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Performance and degradation of gas-gap heat switches in hydride compressor beds

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Abstract

A closed-cycle gas-gap heat switch (GGHS) can function as a variable vacuum dewar for metal hydride compressors to reduce nominal input power to each compressor by ~80% over its lifetime without the use of any moving parts. The hydrogen gas pressure in each GGHS is varied with an independent actuator containing ZrNi hydride. As the GGHS must attain low H_2 gas pressure in its insulating "off" state to function reliably, any accumulation of additional gas in the GGHS can compromise the vacuum causing parasitic heat losses within the system. The effects of such accumulations have been found to be a combination of outgassing from metallic components and hydrogen permeation through the walls of the high-pressure compressor bed when it is heated between 290 K and 670 K. This accumulation has been volumetrically measured over a wide range of operating temperatures and pressures on different versions of hydride compressor beds to provide hydrogen accumulation rates in the GGHS. Correlations with literature values are given, addressing the performance of stainless steel in terms of permeation and outgassing of hydrogen gas.

Keywords: Hydrogen storage materials; Intermetallics; Gas–solid reactions

1. Introduction

A gas-gap heat switch (GGHS) provides variable thermal conduction between two objects by changing the pressure of a gas between their surfaces. The thermal conductivity of this gas, physical dimensions of the gap, and properties of surfaces determine the required "ON" (i.e., conducting) and "OFF" (i.e., insulating) state pressure for the heat switches. Since hydrogen has the highest thermal conductivity of any common gas, it is an excellent choice for use in GGHS applications. The reversible pressure changes generated by alternatively heating and cooling appropriate metal hydrides can allow minimal size and mass for the control actuators when such materials are used. Hydrogen gas-gap heat switches have been previously described for high temperature batteries [1,2], sorption cryocoolers that produce cryogenic refrigeration via a closed-cycle Joule–Thomson (J–T) expansion process [3–5], and other cryogenic applications [6]. GGHS actuators using $ZrNiH_x$ as the hydride have recently been developed [7–9] for a 20 K sorption cryocooler. Since this cryocooler has been designed for a minimum operational life of 1.5 years [10], all systems and components (including the gas-gap actuators) must be power efficient, reliable, and robust. Minimal operating temperatures for the gas-gap actuators that can satisfy required heat transfer rates are necessary to lower input power and ensure stability during extended temperature cycling. ZrNi hydride was previously demonstrated [8–11] to satisfy all these requirements for use in the GGHS actuators of the 20 K Prototype Sorption Cryocooler (PSC) compressor elements (CEs).

As a heat engine, the PSC requires efficient heat rejection as well as excellent thermal isolation in order to allow high performance across its performance envelope. This requirement for variable thermal isolation must be met by the PSC-GGHS, wherein the GGHS space surrounds each CE and communicates directly with a small container filled with $ZrNiH_x$ hydride. Temperature control of this hydride container, the "gas-gap actuator" (GGA), allows for reversible pressurization of the GGHS with hydrogen gas. Heat transfer between the CE sorbent bed and its

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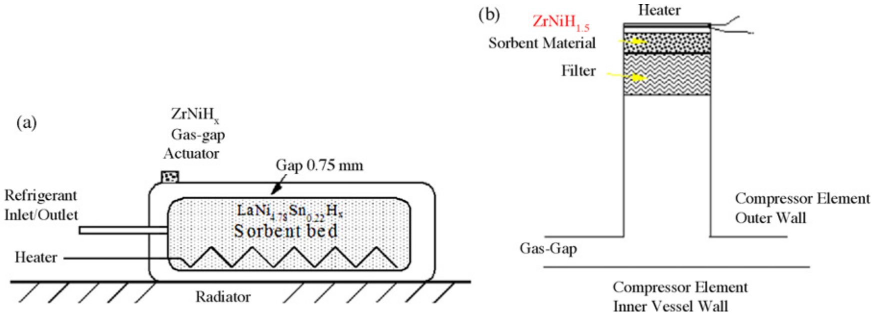

Fig. 1. (a) Schematic representation of a hydride compressor element (CE) showing the LaNi$_{4.78}$Sn$_{0.22}$H$_x$ inner bed, the annular gas-gap heat switch (GGHS) space, and the gas-gap actuator (GGA). (b) Expanded diagram of the GGA, showing connection to the GGHS space. These views are adapted from prior publications by Prina et al. [7–9].

environment is allowed when the GGHS is full, or “on”, and the sorbent bed is isolated when the GGA is “off”, or empty. The GGA thus completely controls the quality of the thermal link between the CEs and the heat rejection radiator. By heating and cooling the GGA to >450 K and <300 K, respectively, the hydrogen pressure in the GGHS may be varied between >1.3 kPa (∼10 Torr) and <1.3 Pa (∼10 mTorr). Schematics of the individual CE/GGHS configurations are shown in Fig. 1, and a completely assembled version of the CE/GGHS is shown mounted on its test radiator plate in Fig. 2.

2. Hydrogen accumulation in the PSC GGHS

2.1. Early findings

Performance evaluation of the PSC GGHS design began with the testing of individual “engineering bread board” (EBB) CEs and was followed by full-up testing of an integrated EBB cryocooler. The results of this testing have been published elsewhere [8,11]. Most importantly, though, it was determined that the GGHS off-state pressure was slowly increasing during the course of running the cooler throughout its operating regime. The extent and behavior of this phenomenon was characterized experimentally, and was determined to be due to hydrogen gas accumulating in the GGHS space from several sources, most significantly due to permeation through the stainless steel walls of the sorbent bed driven by the high-pressure, high-temperature conditions inside, peaking at 5.1 MPa (50 atm) and ∼465 K (192 °C) [12]. This accumulation behavior was seen to agree with literature values for the permeation of hydrogen gas through austenitic stainless steels [13]. Intensive investigations eventually showed that the inner surfaces of the EBB GGHS, which had been plated with layers of electrodeposited nickel and gold for increased thermal performance, were likely sources of the mobile hydrogen and certain other contaminant species, including hydrocarbons, observed during these heating studies [12].

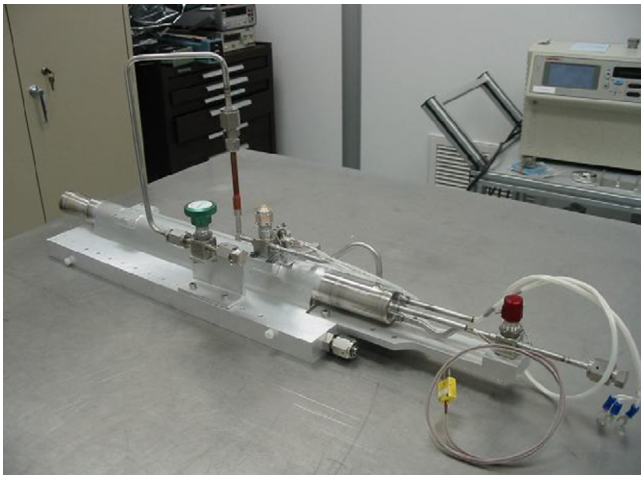

Fig. 2. Photograph of a complete CE mounted on a test fixture with a gas sampling line and valve to monitor pressure in the GGHS during sorbent bed performance and cycling tests.

2.2. Initial pathfinder testing

Following the EBB findings, new CEs were tested with electropolished Al-6061 and SS-316L surfaces without the nickel/gold plating in the GGHS space. The first such CE to be completed was called the “Pathfinder” unit, and was dedicated to thermal performance evaluation and cycle testing of the new GGHS arrangement. To reduce complexity and cost, the Pathfinder CE had no hydriding alloy in its sorbent bed, but was installed in a test facility that would allow the inner bed to be filled with a variety of gas species in order to separate temperature-driven outgassing and permeation behavior from the walls of the inner sorbent bed by excluding through-wall hydrogen permeation as much as possible. Characterizations of hydrogen accumulation behavior were repeated for the Pathfinder unit in a manner essentially identical to that performed previously with the EBB-CE units [12]. Fig. 3 is a summary of the results from this test series, showing various Arrhenius-type relationships of accumulation rate with the Pathfinder’s inner bed temperature. It is notable that the accumulation rates for the “H$_2$-filled” Pathfinder CE at high temperature are comparable with the permeation rates of LeClaire [13], but the Pathfinder’s apparent activation energy (E_a) of 51 kJ/mol for these data is much lower than LeClaire’s reported 65 kJ/mol E_a value. The Pathfinder’s inner bed was also filled with helium gas to isolate the effects of outgassing from metallic structures in the GGHS. Once the overwhelming effects of through-wall hydrogen permeation were eliminated by this procedure, additional detail was revealed in the accumulation rate data. As

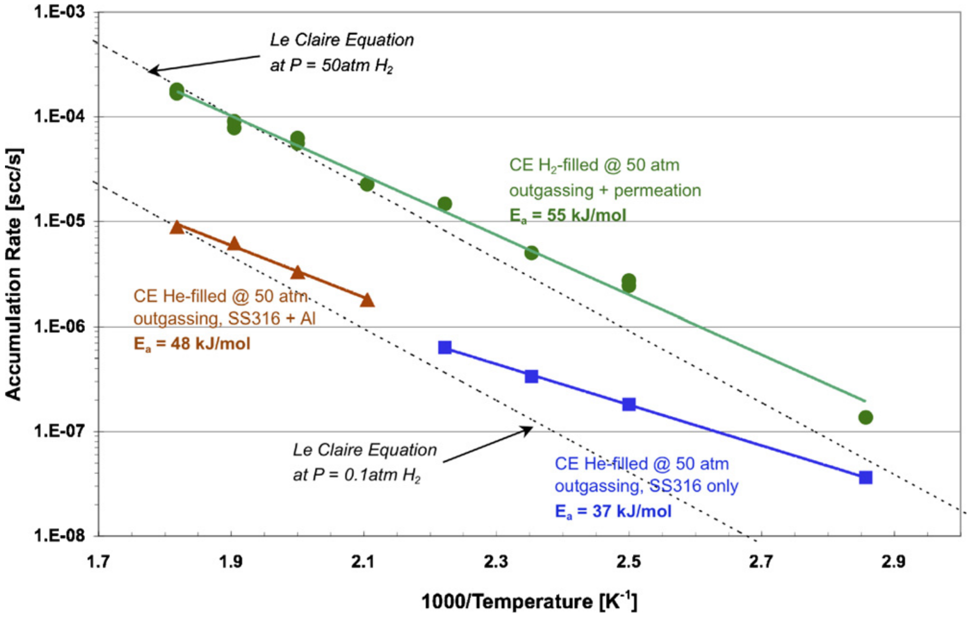

Fig. 3. Hydrogen accumulation data from the first Pathfinder test series, showing the isolation of outgassing- and permeation-dominated behavior. The two different outgassing regimes shown (37 kJ/mol vs. 48 kJ/mol) are thought to show the effects of increased outgassing contributions from additional surfaces in the GGHS as the structure is heated to higher temperatures. Note the rates for outgassing + permeation, which compare favorably at higher temperatures to predictions based upon hydrogen permeation rates in austenitic stainless steels as reviewed by LeClaire [13].

shown in Fig. 3, these data suggest two different regimes; while generally indicating a trend that increases with inner bed temperature, data below approximately 460 K (∼190 °C) show an E_a value of 37 kJ/mol, while data above this temperature indicate a higher value of 48 kJ/mol. This change in behavior is thought to be due to an increased outgassing contribution from ancillary aluminum components in Pathfinder's GGHS space at higher inner bed temperatures. While hydrogen accumulation effects may be dominated by outgassing from the stainless steel walls of the heated inner bed at low temperatures (e.g., below 190 °C), increased temperatures promote heating of other surfaces, including the aluminum outer shell of the Pathfinder CE. These additional outgassing sources may be the cause of the rate shift seen at higher temperatures.

The Pathfinder unit demonstrated, as well, the long-term effects of accumulation on the "off" state of the GGHS during temperature- and pressure-cycling of the unit. After 2509 cycles that simulated GGHS conditions during sorption cooler

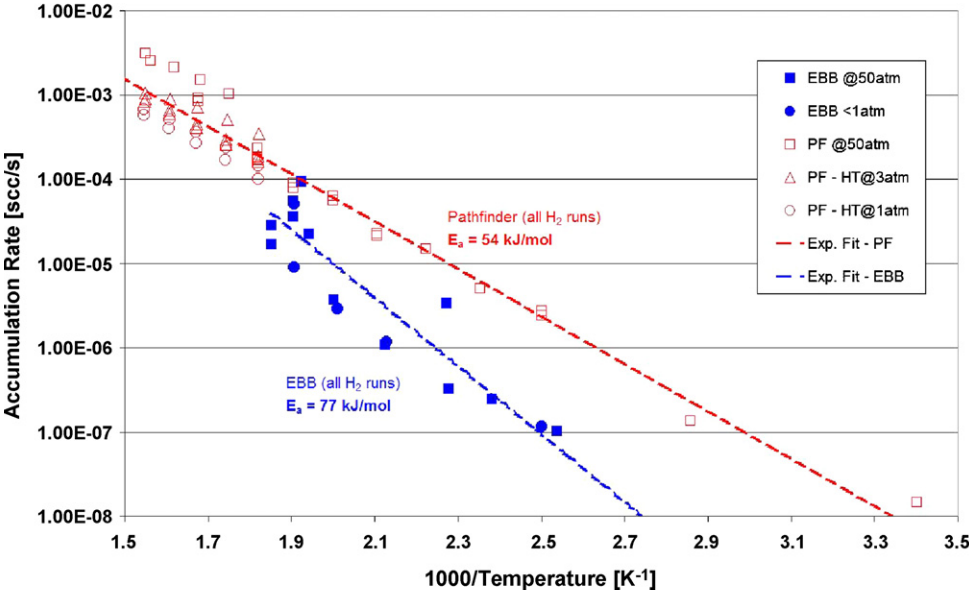

Fig. 4. Hydrogen accumulation data from the "High-T" Pathfinder test series, showing high-resolution runs at the high-temperature end of the scale (upper left), which were made at varied hydrogen source pressures. These data also include all lower-temperature hydrogen permeation data from the earlier Pathfinder series. Data from the earlier EBB test series are also included for comparison; the higher E_a values (77 kJ/kmol vs. 54 kJ/kmol) are thought to reflect inhibited permeation due to the EBBs gold plated GGHS surfaces.

operations [10], volumetric measurements indicated that the $ZrNiH_x$ composition had increased by a Δx of 0.33 from its initial value $x = 1.09$, providing evidence of excess hydrogen uptake during cycling. Furthermore, the "off" state pressure in the GGHS volume was about 0.9 Pa (7 mTorr) with a composition of 54% methane, 27% hydrogen, 10% water vapor, and other trace species in this residual gas as determined by mass spectroscopy. This was the first detailed characterization of operational accumulation behavior, and supplied evidence of further hydrocarbon contamination, which was eventually traced to inefficient cleaning procedures.

2.3. "High-T" pathfinder experiments

For many metal hydride materials (e.g., $LaNi_5H_x$ and its substituted alloys), it is known that repeated desorption/absorption with temperature cycling can present serious problems for long-term use related to capacity reduction as well as greatly distort the isotherms [14]. For most of these hydrides, virtually complete recovery of initial capacity can be achieved through *regeneration*; i.e., the degraded hydride must be annealed at sufficiently high temperatures (i.e., >600 K) to eliminate various defects in the microstructure and reverse the disproportionation reactions [14] that cause a reduction of capacity and other such problems. For such systems that might utilize a GGHS, however, a regeneration event can compromise the switch's "off" state by promoting accumulation of excess hydrogen gas into the closed GGHS vacuum space. Although a hydride-based gas-gap actuator will be open to its GGHS to "soak up" some of the excess hydrogen gas via absorption, it has a fundamentally finite capacity to do.

Furthermore, the performance of the GGA hydride bed is tuned to operate in a particular region of the isotherm plateau, and excess hydrogen in the system would necessarily upset that balance. Clearly, the accumulation expected during a regeneration event would compromise the effectiveness of the GGHS. For this reason, the Pathfinder test series was extended to higher temperatures of 675 K. Results from this test series are shown in Fig. 4, where notably higher H_2 accumulation rates with a smaller E_a value (54 kJ/kmol) were obtained from the Pathfinder unit as compared to the EBB-CE unit (77 kJ/kmol). Comparison of these results suggested that the gold plating of the EBB units, although a certain source of hydrocarbon contamination in their original form, may have been a better barrier to permeation than originally thought.

2.4. Experimental test of regeneration process on GGHS performance

Using previously cycled CE-EBB units [10,11] containing degraded $LaNi_{4.78}Sn_{0.22}H_x$ in the sorbent beds, a regeneration scheme was devised in order to improve the PSCs operational lifetime. Volumetric measurements of the CE sorbent bed and $LaNi_{4.78}Sn_{0.22}H_x$ absorption isotherms at 293 K demonstrated that a 98% recovery requirement of total storage capacity could be obtained [15]. The optimal sorbent bed regeneration profile consisted of 2 h linear heatup to ∼670 K, a temperature soak for 4–5 h with H_2 pressure held below 0.3 MPa (3 bar), and a cooldown to ∼280 K over several hours.

The impact of these regeneration procedures on the performance of the GGHS was assessed using a spare CE identical to the one shown in Fig. 2. Following each step in a regeneration treatment at increasing temperature and time duration, the parasitic heat loss through the GGHS in the "off" state was monitored as shown in Fig. 5. Volumetric measurements of the GGA hydride after completion of these experiments gave a Δx increase of 0.23, indicating hydrogen accumulation equivalent to over 2 months of normal PSC operation. Furthermore,

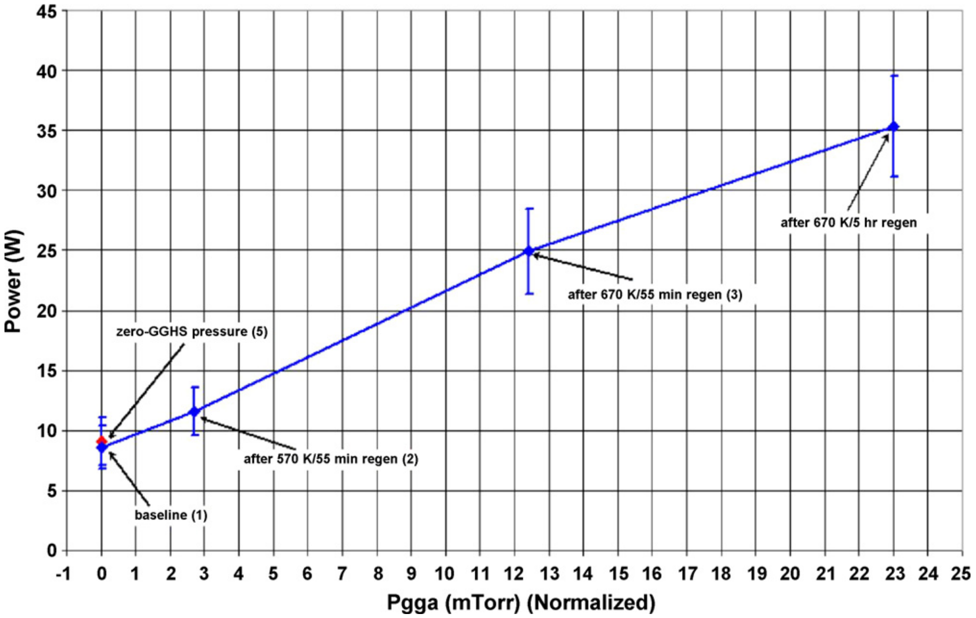

Fig. 5. Impact on the heater power required to maintain the sorbent bed at 445 K following each of several individual regeneration steps. Rise in steady-state power is attributed to reduced isolation in the GGHS due to accumulation of gas in the off-state.

regeneration temperatures in excess of those previously reached during processing and bake-out also produced relatively large amounts of methane and carbon monoxide from previously undetected hydrocarbon contaminant sources in the GGHS; mass spectroscopy indicated between 60% and 70% total content of carbon-bearing species. This residual, non-absorbed gas directly impacts the off-state isolation requirement of the GGHS, yielding increasingly large parasitic losses as shown in Fig. 5.

3. Conclusion

Hydrogen accumulation in the PSC-GGHS is a complex issue. Electroplated Au/Ni barrier coatings can be a rich H_2 outgassing source, but can also suppress permeation-driven accumulation to a certain extent. Activation energies for outgassing and permeation processes in the GGHS are seen to depend strongly on surface properties. Significantly, aqueous electro-processing of metallic structures for high-vacuum systems is seen to present a contrasting set of problems for contamination control and permeation management issues—how best to pre-process these materials is a question that still remains unresolved.

Gas-gap heat switch systems exhibit delicate tradeoffs in terms of overall design and performance. Vacuum bake-out and surface preparation is a sensitive issue that should be performed in excess of expected operating conditions (i.e., higher temperatures), specifically to eliminate mobile contaminant species before operation, especially in the presence of strongly reducing agents such as hydrogen. Barrier coatings can suppress permeation through metallic structures, but can be an outgassing source if not carefully applied. For certain high temperature/pressure applications, like the PSC, it may be found that their use is necessary for controlling H_2 permeation into GGHS vacuum spaces. Since hydrogen accumulation effects may be ultimately unavoidable, hermetically sealed GGHS systems present little opportunity for mitigation of accumulation and/or contamination effects, although including actuators for venting excess gases can significantly increase system mass and complexity. Where permanently sealed GGHS systems are unavoidable, larger hydride actuators can provide additional capacity for H_2 outgassing and permeating from various sources; however, these larger GGAs will suffer from slow dynamic response and require more actuation power. Design and performance trades must be carefully considered in all cases.

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