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IMPROVED COLD SEAL PRESSURE VESSELS TO OPERATE TO 1100°C AT 3 KILOBARS

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The working field of the original Stellite 25 cold-seal pressure vessel apparatus (Tuttle, 1949) has previously been extended both to much higher pressures, using Rene 41 vessels (Luth & Tuttle, 1963), and to higher temperatures, using molybdenum alloy vessels (Williams, 1966). Two improvements to this latter apparatus are reported here: a solid metal sheath now replaces the argon gas jacket, and use of TZM alloy (molybdenum-0.5% titanium-0.08% zirconium) results in more extreme working conditions being possible.

APPARATUS

The original molybdenum alloy vessels were held inside argon filled Nimonic sheaths to prevent oxidation. These gas jackets were an additional complication and insulated the vessels somewhat, resulting in slower quench rates than are normal for cold-seal vessels. At present there is no simple, cheap and sufficiently reliable protective coating which could be used with confidence on molybdenum alloy pressure vessels at high temperatures (Pentecost, 1963). Electroplated films of such metals as nickel and chromium tend both to spall off the substrate, and to diffuse into it, causing loss of strength (Levinstein, 1963). Since molybdenum oxidation products are non adhesive and volatile, even a pinhole flaw in a coating could prove disastrous.

Now the sheath is made from a rod of nickel-based alloy (Nimonic 75), drilled out to be a good fit onto the vessel. It is attached by two bolts to the top of the vessel, and soft gasket cement (Holts, non-hardening, for sealing cylinder heads) makes an air-tight seal to the closure nut (Fig. 1). Alternatively the sheath can be more permanently silver-soldered (and bolted) to the closure nut. Attempts to silver-solder the Nimonic sheath directly to the vessel failed: differential contraction of sheath and vessel caused holes to develop in the joint as the solder cooled. A stainless steel spacer occupies the drilled-out cone in the bottom of the sheath, to minimize trapped air. An exit tube allows this air to escape on heating, thus preventing it from blowing a hole in the soft gasket; this tube is closed when temperature has stabilized.

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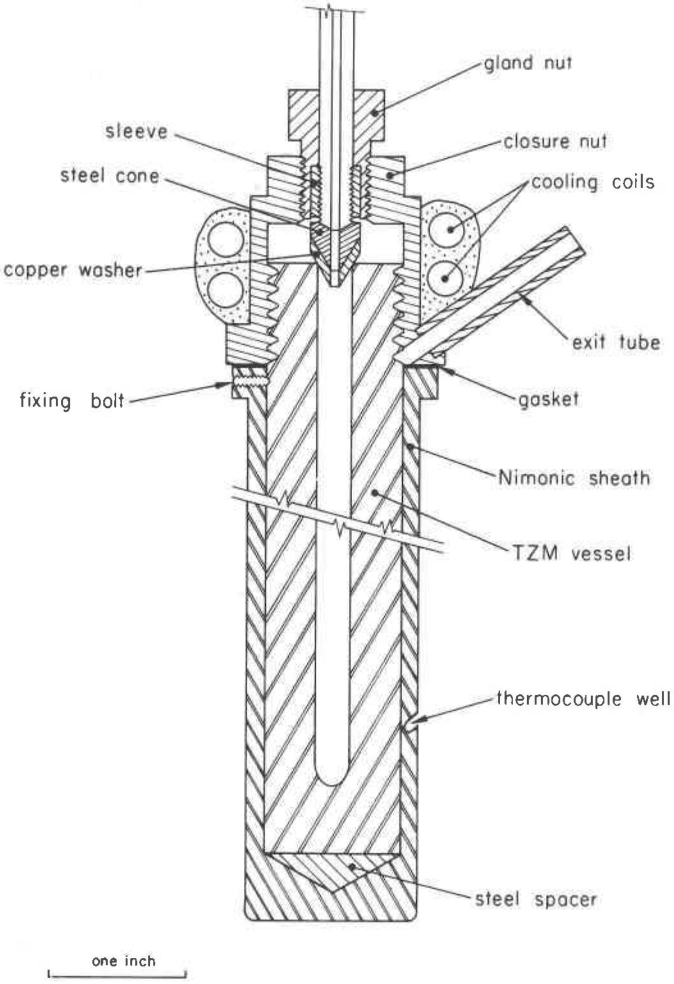

FIG. 1. Sectional view of TZM vessel, sheath and closure.

Contact between vessel and sheath is much less intimate than if the vessel had been plated, especially since the Nimonic sheath expands about ×3 as the molybdenum alloy on heating. This differential expansion, the main cause of the spalling off of electroplated coatings on refractory metal alloys, is allowed for here, since the sheath is free to expand downwards from its single point of attachment.

The 12″ long vessels and closure are essentially the same as those used previously, but the TZM vessels have a 4:1 wall ratio, compared to 3:1

for the original molybdenum-0.5 percent titanium ones. The reasons for the type of closure shown in Figure 1 have been presented elsewhere (Williams, 1966). Once its sheath has been attached, a TZM vessel can be used exactly as a Stellite one, and with the elimination of the gas jacket, quenching procedures and quench rates are similar to those of a normal "Tuttle bomb."

Although some air might be expected to diffuse down the threads of the closure nut into the sheath, both molybdenum-0.5 percent titanium and TZM vessels have been used like this for long periods up to 1100°C, with no detectable oxidation. Until the outer diameter of a vessel begins to swell plastically, a vessel can easily be withdrawn from its sheath for inspection. The solid sheath also provides considerable protection in the event of a violent vessel failure: two molybdenum-0.5 percent titanium vessels which have failed at 2 kbar produced no shrapnel. It is normal practice to use these vessels inside a steel safety room, with all valve and furnace manipulation being carried out from the outside.

VESSEL PERFORMANCE

The original molybdenum-0.5 percent titanium vessels were developed for use at low pressures (1 kbar) at the highest possible temperatures (1200°C), well above the recrystallization temperature of molybdenum alloys. Molybdenum-0.5 percent titanium was used, as it was the cheapest and most readily available molybdenum alloy.

It is well known that strain hardening, induced by hot working below the recrystallization temperature during manufacture, greatly increases the strength of molybdenum alloys over that of fully recrystallized material. The superior strength of such material is retained in subsequent use, so long as the alloy is not heated to its recrystallization temperature. Arc-cast and strain hardened TZM alloy was used for these vessels since it has the highest stress-rupture strength above 1000°C of the molybdenum alloys (Schmidt and Ogden, 1963; Gilbert and Houston, 1962), and a recrystallization temperature at least 100°C higher than molybdenum-0.5 percent titanium. TZM can be used for long periods up to temperatures of 1150°C without loss of strength due to recrystallization (Semchyshen, 1958).

Cold-seal vessel of this type made of many different alloys, having wall ratios of between 3:1 and 5:1, have proved to have very long lives (many hundreds or thousands of hours) if used only up to the 100-hour stress-rupture curve of the alloy of which they are made (Tem-Pres[1]; Williams & Harris, 1968). Therefore the 100-hour stress-rupture curve

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[1] Tem-Pres Research, Inc., InfoCirc. HT-59-2.

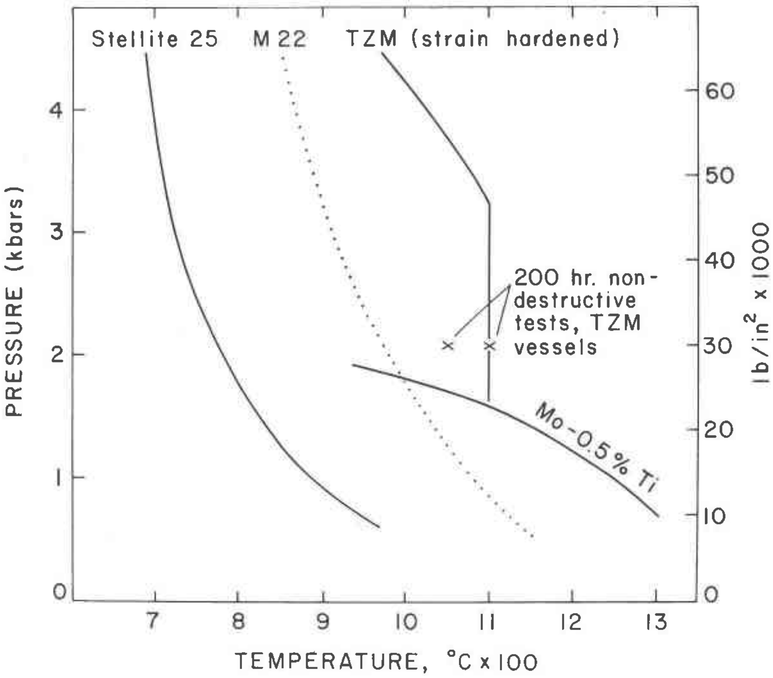

FIG. 2. Solid lines: working fields for vessels of Stellite 25, molybdenum-0.5% titanium (recrystallized) and TZM (strain hardened). Also shown is 100-hour stress-rupture curve for M22 alloy, and test conditions for TZM vessels.

for strain hardened TZM should outline the upper limit of the working field for these vessels, up to the recrystallization temperature.

Tests have been run for several hundred hours at 30,000 lb/in² up to 1100°C (*i.e.*, 50°C below the recrystallization temperature) without failure, or any swelling, or recrystallization occurring. Having confirmed that neither recrystallization nor reaction with the Nimonic sheath occurs under these conditions to weaken a vessel, a conservatively-rated working field has been outlined some $\frac{1}{2}$ kbar below the 100-hour stress-rupture curve for strain hardened TZM, and 50°C below its recrystallization temperature (Fig. 2). The working fields for Stellite 25 (Tem-Pres[1]), and molybdenum-0.5 percent titanium vessels (Williams, 1966) are also shown. (The dotted line is the 100-hour stress-rupture curve for the highest strength nickel-based high temperature alloy, M 22 as shown on the data sheet from International Nickel, London, (1966), indicating the maximum working conditions likely to be reached in vessels of any currently available non-refractory metal alloy). Although the strength of

TZM falls off rapidly above 1150°C, as recrystallization occurs, even when fully recrystallized it is somewhat stronger than molybdenum-0.5 percent titanium. Recrystallized TZM vessels can be expected to withstand slightly higher pressures than those indicated by the line for molybdenum-0.5 percent titanium ones in Figure 2.

Recently experimental melts of tungsten-based alloys have been reported with 100-hour stress-rupture strengths approaching 2 kbar at 1500°C (Climax Molybdenum, 1966). With the commercial availability of such alloys the extension of the working field of refractory metal vessels to much higher temperatures will be in prospect.

TZM vessels should be of interest to experimental petrologists, and those working in allied fields, since their use enables work on all but the most refractory silicate-volatile systems to be done in cold-seal vessels at pressures up to 3 or 4 kbar. Thus the more expensive and complicated internally heated pressure vessels are not required for work below, say, 5 kbar. As the bulk of the work in any study is usually at the lower pressures, more extensive use of TZM vessels should result in considerable savings of both time and always-limited financial resources.

ACKNOWLEDGEMENTS

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