2. Experimental

2.1 Materials

Measurements of the ECP and corrosion rates have been performed on A533 Gr.–B low–alloy steel, Alloy 600, and austenitic Type 304 SS and Type 308 SS weld overlay, in boric acid solutions at temperatures between 95 and 316°C (203 and 600°F). The compositions of the alloys are given in Table 1.

Table 1. Composition of RPV head and nozzle alloys for corrosion studies

Alloy Type	Heat Number	Analysis	Composition (wt.%)									
			Ni	Fe	Si	P	S	Mn	C	N	Cr	Mo
A533 Gr.B[a]	Midland	Vendor	0.50	Bal.	0.17	0.014	0.016	1.28	0.200	–	0.19	0.47
	Lower Head	ANL	0.55	Bal.	0.28	0.025	0.010	1.27	0.220	–	0.19	0.50
304 SS[b]	53319	Vendor	8.88	Bal.	0.59	0.024	0.013	1.69	0.060	0.029	18.33	0.14
		ANL	8.96	Bal.	0.55	0.021	0.008	1.72	0.070	–	18.52	0.16
308 SS	–	Spec.	9-11	Bal.	0.90	0.040	0.030	2.5 max	0.080	–	18-21	0.75
		ANL	9.37	Bal.	0.56	0.027	0.002	1.27	0.029	–	21.08	0.39
Alloy 600[c]	NX8844B33	Vendor	Bal.	8.26	0.24	0.009	0.001	0.26	0.069	0.010	14.97	0.15
		ANL	Bal.	9.01	0.26	–	0.001	0.24	0.080	–	14.68	–

[a]162–mm thick hot–pressed plate from Midland reactor lower head. Austenitized at 871–899°C for 5.5 h and brine quenched; then tempered at 649–663°C for 5.5 h and brine quenched.
[b]Solution annealed pipe.
[c]25.4–mm–thick plate fabricated by INCO Alloys International, Inc., Huntington, WV, for the Electric Power Research Institute (EPRI). Annealed at 872°C for 1 h.

The size and shape of the specimens varied with the environmental conditions and type of test. Cylindrical rods with 3.2 or 6.35 mm (0.125 or 0.25 in.) diameter and up to 100 mm length were employed for ECP measurements and potentiodynamic studies. Ring specimens with 12.7 mm (0.5 in.) diameter and ≈3.2 mm (0.125 in.) wall thickness were used for the corrosion/wastage studies. A schematic drawing of shielded metal arc (SMA) weld overlay on A533 Gr.–B low–alloy steel plate using Type 308 SS filler metal is shown in Fig. 5. Cylindrical rod or ring specimens were fabricated from the weld overlay as shown in the drawing. A photograph of ring specimens and the weld overlay piece that was used for machining the specimens is shown in Fig. 6. Figure 7 shows specimen holder with a set of ring specimens of A533 Gr.–B steel and SMA weld overlay for corrosion/wastage studies in concentrated boric acid solutions at 100°C.

Figure 5. Schematic drawing of the Type 308 SS weld overlay on A533 Gr.-B low-alloy steel.

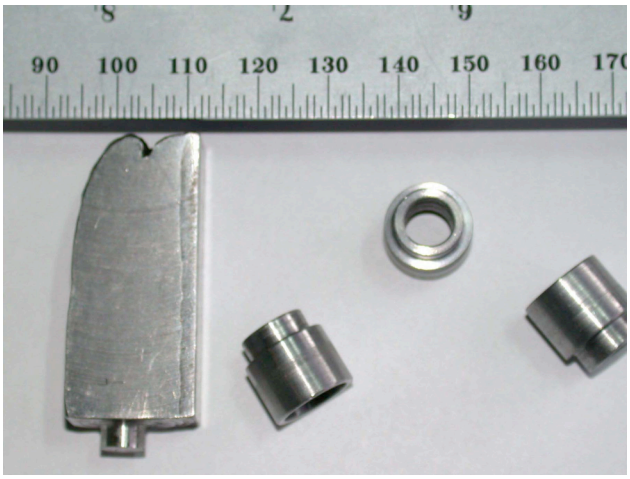

Figure 6.
Ring samples fabricated from the Type 308 SMA weld overlay.

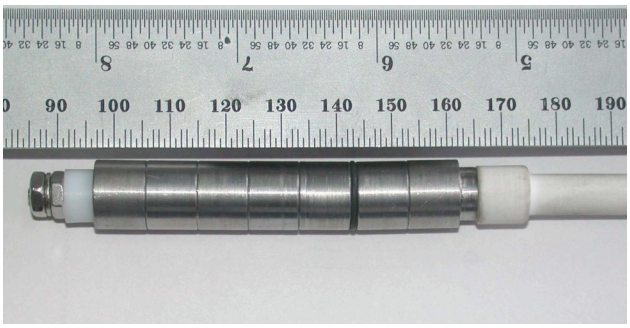

Figure 7.
Assembled set of ring samples of A533 Gr.-B low-alloy steel and Type 308 SS SMA weld overlay for corrosion/wastage tests.

2.2 Test Environments

The various test environments simulate the postulated conditions in the RPV head/nozzle crevice. The environment in the crevice between the RPV head and the Alloy 600 penetration above the J–groove weld (see Fig. 3) depends on what the leak rate is, and whether the nozzle/head annulus is plugged or open. The following three environmental conditions have been investigated in the present study: (i) low–temperature (≈95°C) saturated boric acid solution deaerated and aerated; (ii) high–temperature, high–pressure aqueous environment with a range of boric acid solution concentrations; and (iii) high-temperature (150–300°C) boric acid powder at atmospheric pressure with and without addition of water.

2.2.1 Low–Temperature Saturated Boric Acid Solutions

Near the end of the overall progression of damage, high leak rates through the CRDM cracks provide sufficient cooling of the metal surfaces to allow liquid boric acid solutions to form in the crevice. These solutions will become concentrated in boric acid through boiling and more reactive by infusion of oxygen available directly from the ambient atmosphere.

The solubility of boric acid[6,7] at temperatures up to 100°C (212°F) is shown in Fig. 8. The solubility increases by a factor of ≈8 when temperature is increased from room temperature (RT) to 100°C.

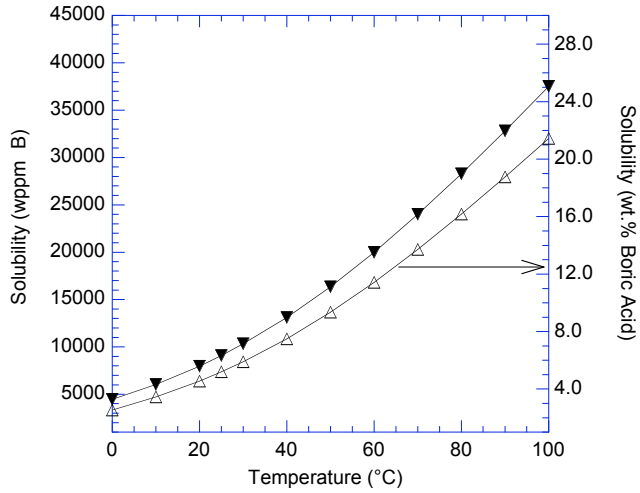

Figure 8.
Solubility of boric acid (wppm B or wt.% boric acid) in water vs. temperature (Ref. 6,7).

Figures 9a–d show the measured pH of aerated and deaerated solutions of boric acid at temperatures up to 100°C. The RT–saturated boric acid solution was prepared by adding more than the required amount of boric acid to ultra–high pure (UHP) water at RT and storing it for a few days. The temperature was measured using a three–digit Omega–digital K–type thermometer which was calibrated. The boiling point for the saturated boric acid solution was measured to be ≈103°C, but the experiments were conducted at 97.5°C. The 100°C–saturated solution was prepared by adding boric acid to UHP water at 100°C until excess boric acid crystals (or agglomerated powder) were presented in the solution. Boric acid solutions saturated at any other temperature between 25 and 100°C were obtained by cooling the 100°C–saturated solution. The solutions were purged with N_2 plus 1% H_2 gas for deaerated condition and were open to air environment for the aerated condition. The exact concentration of DO, measured by CHEMets ampoules, in the deaerated and aerated solutions was <5 and ≈30 ppb, respectively. The DO measurement was made by inserting a glass tip into the solution, opening the tip quickly at temperature to suck the solution, and closing the tip with a rubber cap. The test glass was air cooled to room temperature and DO measured by CHEMets capsules.

The pH of RT–saturated solution of boric acid is plotted as a function of temperature in Fig. 9a. The measured pH of both aerated and deaerated solutions show little or no change with temperature at 25–100°C. The pH of boric acid solutions that were saturated at temperature is plotted as a function of temperature in Fig. 9b and boron concentration in Fig. 9c; the pH decreased with increasing temperature or boron concentration. The pH and solubility of boric acid (wppm B) in water are plotted as a function of inverse temperature in Fig. 9d to gain an understanding of the solution enthalpy for the boric acid in the water and formation energy for the ionization, i.e., $2H_2O + B(OH)_3 = [H_3O]^+ + [B(OH)_4]^-$. The results indicate that the $[B(OH)_4]^-$ ion is stable in the temperature range 25–100°C, and boric acid may be treated to be totally ionized in solutions that are saturated at test temperature.

Another scenario can also create low–temperature saturated solutions of boric acid. Slow leakage into an open crevice or annulus leaves deposits of boric acid in the crevice and also on top of RPV head surfaces (Fig. 4). The annulus between the nozzle and head is then plugged by deposits and/or corrosion products. In the absence of moisture, these deposits will be relatively dry and a layer of molten HBO_2 and solid B_2O_3 will form next to the hot metal surface. Later moisture may be introduced to this pile of deposits either due to unplugging of

the nozzle/head annulus or leakage from the CRDM nozzle flange or continued leakage through the crack. The heat of evaporation will provide cooling and, if the rate at which moisture is added to the pile of deposits is equal to the rate at which moisture evaporates, a concentrated solution of boric acid will form under the pile; the solution temperature may be as high as 150 or 170°C.

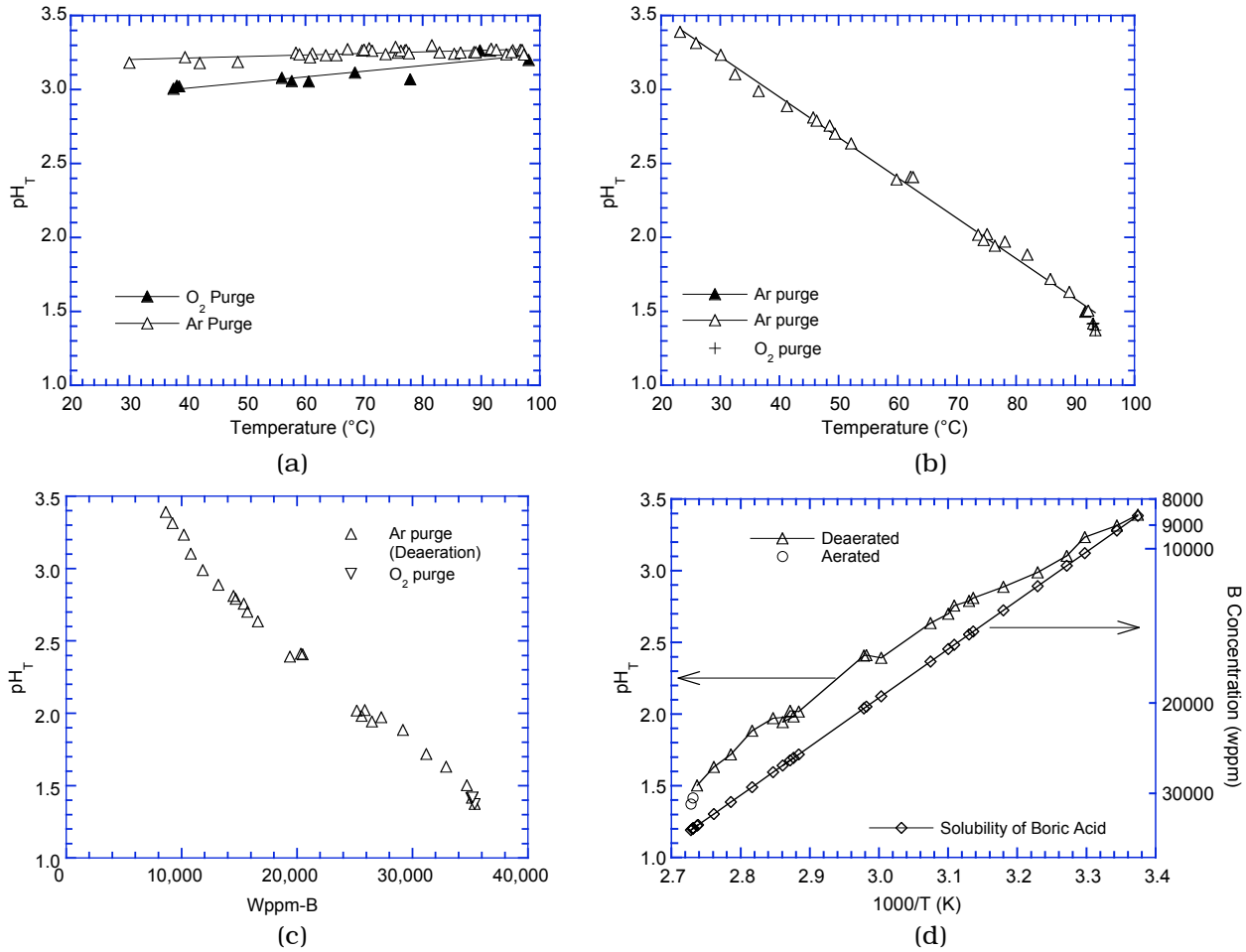

Figure 9. Plots of pH_T vs. temperature in the oxygen and argon gas environments (a) for the RT–saturated solution and (b) the boric acid saturated at T; (c) pH_T vs. wppm B for temperature between RT and 100°C; and (d) pH_T and wppm B vs. inverse temperature.

2.2.2 High–Temperature High–Pressure PWR Environments

Initially, extremely low leak rates result in complete flashing of the coolant to steam. Under this condition, two scenarios are possible based on whether the nozzle/head annulus is plugged by deposits and/or corrosion products or is open to the atmosphere. A plugged nozzle/head annulus will result in a high–temperature, high–pressure aqueous environment in the annulus, i.e., on the OD of the CRDM nozzle. The PWR environment used in the present study consisted of 1000 ppm B, 2 ppm Li, <10 ppb dissolved oxygen (DO), and ≈2 ppm (≈23 cc/kg) dissolved hydrogen. However, depending on how long after the leak that the crevice gets plugged, the concentrations of B and Li in the solution may be significantly greater than the typical values in the PWR environment. Continued leakage into an open crevice will cause a buildup of boric acid deposits in the crevice.

2.2.3 Molten H–B–O Environments at Ambient Temperature

A crevice open to the atmosphere would cause deposits of boric acid on hot metal surfaces (typically at temperatures above 300°C). However, at high temperatures boric acid loses moisture and transforms first to HBO_2 at 169°C and then to B_2O_3 at temperatures above 300°C. The various phases for the H-B-O system at temperatures up to 450°C are listed in Table 2. HBO_2 is molten at temperatures above 236°C and, in the absence of moisture, readily transforms to solid B_2O_3 at temperatures in excess of 300°C; B_2O_3 melts at 450°C. Consequently, deposits of boric acid in contact with hot RPV head surfaces would consist of a mixture of molten HBO_2 and solid B_2O_3.

Table. 2. Melting points and phase transition temperatures in the H-B-O system.

Phases	Temperature (°C)	Reaction with H_2O
H_3BO_3 or $B(OH)_3$	169 (Transition)	$B(OH)_3 + H_2O = [B(OH)_4]^- + H^+$
HBO_2	236 (Melting)	$B(OH)_3 - H_2O = HBO_2$
B_2O_3	300 (Transition), 450 (Melting)	$2HBO_2 - H_2O = B_2O_3$

The moisture content of the H-B-O system is expected to be an important parameter for corrosion studies, since the stability and the presence/absence of a given phase are dictated by the addition or removal of water, as can be seen by the reactions given in Table 2. The temperature dependence of the equilibrium water vapor pressure (pH_2O), calculated for various reactions in the H-B-O system, is shown in Fig. 10. The equilibrium water vapor pressure was calculated using the two equations shown in the figure and thermodynamic data from Ref. 8. Conversion of boric acid into HBO_2 and HBO_2 into B_2O_3 requires removal of H_2O, and maintenance of mixtures of boric acid and HBO_2 or HBO_2 and B_2O_3 dictated significant increases in steam pressure, especially at higher temperatures. Later in this report we discuss various experiments that were conducted to examine the corrosion performance of A533 steel in different H-B-O compounds.

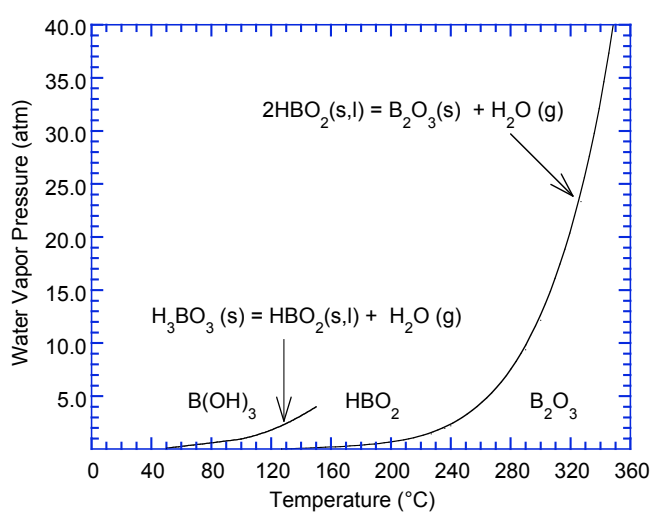

Figure 10.
Plot of equilibrium water vapor pressure vs. temperature for the H-B-O system.

2.3 Test Facilities

2.3.1 Low–Temperature Tests at Ambient Pressure

The electrochemical cell used for the ECP and potentiodynamic measurements in concentrated solutions of boric acid at 95°C (203°F) and ambient pressure is shown in Fig. 11. The cell consists of a 1–L round–bottom Pyrex flask that was modified by the addition of various necks to permit introduction of working, counter, and reference electrodes, pH probe, gas inlet and outlet tubes, and a thermocouple. A saturated calomel electrode (SCE) utilizing a porous plug tip was used as the reference electrode, and a platinum sheet as auxiliary or counter electrode. A Luggin capillary with salt–bridge connection to the reference electrode separated the bulk boric acid solution from the saturated calomel reference electrode. The probe tip could be easily adjusted to bring it in close proximity with the working electrode. A 6.35–mm diameter and 75–mm long rod was used as a working electrode (Fig. 12). The working electrode was tightly intruded with vacuum grease into a PHARMA–50 (Dow Corning) tubing such that only the bottom surface (0.317 cm^2 area) of the electrode was exposed to the solution. The bottom surface was polished with a 600–grit silicon carbide paper.

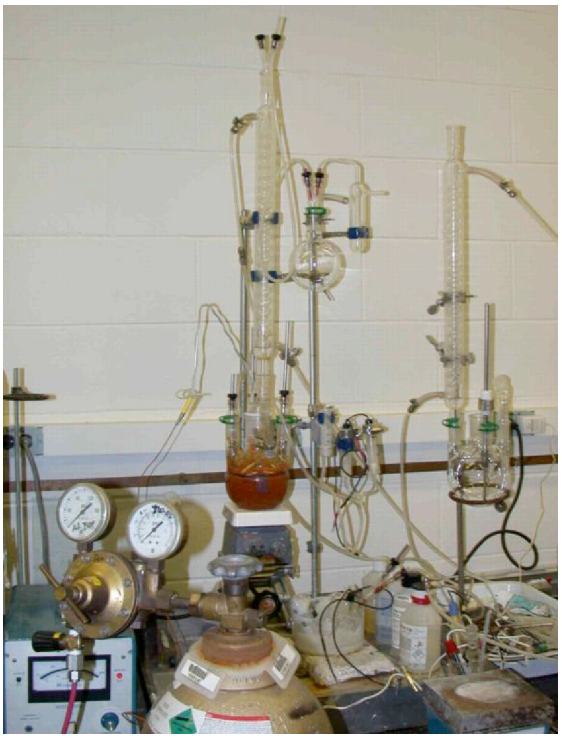

Figure 11. Electrochemical cell for potentiodynamic studies.

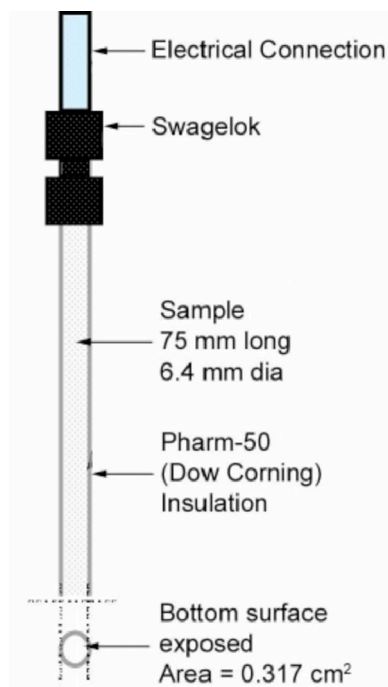

Figure 12. Schematic drawing of the working electrode.

A scanning potentiostat with high input–impedance (10^{12} Ω) was used for the potentiodynamic measurements. The potential was automatically varied at a constant rate between two preset values, and the current and potential were recorded continuously. The tests were conducted in accordance with ASTM Standard Procedure G5–94.[9] A potential scan rate of 0.16 mV/s was used for the test runs; a fast scan rate of 5 mV/s was used to measure the open circuit potential and establish the test conditions. The apparatus was calibrated using a Fe working electrode. The results are presented in Fig. 13. The measured corrosion

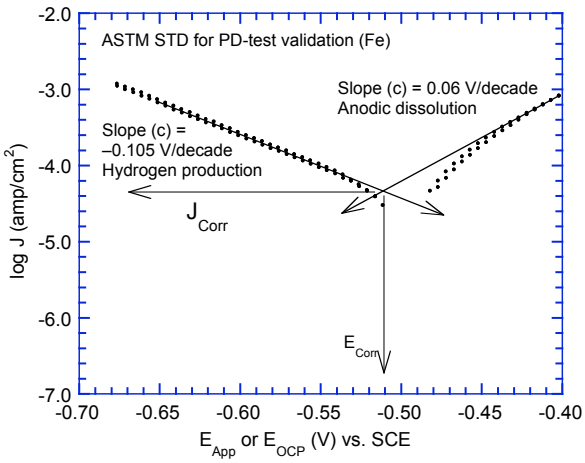

Figure 13.
Calibration of the potentiodynamic test apparatus following with ASTM G5-94 using Fe working electrode and saturated calomel reference electrode.

potential for Fe, –0.512 V, is in good agreement with the standard value of –0.52 V quoted in ASTM G5–94 in terms of SCE. The measured potentials, E_{meas} (V), may be converted to the standard hydrogen electrode (SHE) scale, E_{SHE} (V), by the expression[10]

$$E_{SHE} = E_{meas} + 0.242 - 7.6\text{x}10^{-4}\ \Delta T \qquad (1)$$

where ΔT(°C) is the temperature difference of the salt bridge in the reference electrode (i.e., the test temperature minus ambient temperature).

The apparatus used for corrosion/wastage studies on ring specimens of A533 Gr.–B low–alloy steel, Alloy 600, and Type 308 SS cladding, in concentrated solutions of boric acid at temperatures up to 100°C is shown in Fig. 14. The specimens were rotated at 50 rpm, and material loss or wastage was measured at 24, 76, 100, 311, and 411 h. To prevent possible

Figure 14.
Apparatus for corrosion test in concentrated solutions of boric acid at temperatures up to 100°C.

galvanic interaction, the specimens were separated from each other with an insulator (Teflon gasket) and isolated from the specimen holder by tygon tubing.

The solution was prepared by dissolving 158–g boric acid in 500–mL water at 95–100°C; this is ≈3 g in excess of the estimated solubility of boric acid at 95°C. For ECP and potentiodynamic measurements, the DO in solution was fixed by bubbling air through the solution prior to the test, and for corrosion tests, the solution was open to air. The measured DO content was 600 and 30 ppb, respectively, after bubbling air and when the system was open to air. It seems the DO in the saturated boric acid solution is substantially lower than normally would be present in high–purity water (≈2 ppm). The test specimen was degreased and rinsed in distilled water before immersion into the cell; the salt–bridge probe tip was adjusted to ≈2 mm from the test specimen. Open circuit or corrosion potential was recorded ≈1 h after immersion. Tests were performed on A533 Gr.–B low–alloy steel, Alloy 600, and Type 304 and 308 SS in aerated saturated solution of boric acid at 95°C.

2.3.2 High–Temperature High–Pressure Tests

Figure 15 shows a schematic diagram of the facility for potentiodynamic and ECP measurements in high–pressure solutions of boric acid of varying concentrations at temperatures up to 300°C. The facility consists of a supply tank, high–pressure pump, preheater, heated test chamber, regenerative heat exchanger, Mity Mite™ back-pressure regulator, and drain. The entire system from the storage tank to the drain, including the 25 x 50 mm cross section and 75 mm long test chamber, was constructed of Type 304 SS. Figure 16 shows the configuration of the test chamber with solution inlet/outlet lines, working electrode assembly, Pt counter electrode, 0.1–M KCl/AgCl/Ag external reference electrode, and a thermocouple well. The working electrode assembly consisted of three 3.2–mm (0.125–in.) diameter x 3.2–mm (0.125–in.) long samples of A533 Gr.–B, Alloy 600, and Type 308 weld metal, spot welded to Pt lead wires, plus a fourth Pt wire sample. The lead wires were covered

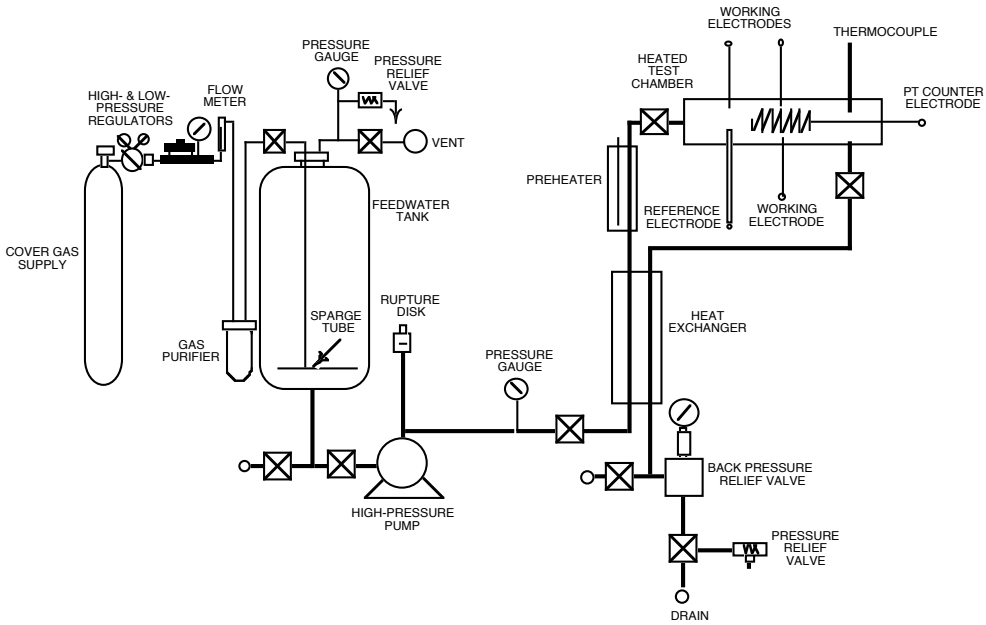

Figure 15. Schematic of the facility for high–temperature high–pressure tests in PWR environments with various concentrations of B and Li.

with teflon spaghetti and secured in a four-hole alumina rod, 9.5–mm (0.375 in.) diameter 127–mm (5 in.) long, such that only the working electrode samples were exposed to the test solutions, Fig. 17.

The simulated PWR solution, consisting of high–purity water containing <10 ppb DO, 1000–9000 ppm B, and ≈2 ppm Li, was circulated through the system at a relatively low flow rate of ≈10 mL/min. The high–purity water was prepared by passing deionized water through a set of filters that comprise a carbon filter, an Organex–Q filter, two ion exchangers, and a 0.2–mm capsule filter. The DO level in the water was reduced to <10 ppb by bubbling pure N_2 and then pure H_2 through the water. The DO level was measured in the feedwater tank and the effluent with a Model 26075 (sensor 21152) Orbisphere DO sensor and monitor. The desired amount of boric acid and lithium hydroxide were dissolved in 20 L of deionized water and this solution was then added to the supply tank to prepare the test solutions.

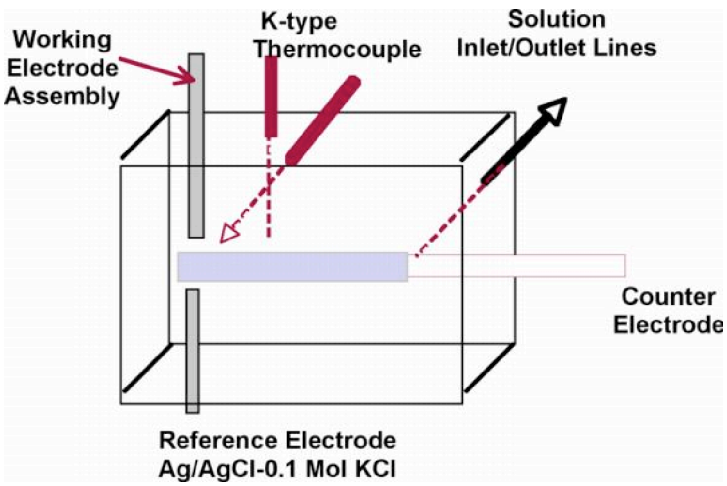

Figure 16. Schematic of the test chamber showing the location of various electrodes, solution inlet/outlet lines, and thermocouple well.

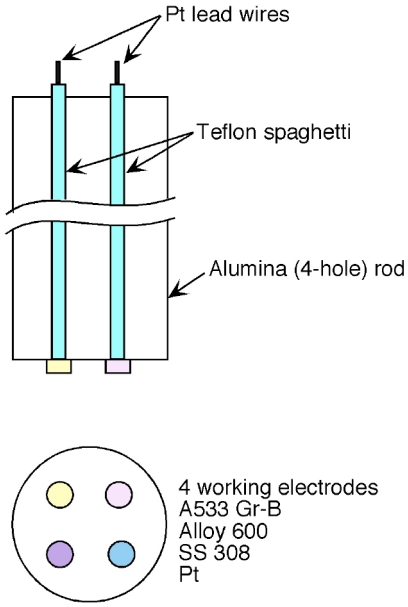

Figure 17. A four hole high–purity alumina rod containing four working electrodes.

The corrosion/wastage rates of A533B low–alloy steel, Alloy 600, and Type 308 SS cladding were performed in boric acid solutions of varying concentrations at 95–316°C (203–600°F). The concentration of B in the solutions ranged from the typical value for normal PWR water, e.g., 1000 wppm, to RT–saturated boric acid solution containing 9090 wppm B. All solutions contained 2 wppm Li, and a 34–kPa overpressure of pure H_2 was maintained above the supply tank to obtain ≈2 ppm (≈23 kg/cc) dissolved H_2 in the solution. A schematic diagram of the specimen holder and disc–shaped specimens used for the study is shown in Fig. 18. Specimens, 6.4–mm (0.25–in.) diameter and 1-mm thick, were supported by an alumina rod and connected with 0.25–mm (0.01–in.) diameter SS wire. After the tests, specimen weight was measured to determine corrosion rates. The specimens were also examined by scanning electron microscopy and energy-dispersive x-ray spectroscopy (SEM/EDS); x-ray diffraction studies were also conducted for some A533 Gr.–B specimens.

Figure 18. Schematic of the test specimen holder for high-temperature, high-pressure corrosion tests in a flowing boric acid solution under the hydrogen cover gas.

2.3.3 Tests in Molten H–B–O Environment at Ambient Pressure

The facility used for potentiodynamic and ECP measurements in molten HBO_2/B_2O_3 environments at 240 and 290°C and ambient pressure is shown in Fig. 19. The melt was prepared in a 125–mL Type 304 SS beaker with its lip cut off. The test beaker was placed inside a 1.2–L SS environmental chamber, alumina blocks were used to provide electrical insulation between the two vessels. The environment above the test vessel was controlled by a constant supply of Ar or air through the environmental chamber.

For each potentiodynamic or ECP measurement, ≈300 g of boric acid was used to prepare ≈40–mm–deep (≈1.6–in.) melt in the test vessel. Typically, only 100 g boric acid could be melted in the 125 mL beaker. The process was repeated three times to collect the total volume of melt for each test. The molten salt was totally transparent and appeared like clear glass.

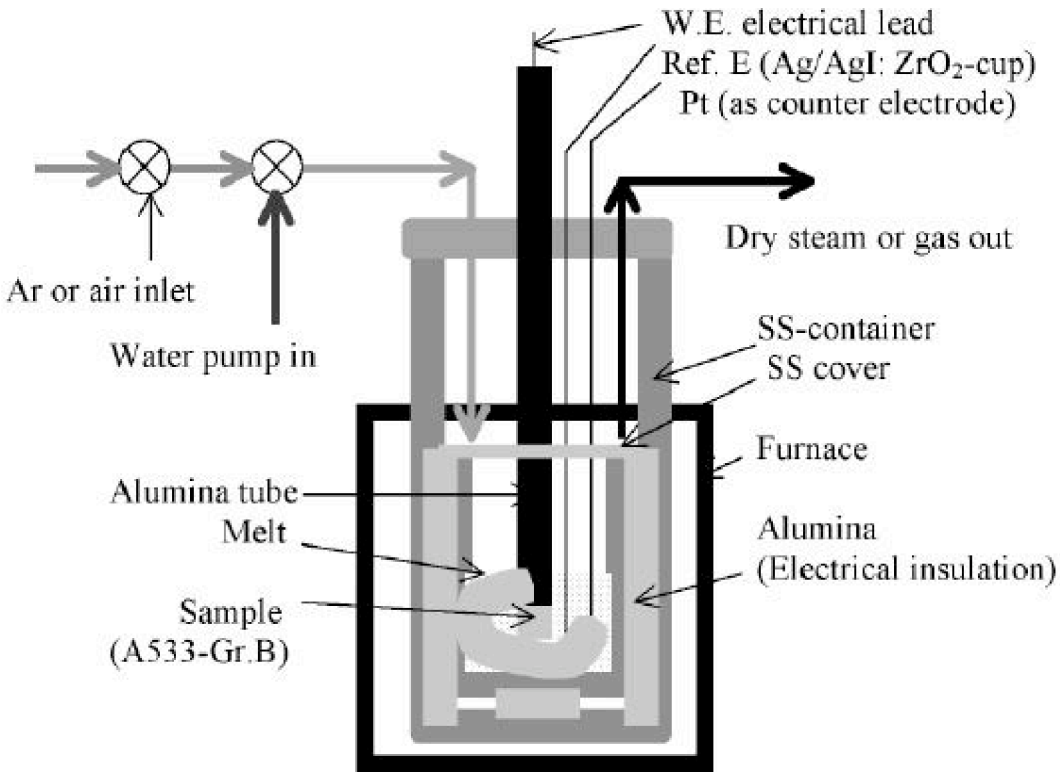

Figure 19. Schematic of the facility for potentiodynamic and ECP measurements in mixtures of molten boric acid and boric oxide at temperatures up to 300°C.

As discussed earlier, when heated, boric acid transforms first to HBO_2 and then to B_2O_3; it loses weight as H_2O evaporates. This is demonstrated in Fig. 20, which shows the thermogravimetric analysis (TGA) for a 180–mg sample of boric acid as it was heated from 25 to 420°C in air. After ≈1500 s the sample exhibited an erratic behavior in weight change due to formation and escape of bubbles from the melt. The results indicate that at up to 350°C the observed sample weight is in agreement with the expected weight for the B_2O_3 phase. At temperatures >350°C the sample weight decreased further; additional tests are needed to examine the phase stability at higher temperatures. The change in weight with time of another ≈100–g sample of boric acid at 280°C in air is shown in Fig. 21; the estimated weights for HBO_2 and B_2O_3 are identified in the figure.

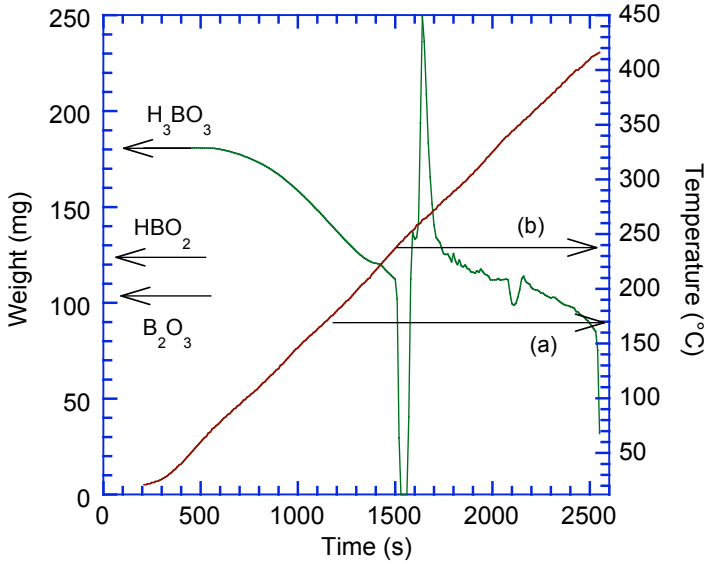

Figure 20.
Change in weight of boric acid when heated from 25 to 450°C in an air environment, (a) corresponds to transition to HBO_2 and (b) represents melting point of HBO_2.

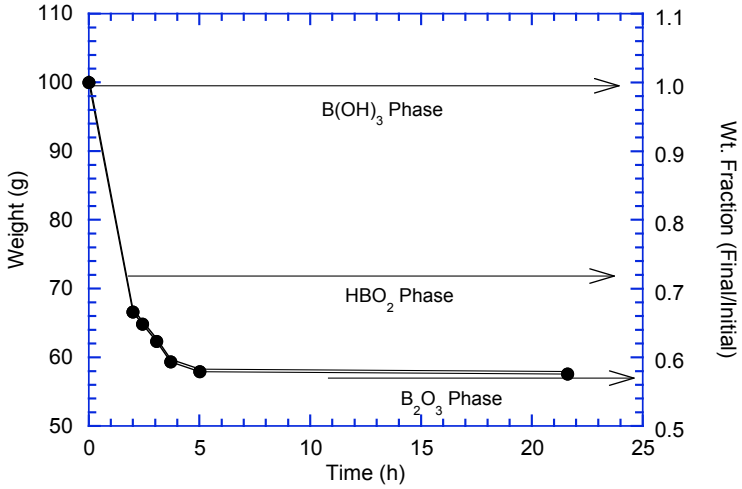

Figure 21.
Weight change vs. time at 280°C in air atmosphere. Boric acid turns to HBO_2 and mostly B_2O_3 phase.

Figure 22 shows the schematic diagram of the working electrode used in the present study. It consists of a 6.4–mm (0.25–in.) diameter x 6.4–mm (0.25 in.) long sample of A533 Gr.–B steel spot welded with silver to a SS lead wire and inserted into the end of a 6.4–mm (0.25 in.) OD alumina tube. A heat sink was used during welding to prevent overheating of the sample. The welded end of the electrode was carefully machined to provide a

leak–tight seal with the alumina tube. The total area of the working electrode exposed to the solution was 2.3 mm^2. A 3–mm wide Pt strip was used as counter electrode. The reference electrode (shown in Fig. 23) consisted of Ag/AgI electrolyte contained in a porous ZrO_2 cup. The AgI electrolyte was allowed to soak into the ZrO_2 cup at 700°C for ≈600 s before contact with the H-B-O melt. The activity of AgI in solid state is unity, and at >147°C AgI becomes an ionic conductor with a transport number for Ag of 1.

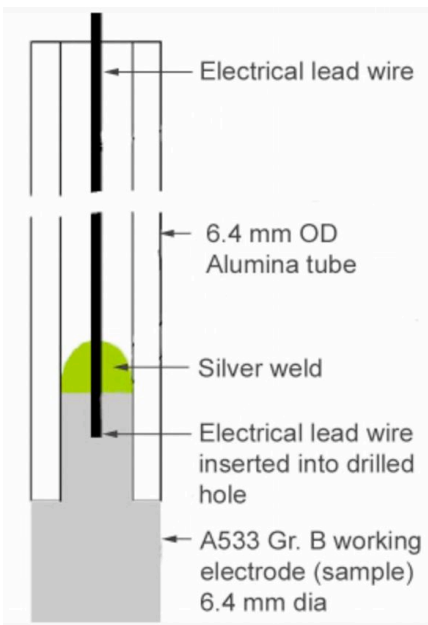

Figure 22. A533 Gr.–B low–alloy steel working electrode.

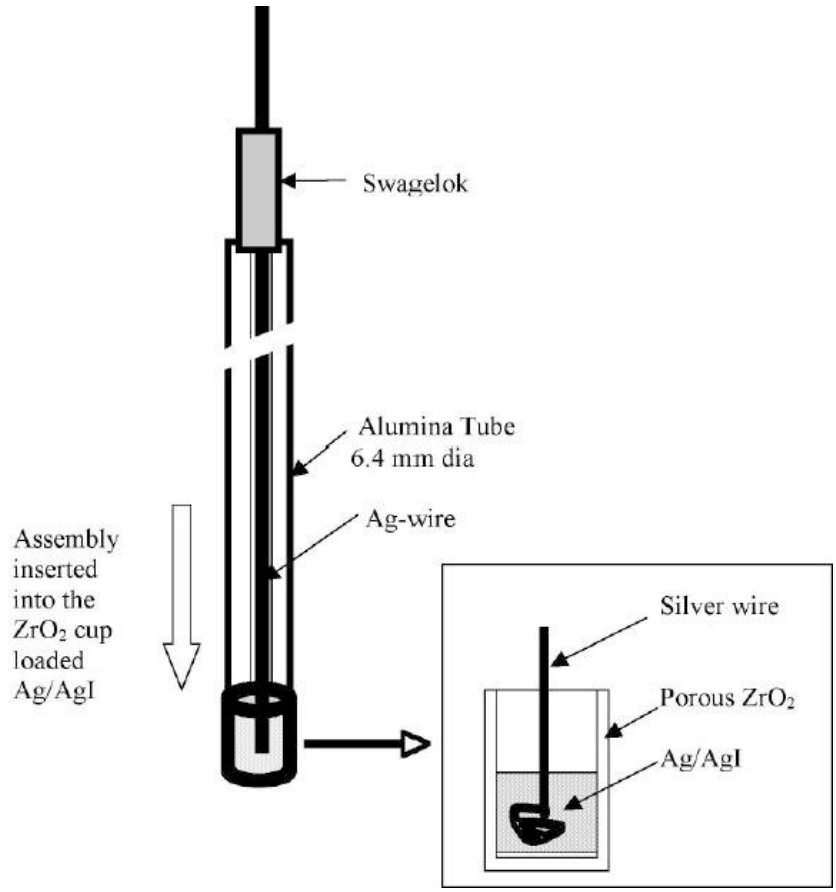

Figure 23. Reference electrode consisting of Ag/AgI electrolyte contained in a porous sintered ZrO_2 cup.

Figure 24 shows the apparatus for conducting corrosion tests in boric acid powder at 150–300°C, with and without the addition of water. It consists of a 63.5–mm (2.5–in.) diameter, 572–mm (22.5–in.) long SS chamber, the bottom ≈250 mm (10 in.) of which was heated in a furnace. A long 6.35-mm (0.25–in.) diameter SS tube was used both as the specimen holder and for addition of water to the system. A stack of three ring samples was mounted at the end of the tube; the stack was rotated at ≈50 rpm during the test.

For each corrosion test, the SS chamber was densely packed with boric acid powder to a depth of ≈356 mm (≈14 in.). A stack of samples was inserted into the boric acid powder by slowly rotating the stack and pushing it in. The furnace was then heated to 300°C to create a temperature gradient in the column of boric acid powder inside the test chamber; the temperature of the column was monitored at 6 locations. Under steady state the top of the

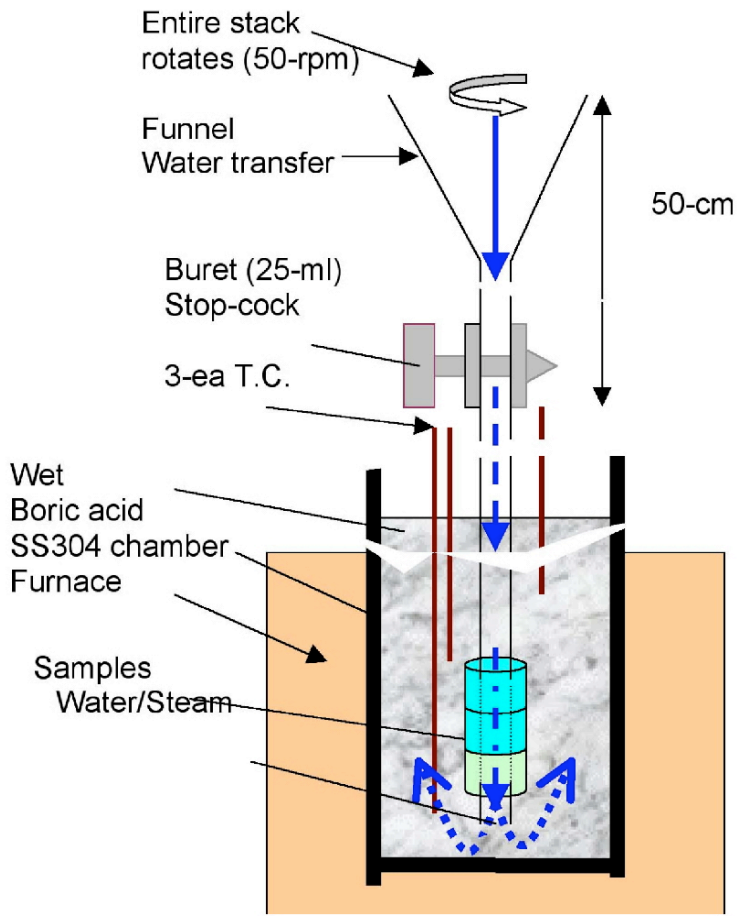

Figure 24.
The apparatus for conducting corrosion tests in molten H-B-O system with water additions.

column was at room temperature and the bottom at 300°C. Based on the information presented in Table 2 and Fig. 10, the environment at different depths of the test chamber is expected to be a molten mixture of B_2O_3 + HBO_2 at 300°C, molten HBO_2 at 260°C, and a dry powder of HBO_2 + H_3BO_3 at 150°C. For the tests without addition of water, a stack of ring specimens was exposed for 24 h in these three temperature zones.

A similar procedure was followed for the corrosion tests with addition of water. A densely packed column of boric acid with a stack of corrosion specimens was heated at the bottom to 300°C. Then, 200–250 mL of water was poured into the system through the specimen holder tube. After the initial reaction when water flashed to steam, the system cooled rapidly, and the entire column of boric acid in the test chamber was covered with water. Additional water was added on top of the boric acid to ensure that the entire column of boric acid powder/melt was covered with water for the duration of the test. Under steady state, the test chamber consisted of saturated solution of boric acid at room temperature at the top of the chamber and at 150 or 170°C at the bottom of the chamber. A photograph of the solid boric acid crust that was left at the bottom of the test chamber after the corrosion test with water addition is shown in Fig. 25.

Figure 25.
Photograph of the solid boric acid crust left at the bottom of the test chamber after the corrosion test with water addition.

2.3.4 Capsule Test

Capsule corrosion tests were conducted on A533 Gr.–B, Alloy 600, and Type 308 SS samples to study corrosion under equilibrium conditions in the H-B-O system at high temperatures and pressures. The test capsule consisted of a heavy-wall Type 304 SS tube, 12.7 mm (0.5 in.) diameter and 50 mm (2 in.) long, enclosed with Swagelok caps at each end, Fig. 26. The capsules heated to 294 and 316°C had bulged significantly because of buildup of high pressure inside the capsules that were heated to high temperatures. Disk–shaped samples, 6.35 mm (0.25 in.) diameter and 0.25 mm (0.01 in.) thick, were used for the tests. The capsules were filled with room–temperature saturated boric acid solution, and were sealed and heated to temperatures between 170 and 316°C in an Ar–purged furnace. All corrosion tests were of 68–h duration. The samples were removed from the capsules after the tests, ultrasonically cleaned in ethanol, and examined by SEM and X-ray analysis.

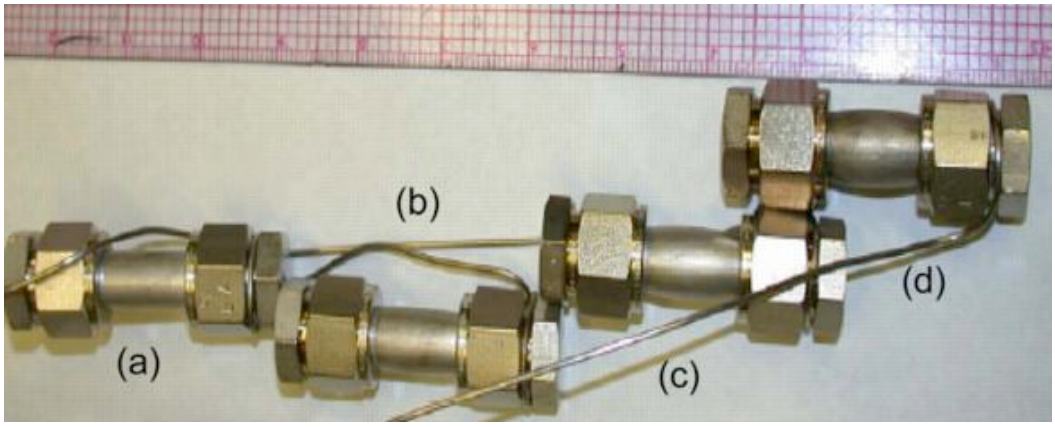

Figure 26. Test capsules 12.7 mm (0.5 in.) in diameter and 50 mm (2 in.) long, loaded with a boric acid solution saturated at room temperature and tested at (a) 172°C, (b) 235°C, (c) 294°C, and (d) 316°C.