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Assessment of Zr–V–Fe getter alloy for gas-gap heat switches

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Abstract

A commercial Zr–V–Fe alloy (i.e. SAES Getters trade name alloy St-172) has been assessed as reversible hydrogen storage material for use in actuators of gas-gap heat switches. For applications involving hydride compressors in closed-cycle Joule–Thomson sorption cryocoolers, the actuator need to produce a conducting (i.e. ON) state pressure above 670 Pa and an insulating (i.e. OFF) state pressure below 0.13 Pa in the gas-gap switch with switching times ~200 s between the two states. Pressure–composition–temperature isotherms have been measured for the SAES St-172 material to define power efficient baseline performance at appropriate hydrogen concentration for these heat switch actuators. Two prototype actuators containing the SAES St-172 material were built and operated for several thousand cycles to evaluate performance of the metal hydride system under conditions simulating heat switch operation.

Keywords: Hydrogen storage; Zr–V–Fe hydrides; Reversible thermal switch; X-ray diffraction; *P–C–T* isotherms; Hydrogen getters

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1. Introduction

Gas-gap heat switches are devices that provide 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 [1]. Since hydrogen has the highest thermal conductivity, it is an excellent choice for use in a gas-gap heat switch. The reversible pressure changes generated by alternatively heating and cooling appropriate metal hydrides allow minimal size and mass for the control actuators. Hydrogen gas-gap heat switches have been described for high temperature batteries [2,3], sorption cryocoolers that produce cryogenic refrigeration by closed-cycle Joule–Thomson expansion process [1,4–6], and other cryogenic applications [7]. Hydride actuators are currently being developed [5,6] for a 20-K sorption cryocooler to provide cooling of detectors that will map the anisotropy of cosmic microwave radiation for the Planck cosmology mission. Since this instrument [6,8] will be operating on a spacecraft for a minimum duration of 1.5 years in space, all systems and components (including the gas-gap actuators) must be power efficient, reliable, and robust. A summary of the parameters expected for the hydride actuators are given in Table 1. 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.

SAES Getters S.p.A. (Milan, Italy) has developed numerous Zr-based alloys as nonevaporable gettering (NEG) media for the purification of various types of vacuum systems [9] as well as the recovery, purification, and processing of hydrogen isotopes [10–12]. In order to be effective, most of these NEG alloys need to be activated

Table 1
Properties expected from a metal hydride actuator for a gas-gap heat switch to be used in the Planck 20 K sorption cryocooler (from Refs. [5,6,8])

Property/parameter	Desired value/range
ON state pressure (Pa)	>1300
OFF state pressure (Pa)	<1.3
Maximum desorption temperature (K)	<625
Minimum absorption temperature (K)	>280
Input power for ON state (W)	<10
Switch time: OFF→ON (s)	<300
Switch time: ON→OFF (s)	<180
Minimum number of cycles	$>16\,000$

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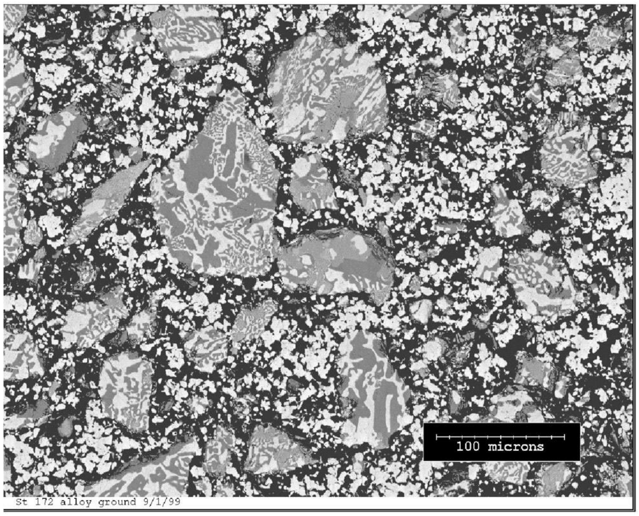

Fig. 1. Photomicrograph of SAES St-172 Zr–V–Fe alloy showing presence of three phases (i.e. brightest is nearly pure Zr and two gray components with differing Zr:V:Fe ratios) in an epoxy matrix (darkest regions).

and operated at temperatures well above 650 K. The SAES getter alloy St-707 with nominal weight composition 70% Zr–24.6% V–5.4% Fe is a mixture of α-Zr metal and the cubic C15 pseudobinary $Zr(V_{0.83}Fe_{0.17})_2$ intermetallic Laves phase [13] and has shown reversible hydrogen sorption at somewhat lower temperature [11,12]. The SAES getter alloy St-172 is a sintered porous mixture of approximately equal portions of Zr metal (Fig. 1) and the St-707 Zr–V–Fe alloy that is described in company product literature [14] as retaining excellent hydrogen sorption capacity and kinetics down to room temperature while needing less stringent activation. This St-172 alloy was thus deemed as a promising candidate for a gas-gap actuator material that could meet the requirements given in Table 1. The remainder of this paper reports our observations on the hydriding behavior of SAES St-172 when used for gas-gap heat switches.

2. Characterization of St-172 getter alloy

The St-172 alloy was obtained from SAES Getters/USA, Inc. (Colorado Springs, CO, USA) in form of sintered pellets mounted on Kovar rods. In an argon-filled glovebox, the active material was separated from its supports and ground into a coarse powder for characterization and filling gas-gap actuators. The alloy was examined by scanning electron microscopy (SEM) with electron-induced X-ray fluorescence capability and powder X-ray diffraction (XRD) with internal silicon standards to identify phase composition and lattice parameters. As expected [13,14], the alloy mainly consisted of an α-$Zr_{0.984}V_{0.01}Fe_{0.006}$ phase ($a = 0.3244$ nm and $c = 0.5166$ nm) and the C15 Laves $Zr(V_{0.84}Fe_{0.16})_2$ phase ($a = 0.7359$ nm). However, we also found a substantial fraction (i.e. ~30+%) consistent with the cubic ($a = 1.2102$ nm) $Zr_3(V_{0.84}Fe_{0.16})_3O_y$ phase [15] as well as small amounts (<1–2%) of the cubic ZrO_y and tetragonal ϵ-$ZrH_{\sim 2}$ phases.

Since the only available hydrogen isotherm data [14] for the St-172 alloy are at hydrogen contents <0.1 mg g_{alloy}^{-1} and $T > 673$ K (see insert in Fig. 2), we have measured the hydrogen absorption and desorption isotherms at greater

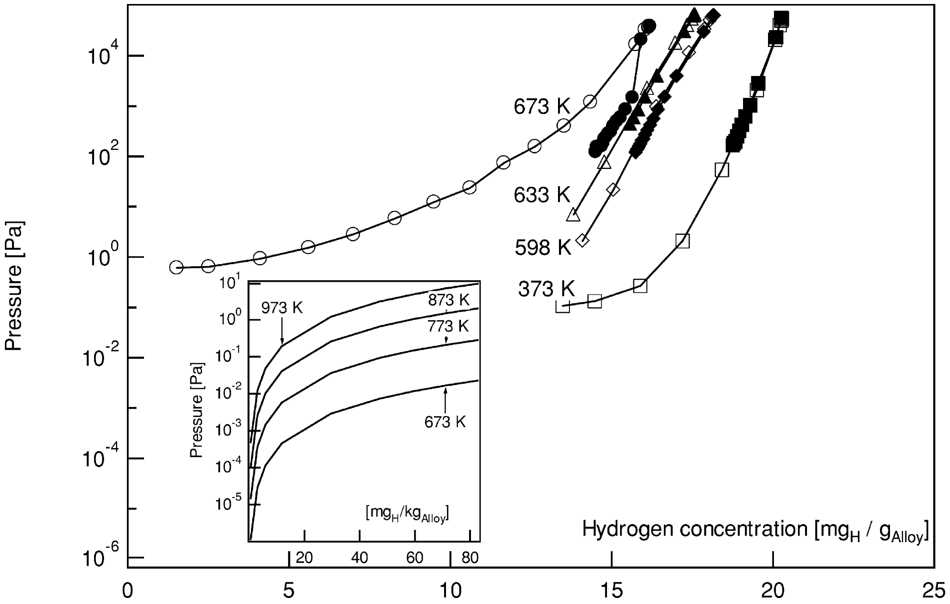

Fig. 2. Hydrogen absorption (open symbols) and desorption (filled symbols) isotherms for Zr–V–Fe alloy (SAES St-172). Insert summarizes isotherms at very low hydrogen contents from Ref. [14].

hydrogen contents and lower temperatures. A precise, computer controlled, all-metal Sieverts' system [16] based upon oil-free vacuum pumps was used for these experiments. The initial hydrogen absorption done at 673 K was followed by a desorption which exhibited a large hysteresis difference as shown in Fig. 2. This effect has been seen in other Zr alloys [17,18] and was attributed to generation of defects during the activation absorption reaction. As also found by others [17,18] for two-phase Zr alloys, it is extremely difficult to remove all the hydrogen from the ZrH_x phases even using active vacuum pumping at $T>800$ K. Consequently, hydrogen concentrations for the other isotherms in Fig. 2 were fixed by taking the system to 673 K following desorption and assigning the final hydrogen content to corresponding pressure for the initial desorption isotherm. There are no plateaus observed for any of the isotherms in Fig. 2 and also no hysteresis between absorption and desorption after the first 673 K one. These results indicate there are no two-phase hydride regions at these temperatures and concentrations with hydrogen forming solid solutions in the $Zr(V_{0.84}Fe_{0.16})_2$ and $Zr_3(V_{0.84}Fe_{0.16})_3O_y$ phases. The pressures are, however, sufficiently high to satisfy the ON state requirements for heat switch actuators in Table 1 when the total hydrogen content is greater than ~15 $mg_H\ g_{alloy}^{-1}$. After completion of the isotherm measurements, the sample was saturated with hydrogen and cooled to room temperature. Powder X-ray diffraction of this hydride material indicate three predominant phases: ϵ-$ZrH_{\sim 2}$ ($a=0.4979$ nm and $c=0.4451$ nm); $Zr(V_{0.84}Fe_{0.16})_2H_x$ ($a=0.7776$ nm); and $Zr_3(V_{0.84}Fe_{0.16})_3O_yH_x$ ($a=1.2481$ nm) had been formed. The lattice parameter expansions for the latter hydrides are consistent with other AB_2H_x and $A_3B_3O_yH_x$ phases [15,19]. Furthermore, the hydrogen contents for these phases are estimated within ~10–20% to be $Zr(V_{0.84}Fe_{0.16})_2H_{3.0}$ and $Zr_3(V_{0.84}Fe_{0.16})_3O_yH_{5.3}$ from a correlation of their volume expansion (i.e. $\Delta V/V_{alloy}$) to literature trends for similar hydrides [19,20].

3. Fabrication and testing of actuators

In an initial assessment of St-172 for a heat switch actuator, the alloy was tested as a reversible hydrogen pump for more than 500 cycles with no substantial changes found in its behavior. This test was conducted utilizing the sintered solid pellet as supplied by the manufacturer with a built-in heater and charged at a low hydrogen concentration (~1.2 $mg_H\ g_{alloy}^{-1}$) to avoid hydrogen embrittlement [9,10,14]. During these tests, the temperature required to desorb hydrogen at a pressure above 270 Pa was almost 1000 K, requiring a large heater power (34 W). Despite the high temperature needed to run it, the alloy did not show any degradation and, in addition, fast kinetics were observed. This design was not evaluated further due to its large power consumption and to the high temperature necessary for the ON state that would impose high thermal stress on other components of the actuator (i.e. heater, heater leads, temperature sensors, etc.).

The configuration of a heat switch actuator that was adapted from the design previously used [5] for ZrNi and uranium (U) metal as the sorbent alloys is presented in Fig. 3 where an expanded view of the hydride container is shown above its test assembly. The actuator includes a conductive calibrated thermal conductance (i.e. a thin wall tube) with a heater and temperature sensor (platinum resistance thermometer) located on the cap. The porous 316L stainless steel (SS) filter has a thickness of 0.78 mm and a porosity of 0.5 μm in order to contain the St-172 material after it is transformed into fine powder by the reaction with hydrogen. All the parts in contact with hydrogen gas are made of electropolished 316L SS that had been carefully cleaned and vacuum baked. After the hydride container was filled with a specified amount (~0.3 g) of alloy, the tube, with the filter mounted on top, was slid into place. The actuator assembly was joined together by electron-beam welding. The thin wall tube had been previously e-beam welded onto a concentric reducer (i.e. 12.7–6.35 mm) mounted to a VCR fitting for connection to the rest of the test assembly in Fig. 3. After passing a helium leak check, the test assembly was then removed and connected to a hydrogen charging station containing a turbomolecular vacuum pump and baked out under vacuum at 523 K overnight to reduce the gases adsorbed on the internal surfaces of the test actuator assembly. An Omega type WS81 resistance heater was attached to the cap via a copper post using a high temperature braze. The test actuator unit was now ready to be reacted with research grade hydrogen gas further purified with a NanoChem resin filter. The hydride material was initially reacted with a known amount of hydrogen and the final concentration was reduced by desorption into the calibrated volume. Sample St-172-1 was filled to a hydrogen concentration of ~18 mg g^{-1} alloy and sample St-172-2 to 14.3 mg g^{-1} alloy. During desorption the quantity of hydrogen evolved from the hydride in an actuator to generate a 1.0-kPa pressure in the test volume shown in Fig. 3 would be ~3–5% of its total hydrogen content. Before inserting the actuator assembly into lifetime testing system (i.e. performing the ON–OFF state cycling by heating and cooling actuators in a vacuum test chamber), the temperature sensor was attached on the cap using Aremco Ceramabond 571 cement. Additional information on fabrication and testing procedures are given elsewhere [16].

Some representative pressure and temperature profiles for the two actuators containing hydrided SAES St-172 alloy are shown in Fig. 4. These traces cover nearly the total range of cycles performed. For temperature changes from 300 to 525–625 K, the pressures vary by factors between 1000 and 10 000 — as desired in a gas-gap heat switch. The OFF state pressures for temperatures below ~375 K are too low to measure (the ~0.4-Pa pressure seen in the absorption stage during the 4068th cycle in Fig. 4b

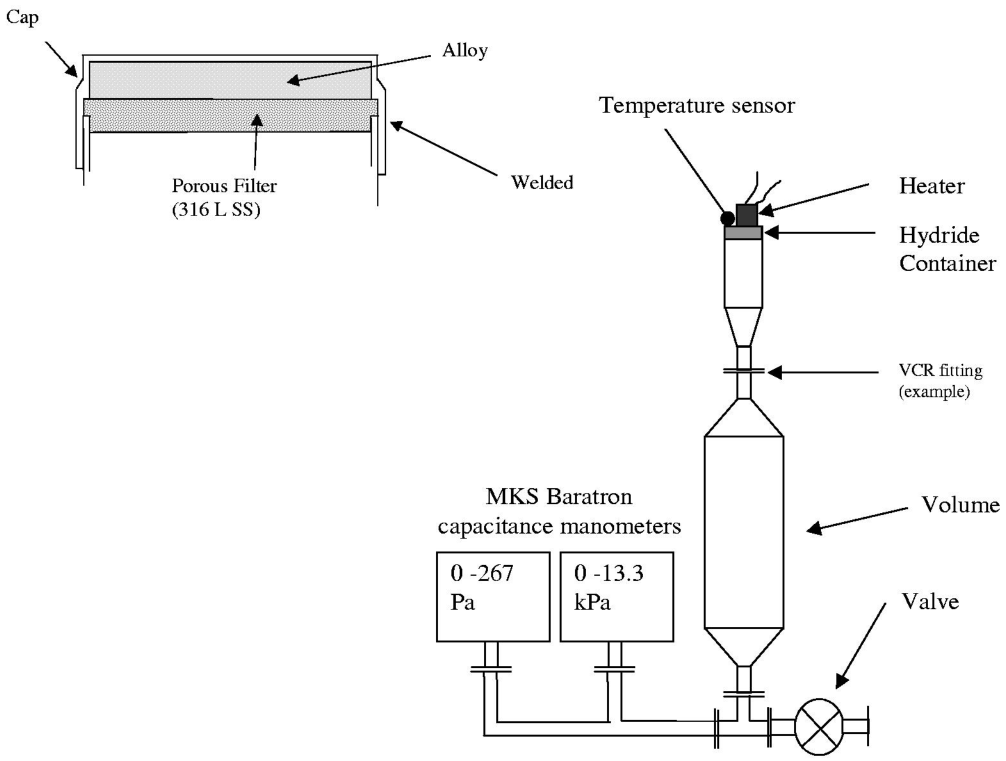

Fig. 3. Schematic drawings of hydride container for actuator (upper) of gas-gap heat switch and test assembly (lower).

is due to zero-drift of the gauge) with the available gauges. Both the drops and rises in pressure for these actuators are within the desired ON–OFF and OFF–ON switching times, respectively, given in Table 1. It was observed that the kinetics of the hydrogen absorption and desorption become somewhat slower as cycling progress — especially for St-172-1, which was cycled to a higher pressure than St-172-2. However, the pressure change ratios would still provide acceptable ON–OFF time constants. For both the samples, the thermal cycling deteriorated the heater attachment (as well as for the temperature sensor on St-172-1 after <50 cycles) such that heaters failed after ~4500 cycles (a new heater was attached to St-172-1 and cycling was continued until it also failed). It should be noted that when this new heater was attached, a different pressure–temperature relationship was observed due to alterations in thermal transfer characteristics. The kinetics for St-172-2 desorption show a constant degradation of the ON state along with lower pressures and lower temperatures reached for the ON state as cycling continues, but no major degradation of the hydrides is indicated. Rather a change in heat conductance into the alloy occurred from variations in thermal contacts of the heater and temperature sensor with the hydride container cap [16]. It is believed that the much lower ON state cycling temperature and the shorter time of cycling has avoided any large changes in hydrogen absorption/desorption kinetics for St-172-2.

Reported in Fig. 5 are the end points of the ON state (i.e. pressure, input power, and temperature data monitored during the thermal cycling) for both tested actuators. It can be observed that ON state pressures decrease during cycling (especially after about 5000 cycles for St-172-1, where changes in power levels and temperature are also seen). However, as can be predicted from the isotherms in Fig. 2 lower pressures are observed for St-172-2 which has the smaller hydrogen content. The instability and fluctuations are believed [16] to be mainly caused by variations in the thermal contact for heaters and temperature rather than behavior of the hydride phases. However, the fact that isotherms for the St-172 alloy do not have plateau regions make them more vulnerable to inadvertent changes in hydrogen content than for hydrides operating across two-phase regions such as $ZrNiH_x$ and UH_x previously evaluated [5] for heat switch actuators.

After cycling ended, the actuators were opened and the powder was examined by XRD. The contents of St-172-1 were ϵ-$ZrH_{\sim 2}$ (unchanged from initial preparation); $Zr(V_{0.84}Fe_{0.16})_2H_{1.6}$ ($a=0.7582$ nm); and $Zr_3(V_{0.84}Fe_{0.16})_3O_yH_{4.2}$ ($a=1.400$ nm). The contents of St-172-2 were ϵ-$ZrH_{\sim 2}$; $Zr(V_{0.84}Fe_{0.16})_2H_{1.2}$ ($a=0.7527$ nm); and $Zr_3(V_{0.84}Fe_{0.16})_3O_yH_{3.5}$ ($a=1.2362$ nm). The material from both cycled actuators was very fine powder, but with no evidence of contamination.

4. Conclusions

These studies have demonstrated that the SAES Zr–V–Fe St-172 alloy is a viable candidate for use in actuators of gas-gap heat switches in sorption cryocoolers if the

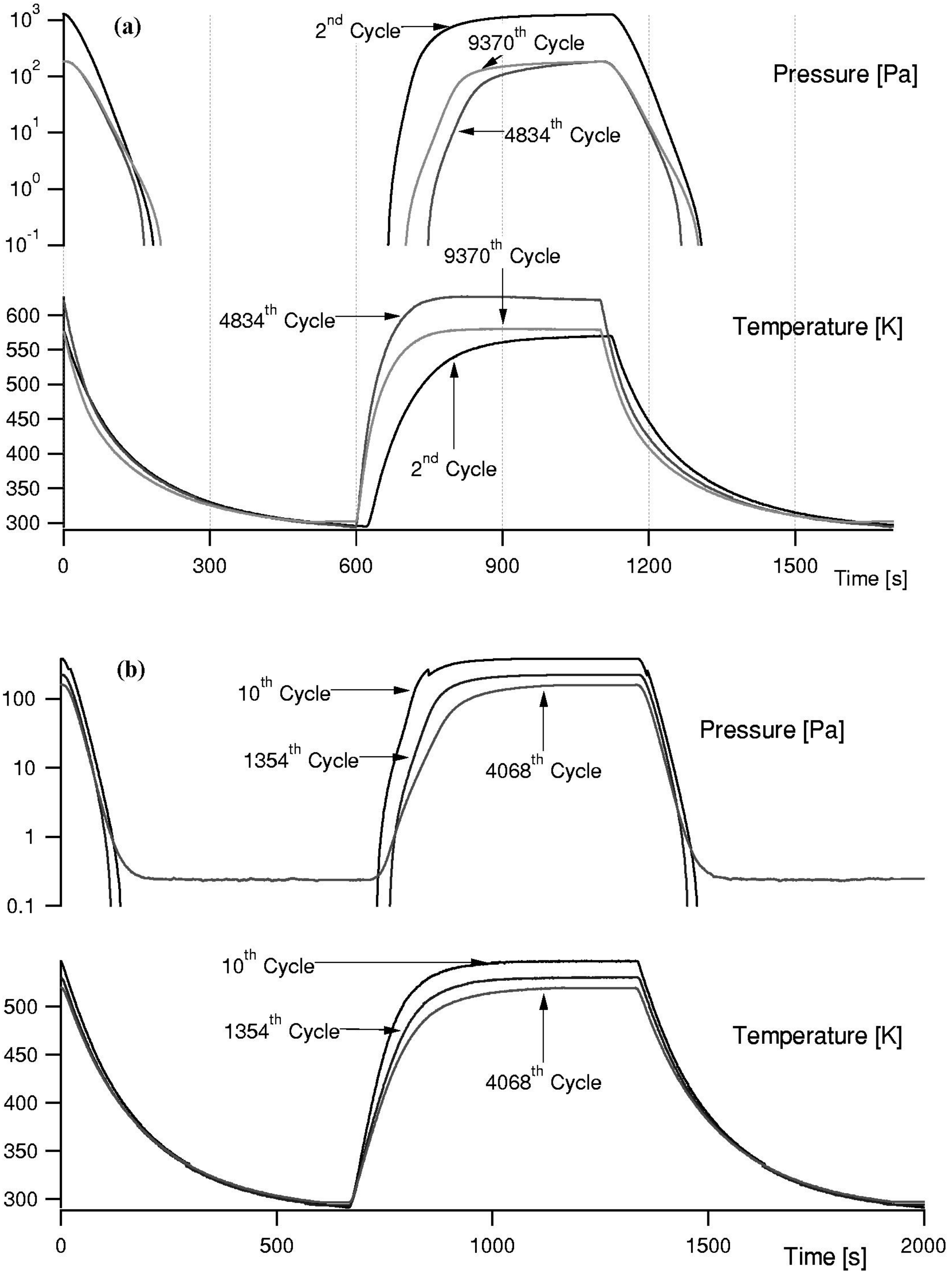

Fig. 4. Pressure and temperature profiles observed from actuator (a) St-172-1 during cycles 2, 4834, and 9370 and (b) St-172-2 during cycles 10, 1354, and 4068.

hydrogen content is sufficiently high (i.e. >15 $mg_H\ g_{alloy}^{-1}$). The OFF state low pressures are easily met and both the absorption and desorption kinetics are sufficiently rapid. The alloys are also very tolerant to impurities and require minimal activation. Fairly high temperatures (i.e. >600 K) are needed for ON state pressures above 1.3 kPa. All of the hydrogen transfers during the heating and cooling cycles are associated with the $Zr(V_{0.84}Fe_{0.16})_2H_x$ and $Zr_3(V_{0.84}Fe_{0.16})_3O_yH_x$ phases as the equilibrium pressure for ϵ-ZrH_x is much too low [17,18] to contribute below 700 K. However, reliable and durable attachment of heaters and temperature sensors to the actuator cap is a major challenge that is exacerbated by the necessary high operating temperature for the ON state. Furthermore, the

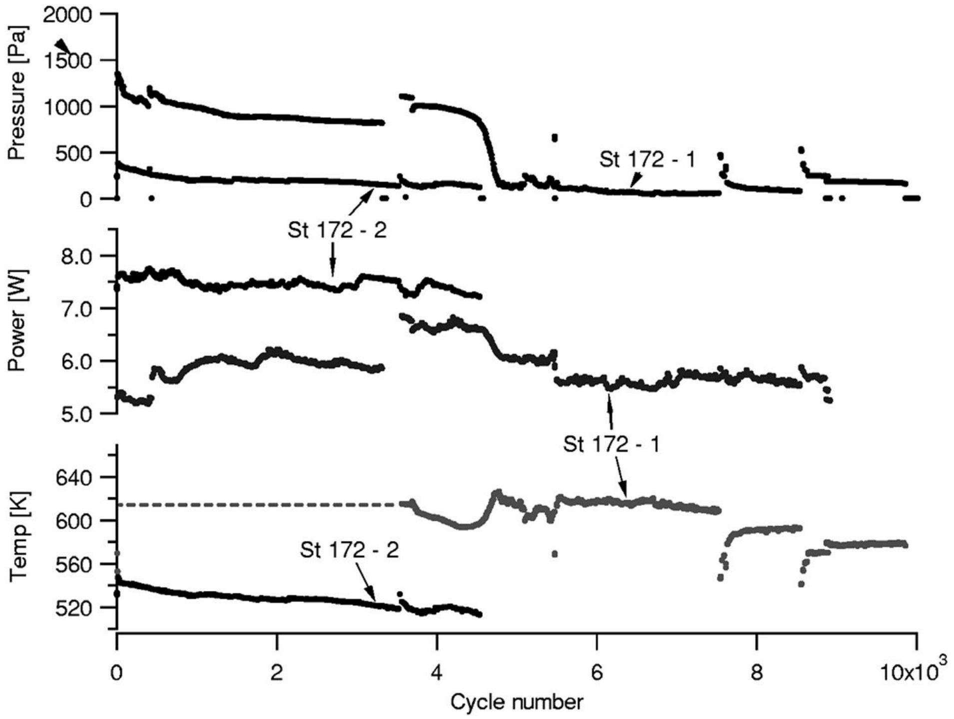

Fig. 5. On state pressures, input power levels, and maximum temperatures for actuators St-172-1 and St-172-2 observed during cycling until heater failures for both units.

rapid variation of pressure with hydrogen content (i.e. no plateau region) apparently contributes to instability. Current efforts for developing these heat switch actuators are directed towards hydrides with two-phase regions and higher pressures (i.e. $ZrNiH_x$).

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