Micro-mechanical and microstructural underlying causes of decrepitation in intermetallic compounds dedicated to solid state hydrogen storage

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EXTENDED ABSTRACT

In the context of the climate transition, hydrogen is regarded as a key energy carrier for the decarbonization of numerous industrial sectors. However, the development of safe and energy-efficient storage solutions is a prerequisite for its sustainability and large-scale deployment. Solid-state hydrogen storage relies on the reversible hydriding of intermetallic alloys, typically in powder form. This technology offers intrinsically safe hydrogen storage with high energy efficiency, enable by mild operating conditions (P ∈ [1–30] bar; T ∈ [10–80] °C for TiFe), which limit compression requirements and leakage compared to compressed hydrogen storage, while imposing less safety and thermal management constraints than cryogenic storage.

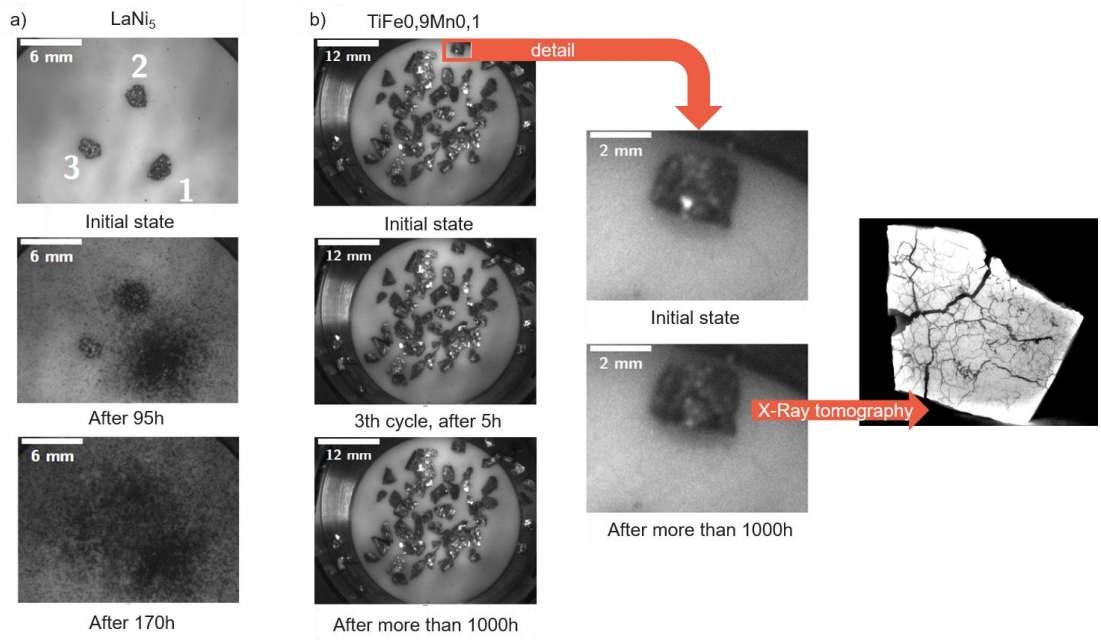

Figure 1 : Hydriding observations under 30 bars of H_2 : a) Severe degradation of LaNi5 particles until complete pulverization b) No apparent change of the particles of TiFe0.9Mn0.1 whereas X-ray tomography of a sample particle reveals significant internal damage.

Hydridation is a solid-state transformation that causes the crystal lattice to expand under H2, with local expansion reaching up to ΔV≈17% for TiFe [1]. This induces decrepitation, i.e. successive self-fragmentation of particles during cycles due to a lack of elastic accommodation

of local strains. The particle size decreases as the powder bed gradually settles. At the same time, the intra-particle microstructure is likely to evolves during cycles, with trapped hydrogen, changes in crystallites size or twinning, or the development of dislocation networks. Although decrepitation is widely observed [2] and likely to critically affect storage system durability [3], it remains insufficiently understood.

This study investigates the mechanical, microstructural, and granulometric characteristics of three intermetallic compounds ($TiFe_{0,9}Mn_{0,1}$, $TiMn_{1,5}$ and $LaNi_5$) in order to elucidate the mechanisms and consequences of decrepitation. To this end, a comprehensive experimental approach combining SEM/EDS, nanoindentation [4], and particle size analysis, is employed to establish correlations between microstructure, heterogeneity within the particle and stability of storage performances. In addition, the in-situ visualization of particle degradation during its first absorption is proposed (Figure1). Contrasted behaviours are observed. LaNi5 undergoes severe pulverization of particles, whereas $TiMn_{1,5}$ and $TiFe_{0,9}Mn_{0,1}$ exhibit only sparse limited particle movement without projection. Nevertheless, X-ray tomography of an isolated $TiFe_{0,9}Mn_{0,1}$ particle reveals a dense, interconnected cracks network. We therefore attempt here to link these very different modes of decay to microstructures and fields of mechanical properties, particularly elastic properties, at the intraparticle scale.

FUNDINGS

This work has been supported by the EIPHI Graduate School (contract ANR-17-EURE-0002), the Region Bourgogne Franche-Comté (CYCLAHMID Project) and by the French RENATECH network and its FEMTO-ST technological facility. The authors would like to thank the AMETISTE platform for access to the equipment.

REFERENCES

[1] L. Mohammedi, B. Daoudi, et A. Boukraa, « Ab-initio structural and electronic properties of the intermetallic compound TiFeH2 », *Comput. Condens. Matter*, vol. 2, p. 11-15, mars 2015, doi: 10.1016/j.cocom.2014.12.001.

[2] J.-M. Joubert, M. Latroche, R. Černý, A. Percheron-Guégan, et K. Yvon, « Hydrogen cycling induced degradation in LaNi5-type materials », *J. Alloys Compd.*, vol. 330-332, p. 208-214, janv. 2002, doi: 10.1016/S0925-8388(01)01640-1.

[3] K. Nasako, Y. Ito, N. Hiro, et M. Osumi, « Stress on a reaction vessel by the swelling of a hydrogen absorbing alloy », *J. Alloys Compd.*, vol. 264, nº 1, p. 271-276, janv. 1998, doi: 10.1016/S0925-8388(97)00246-6.

[4] L. Bebon, A. Maynadier, Y. Gaillard, et D. Chapelle, « Multiscale Elastic Modulus Characterization of Ti0.5Fe0.45Mn0.05, an Iron–Titanium–Manganese Alloy Dedicated to Hydrogen Storage », *Materials*, vol. 17, nº 24, p. 6100, déc. 2024, doi: 10.3390/ma17246100.