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Title: High Temperature Moderator Cladding Report

Author(s): O'Brien, Lindsay Beth
Luther, Erik Paul

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High Temperature Moderator Cladding Report

Lindsay O'Brien and Erik Luther

Summary

The hydrogen permeation system at LANL has been modified and improved to perform high temperature testing of metals and metal/ceramic samples. This will allow us to demonstrate the ability to reduce hydrogen permeation for microreactor materials. For this program, two metals have been chosen for analysis, stainless steel as a base metal and TZM based on its high temperature properties and anticipated higher H permeation resistance. Samples have been fabricated and coated with Al_2O_3 via atomic layer deposition in order to evaluate the potential to reduce hydrogen permeation with a thin layer ceramic coating. Current efforts include literature review of systems and sample fabrication to demonstrate feasibility, future work will focus on collecting hydrogen permeation data.

Introduction

Microreactor technologies will likely utilize high temperature, solid moderators such as hydrides; e.g., zirconium and yttrium hydride. This will allow for operating temperatures to reach much higher than typical light water reactors, which will improve the performance of these reactors. As hydride moderators are expected to de-hydride at temperatures close to these operating temperatures, additional means of containing hydrogen are needed. Cladding the moderator or coatings applied to the moderator is thus of interest in order to limit hydrogen migration.

The goal of this study is to evaluate potential candidates for high temperature claddings or coatings of hydride moderators in order to limit the permeation of hydrogen. A variety of metals, ceramics, and metal-ceramic combinations have been considered on the basis of high temperature properties, nuclear compatibility, and available hydrogen permeation/diffusion data. Due to the limited scope of the effort, two metals and one coating were down selected for testing. A permeation testing rig, previously used to measure the permeation of deuterium through iron-chromium-aluminum (FeCrAl) alloys, was returned to service and modified to extend its capability to testing up to 800°C.

Background

Significant information is available in the literature regarding the hydrogen permeability properties of metals and ceramics. Criteria for consideration were: 1) relatively low hydrogen permeability, 2) relatively high melting temperature, 3) neutron transparency. Neutron transparency is more important for a cladding which is relatively thick vs a coating which is expected to be thin (on the order of microns or less). This evaluation is not exhaustive and additional considerations are relevant, such as chemical compatibility, radiation dependent beahvior etc.

Steels, such as 304L SS, are well understood and characterized, especially in radiation environments. 304L SS has been included in this study due to the ability to compare with the open literature and as a substrate for coatings. TZM is also considered due to available literature data and its high temperature mechanical properties. Although TZM shows reasonably low hydrogen permeation rates at lower temperatures, recent unpublished results indicate that at higher temperatures (>600°C), TZM alone may not show adequate permeability behavior (Reference 1).

FeCrAl alloys such as APM are expected to have good high temperature mechanical properties. Hydrogen permeability data is limited in these alloys, but prior testing performed by LANL, shown in Figure 1, shows similar results to those presented in Reference (2); both results indicate a decreased hydrogen permeation relative to zirconium alloys. FeCrAl was not included in this study due to its limited scope; however, additional investigations into FeCrAl should be considered.

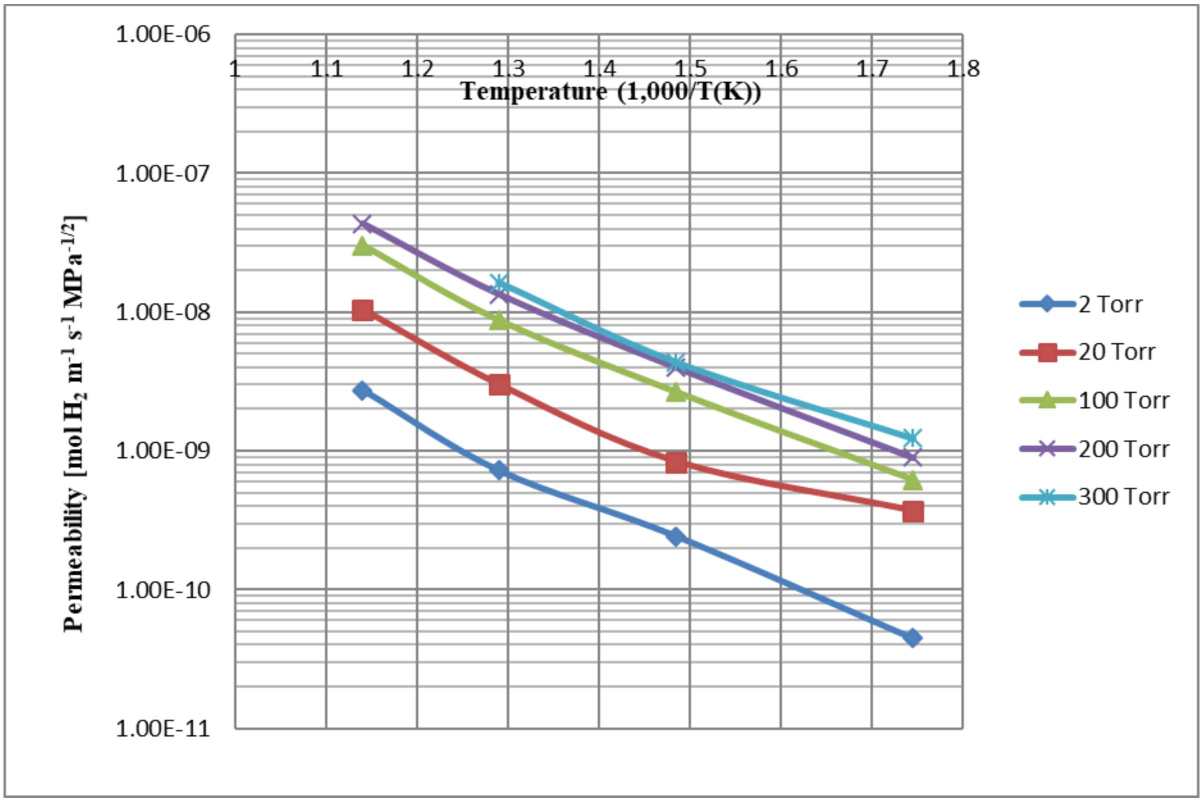


Figure 1 Hydrogen permeability of FeCr13.5Al5Y0.15 (AT35Y2). These results were produced using a "can"-type specimen design.

Due to the relatively poor hydrogen retention capabilities of candidate cladding, low permeability coatings are also considered. Since a successful coating must be hermetic to prevent hydrogen loss, it is recognized that the deposition method for coatings is likely as important as the material chosen. The hydrogen permeability of ceramics (oxides, carbides, nitrides, etc.) have been shown to be relatively low compared to metals particularly at high temperatures. For example, researchers have shown success in reducing the hydrogen permeation of zirconium based alloys with ceramic coatings, References (4-6). In order to be successful in this application properties such as coefficient of thermal expansion and defect density become important. For this limited study, we elected to show preference for the coating method believed to be capable of the most conformal coating. ALD is known to produce thin coatings with limited defects. Thin coatings are likely necessary to minimize thermal stresses due to inevitable, albeit small differences in coefficient of thermal expansion. Once ALD had been downselected, we identified aluminum oxide as the most easily deposited by our partner (Colorado School of

Mines). While we recognize that the CTE mismatch of alumina with stainless or moly is significant and is therefore unlikely to be the best solution, we chose it to prove feasibility of the process.

Permeation Rig

A related program has brought the hydrogen permeation rig back to operating conditions and improved the system. The basic operation of the rig uses a deuterium source on one side of the sample, held at a constant pressure, with a high vacuum (<10^{-7} torr) maintained on the opposite side. The system utilizes a Stanford Research Systems residual gas analyzer (RGA) to measure deuterium, and the RGA is calibrated using certified deuterium leaks. A tube furnace is used to control the sample temperature. A schematic of the rig with the original can-type sample holder is shown in Figure 2.

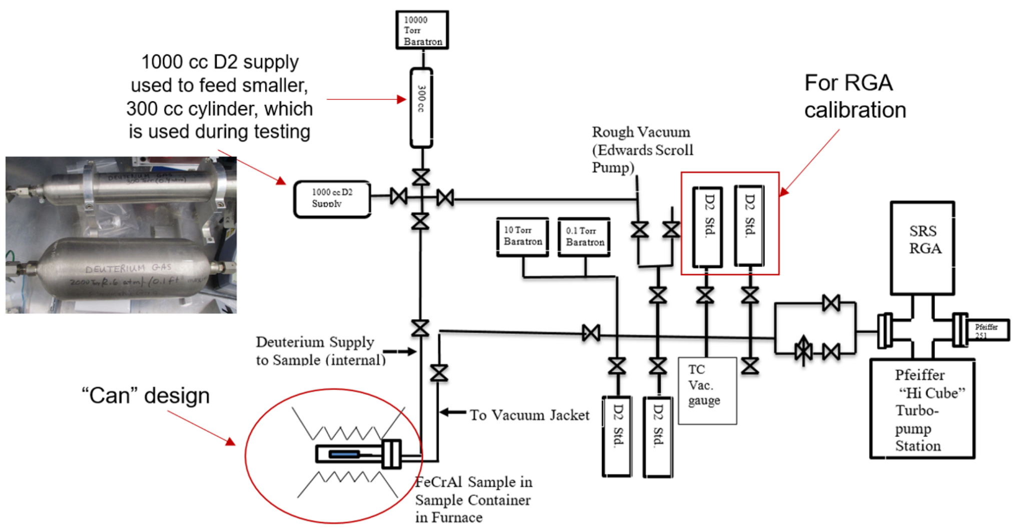


Figure 2. Schematic of Permeation Rig.

Prior testing has been performed utilizing a can-type sample design, shown in more detail in Figure 3. While this sample design was successful, a simpler design has been implemented in order to allow the testing of coatings. The new design does not require any welding, and utilizes a very small quantity of material by replacing a typical Swagelok gasket in a female VCR fitting with a round sample that matches the outside diameter of the gasket. The retainer gasket is used to hold the sample in place during assembly. The new design is shown in Figure 4, and will be integrated into the system via the Swagelok fitting that is shown by a circle in Figure 3.

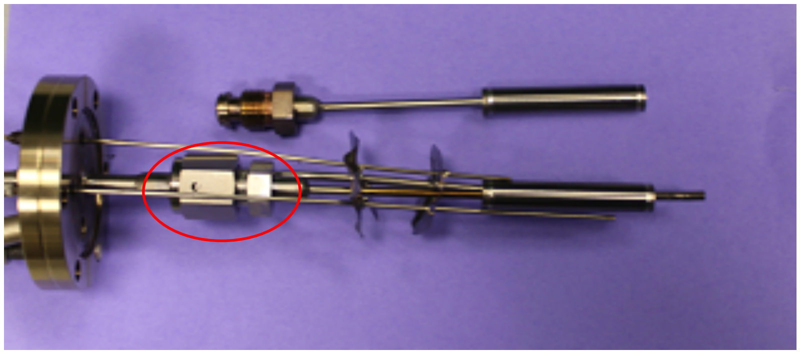


Figure 3. Can-type Specimen Design. The red circle shows where the new VCR fitting specimen assembly will be attached.

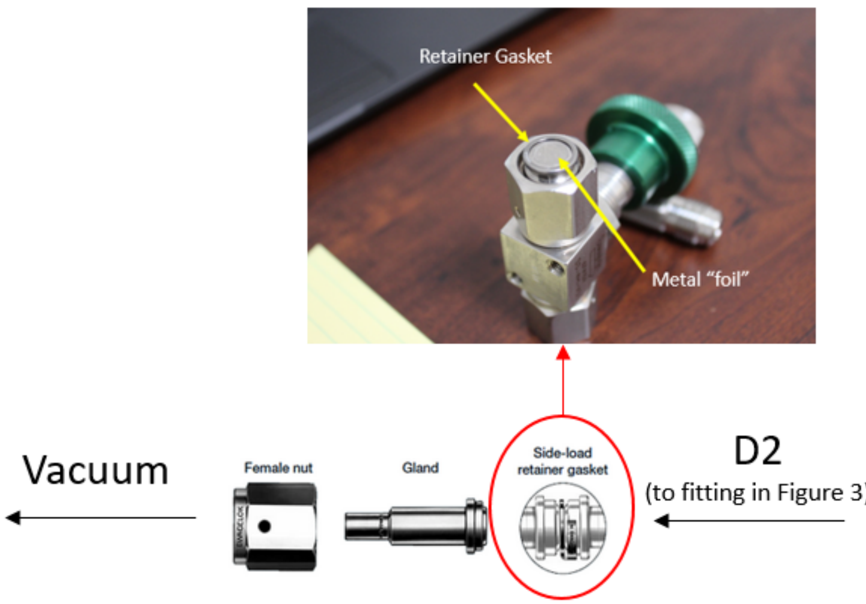
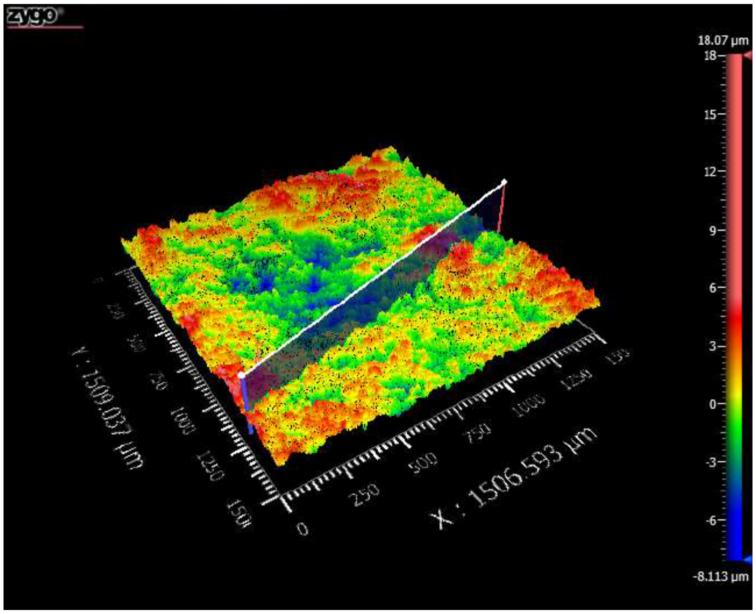


Figure 4. Example of VCR Fitting Design. The sample, shown above and labelled "Metal foil", will be held in place by the retainer gasket.

Progress

Circular blanks (samples) were cut from 304SS and TZM via stamping to a diameter of 3/8" (9.5 mm). ALD builds coatings via a layer by layer process, therefore, it can handle rough sample topography. In this initial effort, no surface preparation such as electropolishing was performed prior to coating only degreasing. Coating of TZM and 304SS was performed to nominal thicknesses of 50 and 100nm. Figure 5 shows the topography of the TZM as prepared sample. No imaging of the 304SS was performed.



TZM,

As received

S_a (µm)1.740

Figure 5. Surface Roughness of TZM Sample. The surface roughness, expressed by the 3D S_a, or average surface roughness.

Preliminary scanning electron microscopy (SEM) investigation of the surface quality after ALD was performed. No conductive coating was applied to the alumina surface, therefore, charging occurred during imaging. Figure 6a shows the TZM sample with a 50 nm deposition. The coating appears to be relatively homogeneous. The 304L SS sample, Figure 6b was significantly different in appearance; the coating appeared to follow machining lines, and non-conductive "streaks" were observed on the surface. These streaks may be the result of a residue or cleaner applied post-ALD, and it is not clear at this time whether these streaks are the result of ALD or some other process.

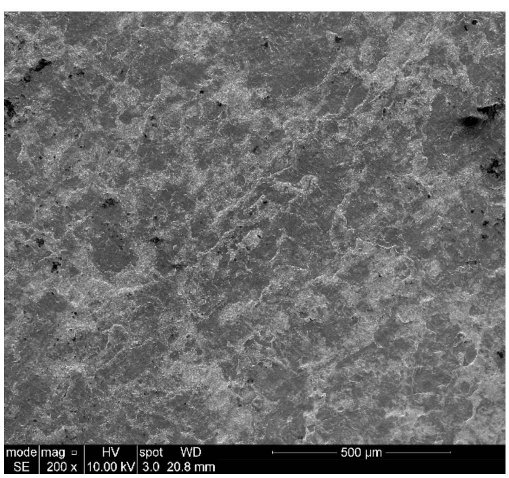


Figure 6a, TZM sample with 50 nm Al_2O_3 coating.

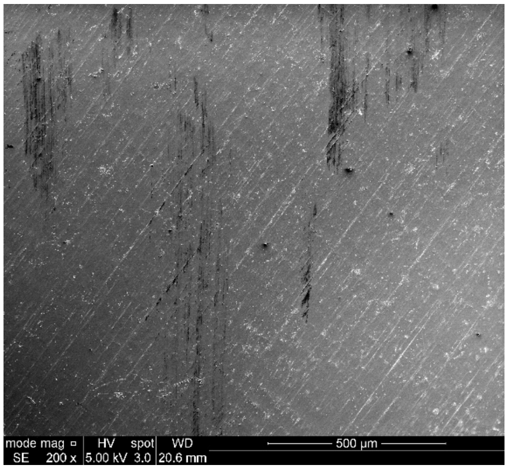


Figure 6b, 304L SS sample with 100 nm Al_2O_3 coating.

Future Work

The hydrogen permeation system will be run up to 800°C in the near future, with uncoated TZM and 304SS samples to confirm that the sample design can maintain vacuum and produce permeability data comparable to the open literature. Ceramic coated samples will be tested to evaluate the ability of the ceramic coating to withstand the load from the VCR fitting. If damage is found to occur, a thin layer of gold will be deposited around the outer diameter of the sample to mate with the VCR edge, which should relieve load on the ceramic. Since gold has very low permeability, it should be possible to deconvolute any effects of this deposition.

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