Material Classification Regulations and their Impact on Reversible Metal Hydride Hydrogen Storage Systems

Presented by

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Review of Reversible Metal Hydride Technology for Hydrogen Storage

- $MH_{x\ (solid)}$ + heat $\Leftrightarrow$ $M_{\ (solid)}$ + x/2 $H_{2\ (gas)}$
- Hydrogen chemically bonded within metal lattice
- Hydrogen desorption – endothermic
- Hydrogen absorption – exothermic
- Lower temperature – lower plateau pressure
- Higher temperature – higher plateau pressure
- Expansion/contraction on hydriding/dehydriding

Review of Reversible Metal Hydride Technology for Hydrogen Storage

Key Items to Note for Ambient Temperature Storage Materials:

- Need to have an overpressure of hydrogen
- If pressure is lowered – hydride disproportionates
- If pressure is increased – absorption occurs up to capacity limit
- Pressure highly dependent on temperature
  - pressure changes much greater than for ideal gas over identical temperature ranges

Transportation of Hazardous Materials within the U.S.

- Regulated by the U.S. Department of Transportation
- Regulations found in Title 49 of Codes of Federal Regulations, parts 100-185
- *Hazardous Materials Table* found in § 172.101

Sym-bols	Hazardous materials description and proper shipping names	Hazard class or Division	Identifi-cation Numbers	PG	Label Codes	Special Provisions (§ 172.102)	(8) Packaging (§ 173.***)			(9) Quantity limitations		(10) Vessel stowage	
							Excep-tions	Non-bulk	Bulk	Pass-enger Aircraft/ rail	Cargo aircraft only	Loca-tion	Other
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8A)	(8B)	(8C)	(9A)	(9B)	(10A)	(10B)
	Hydrogen and Methane mixtures, compressed	2.1	UN2034	……	2.1 ……		306…..	302…	302….	Forbidden	150 kg	E	40
	Hydrogen, compressed	2.1	UN1049	……	2.1 ……		306…..	302… .	3.2....	Forbidden	150 kg	E	40,57
	Hydrogen, refrigerated, liquid *(cryogenic liquid)*	2.1	UN1966	……	2.1 …..	T75, TP5	None…	316…	318…	Forbidden	Forbidden	D	40

Hazard Class numbers, names and 49 CFR references.

Class No.	Division No. (if any)	Name of class or division	49 CFR reference for definitions
None		Forbidden materials	173.21
None		Forbidden explosives	173.54
1	1.1	Explosives (with a mass explosion hazard)	173.50
1	1.2	Explosives (with a projection hazard)	173.50
1	1.3	Explosives (with predominately a fire hazard)	173.50
1	1.4	Explosives (with no significant blast hazard)	173.50
1	1.5	Very insensitive explosives; blasting agents	173.50
1	1.6	Extremely insensitive detonating substances	173.50
2	**2.1**	**Flammable gas**	173.115
2	2.2	Non-flammable compressed gas	173.115
2	2.3	Poisonous gas	173.115
3		Flammable and combustible liquid	173.120
4	**4.1**	**Flammable solid**	173.124
4	**4.2**	**Spontaneously combustible material**	173.124
4	**4.3**	**Dangerous when wet material**	173.124
5	5.1	Oxidizer	173.127
5	5.2	Organic peroxide	173.128
6	6.1	Poisonous materials	173.132
6	6.2	Infectious substance (Etiologic agent)	173.134
7		Radioactive material	173.403
8		Corrosive material	173.136
9		Miscellaneous hazardous material	173.140
None		Other regulated material: ORM-D	173.144

Hazardous Classification for Metal Hydride Hydrogen Storage Systems

- Contains:
  - Gaseous Hydrogen
    - 2.1 Compressed Flammable gas, hydrogen, n.o.s.
  - Solid material, which could be:
    - hydrided, partially hydrided or *non-hydrided*
    - flammable, spontaneously combustible or water-reactive
- Therefore a mixture:
  - precedence listing found in § 173.2a
  - 2.1 compressed flammable gas takes precedence over all class 4 solid hazards

How to determine Class 4, Division 4.1, 4.2 and 4.3 Solid Hazards

- Definitions found in § 173.124
- Packing group assignment found in § 173.125
- Referenced tests found in the

  UN Manual of Test and Criteria
  - 4.1: Flammable solids
  - 4.2, pg I: Pyrophoric solids
  - 4.2, pg II & III: Self-heating solids
  - 4.3 : Dangerous when wet / Water-reactive solids
- None of the tests can be performed with an overpressure of hydrogen!

Question: What is the true hazard associated with the solid material?

- 4.1, 4.2 and 4.3 solid hazards are possible
- Properties/hazard class may change depending on state-of-charge

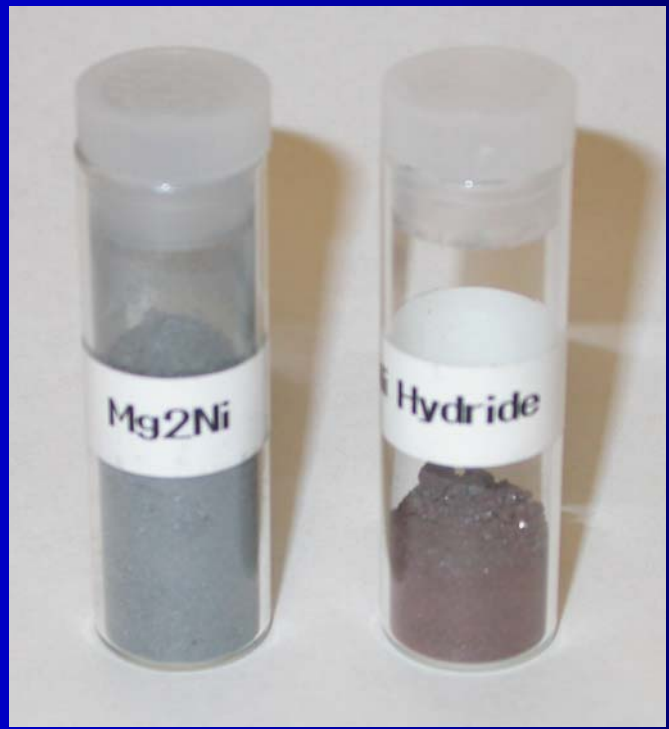
Type	Formula	Results
AB – Commercially obtained	TiFe	Non-pyrophoric
AB_2 – Commercially obtained	$Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$	Pyrophoric
AB_2 – Proprietary Ovonic™ alloy	OVB94	Non-pyrophoric
AB_5 – Commercially obtained	$MmNi_{4.5}Al_{0.5}$	Non-pyrophoric
A_2B – Commercially obtained	$Mg_{2.4}Ni$ – non-hydrided	Pyrophoric
A_2B – Commercially obtained	$Mg_{2.4}Ni$ – hydrided	Non-pyrophoric
Proprietary Ovonic™ alloy	TC04 – non-hydrided	Pyrophoric
Proprietary Ovonic™ alloy	TC04 – hydrided	Non-pyrophoric

Different Hazard Class and Packing Group Possible within an Alloy-type

Video of Pyrophoricity tests of a commercially available AB_2 alloy (pyrophoric) and of a Proprietary Ovonic™ AB_2 alloy (non-pyrophoric), demonstrating that different hazard classes can exist even within a material class.

Reactivity May Change Between Hydrided and non-Hydrided States

- Mg_2Ni – activated (gray-black) versus Mg_2NiH_4 (red)



Reactivity May Change Between Hydrided and non-Hydrided States

Video of Pyrophoricity tests of a Proprietary Ovonic™ AB_2 alloy, with a low plateau pressure, in each the hydrided and non-hydrided states (material had been activated and cycled in each case) demonstrating that the hazard class may change with state-of-charge.

Question: What is the true hazard associated with the solid material?

- 4.1, 4.2 and 4.3 solid hazards are possible
- Properties/hazard class may change depending on state-of-charge

Therefore

- Unable to use a single solid hazard description for all metal hydride hydrogen storage systems
- Any description might be ambiguous due to:
  - Changes in properties with state-of-charge
  - Effects of the dehydriding reaction when hydrogen overpressure is removed

The U.S. DOT's Solution

- All metal hydride hydrogen storage products will need an exemption – **No Party Status Allowed**
- Description
  - Proper Shipping Name:
    Hydrogen, absorbed in metal hydride
  - Hazard Class/Division: 2.1
  - Identification Number: NA9279
  - Packing Group: N/A

The U.N. Sub-Committee of Experts for the Transport of Dangerous Goods' Solution

- Includes special provision that "storage systems shall always be considered as containing hydrogen"
- Description
  - Proper Shipping Name:
    Hydrogen in a metal hydride storage system
  - Hazard Class/Division: 2.1
  - Identification Number: UN3468
  - Packing Group: N/A
- Considered special provision to allow inclusion of subsidiary risks.

Other Standard Development Activities for Metal Hydride Systems

- ISO/TC 197, Working Group 10 –
  - Transportable Gas Storage Devices – Hydrogen absorbed in reversible metal hydrides
- CGA, Metal Hydride and Alternate H_2 Fuel Technology Committee
  - Several activities including guidelines to classification as well as product safety design standards
- SAE, Fuel Cell Standards Committee – Safety
  - J2579 - Recommended Practice for Fuel Systems in Fuel Cell and Other Hydrogen Fueled Vehicles

Summary

- UN Sub-Committee of Experts for the Transport of Dangerous Goods:
  - Hydrogen in a Metal Hydride Storage System, 2.1
  - UN Identification number to be assigned
- US DOT:
  - Hydrogen, absorbed in a metal hydride, 2.1, NA9279
  - Exemption required for all products, No Party Status Allowed
- ISO/TC 197, CGA and SAE all have standard development activities underway concerning metal hydride products

Closing Remarks

- Current prescribed tests are not adequate to determine the true hazard of metal hydride hydrogen storage systems
- New tests need to be developed to determine potential hazards
- All manufacturers should test their materials with current test methods to understand, at least, the hazard without hydrogen – useful for emergency response personnel
- All manufacturers should understand and keep up with current regulations and comply with them
- All manufacturers and system developers should get involved with the product standard development efforts

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