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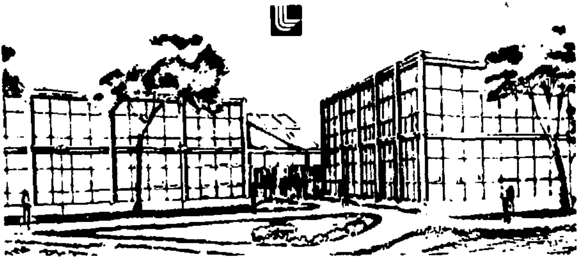

HIGH PRESSURE APPARATUS FOR HYDROGEN ISOTOPES TO PRESSURES OF 345 MPa (50,000 psi) AND TEMPERATURES OF 1200°C*

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INTRODUCTION

A functional new high pressure, high temperature apparatus for hydrogen isotopes uses an internally heated pressure vessel within a larger pressure vessel. The pressure capability is 345 MPa (50 K psi) at 1200°C. The gas pressure inside the internal vessel is balanced with gas pressure in the external vessel. The internal vessel is attached to a closure and is also the sample container. Our design allows thin-walled internal vessel construction and keeps the sample from "seeing" the furnace or other extraneous environment. The sample container together with the closure can easily be removed and loaded under argon using standard glove-box procedures. The small volume of the inner vessel permits small volumes of gas to be used, thusly increasing the sensitivity during pressure-volume-temperature (PVT) work.

* Work performed under the auspices of the U. S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

Pressure Vessel

The overall views of the pressure vessel are shown in Figures 1 and 2. The vessel rests on a trunion so that loading may be done vertically. In actual operation, the vessel is positioned horizontally to reduce internal convection currents. The cylindrical space available inside the 24.13 cm o.d. vessel measures 7.62 cm i.d. and 43.2 cm in length. The body is constructed of AISI 4340 steel and is water cooled externally. Within the body are two concentric liners, each 6.5 mm thick, fabricated of Type 316 stainless steel. The innermost liner is circumferentially grooved and the grooves are criss-crossed for greater assurance of venting of outward diffusing hydrogen. The vented H_2 is never in contact with the wall of the outer pressure body. If only one liner were used, and if it is grooved on the O.D., it would not distribute the pressure uniformly. The interface area is reduced by the grooves but more importantly, there will be stress risers at the edge of the grooves.

The liners are autofrettaged in place, locking in favorable oriented compressive stresses that increase resistance to fatigue and diminish the magnitude of the S_t^* peak stresses. The liner has a finite life of many thousands of stress cycles - 9,000 to 15,000 estimated.

Stresses

The AISI 4340 used in the pressure vessel body has a tensile strength of 160,000 psi at 260°C. The Type 316 stainless steel tensile strength is 75,000 psi. The stresses calculated for the vessel are listed in Table I. Thermal stresses and strains are superposable on those resulting from pressure but are not shown.

*S_t - tangential stress

Table I. Calculated Stress Values* For 137.9 MP Pressure Vessel (Harwood Engineering Co. Data)

Type of Stress	Location	Value in psi
Tangential Stress, S_t	At inside radius of innermost 316 liner	61,200
Tangential Stress, S_t	Inner radii of AISI 4340 body	36,900 (Max stress on body)
Tangential Stress, S_t	Outermost radii of AISI 4340 body	11,100
Radial Stress, S_r	At inner radii of innermost 316 liner	-50,000
Radial Stress S_r	At inner radii of AISI 4340 body	-25,800
Radial Stress S_r	At outer radii of AISI 4340 body	0

NOTES:

a. The pressure to rupture the outer cylinder = 138,000 psi [1,2]

b. The pressure to rupture the inner cylinder = 21,600 psi [1,2]

c. The pressure to rupture composite cylinder 138,000 + 21,600 psi

d. Factor of safety against rupture of composite cylinder = 159,600/50,000 = 3.19

e. Factor of safety against rupture of outer cylinder = 138,000/25,800 = 5.35

f. Tensile strength outer cylinder/maximum tensile stress = 160,000/36,900 = 4.34

* For Formulae, see Harwood Engineering Co. Stress Strain Table, "Collected Stress Strain Formulae for Thick Hollow Cylinders in the Elastic State".

Vessel Closures

The two vessel closures, shown on the right and left in Figure 3, are machined from A-286 steel. The closure seals consist of a bronze wedge ring; a lead ring (square in cross section); a Viton* spring-loaded Bal-Seal+; and a Spirulox retainer ring. All metal rings were coated with Teflon++ to reduce friction in assembly and disassembly and to prevent scoring of the vessel bore, which is honed to an 8 μ in. finish.

Electrical Leads

Electrical leads (with bayonet-type disconnects, Figure 2) and furnace control thermocouples enter the closure through BeCu cones. These cones are electrically insulated from the closure with BN coated with 2902 epoxy.++

Inner Pressure Vessel

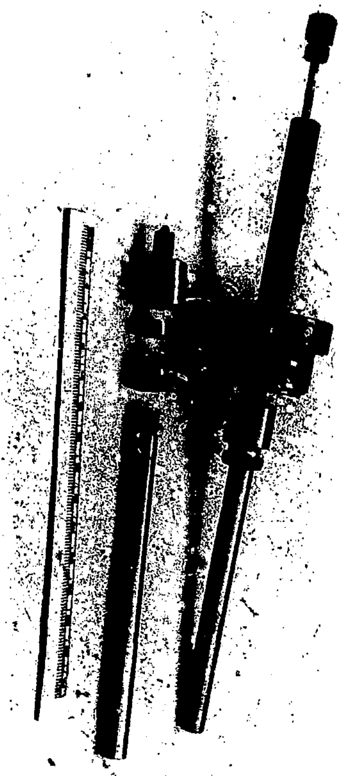
The inner pressure vessel - sample container is shown in Figure 4. It is shown attached to the closure and also in a disassembled position. The inner vessel measures 1.8 cm o.d. by 1.15 cm i.d. Figure 5 shows the same vessel together with an inner spacer, a molybdenum protective tube for the internal thermocouple, and a sample and cylindrical crucible. The spacer is used to cut down convection currents. The inner pressure vessels have been made from molybdenum bar stock or chemical vapor-deposited tungsten.

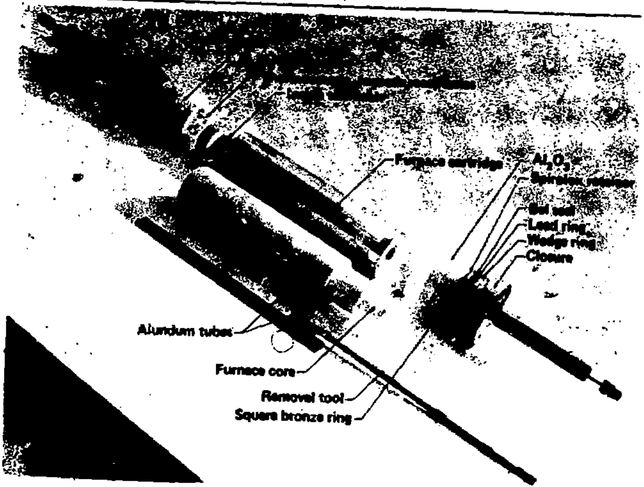
* Reference to a company or product name does not imply approval or recommendation of the product by the University of California, or the U. S. Energy Research and Development Administration to the exclusion of others that may be suitable.

\+ Bal Seal Engrg. Co. Series 506/2.622/GWO .199

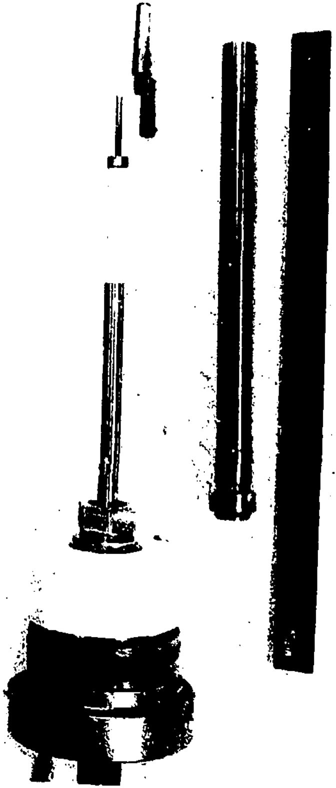
++ TFF Coating # 6070, Crown Industrial Products Company

†† Tra-Con, Inc.





Furnace cartridge
Lead ring
Wedge ring
Closure
Alundum tubes
Furnace core
Removal tool
Square bronze ring



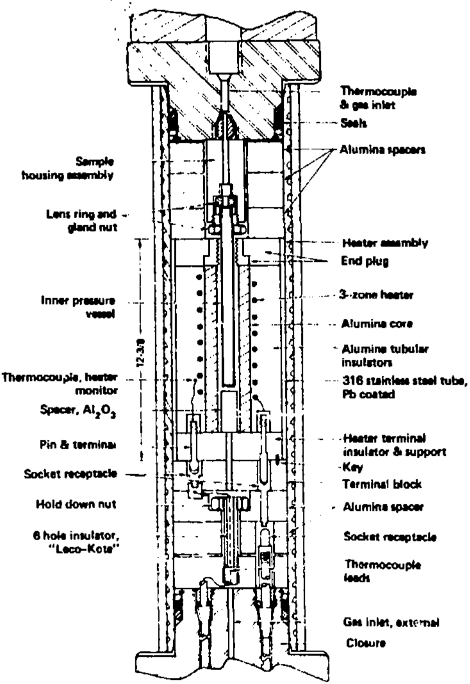
The end of the tubular vessel is sealed into its fitting with either a flat copper washer or a copper lens-ring. Both are silver plated. The tubular inner vessel and the fitting are then sealed into the pressure vessel closure via a 59° cone angle and which can be seen on the end of the fitting. The seals do not become heated, so that there is no expansion and contraction resulting in a leak. A fine SAE thread in the fitting also aids in maintaining the seal. A Mo tubular vessel of the above dimensions has been exposed to instantaneous overpressures of 60 atm at 930°C without failure.

Cartridge Heater

The cartridge heater has been shown previously in Figure 3. Figure 6 shows a schematic drawing of its installation in the pressure vessel. The sockets for the bayonets on the cartridge heater can be seen in the upper left hand portion of the photo. The sockets and bayonets are made of BeCu. The windings are made of 0.038 cm diameter KW Mo wire. The furnace core is Alundum*, with dimensions of 1.9 cm i.d. x 2.54 cm o.d., 0.079 cm groove depth, 0.079 groove width, and 16 turns per 2.54 cm. The wall of the Alundum core is 0.3 cm thick. Each Mo winding of a 3-zone furnace has 2 Ω of resistance at ambient temperature.

The thermocouples for the heater controls are inserted into alumina tubes and are laid across the windings. Norton RA 4139 cement insulates the windings and thermocouples. The entire sub-assembly is encased in two alumina tubes and a slurry of Al_2O_3 is poured in the void spaces between insulated winding and the adjacent tube. A 316 stainless steel tube with

* Norton Co., RA 4139 Alundum



Thermocouple & gas inlet
Seals
Alumina spacers
Sample housing assembly
Lens ring and gland nut
Heater assembly
End plug
Inner pressure vessel
3-zone heater
Alumina core
Alumina tubular insulators
12-3/8
Thermocouple, heater monitor
316 stainless steel tube, Pb coated
Spacer, Al_2O_3
Pin & terminal
Heater terminal insulator & support
Key
Socket receptacle
Terminal block
Hold down nut
Alumina spacer
6 hole insulator, "Leco-Kote"
Socket receptacle
Thermocouple leads
Gas inlet, external
Closure

two alumina end pieces (Coors, AD 85) encases the complete assembly. Lead plating is used on the outer surface of the stainless steel tubing to avoid scratching the vessel bore when the cartridge is inserted. A special tool, shown at the bottom of Figure 3, is used to insert and withdraw the cartridge.

The cartridge heater design allows removal of the furnace for repair without removing the bottom closure into which it fits. With water cooling, the temperature of the uppermost surface of the outer vessel does not rise above 40°C when the sample temperature is at 1000°C and 137.9 MPa (20 K psi) At no time did the lead plate melt For operation at these conditions, the power consumption for each heater was 1100*, 920, and 1368 W respectively.

A heater like the one described was cycled through eleven runs before failure occurred in the center winding. These heaters are operated above their normal power rating which accounts for the shorter lifetime. As with Pt wound furnaces, these windings need to be brought up to temperature slowly (~200°C/hour) until sufficient resistance is obtained, otherwise burn-out will occur because of excessive initial wattage.

Thermocouples

A high temperature, high pressure H_2 environment affects thermocouple wire in two ways. Changes in calibration occur due to pressure alone. The other is hydrogen attack by itself or in combination with O_2. The degree of deterioration depends on temperature.

The best behavior was found in W-Re and Geminol P/N+ thermocouples, although Cr-Al++ was also used when temperatures were not severe (<600°C).

* winding nearest the terminal end

\+ Driver Harris Co.

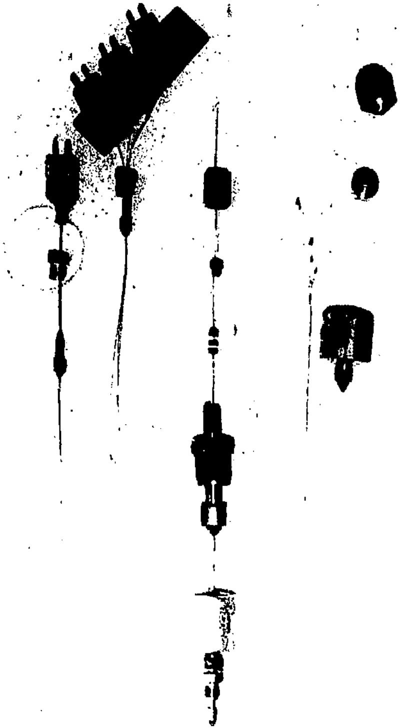
++ Hoskins Mfg. Co.

Four thermocouples designs are shown in Figure 7. Counting from the bottom, sets 1 and 2 are bare-wire thermocouples and sets 3 and 4 are metal-MgO sheath thermocouples. In the first two sets, 0.036 cm diameter wire is threaded into 0.0397 cm holes in a 0.158 cm diameter alumina insulator. In the first set, the wire is also threaded through 16° (included angle) BeCu cones and brazed in place. The cone insulators are pyrophyllite or BN. The small cones with their insulators are then placed into a larger 59° (included angle) metal cone and thence into a fitting which is subsequently held in position by a gland nut (lower right). This sealing arrangement is good for the pressure rating of the fitting used.

The pair of thermocouples in set 2 use 1.43 cm o.d. pressure tubing to house flat gaskets. It is satisfactory to 414 MPa. The gaskets are Teflon and Micarta. The fitting above the gaskets is designed so that the flats on it prevent its rotation inside as it is pushed onto the gaskets by gland-nut rotation. Thus, there is no rotation of the gaskets causing shearing of thermocouples wires. A four-hole alumina insulator is used for the bare wire insulation.

The thermocouples in sets 3 and 4 are commercially available, metal-sheath, MgO insulated. The ones shown are 0.0794 cm and 0.159 cm diameter. They are brazed into a standard 59° cone high pressure fitting. Hydrogen has permeated our metal sheath couples at elevated temperatures (~800°C) and pressures (~70 MPa). The conditions under which this occurs are not reproducible.

The bare wire Geminol P/N couple has been the most versatile in a reducing atmosphere to temperatures of 1200°C. After 212 hours of exposure at 954°C, the change in emf is only 0.13 MV. The hot junction can



be made with an oxy-acetylene torch. The mv output of this thermocouple is less than that of Chromel-Alumel. The W3Re - W26Re couple is also excellent for use in H_2 atmospheres but the hot junction must be made in an inert atm.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1. Hydrogen pressure vessel in operating position. External pressurizing manifold is on the left, sample and internal vessel are introduced on the right side. (Harwood Engineering Co. vessel and trunion).

Fig. 2. Hydrogen pressel vessel in the loading position. Electrical leads and thermocouple compensators are shown in the lower left. (Harwood Engineering Co. vessel and trunion).

Fig. 3. Pressure vessel closures and 2-zone cartridge furnace. Rod in lower right is a tool used for removal of the cartridge furnace.

Fig. 4. Inner pressure vessel in operating position (upper view) and in telescopic view. Sealing washer is not shown.

Fig. 5. Spacers used to reduce convection currents within inner pressure vessel. On the right are a sample and crucible. The seals (starting from left) are a wedge ring, lead ring, Bal seal, bronze ring, and retainer ring.

Fig. 6. Cartridge heater installed in the vessel bore, schematically shown.

Fig. 7. Thermocouple assemblies. The bottom two sets use bare wire in ceramic insulators. The top 2 sets use metal sheaths and MgO.