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Experimental and theoretical investigations for mitigating $NaAlH_4$ reactivity risks during postulated accident scenarios involving exposure to air or water

Y.F. Khalil[*], *S.M. Opalka*, *B.L. Laube*

United Technologies Research Center (UTRC), 411 Silver Lane, MS 129-30, East Hartford, CT 06108, USA

ABSTRACT

Experimental and theoretical studies were conducted to investigate the pyrophoricity and water-reactivity risks associated with employing sodium alanate ($NaAlH_4$) complex metal hydride in on-board vehicular hydrogen (H_2) storage systems. The ignition and explosivity of $NaAlH_4$ upon exposure to oxidizers in air or water were attributed to the spontaneous formation of stable hydroperoxyl intermediates on the $NaAlH_4$ surface and/or H_2 production, as well as the large driving force for $NaAlH_4$ conversion to favorable hydroxide products predicted by atomic and thermodynamic modeling. The major products from $NaAlH_4$ exposure to air: $NaAl(OH)_4$, gibbsite and bayerite $Al(OH)_3$, and Na_2CO_3 observed by XRD, were identified to be formed by surface-controlled reactions. The reactivity risks were significantly minimized, without compromising de-/re-hydrogenation cyclability, by compacting $NaAlH_4$ powder into wafers to reduce the available surface area. These core findings are of significance to risk mitigation and H_2 safety code and standard development for the safe use of $NaAlH_4$ for on-board H_2 storage in light-duty vehicles.

Keywords: Metal hydrides; Sodium alanate; Risk mitigation; Powder compaction; Pyrophoricity; Water reactivity; On-board reversible

1. Introduction

For over a decade, a significant body of research has been focused on complex metal hydrides with de-/rehydrogenation reversibility at moderate temperatures and pressures for application as solid-state hydrogen (H_2) storage media for the proton exchange membrane (PEM) fuel cell powered light-duty vehicles. While complex hydride candidates based on light metals have the potential for high gravimetric H_2 storage capacity, there have been concerns raised about their safe implementation in the transportation sector. Many of these complex hydrides are highly reactive to air or water, and can ignite or explode upon exposure during postulated accidents (Khalil, 2010a,b, 2011a). In particular, extensive risk mitigation testing has confirmed the flammability, pyrophoricity and water reactivity characteristics of sodium alanate ($NaAlH_4$) powder (Khalil, 2010a; Mosher et al., 2007; Tanaka et al., 2009; Lohstroh et al., 2009).

We have developed formal qualitative and quantitative risk analyses (Khalil, 2011a; Khalil et al., 2010a; Khalil and Modarres, 2010) as well as a comprehensive safety testing program (Khalil, 2010b, 2011a; Khalil et al., 2010b) to investigate the reactivity and safety-significant characteristics of candidate solid-state H_2 storage media of interest to the U.S. Department of Energy (DOE) H_2 safety program. Our risk analysis for on-board reversible H_2 storage systems led to identifying potential safety-significant failure mechanisms and accident scenarios that challenge the storage vessel integrity of on-board reversible systems (Fig. 1). As can be seen in this figure, specific postulated accident scenarios have been deemed to be credible from a probabilistic standpoint, especially: (a) air or water intrusion/in-leakage into the vessel leading to air/hydride or water/hydride reactions driven by the strong pyrophoricity and water reactivity of $NaAlH_4$ loose powder, and (b) catastrophic rupture of the hydride storage vessel leading to dispersing the stored hydride powder into the ambient air.

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[*] *Corresponding author*. Tel.: +1 860 610 7307; fax: +1 860 660 9574.
E-mail address: khalilyf@utrc.utc.com (Y.F. Khalil).

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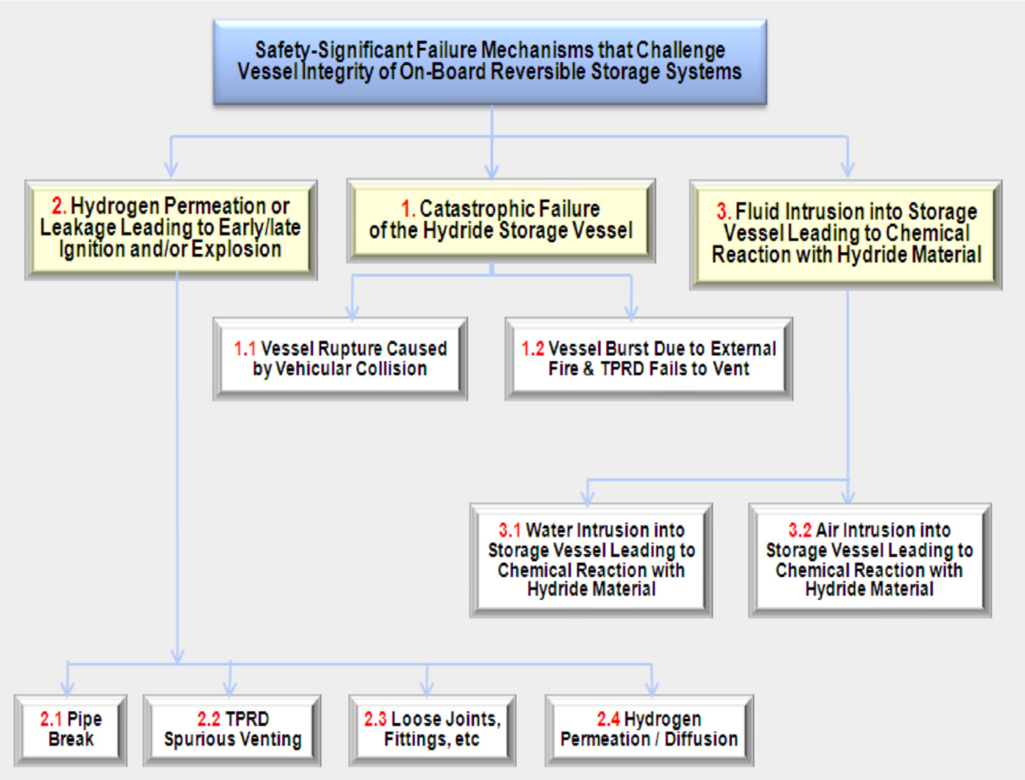

Fig. 1 – Safety-significant failure mechanisms and accident scenarios that challenge the integrity of on-board reversible storage system (Khalil, 2010a, 2011a).

In addition to our experimental investigation, we developed a theoretical understanding of the reaction mechanisms of $NaAlH_4$ with the oxidizing compounds in ambient atmospheres: molecular oxygen (O_2) and water (H_2O), as well as carbon dioxide (CO_2), and also with liquid H_2O, as a basis for developing a risk mitigation method for safe $NaAlH_4$ containment in an on-board H_2 storage system. Atomic and thermodynamic modeling were conducted to identify the key reaction steps that initiate the highly exothermic reactions of $NaAlH_4$ with O_2 and H_2O. Based on our understanding of these reaction mechanisms, we developed a powder compaction method to suppress $NaAlH_4$ reactivity with O_2 and H_2O, without compromising H_2 storage reversibility. Our experimental investigation of the air and water reactivity of $NaAlH_4$ powder and compacted wafers confirmed the efficacy of this risk mitigation method. A fundamental reaction scheme for the progressive $NaAlH_4$ oxidation reactions was established by combining insights from the fundamental modeling and X-ray diffraction (XRD) observations of $NaAlH_4$ oxidation products.

2. Methods

Section 2.1 discusses the safety-related material reactivity test methods, Section 2.2 describes the H_2 cycling testing, Section 2.3 summarizes the types of material characterization tests that were employed, Section 2.4 describes thermodynamic modeling of chemical reactions and phase equilibria and Section 2.5 discusses the atomic modeling of $NaAlH_4$ surface reactions. The thermodynamic and atomic modeling techniques were employed to identify possible reaction pathways, the thermodynamic feasibility of each reaction pathway, and the potential formation of passivation surfaces that prevent the progression of chemical reactions when $NaAlH_4$ contacts O_2, H_2O, and/or CO_2.

2.1. *Safety-related material reactivity tests*

A series of tests have been conducted on 4 mol% titanium chloride ($TiCl_3$)-catalyzed $NaAlH_4$. Part of those tests focused on investigating the pyrophoricity of this material, both in loose powder and in powder compacts pressed into 1-g wafers. The remaining tests focused on investigating the water reactivity of this complex hydride both in loose powder and powder compact forms.

To prepare the test samples, commercial-grade $NaAlH_4$ powder, purchased from the Albemarle Corporation, was mixed with 4 mol% $TiCl_3$ using high-energy SPEX ball milling for 3 h under an inert environment (nitrogen, N_2 gas). The storage and transfer of the test samples were performed under a high-purity N_2 environment inside a glove box with an O_2 concentration <10 ppm. To prepare the powder compact (wafers), the loose hydride powder was pressed into 0.4 in. (~10 mm) diameter and 0.08 in. (~2 mm) thick wafers (Fig. 2) using a 10-ton Carver press inside the glove box.

In the pyrophoricity (air-reactivity) tests, both the loose powder and the wafers were exposed to ambient air. During the exposure tests, the air ambient temperature ranged from 23 to 30 °C and the relative humidity ranged from 31 to 49%. In the water-reactivity tests, 1-g samples of loose powder and powder compacts (wafers) of the hydride material were

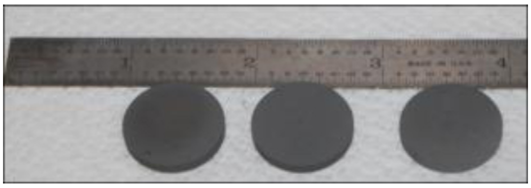

Fig. 2 – Sodium alanate powder compact (wafers).