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High-temperature hydrogen permeation in nickel alloys

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Abstract – *In gas cooled Very High Temperature Reactor concepts tritium is produced as a tertiary fission product and by activation of graphite core contaminants, such as lithium; of the helium isotope, He-3, that is naturally present in the He gas coolant; and the boron in the B4C burnable poison. Because of its high mobility at the reactor outlet temperatures tritium poses a risk of permeating through the walls of the intermediate heat exchanger (IHX) or steam generator (SG) systems, potentially contaminating the environment and in particular the hydrogen product when the reactor heat is utilized in connection with a hydrogen generation plant. An experiment to measure tritium permeation in structural materials at temperatures up to 1000 C has been constructed at the Idaho National Laboratory Safety and Tritium Applied Research (STAR) facility within the Next Generation Nuclear Plant program. The design is based on two counter flowing helium loops to represent heat exchanger conditions and was optimized to allow control of the materials surface condition and the investigation of the effects of thermal fatigue. In the ongoing campaign three nickel alloys are being considered because of their high-temperature creep properties, alloy 617, 800H and 230. This paper introduces the general issues related to tritium in the on-going assessment of gas cooled VHTR systems fission product transport and outlines the planned research activities in this area; outlines the features and capabilities of the experimental facility being operated at INL; presents and discusses the initial results of hydrogen permeability measurements in two of the selected alloys and compares them with the available database from previous studies.*

I. INTRODUCTION

The U.S. Department of Energy has selected the very high temperature reactor (VHTR) concept for the Next Generation Nuclear Plant (NGNP). Conceptually, the NGNP can produce electricity, generate hydrogen, and provide industrial process heat at temperatures up to 850°C. The NGNP design is conceptually a graphite reactor core in which the primary coolant is re-circulating helium gas. The very high

planned outlet temperatures impose severe service requirements on the structural components of the reactor and intermediate heat exchanger. The need for resistance to high temperature creep severely limits candidate alloys to high-nickel alloys. Presently, alloys that are candidates for high-temperature structural components are Incoloy 800H, Inconel 617, and Haynes 230.

Containment of fission products is a paramount concern in the operation of a nuclear reactor. The containment of tritium, a gaseous fission product, is of special concern in the NGNP because of its high relative mobility in the core at the high operating temperatures. Tritium will be produced in the NGNP reactor as a tertiary fission product and by activation of graphite core contaminants such as lithium (Li-6 and Li 7); of the helium isotope, He-3, which is naturally present in the helium gas coolant; and the boron in the B4C burnable poison. Tritium is a radioactive isotope of hydrogen. It is an internal radiological hazard to humans, whose release is stringently limited by federal regulations. Because of its potentially high mobility at the reactor outlet temperatures, the tritium poses a risk of permeating through the walls of the intermediate heat exchanger and steam generator systems, potentially contaminating the environment and the hydrogen product. Therefore, the stringent environmental regulatory limits require that the design of the core and the plant system effectively contain the tritium produced by fission and activation.

The design of an acceptable containment system requires the selection of materials that allow the control of fission product permeation. This is particularly important for the alloys comprising the high-temperature service components of the NGNP system such as the intermediate heat exchanger and the steam generator. Most gases, including hydrogen and tritium, have a finite permeation rate through materials, which generally increases exponentially with temperature. The magnitude of the permeation rate at any temperature is a function of the activation energy and the permeation constant (the Arrhenius frequency factor or pre-exponential factor), which are characteristics determined by the elemental composition, phase composition, microstructure, and surface coatings of the alloys and materials. The characterization of the permeation process is therefore essential for the design of control systems that ensure that emission limits are satisfied under all credible circumstances.

The permeation of hydrogen through the more common metals and alloys has been investigated extensively over the last 50 years. Permeation data have been published for a number of metal alloys, including ferritic steels, austenitic steels, copper alloys, aluminum alloys, some high-nickel alloys, and metals such as nickel, gold, and palladium for temperatures up to 600–900°C, as shown in Figure 1 [1].

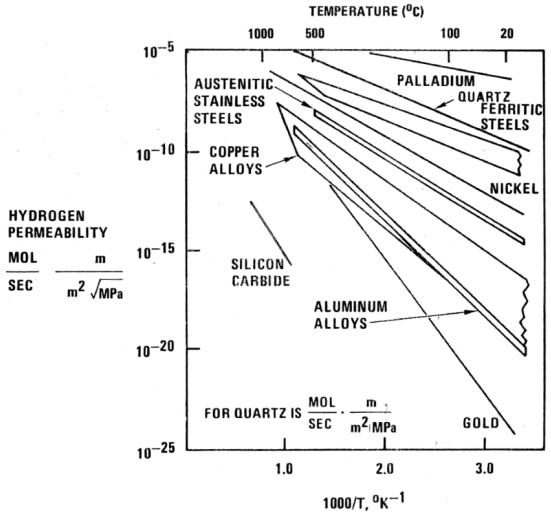

Fig. 1: Hydrogen permeability of some metals, classes of alloys, and ceramics as a function of temperature

In general, the hydrogen permeability in metals is an exponential function of temperature, increasing as much as five orders of magnitude between 20 and 800°C. In addition, while the range of permeability for various groups of alloys spans many orders of magnitude at 20°C, the range decreases to a spread of only a few orders

of magnitude at high temperatures (>500°C). The hydrogen permeability of the candidate alloys for NGNP structural components is not as well defined. Of the three candidate high-nickel alloys, only Incoloy 800/800H has been significantly tested for permeation, with several reports in the literature [2-10]. By comparison, only two groups have reported hydrogen permeability data for Inconel 617 and none for Haynes 230 [5,7]. Tritium permeation has been reported only for Incoloy 800/800H, and only by two groups [5,12,13]. Furthermore, the literature data generally pertain to hydrogen partial pressures greater than 0.1 atm, with the exception of the data of Roehrig et al. [4], a range substantially higher than hydrogen and tritium pressures typical of the steady-state conditions within a VHTR core. These data must be generated experimentally to support the design of the NGNP systems.

II. EXPERIMENTAL FACILITY

The NGNP project designed and assembled a system for the measurement of the permeation characteristics of hydrogen and tritium through metal samples at high temperatures at the INL Safety and Tritium Applied Research (STAR) facility. The measurement system consists of two counter-flowing helium gas flow loops separated by the heated tubular test sample. The thin-walled tubular sample, mounted within a sealed quartz sample chamber, is the permeation interface separating the counter-flowing helium gas streams of the primary and secondary gas loops (Figure 2). The probe gas mixture (helium and hydrogen) in the primary gas loop flows through the bore of the tubular test sample, while the helium of the secondary gas loop, which includes the volume of the test chamber, flows over the external surface of the tubular sample to sweep away the permeated gas. The concentration of the permeated gas in the helium of the secondary gas loop is measured by a quadrupole mass spectrometer specially designed to sample with high sensitivity from high-pressure gas flows (Compact Process Monitor by Inficon, Inc).

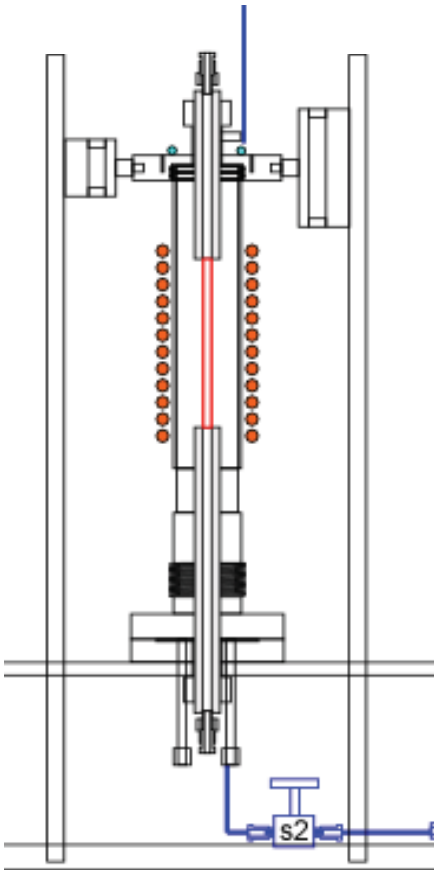

Fig. 2: Test section schematic

The test sample is directly heated by a radio frequency induction heater, with the copper coils external to the quartz chamber and surrounding the thin-walled section of the test sample. The induction heater heats the sample to temperature rapidly, within a few tenths of a second, defining a sharp temperature transition and avoiding the long temperature ramps that are common with resistance heaters. The control signal is acquired by a thermocouple in contact with the inner surface of the sample wall, which is also used for calibration and verification of the sample surface emissivity. The temperature of the heated area is then monitored by an infrared thermal imaging system mounted externally

to the quartz tube and the glove box. The system yields two-dimensional maps of the temperatures of the heated sample area that is visible in the gaps between the induction heater coils (Figure 3).

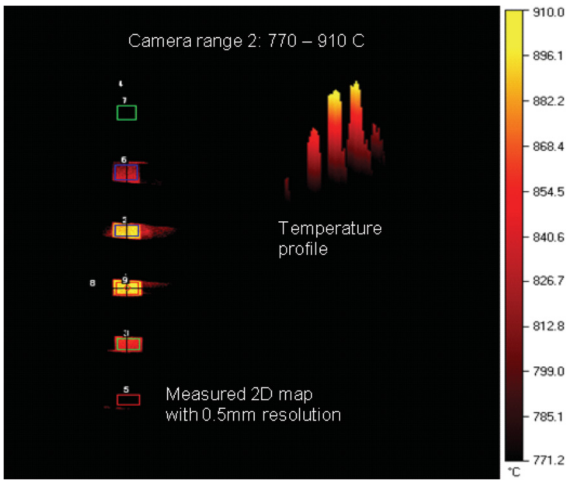

Fig. 3: Example of temperature distribution mapping during permeation tests

II.A. Test samples

The three alloys tested for hydrogen permeability are Incoloy 800H, Inconel 617, and Haynes 230. They were purchased from a commercial vendor (Century Tubes, Inc.) and tested after cleaning but without further surface conditioning. The alloy tube stock was obtained in two wall thicknesses, nominally 0.010 and 0.030 in. (0.254 and 0.762 mm). The diameter of the tube stock is 0.25 in. (6.35 mm). The actual wall thickness of the alloy tube stock was determined by scanning electron microscopy (SEM) of radially sectioned and polished samples.

The sample configuration is shown in Figure 4, and consists of a 4 to 6-in.-long test section of Incoloy 800H, Inconel 617, or Haynes 230 tube welded to upper and lower thick-walled barrels of Inconel 600. The Inconel 600 tubes are 0.75 in. (19.1 mm) outer diameter and 0.25 in. (6.35 mm) inner diameter; the tubes were gun-drilled from round bar stock. The center portion of the thin-walled test section is the heated permeation zone. The thickness of the barrels and their location outside the heated zone ensure that they do not contribute measurably to the flux of permeating gas. The thick-walled barrel sections of the test sample are sealed by compression O-ring seals to the upper and lower mounting flange of the sample chamber, thereby isolating the primary flow loop from the secondary flow loop.

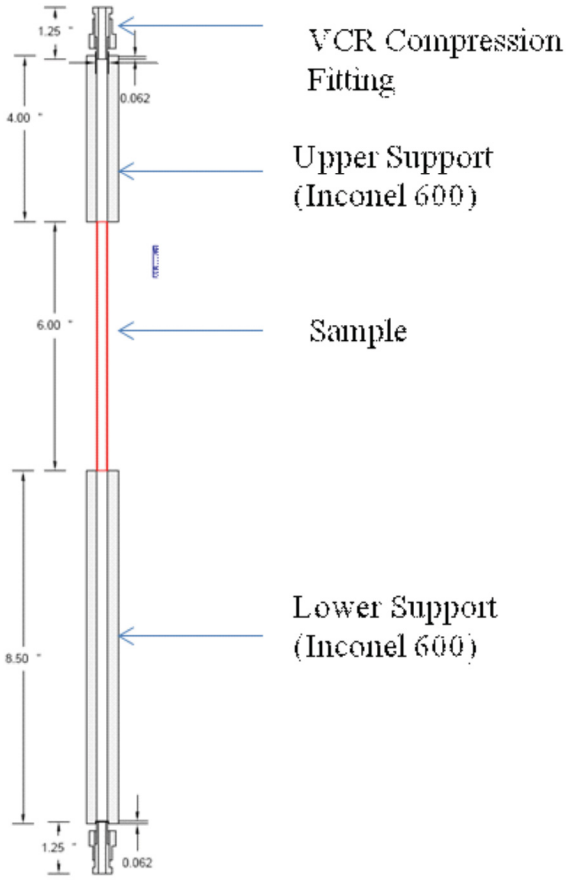

Fig. 4: Configuration of the test samples

III. INITIAL RESULTS AND DISCUSSION

Steady-state hydrogen permeation through thin-walled metallic tubes can be described by a simple permeation model [4,5,10,11]:

$$J_{H_2} = \frac{K_{H_2}}{x}(\sqrt{p_1} - \sqrt{p_2}) \qquad \text{(eq. 1)}$$

where J_{H2} is the hydrogen flux through the sample, K_{H2} is the hydrogen permeability of the sample, x is the thickness of the sample, p_1 is the input pressure of hydrogen permeation gas on the primary (high partial pressure) side of the sample, and p_2 is the pressure of permeated hydrogen on the secondary side. The hydrogen flux through the sample is measured as the area-normalized volumetric flow rate of the permeated hydrogen:

$$J_{H_2} = \frac{C_{H_2} \cdot \dot{V}_{He}}{A} \qquad \text{(eq. 2)}$$

where C_{H2} is the hydrogen concentration in the He sweep flow, V_{He} is the secondary loop flow rate and A is the heated are of the sample. Combining eq. 1 and eq. 2, the material permeability is calculated as:

$$K_{H_2}(T) = \frac{c_{H_2} \cdot \dot{V}_{He} \cdot x}{A \cdot (\sqrt{p^1_{H_2}} - \sqrt{p^2_{H_2}})} \qquad \text{(eq. 3)}$$

and expressed in Arrhenius form as:

$$K = K_0 \cdot e^{-\frac{Q}{RT}} \qquad \text{(eq. 4)}$$

once the assumed dependence from the input partial pressure (Sievert's Law) is verified. The initial results for the 800H and 617 alloys are presented in Figure 5 and Figure 6 respectively and compared to the literature data listed in the introduction. The tests have been performed with three different certified mixture of hydrogen in helium on the primary side, with hydrogen partial pressures of 100 ppm, 1000 ppm and 10000 ppm. However, permeability data obtained with the lowest input concentration showed a significantly higher statistical error in the measured concentration due to the low signal to noise ratio of the mass spectrometer. This sensitivity issue will be overcome by the planned use of tritium, for which radiation counters can be applied. The current set of hydrogen results is therefore derived in the 1000 ppm to 10000 ppm range. The temperature range consider is between 700 and 950 C.

The Incoloy 800H permeability data from this work compare well with published literature values for Incoloy 800 and 800H (the two alloys have the same elemental composition specifications and differ only in heat treatment) despite the lower hydrogen partial pressure range in which they were obtained. This means that the permeation processes are essentially the same. The Arrhenius plot of the permeability data obtained from this work has a pre-exponential constant similar to the low end of the published range of values and exhibit a slightly higher activation energy and therefore slightly higher temperature dependence. This is likely due to a better account of the temperature distribution in the experimental set up due to the two dimensional capability of the infrared system.

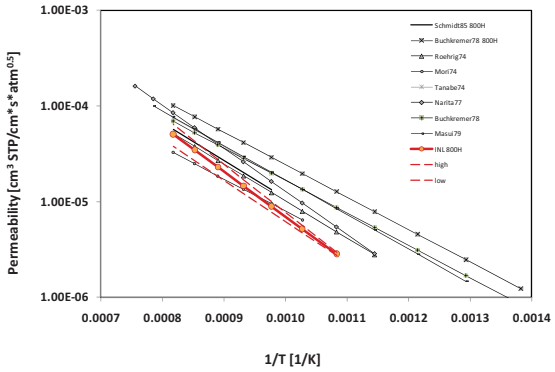

Fig. 5: alloy 800H permeability data

A similar analysis can be derived for the Inconel 617 permeability compared with references [7, 5] obtained at higher pressure ranges. Also in this case the Arrhenius plot shows a higher activation energy. Incoloy 800H has significantly lower nickel and higher iron content, 30.8 and 46.6 wt%, respectively in comparison with 53 wt% Ni for Inconel 617. The results of this work show that while the permeation activation energies of the two alloys are similar, the permeation constants for Inconel 617 is about 50% greater than the permeation constant for Incoloy 800H, as shown in Figure 6. These results are consistent with the observation that hydrogen permeability of alloys generally increases with

increasing nickel content, although the correlation is not a sensitive one [3,14].

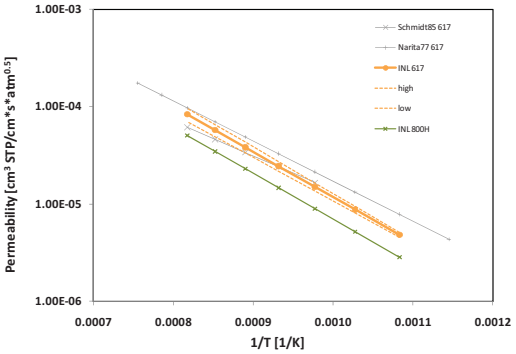

Fig. 6: alloy 617 permeability data

III. CONCLUSIONS

A system was designed, fabricated, and tested at the Idaho National Laboratory to measure the permeability of metal alloys at high temperatures. The operation of the system was tested and validated using Inconel 800H, for which hydrogen permeation data have been published in several journal articles. Using this system, the temperature-independent permeability constant and permeation activation energy were found to be 0.359 cm3 hydrogen (STP)/cm·sec·atm1/2 and 21.6 kcal/mol, respectively, comparable to the published values for this alloy.

The system was then used to measure the permeability of Inconel 617 at hydrogen partial pressures of 10-3 and 10-2 atmospheres, significantly below the hydrogen pressures used in the published data. The temperature-independent permeability constant and the activation energy were measured as 0.539 cm3 hydrogen (STP)/cm·sec·atm1/2 and 21.3 kcal/mol, respectively, in good agreement with the two sets of published values obtained at hydrogen pressures at one atmosphere and greater. These results indicate that hydrogen permeability of Inconel 617 is about 50% higher than for Incoloy 800H, and that temperature sensitivity is comparable.

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