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Development of metal hydride beds for sorption cryocoolers in space applications

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Abstract

The development of hydrogen sorption cryocoolers over the past 30 years is briefly reviewed. The behavior of the metal hydride sorbent beds used in the sorption compressors dominates both the performance and reliability of these closed-cycle Joule–Thomson cryocoolers. Improved compressor elements have been recently designed to minimize their input power requirements and to enhance hydride durability during extended temperature cycling while in operation. ZrNi hydride is used to provide variable gas pressure in the gas-gap heat switches for each compressor element. Characterization tests have been performed on the compressor elements built for an engineering breadboard (EBB) cryocooler to evaluate the behavior of both the sorbent bed and gas-gap switches under conditions simulating flight operation for the future Planck mission of the European Space Agency (ESA). Operation of the Planck EBB sorption cryocooler has produced a cooling capacity of 1.0–1.7 W at a temperature of 17.7 K during initial laboratory tests.

Keywords: Hydrogen storage materials; Gas–solid reactions; Heat conduction

1. Introduction

In 1972 Van Mal reported the first liquefaction of hydrogen via Joule–Thomson (J-T) expansion with a metal hydride sorption compressor [1,2], which utilizes a thermochemical cycle whereby sorbent beds are heated to provide gas at high pressure to the inlet of the J-T expander while the gas leaving the cryostat is recovered in a cooled sorbent bed. This method eliminates essentially all of the vibrations and electromagnetic sources that are inherent with mechanical compressors. Hence, these sorption cryocoolers are very attractive for space applications [3] where reliable and stable operation is very important. Operation of a sorption compressor is inherently an intermittent process with generation of high-pressure gas from a hot sorbent bed alternating with absorption by a cool bed. Continuous refrigeration is achieved by the sequential phasing of several sorbent beds. Fig. 1a illustrates the sorption cycle using the pressure–composition–temperature (PCT) isotherms [4] for the representative $LaNi_{4.8}Sn_{0.2}H_x$ system. The general configuration of sorption cryocooler that would be suitable for producing liquid hydrogen during a space flight is shown in Fig. 1b. Since the sorbent hydride and its container must be heated together, a significant amount of power is needed during heat up and desorption that is rejected by radiators during the compressor element cool down. Gas gap heat switches [5] can minimize excessive heat loss to improve efficiency and reduce the input power.

Over the years various organizations have built and tested hydride sorption cryocoolers. These demonstrations [1,2,6–13] are summarized in Table 1. Several important parameters are presented in this table, while further details on the configurations and performance of these systems can be found in the original references. Although the continuous production of liquid hydrogen has been the primary focus for most of these cryocoolers, the possibility of the periodic formation of solid hydrogen at ~10 K was seen as a desirable goal for rapid, on-orbit cooling of long wavelength infrared (LWIR) sensors for space surveillance applications [3]. The feasibility of this approach was proven in the laboratories at Aerojet [3,9] and the Jet Propulsion Laboratory (JPL) [10] that ultimately led to the development of the Brilliant Eyes Ten-Kelvin Sorption Cryocooler Experiment (BETSCE) [14,15] flown on a

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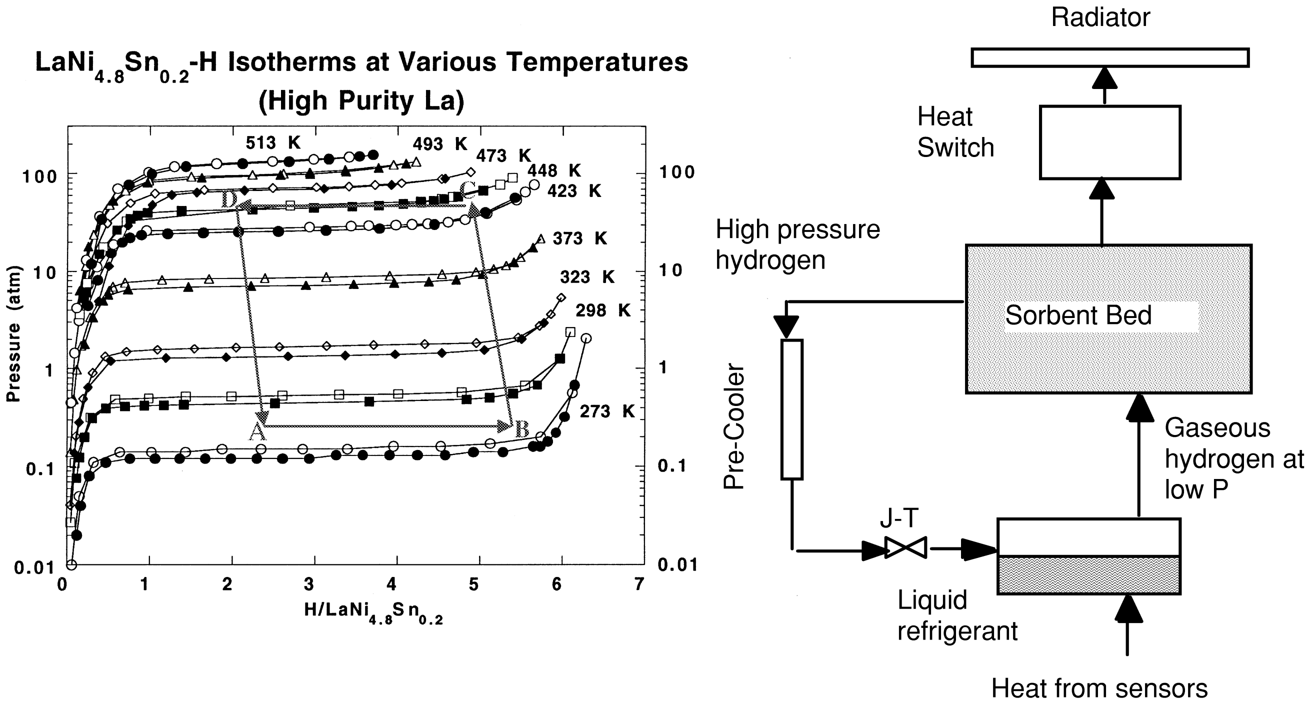

Fig. 1. (a) The idealized sorption cycle for the 18 K Planck compressor superimposed on the isotherms for the $LaNi_{4.8}Sn_{0.2}$ hydrogen where line A–B is absorption and line C–D is desorption. (b) Schematic diagram of a single-stage sorption cryocooler producing liquid hydrogen.

Space Shuttle mission in 1996. JPL is currently developing a metal hydride sorption cooler [16] to provide continuous 1.1 W cooling at ~18 K to the ESA Planck Mission for high resolution mapping of the cosmic microwave background. Initial operation of an engineering breadboard (EBB) version of this JPL cooler was successfully started

Table 1
Summary of laboratory demonstrations of metal hydride–hydrogen sorption cryocoolers that had produced cryogenic liquid or solid

Organization	Philips	JPL	Aerojet	Kawasaki	Aerojet	JPL	Acad. Science	JPL
(Country)	(Netherlands)	(USA)	(USA)	(Japan)	(USA)	(USA)	(PRC)	(USA)
Year reported	1972	1984	1986	1989	1994	1994	1995	2002
Type	Continuous	Continuous	Continuous	Continuous	Periodic	Periodic	Continuous	Continuous
Number beds in compressor	3	3	4	6 (each with 3 alloy beds)	1 or 2	1	3	6
Sorbent alloy[a]	$LaNi_5$	$LaNi_5$	$LaNi_5$	$MmNi_{4.75}Al_{0.25}$, $DiNi_5$, $LaNi_{4.75}Al_{0.25}$	Vanadium, $La_{1.1}Ni_{4.7}Sn_{0.3}$, ZrNi	ZrNi	$LaNi_5$	$LaNi_{4.78}Sn_{0.22}$
Compressor parameters								
Absorption temp. (K)	290	313	273	293	280	280	290	270
Desorption temp. (K)	430	393	402	353	373–500	523	363	470
Low pressure (MPa)	0.4	0.4	0.4	<0.05–0.1	0.03–0.5	0.00013	0.3	0.06
High pressure (MPa)	4.5	6.0	3.4	4.0	0.1–0.5	N.A.	1.4	5.0
Input power (W)	~1000	162	N.A.	N.A.	N.A.	N.A.	N.A.	364
Precooling method	LN2	LN2	LN2	LN2	LN2	LN2	LN2	GM cooler
Precooling temp. (K)	78	77–80	80	78	65	63–78	78	45–60
H_2 flow rate (mg/s)	10	2.7	5.0–28	15	18	0.6	28	5.9
Type J-T valve	Capillary tube	Check valve	Spring-loaded ball	N.A.	Metering (modified)	Orifice (0.41 mm)	N.A.	PSSSF[b]
Cold tip parameters								
Temperature (K)	26	14–29	26.6	16.5–20.4	17.1–30	9.3–11.0	25	17.7
Cooling capacity (W)	0.6–0.8	0.14	0.21	1.2 (20 K) 0.6 (17.5 K)	N.A.	0.15 (solid H_2)	0.4	1.0–1.7
Refs.	Van Mal [1,2]	Jones [6]	Karperos [7]	Kumano [8]	Bowman [9]	Wu [10]	Zhang [11]	Prina [12,13]

[a] Mm, Misch metal, natural mixture of rare earth metals (mostly, Ce and La); Di, didymium—another unprocessed rare earth metal mixture.
[b] PSSSF, porous sintered stainless steel filter.

in January 2002 with launch of the Planck spacecraft currently planned for 2007.

2. Description of BETSCE cryocooler

BETSCE was the first space-flight demonstration [15] of chemisorption cryocooler technology and was undertaken to develop a complete closed-cycle periodic 10 K sorption cryocooler suitable for operation in earth orbit. The BETSCE instrument contained three distinct metal sorbent beds [14]. The fast absorber sorbent bed containing $LaNi_{4.8}Sn_{0.2}H_x$ was able to absorb the excess hydrogen gas and dissipate the heat of reaction during the 2-min cooldown phase while maintaining the backpressure typically below 0.35 MPa. The low pressure sorbent bed containing $ZrNiH_x$ demonstrated that it could solidify the hydrogen within the J-T reservoir in less than 10 s and to produce temperatures as low as 9.44 K. Finally, the high pressure sorbent bed, which contained $LaNi_{4.8}Sn_{0.2}H_x$ in an Al foam matrix, compressed hydrogen from pressures around 0.07 MPa to greater than 10 MPa for transfer into the high pressure storage volume allowing repeated periodic J-T expansions [14,15]. The BETSCE instrument was launched into orbit on Shuttle Mission STS-77 (Orbiter Endeavour) in May, 1996. Fig. 2 shows the initial on-orbit 10 K cooldown for BETSCE. The cooldown from 70 to 11 K was completed in less than 2 min, and a 100 mW heat load was sustained at below 11 K for 10 min, thus meeting the primary system performance objectives for the BETSCE flight [15]. The BETSCE hardware development experience and the BETSCE ground and flight test results have led to improved sorption coolers. The BETSCE instrument was essentially an adaptable test bed that allows extensive characterization testing of an experimental 10 K sorption cryocooler system within the highly constrained Shuttle safety and interface requirements. Microgravity operation was found to have no adverse effects on the ability to retain liquid and solid hydrogen, and the sorption compressors demonstrated similar heat and mass transfer characteristics as determined in ground testing before and after its space flight.

3. Hydride compressor beds for the Planck 18 K sorption cooler

JPL is currently developing hydrogen sorption coolers [16] to provide continuous cooling at a nominal temperature about 18 K. The cooler is sized to achieve a 2-year operating life. Each cooler input power is predicted to be 520 W at end-of-life plus an additional 30 W estimated for the cooler electronics. Passive check valves that are protected by porous sintered disc filters to prevent leaks by entrapped particles direct hydrogen flow in the cooler. The principal cryostat components include the J-T expander and two liquid reservoirs interfaced [16] to the Planck instruments and a third reservoir used to boil off excess liquid hydrogen. The compressor contains six compressor elements (CE) filled with $LaNi_{4.78}Sn_{0.22}$ alloy. The CEs are independently heated and cooled through a series of heat-up, desorption, cool-down, and absorption steps to provide compression and circulation of the hydrogen refrigerant gas during a closed-cycle J-T process that generates liquid hydrogen in the cryostat. The CEs are directly mounted to a radiator that is sized to reject the heat from the input power and exothermic hydrogen absorption by the alloy at $270\ K+10\ K/-20\ K$. Each CE uses a gas gap heat switch to isolate the sorbent bed during heating and desorption while permitting heat removal during cool down and absorption. The gas gap actuator (GGA) uses $ZrNiH_{\sim 1.5}$ to reversibly vary hydrogen pressure between >1.3 kPa and <1.3 Pa by alternately heating and cooling this hydride between >450 and <300 K, respectively.

A cross sectional view of the assembled compressor element is shown in Fig. 3 and illustrates the 0.75 mm gas gap separation between the inner sorbent bed and outer

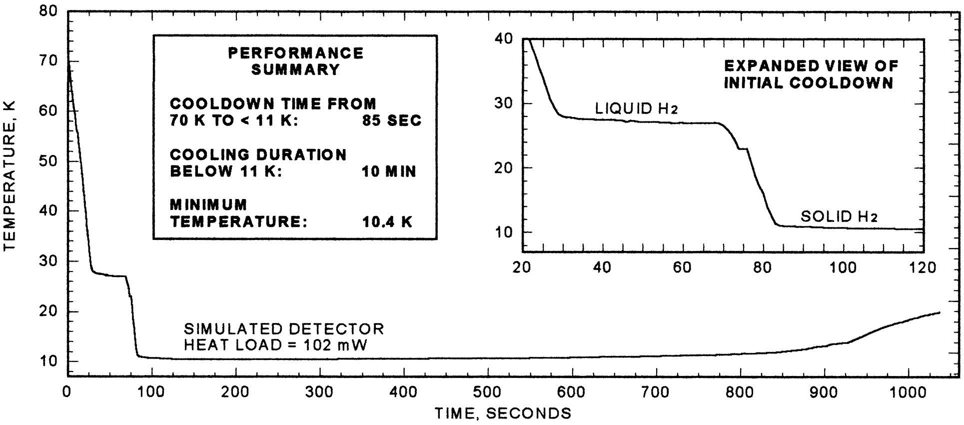

Fig. 2. Summary of the behavior for the BETSCE cryocooler during its on-orbit 10 K cooldown during a Space Shuttle flight (Ref. [15]).

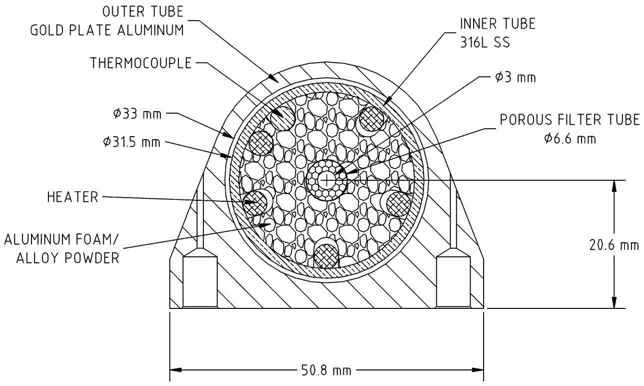

Fig. 3. Cross sectional view of the Planck EBB compressor element showing the gas gap spacing of 0.75 mm between inner bed that contains the sorbent alloy in an Al foam matrix and the outer housing.

housing attached to the radiator. The porous filter tube ensures that hydride powder contained in the Al foam does not migrate from the sorbent bed during the temperature and pressure cycling. Tight physical contact of the Al foam with the inner surface of the tube wall provides heat transfer from the sorbent bed to the gas gap. The sorbent bed is attached to the outer housing only at the ends using supports that limit parasitic heat transfer. A photograph of an assembled CE with its GGA attached is shown in Fig. 4. A more comprehensive description of the CEs fabricated for the EBB cryocooler along with extensive test results have been recently reported [17].

The Planck compressor elements will undergo ~20,000 cycles between 270 and 470 K during ground testing and flight operation [16]. The degradation of the sorbent and gas gap hydrides has been a concern and considerable efforts have been made to evaluate their behavior during accelerated aging studies [17,18]. The CE design includes storage margin that accounts for anticipated [16] rates of hydride degradation. The stoichiometric alloy (i.e. [Ni+Sn]/La ratio=5.0) used in the EBB-CE sorbent beds has smaller rates of degradation than previously available material [18] used in earlier Planck sorbent beds. To date there has been no indication of hydride degradation on the performance of the EBB compressor elements during their characterization tests [17] or initial operation of the EBB cooler [12,13].

Operation of Planck CE beds over several thousand cycles has shown [17] methane in the concentration range of 200–370 ppm relative to the total hydrogen content. The beds had been initially filled with research grade hydrogen gas (i.e. 99.999+% purity) that was further purified by flowing it through a chemical purifier and a carbon cold trap cooled in liquid nitrogen. Hence, the impurities seen after cycling were probably generated from residual hydrocarbons on surfaces of filters, foam, and other components even though vacuum and purge gas cleaning was performed during activation. The hydride may act as a catalyst for the conversion of condensed impurities into methane, water, and CO. Since all these molecular species will form solids well above the temperature of liquid hydrogen, they would likely cause plugging at the J-T expansion valve. The Planck sorption coolers contain chemical purifiers/getters and a carbon trap cooled to 50 K to remove these condensable species from the hydrogen gas before entering the cold system and the J-T valve region [16]. A combination of initial cycling, evacuation and refilling with pure hydrogen may prove to be a viable means of eliminating long-term creation of methane and the other species.

Since the OFF-state (i.e. thermal insulating) pressure in the gas gap must lie below 1.3 Pa to minimize excessive parasitic heat leaks [5] to the outer shell and radiator, hydrogen outgassing or permeation from the heated sorbent bed is a serious issue. Because the $ZrNiH_x$ gas gap sorbent was configured to work in the middle of its plateau region during heat switch cycling, it can accommodate a certain amount of additional hydrogen without significant performance impact. However, its capacity is limited and increasing the mass and size of the actuator will require additional power to activate the heat switches. Consequently, quantitative assessment of the amount of hydrogen has become imperative before the design of the compressor elements is finalized and the flight units fabricated. Measurements of the rate of pressure increase

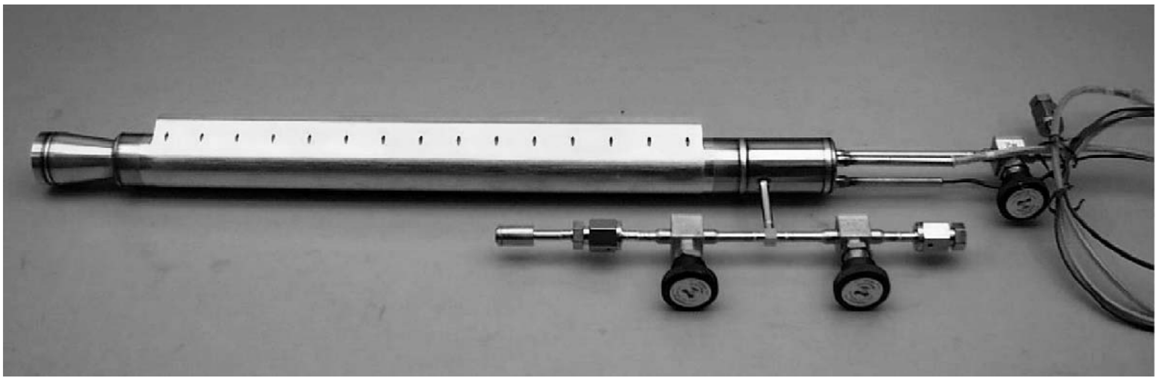

Fig. 4. Photograph of an assembled EBB compressor element with a ZrNi hydride gas gap actuator installed.

in the gas gap volumes of two of the EBB compressor elements have been done under various conditions [17]. The rates range from 4.5×10^{-8} scc/s at 293 K to 1.1×10^{-5} scc/s at 470 K. The information on hydrogen content in the structural materials and outgassing/permeation rates will be used to properly size the gas gap actuators and make any other modifications to provide efficient heat switch performance during the planned operational life of the Planck sorption cooler.

The complete Planck EBB sorption cooler has been built [12] and is undergoing testing to evaluate component performance and interactions prior to fabrication of the flight units. Representative parameters from the first tests on this integrated cryocooler are summarized in Table 1. Additional testing will map the relationships of input power, precooling temperature, and various sorbent bed parameters on cooling capacity and temperature stability at the liquid hydrogen reservoirs.

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References

[1] H.H. van Mal, A. Mijnheer, in: Proceedings 4th International Cryogenic Engineering Conference, IPC Science and Technology Press, Guildford, UK, 1972, p. 122.
[2] H.H. van Mal, Philips Res. Rep. (Suppl. 1) (1976) 1.
[3] B.D. Freeman, E.L. Ryba, R.C. Bowman Jr., J.R. Phillips, Int. J. Hydrogen Energy 22 (1997) 1125.
[4] S. Luo, W. Luo, J.D. Clewley, T.B. Flanagan, R.C. Bowman Jr., J. Alloys Comp. 231 (1995) 473.
[5] M. Prina, J.G. Kulleck, R.C. Bowman Jr., J. Alloys Comp. 330–332 (2002) 886.
[6] J.A. Jones, P.M. Golben, Cryogenics 25 (1985) 212.
[7] K. Karperos, in: G. Green, G. Patton, M. Know (Eds.), Proceedings 4th International Cryocoolers Conference, David Taylor Naval Ship Research and Development Center, Annapolis, MD, 1986, p. 1.
[8] T. Kumano, B. Tada, Y. Tschida, Y. Kuraoka, T. Ishige, H. Baba, Z. Physik. Chem. N.F. 164 (1989) 1509.
[9] R.C. Bowman Jr., E.L. Ryba, B.D. Freeman, Adv. Cryogenic Eng. 39 (1994) 1499.
[10] J.J. Wu, S. Bard, W. Boulter, J. Rodriguez, R. Longsworth, Adv. Cryogenic Eng. 39 (1994) 1507.
[11] Z. Feng, B. Deyou, J. Lijun, Z. Liang, Y. Xiaoyu, Z. Yiming, J. Alloys Comp. 231 (1995) 907.
[12] M. Prina, G. Morgante, A. Loc, M. Schmelzel, D. Pearson, J.W. Borders, R.C. Bowman, A. Sirbi, P. Bhandari, L.A. Wade, A. Nash, in: 11th International Cryocooler Conference, Cambridge, MA, USA, 2002.
[13] D. Pearson, J. Borders, M. Prina, G. Morgante, P. Bhandari, R.C. Bowman, A. Loc, in: 19th International Cryogenic Engineeering Conference, Grenoble, France, 2002.
[14] S. Bard, J. Wu, P. Karlmann, P. Cowgill, C. Mirate, J. Rodriguez, in: R.G. Ross Jr. (Ed.), Cryocoolers, Vol. 8, Plenum, New York, 1995, p. 609.
[15] S. Bard, P. Karlmann, J. Rodriguez, J. Wu, L. Wade, P. Cowgill, K.M. Russ, in: R.G. Ross Jr. (Ed.), Cryocoolers, Vol. 9, Plenum, New York, 1997, p. 567.
[16] L.A. Wade et al., Adv. Cryogenic Eng. 45A (2000) 499.
[17] R.C. Bowman Jr., M. Prina, D.S. Barber, P. Bhandari, D. Crumb, A.S. Loc, G. Morgante, J.W. Reiter, M.E. Schmelzel, in: 11th International Cryocooler Conference, Cambridge, MA, USA, 2002.
[18] R.C. Bowman Jr., C.A. Lindensmith, S. Luo, T.B. Flanagan et al., J. Alloys Comp. 330–332 (2002) 271.