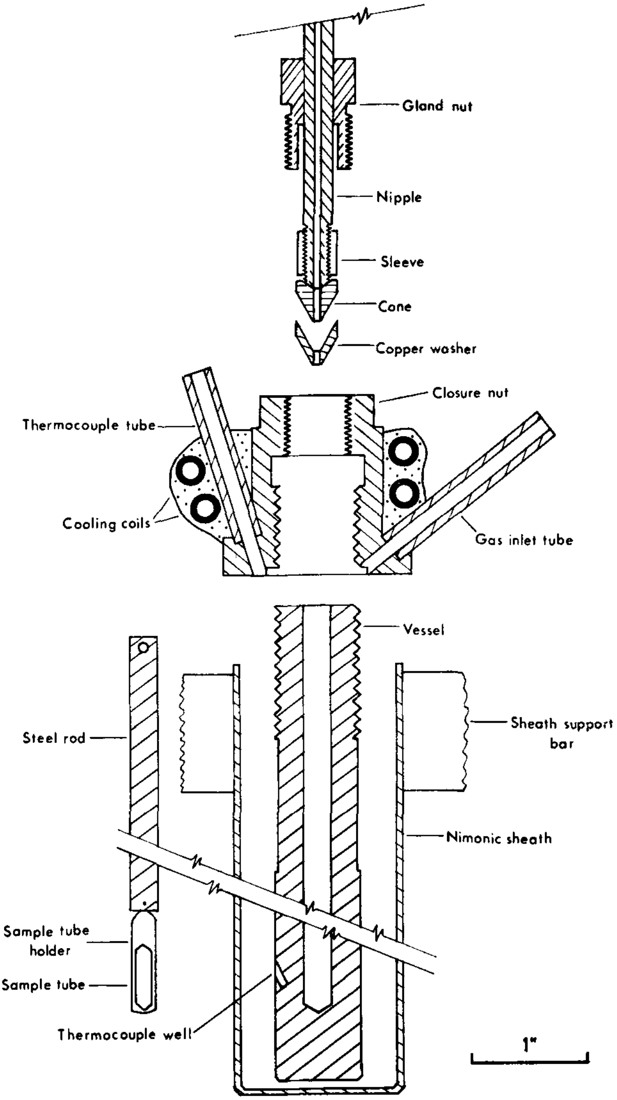

FIG. 1. Exploded sectional view of the apparatus.

Description of apparatus

The molybdenum–titanium vessels themselves are similar to conventional cold-seal ones. They are made from a 12-in. long rod of $\frac{3}{4}$ in.

diameter, which has a $\frac{1}{4}$ in. axial hole drilled from the top to within $\frac{9}{16}$ in. of the bottom. A thread is cut around the top, and a small thermocouple well is drilled opposite the base of the central cavity. There are also two small flats just below the thread (fig. 1).

The closure nut is more complex than for a conventional cold-seal vessel, because it forms the top of the argon gas jacket as well as the high-pressure closure. It is also necessary to have a gas inlet to, and a gas-tight thermocouple exit from, the argon jacket, and these are most conveniently situated in the closure nut. These latter are two short brass tubes, silver-soldered to the closure nut at one end, and both carry rubber tubing connexions at the other end. The thermocouple wires are insulated by alumina sheathing up to the top of the brass tube, and from here they leave the jacket through a clipped rubber tube. The closure nut is made of stainless steel, and has to be water-cooled to keep the high-pressure closure at constant temperature throughout run and quench. Otherwise, differential contraction of vessel and closure nut during the quench causes leakage at the closure. (Molybdenum alloys have coefficients of thermal expansion roughly one third that of steel.) Cooling has the advantage also that the two brass tubes to the argon jacket can be fairly short. Water cooling was not required to prevent leakage when a closure nut and high-pressure connexion of the same alloy as the vessel were used, but then the two brass tubes had to be much longer than convenient to be cool enough to take their rubber connexions.

The closure nut carries two internal threads, the larger to take the pressure vessel, the smaller for a standard $\frac{1}{4}$ in. high-pressure fitting of gland nut, sleeve, and nipple (fig. 1). The nipple has a small steel cone silver-soldered to it, and the seal between this cone and the vessel, through a conical copper washer, is made by tightening the gland nut against the closure nut, which carries flats for a spanner. A copper cone is used here because, though easily indented by the harder metal of the vessel the first time it is used, little force is required for subsequent closures. If the steel cone alone is used, it is also indented by the molybdenum alloy, and increasing force is needed for successive closures. This type of closure makes it unnecessary to hold the vessel in a vice to obtain the high-pressure seal. Also, by removing the gland nut and nipple, and hooking out the stainless steel rod and sample tube container, samples can be changed without disturbing the argon gas jacket or removing the thermocouple on the vessel.

For the outer sheath of the argon gas jacket either a ceramic or metal tube is used, the latter being either semi-permanently bolted to the closure nut or merely held against it so that it can be quickly removed. Normally the bolted-on sheath is used, which consists of a blind tube, rolled and welded from Nimonic sheet (alloy no. 75), with a steel flange silver-soldered to its open end. Bolts through this flange and a similar flange on the closure nut fix it in position, and a thin copper gasket ensures a gas-tight seal. This seal is not normally disturbed for many runs, until, for example, the thermocouple has to be checked or the vessel fails. Provided there is an argon pressure slightly above atmospheric in the jacket whenever the vessel is heated, this unit can be treated exactly as a normal cold-seal vessel. It is cooled by applying to the Nimonic sheath a blast of compressed air for a few minutes, followed by a can of cold water. The insulation provided by the gas jacket results in somewhat slower cooling rates than for conventional vessels cooled in this manner (from 1100° C to 400° C takes approximately 10 minutes). If a fast quench is required, a removable Nimonic sheath is used (fig. 1). This consists of a similar tube to the above, with two steel support bars silver-soldered to it. These bars can be fixed to two vertical rods on either side of the furnace (the rods that support the furnace) to hold the sheath in position against the bottom of the closure nut. The seal between sheath and closure nut is made by applying a little gasket cement to the join. For quenching the sheath is dropped away with the furnace, to expose the vessel to take the compressed air blast and quench water directly. This does cause a little surface oxidation of the vessel, but a single vessel can be repeatedly quenched in this way with no appreciable increase in the thickness of the oxide layer after the first few times.

When a platinum-wound furnace is used, especially one where the windings are embedded in the refractory cement adjacent to the vessel sheath, a ceramic sheath is used to enclose the gas jacket, as a metal one might contaminate the windings or allow them to short to earth. This sheath is an aluminous porcelain combustion tube, which passes through the furnace and is closed and supported at the bottom by a rubber bung. Again, a little gasket cement makes an air-tight seal between the top of the sheath and the closure nut. For normal quenching, the furnace is first lowered and the vessel allowed to cool for a few minutes in the gas jacket before the sheath is dropped away, exposing the vessel to take the air blast and quench water. Faster quenching is possible by dropping the sheath with the furnace, and applying the air blast immediately to the vessel.

Nimonic sheaths are used whenever possible because, being much more durable than the ceramic ones, they provide a degree of protection to both personnel and furnaces in the event of a violent vessel failure. A pressure of approximately half a pound per square inch above atmospheric is maintained in the gas jacket throughout a run, being monitored by a manometer on the argon supply line.

The volume of high-pressure gas in a vessel is kept to a minimum by filling the cavity above the sample with a stainless steel rod. This reduces both the explosion hazard, and the amount of pumping required. Argon is raised from cylinder pressure to 1000 bars by a simple hand pump (Pressure Products Inc.), and from 1000 bars to higher pressures by a hydraulic intensifier. A vessel can be raised to 1000 bars with about 25 strokes of the pump, and a few strokes during the quench maintain run pressure. Pressures are registered on bourdon tube gauges, and these, together with all the high-pressure gas are inside a steel cubicle. All pumping and valve manipulation is carried out by an operator outside this cubicle. Similarly the furnaces can be raised and lowered, and the cooling air switched on, from outside the cubicle. It is important that no-one is exposed directly to a pressurized vessel, especially to one enclosed only in a ceramic sheath.

The vessels are heated in tubular electric furnaces, kanthal wound for run temperatures of up to 1150° C, and platinum wound for higher temperatures. Two platinum/platinum–13 %-rhodium thermocouples are used; one near the furnace winding actuates a temperature controller, the other, in the well in the vessel wall, is connected to one channel of a multipoint recorder. Temperatures can be reported with an accuracy of ±5° C.

Samples are sealed into platinum capsules in the normal way, and these are then placed inside a second loosely fitting platinum tube. This outer tube is to protect the sample tube from contamination by the material of the vessel, and to attach it to the stainless steel rod. Similarly, a small pad of platinum at the bottom of the thermocouple well protects the hot junction of the thermocouple from contamination.

Working range of the vessels

The pressure and temperature limits within which a cold-seal vessel can be used for long runs depend on the long-term hot-rupture strength of the vessel material. Fig. 2 compares the 100-hour stress-rupture curves for Stellite 25, René 41, and molybdenum–0·5 %-titanium alloy, together with the recommended upper limits of use of vessels of Stellite 25 and molybdenum-0·5 %-titanium. At temperatures approaching

1000° C René vessels have a working field similar to that for Stellite ones. Also shown on fig. 2 are the results of some of the tests carried out on molybdenum–titanium vessels in the fully recrystallized condition.

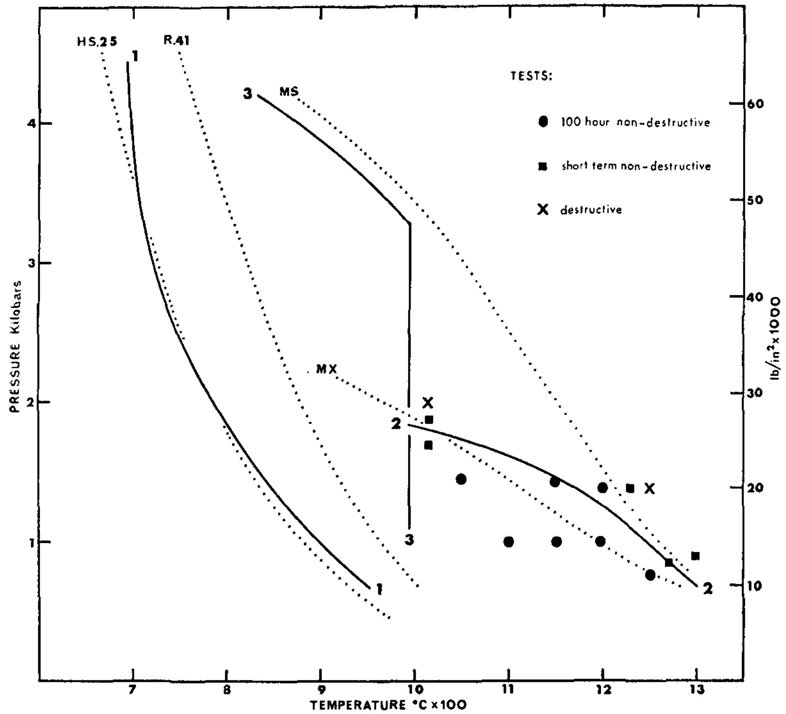

FIG. 2. Working ranges of cold-seal vessels and stress-rupture data for vessel materials. 100-hour stress-rupture curves, dotted (after Cross and Simmons, 1954; Semchyshen, 1958; and Weinberg, 1963): HS. 25—Stellite 25; R. 41—René 41; MS—stress-relieved molybdenum–0·5 %-titanium alloy; MX—recrystallized molybdenum–0·5 %-titanium alloy. Limits of working ranges of vessels for long runs, solid lines: 1—Stellite (Tem-Pres Research Inc.); 2—recrystallized molybdenum–titanium (this work); 3—stress-relieved molybdenum–titanium (estimated). The test results shown are for recrystallized molybdenum–0·5 %-titanium vessels.

It is well known that the strength of a molybdenum alloy varies greatly according to its physical state, which depends on the work history of the material. During the hot swaging stage of manufacture, in which the original ingot is reduced to rod, a fibred microstructure develops that gives the alloy its very high strength. After a short stress-relief, which has little effect on the structure, the alloy is ready for use, and it is material in this stress-relieved condition that has the high strength shown by line 'MS' in fig. 2. If the alloy is then held at elevated temperatures for long periods, however, it begins to recrystallize and lose much of its strength. Line 'MX' in fig. 2 is for completely recrystallized material. For molybdenum-0·5 %-titanium rod of 1 in. diameter the rate of recrystallization at 1000° C is very slow, causing little loss of strength over a few hundred hours; at 1100° C it is almost complete in 100 hours, and at 1300° C it is complete in one hour (Semchyshen, 1958; Cross and Simmons, 1954).

The crucial long-term tests that were carried out to determine the upper limits of these vessels were performed on vessels that had already spent more than 100 hours above 1100° C, and were, therefore, in the fully recrystallized condition (this was confirmed when one of the vessels broke, exposing many crystals 2 mm long, and a few 4 mm long). As can be seen from fig. 2, these vessels can withstand conditions slightly in excess of the 100-hour stress-rupture curve for recrystallized rod (compare lines 'MX' and '2'), even though they only have a 3:1 wall ratio. It is not expected, therefore, that significantly more severe pressure-temperature conditions would be possible with larger vessels, with a 4:1 or 5:1 wall ratio, especially since such vessels would have to be made from less heavily worked and, therefore, probably weaker rod. Line '2' in fig. 2 is the upper limit of the normal working field for long runs in these vessels, although short runs are possible under more severe conditions, for example, 800 bars at 1270° C for one hour, with no harm to the vessels resulting. These vessels can, therefore, be used for long runs at pressures up to 1500 bars at temperatures 300 to 350° C higher than conventional cold-seal vessels.

There remains the possibility of using vessels of this material that are kept in essentially the stress-relieved condition by never heating them above 1000° C. When further supplies of vessels become available, the upper limits of vessels in the stress-relieved condition will be determined. The likely limits of the working field for long runs is shown by line '3' in fig. 2, and conditions of 950° C at 3000 bars can be expected to be routine.

It is not possible to set a definite life span for these vessels, especially as this must depend to some extent on the number and severity of the quenches, the degree of recrystallization reached, etc. However, a single vessel has given several hundred hours service at conditions along line '2' on fig. 2, and withstood repeated quenching.

The rate at which equilibrium is attained in silicate systems in the presence of water vapour, at temperatures above 1000° C, is very much faster than at temperatures at which conventional cold-seal vessels are used. For example, Tuttle and Bowen (1958), working on systems of granitic composition in the presence of water vapour at temperatures between 700° C and 800° C, found that several days were required for equilibrium. Yoder and Tilley (1962), doing similar work on basaltic rocks, found that equilibrium was reached in a few hours at 1000° C to 1100° C. This being so, one can expect to complete many more runs in, say, 100 hours of vessel life with a molybdenum–titanium vessel, than with a conventional cold-seal vessel. In some cases it may even be more economic to use these vessels in excess of the conditions recommended in fig. 2, in expectation of a higher failure rate, rather than using internally heated apparatus.

Tungsten vessels and future developments

Pure tungsten has a slightly higher long-term rupture strength than molybdenum–0·5 %-titanium alloy at temperatures above 1200° C (Schmidt and Ogden, 1963). Several tungsten vessels have been tested; they were similar in all respects to the molybdenum–titanium ones, except that they were only 8 in. or 10 in. long. Of six vessels tested only one has survived more than a few hours at 250 bars at temperatures between 1100° C and 1200° C. Tungsten is known to be very brittle at room temperature, and can be very easily cracked by small blows, or even by being gripped in a vice. This brittleness causes the metal on the top of the vessels around the high pressure seal to be visibly distorted, or even to flake off, under the pressure of the copper closure washer. These tungsten vessels have proved unsatisfactory because small flaws, developed either in the original sintering process, or later by chance blows, cause the vessels to fail at conditions well below the 100-hour stress-rupture curve. It is likely that vacuum-arc-melted tungsten will give much better results than this powder-metallurgy material, but the former is much more expensive. It is also possible that vessels made from thoriated tungsten (powder-metallurgy material, prepared from tungsten powder containing 1 % or 2 % thoria) will be less easily cracked. This latter material has a slightly higher strength above 1200° C than pure tungsten, and is less subject to failure due to intergranular oxide formation (Weinberg, 1963).

As new alloys, with higher strengths at elevated temperatures, become available commercially, it should be possible to extend the working range of the cold-seal apparatus. Vessels of another molybdenum alloy, viz. TZM alloy (molybdenum–0·5 %-titanium–0·1 %-zirconium), are now being tested. In the recrystallized state this alloy is approximately 10 000 pounds per square inch stronger than the one now in use, over the temperature range 900° C to 1100° C, and it is also slightly stronger in the stress-relieved state. A more important advantage is that the recrystallization temperatures for TZM are approximately 100° C higher than those for molybdenum–0·5 %-titanium (Semchyshen, 1958). Vessels of TZM in the stress-relieved condition can be expected to withstand long periods of heating at temperatures up to 1100° C without loss of strength due to recrystallization.

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References

Cross (H. C.) and Simmons (W. F.), 1954. Alloys and their Properties for Elevated Temperature Service. *In* Utilisation of Heat Resistant Alloys, Amer. Soc. Metals, Cleveland, Ohio, p. 55.

Luth (W. C.) and Tuttle (O. F.), 1963. Amer. Min., vol. 48, p. 1401.

Miller (G. L.) and Cox (F. G.), 1961. Development of Oxidation Resistance of some Refractory Metals. *In* Niobium, Tantalum, Molybdenum and Tungsten (ed. A. G. Quarrell), Elsevier, Amsterdam, p. 234.

Pentecost (J. L.), 1963. Coating Materials and Coating Systems. *In* High-Temperature Inorganic Coatings (ed. J. Huminik, Jr.), Rheinhold Publishing Corporation, New York, p. 10.

Schmidt (F. F.) and Ogden (H. R.), 1963. The Engineering Properties of Tungsten and Tungsten Alloys. Report no. 191, Defense Metals Information Center, Columbus, Ohio.

Semchyshen (M.), 1958. Development and Properties of Arc-Cast Molybdenum-Base Alloys. In The Metal Molybdenum (ed. J. J. Harwood), Amer. Soc. Metals, Cleveland, Ohio, p. 281.

Tem-Pres Research Inc., Information Circular HT–59–2.

Tuttle (O. F.), 1949. Bull. Geol. Soc. Amer., vol. 60, p. 1727.

—— and Bowen (N. L.), 1958. Mem. Geol. Soc. Amer. no. 74.

Weinberg (H. P.), 1963. Structural Materials for High-Temperature Use. *In* High-Temperature Inorganic Coatings (ed. J. Huminik, Jr.), Rheinhold Publishing Corporation, New York, p. 110.

Yoder (H. S.), 1950. Trans. Amer. Geophys. Union, vol. 31, p. 827.

—— and Tilley (C. E.), 1962. Journ. Petrology, vol. 3, p. 342.

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