



**HAL**  
open science

## Modeling progressive absorption of an hydride material particle submitted to hydrogen

Ludovic Bebon, Anne Maynadier, David Chapelle, Frédéric Thiébaud

► **To cite this version:**

Ludovic Bebon, Anne Maynadier, David Chapelle, Frédéric Thiébaud. Modeling progressive absorption of an hydride material particle submitted to hydrogen. *International Journal of Hydrogen Energy*, 2021, 46 (18), pp.10830 - 10837. 10.1016/j.ijhydene.2020.12.160 . hal-03359919

**HAL Id: hal-03359919**

**<https://hal.science/hal-03359919v1>**

Submitted on 22 Jul 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

# Modeling progressive absorption of a hydride material particle submitted to hydrogen

*Ludovic Bebon, Anne Maynadier, David Chapelle\*, Frédéric Thiébaud*

*Univ. Bourgogne Franche-Comté, FEMTO-ST Institute, CNRS/UFC/ENSMM/UTBM, Department of Applied Mechanics, 25000 BESANCON-FR*

*Members of the Federation for Fuel Cell Research FCLAB (FR CNRS 3539)*

## Abstract

The present study deals with the modeling of a single intermetallic powder particle likely to form reversibly a hydride material while submitted to hydrogen gas. These materials that make part of the so-called hydrogen solid storage family are one of the most employed media used in order to store hydrogen. During hydrogenation cycling, the initially coarse powder expands due to hydrogen absorption and shrinks over hydrogen desorption. The powder granularity also decreases with the number of cycles but seems to stabilize to reach a mechanical limit. One plausible explanation is that large particles decrepitate into smaller ones because, only due to their geometry, they are less able to accommodate large volume changes and thus, internal stresses are higher than in small particles. This is the hypothesis we intend to discuss in the present work, hypothesis that has never been investigated, in our knowledge, from a mechanical point of view. Within the framework of a simple analytical model, several parameters (initial particle size, material behavior parameters...) are varied in order to evaluate their influence on the propensity of the particle to decrepitate. After introducing the context, the model that allows describing the fragile elastic mechanical response of a single spherical particle submitted to hydrogen is presented. Computed stress and strain along the radius of particles with different size or elastic properties lead to the main conclusion: considering a spherical particles made of an undamaged uniform elastic brittle two phase material is insufficient to evidence dependency of the mechanical response on the particle size. Consequently, this primary model is unable to validate our hypothesis, according which the limit size of decrepitating is driven by the mechanical accommodation of volume changes. This implies that a description of heterogeneities or geometric irregularities must be introduced to account for the phenomenon of particle size stabilization during decrepitating. After results are presented and discussed, opportunities to deepen the present analysis are proposed to account for physical observations of the decrepitating phenomenon, and are to be developed in forthcoming publications.

*Keywords: Absorption modeling, decrepitation, continuum mechanics, hydrogen storage*

*E-mail of the corresponding author: david.chapelle@univ-fcomte.fr*

## Introduction

Since several decades, hydrogen is foreseen as a good energy vector susceptible to play a relevant role in future energetic mix and enabling to diversify our energy sources. Even if hydrogen is the most abundant element, it is also the smallest and it is consequently rather difficult to store. Three main technologies have been developed to store hydrogen: gaseous storage, liquid state storage and solid state storage each one with advantages and drawbacks [1].

This work is focused on solid storage [2]: a tank, partially filled with metallic alloy crushed into powder, is exposed to dihydrogen gas. If the pressure is sufficient, the alloy absorbs hydrogen to form a solid solution, if the pressure exceeds a certain threshold, the absorption pressure, the phase transformation reaction occurs. When hydrogen pressure drops, the metallic alloy releases hydrogen by both reversing the phase change and depletion of the solid solution. Absorption and desorption pressures can be characterized with Pressure Composition Isotherm (PCI) curves schematized Fig 1. These curves determine for an alloy the capacity of hydrogen absorption, absorption pressure and desorption pressure.

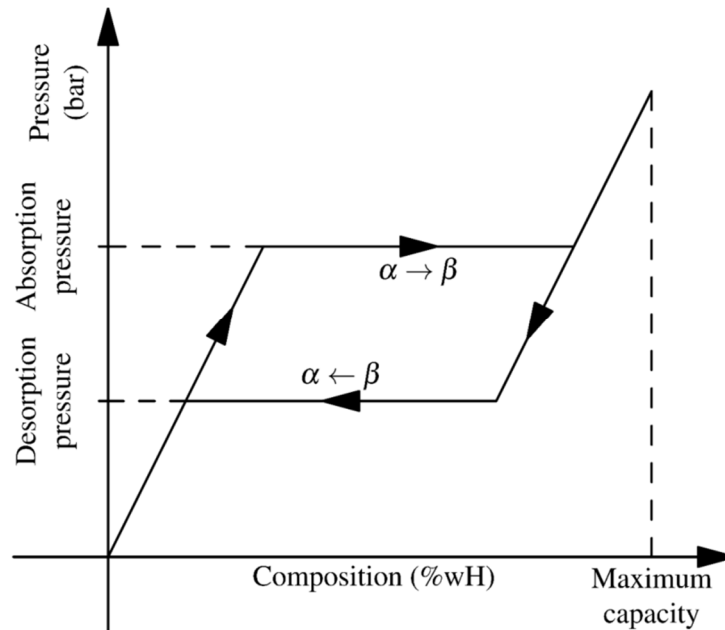


Fig 1 : PCI idealized curve with absorption and desorption pressure plateau. Each pressure plateau correspond to a phase transformation

Different models describe the way a single particle absorbs hydrogen: multi-layer or nucleation. For both models [3], [4], dihydrogen gas is adsorbed on particles surface, the two atoms are split and then diffuse into crystalline structure to form the  $\alpha$ -phase. Once this phase is saturated in hydrogen, crystalline structure changes to become  $\beta$ -phase. This exothermic phase transformation induces a volume change into the crystal lattice different for each material and up to 30% [5], [6].

Metal hydride in tank is subjected to multiple cycles of absorption / desorption. During those cycles, granularity of powder changes, particles are fracturing into smaller particle [7], [8]. Repetition over a large number of cycles shows that a minimum size of particle exists and granularity seems to stabilize [9], [10]. Mechanisms of decrepitation coupled with increase and decrease of particle volume induce mechanical cyclic stresses on the container walls that can induce, after a large number of cycles, plasticity within the constituent materials of the tank till rupture [9], [11].

This issue of spherical solid undergoing self-fracture due large strain, induced by phase transformation is rarely addressed in the literature, and even more rarely considering the hydrogen storage application. Nonetheless, Freidin *et al.* [12] propose the analysis of stress-assisted chemical reactions in spherically symmetric problems of mechano-chemistry. Here, the used framework is the thermodynamics general framework allowing to link energy dissipation to strains. Attention is thus paid on the chemical reactions kinetics front depending on the deformable solid constituents and on boundary conditions. This work is unfortunately not extended to consider induced damage or cracking. In geomaterials, the serpentinisations of the peridotite or periclase mantle rock hydration

into brucite are quite similar even if different phenomena: hydration and carbonization reactions cause volume changes, induce stresses and finally micro-cracks which, in turn, promotes the phenomenon of weathering by enhancing the transport of reactants. Ulven *et al.* [13, 14] proposes a numerical model combining FDM, FEM and DEM to simulate the profile of concentration, the stress state and, above all, the cracking pattern in 2D model of a grain of olivine. It demonstrates that the magnitude of volume increase is main parameters with the thinness of the transformation interface. L. Zhang, C. Nasika, F.V Donzé *et al.* [15] propose a DEM numerical study taking into account the coupling between stress and temperature on the chemical reaction through the volumetric local expansion. They concluded that the hydration reaction advancement, once the reaction has started, depends on the nucleation and growth of fractures and the micro-cracks damage linked to the porosity. They highlighted the slow-down effect on the stress on the reaction rate. Those modelling studies are inspiring for the study of the decrepitation of storage alloy under hydrogen cycling, but it consists on sophisticated numerical simulations difficult to develop, for a phenomenon that seems, maybe wrongly, easily mechanically describable. The present work that consider the problem in a rather simple formulation of the continuum mechanics framework, with classic assumptions, show that the representation of the decrepitation and the particle size thresholding during cycles is not easily obtained.

Consequently, designing properly a storage tank and ensuring versatility become crucial in a context application of hydrogen energy are extensively growing worldwide. To do so, our research goal is to increase our knowledge concerning the hydride powder media when it is placed in the tank and submitted to hydrogen cycle. Our approach, in an original way, deals the mechanical aspects of the phenomena induced by the chemical reactions of absorption and desorption. As a limit size of particle is observed during cycling, we here intend to assess the ability of the particle to accommodate the hydrogen induced deformation and we expect this ability to be dependent on the particle size. This would allow predicting a limit size of particle during absorption/desorption cycling, in accordance with the experimental observations cited above. Thus, an analytical model describing the hydridation of a single spherical particle is developed in order to estimate displacement, strain and stress evolution during hydriding phenomenon, considering the material behaves as a fragile elastic material. We assume a layered penetration of hydrogen within the particle. Our main objective is to investigate if a rather simple and direct continuum mechanics formulation can give account of the threshold effect on the size of the particles while decrepitating: if the calculated maximum stress depends on the initial size of the modeled spherical particle then a simple comparison with a threshold, by considering an elastic-brittle material, is enough to account for the phenomenon. If the stresses always turn out to be identical then either the model must be enriched (material behavior, model of penetration of H in the alloy, damage ...), or it will be necessary to resort to numerical tools allowing a fine discretization and taking into account heterogeneities

In a first part, the model and assumptions are presented. After presenting the obtained results in term of maximum induced stress and strain, we discuss them in relation with the assumptions. In a first approach, one could assume that the self-fracturing of the particles is induced by internal stresses, and occurs when the brittle-elastic yield stress is reached, while the hydriding phenomenon is going on. The presented work demonstrates that a classical model based on an elastic-brittle continuum mechanics framework is not relevant enough to give account of the limit size of particle during decrepitation. Finally, we suggest perspectives to deepen this study, for

example by considering heterogeneities or discontinuities, based on experimental investigations and involving numerical modeling.

## Theory

Hypotheses of this work are classical hypotheses of continuum mechanics. Material is considered elastic, isotropic and brittle. Each phase is described with two material parameters: Young modulus and Poisson ratio respectively denoted as  $E$ , and  $\nu$ . Geometry of particle is a perfect sphere defined by its radius  $r$ .

We assume absorption phenomenon takes place according to a double-layer model [3]. Initially, while hydrogen penetrates the particle from the outside, the particle is a single  $\alpha$ -phase particle, i.e. a solid-state solution of hydrogen in metal. Diffusion of hydrogen is going on till a threshold is reached, a high enough hydrogen concentration leading to the phase transformation and the appearance of  $\beta$ -phase. For this double-layer model, during hydrogen absorption the  $\beta$ -phase layer thickness increases while during hydrogen desorption the  $\alpha$ -phase thickness increases. In both cases, the frontier displaces from the surface to the middle of the particle during absorption as shown in Fig 2.

Effects of hydrogen penetrating the particle are taken into account in each phase by a dilatation coefficient,  $\kappa$ . Volume expansion in each phase is proportional to the rate of hydrogen and its expansion coefficient. A huge difference between  $\alpha$  and  $\beta$ -phase is the volume of crystalline structure denoted by  $\Delta V$ . Considering the mechanical properties gradient at the frontier between  $\alpha$  and  $\beta$ -phase, we expect the developed model to reveal internal mechanical effects such as stress gradient or maximum stress that are dependent on the particle size.

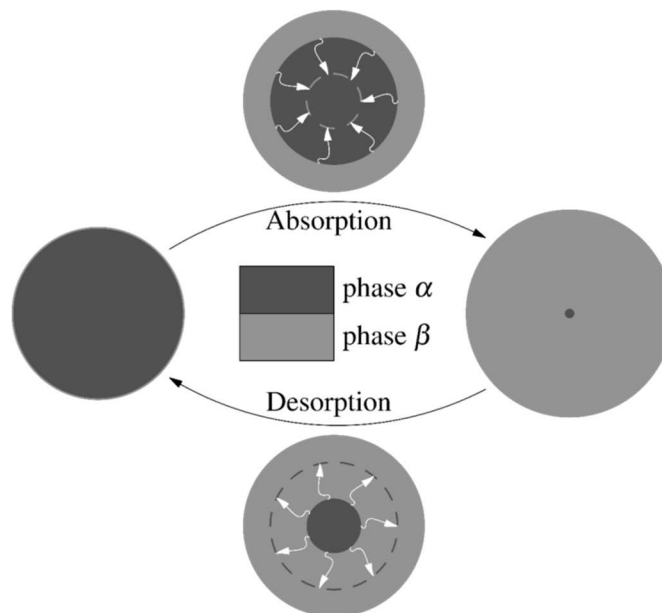


Fig 2 : Schematics representation of absorption and desorption process. We consider here a layer by layer phenomenon with  $H_2$  transfer from the outside to the inside for absorption and from the inside to the outside for desorption.

As particle is considered as a perfect sphere, we use a spherical coordinate system  $(r, \theta, \varphi)$ . Material is isotropic, so we assume displacement  $\mathbf{U}$  has only one component along  $r$  axis,  $U_r(r)$ . After simplification, considering independence in  $\theta$  and  $\varphi$  and small deformations, strain tensor  $\underline{\underline{\epsilon}}$  is expressed in a spherical particle as:

$$\underline{\underline{\epsilon}} = \text{Grad } \mathbf{U} = \begin{pmatrix} \frac{dU_r}{dr} & 0 & 0 \\ 0 & \frac{U_r}{r} & 0 \\ 0 & 0 & \frac{U_r}{r} \end{pmatrix}_{(r,\theta,\varphi)} \quad 1)$$

As a quasi-static state is assumed and gravity is neglected, the equilibrium equations become.

$$\begin{cases} \frac{d\sigma_{rr}}{dr} + \frac{2}{r}(\sigma_{rr} - \sigma_{\theta\theta}) = 0 \\ \sigma_{\theta\theta} = \sigma_{\varphi\varphi} \end{cases} \quad 2)$$

Due to elastic consideration, the link between stress and strain is the classic Hook's law expressed as:

$$\underline{\underline{\sigma}} = 2\mu\underline{\underline{\epsilon}} + \lambda \text{tr}(\underline{\underline{\epsilon}}) \underline{\underline{Id}} \quad 3)$$

Deformations are caused by several mechanisms: first, the deformation due to hydrogen diffusing into the crystalline structure, second the volume difference between  $\alpha$  and  $\beta$ -phases. We consider both mechanisms by decomposing strain tensors in different parts. On the  $\alpha$ -phase, strain tensor has two contributions: elastic part and dilatation part as seen in (4).

$$\underline{\underline{\epsilon}}_{\alpha} = \underline{\underline{\epsilon}}_{\alpha}^{\text{el}} + \underline{\underline{\epsilon}}_{\alpha}^{\text{di}} \quad 4)$$

On the  $\beta$ -phase, we add the volumetric expansion contribution with another constant part

$$\underline{\underline{\epsilon}}_{\alpha \rightarrow \beta} = \begin{pmatrix} \Delta V & 0 & 0 \\ 0 & \Delta V & 0 \\ 0 & 0 & \Delta V \end{pmatrix}_{(r,\theta,\varphi)} \quad 5)$$

Moreover, we express the strain tensor on the  $\beta$ -phase as in (6) :

$$\underline{\underline{\epsilon}}_{\beta} = \underline{\underline{\epsilon}}_{\beta}^{\text{el}} + \underline{\underline{\epsilon}}_{\beta}^{\text{di}} + \underline{\underline{\epsilon}}_{\alpha \rightarrow \beta} \quad 6)$$

For each phase, we apply the Hook's law to the elastic part of strain tensor. After computation, displacements on each phase are linked to the hydrogen concentration by the following differential equation (7). The  $\phi$  index denotes either  $\alpha$  or  $\beta$ -phase.

$$\frac{d^2 U_{r\phi}}{dr^2} + \frac{2}{r} \frac{dU_{r\phi}}{dr} - \frac{2}{r^2} U_{r\phi} - \kappa_{\phi} \frac{2\mu_{\phi} + 3\lambda_{\phi}}{2\mu_{\phi} + \lambda_{\phi}} \frac{dC}{dr} = 0 \quad 7)$$

Equation (7) has a trivial solution expressed as:

$$U_{r\phi}(r) = \kappa_{\phi} \frac{2\mu_{\phi} + 3\lambda_{\phi}}{2\mu_{\phi} + \lambda_{\phi}} \frac{1}{r^2} \int r^2 C(r) dr + rA_{1\phi} + \frac{A_{2\phi}}{r^2} \quad 8)$$

To settle the different constants, boundary conditions and continuous conditions due to first hypothesis are suggested: the center of particle is fixed, stress at free boundary is null, as we do not consider hydrogen pressure on particle. At boundary  $a$  between  $\alpha$  and  $\beta$  phase, displacement and stress are equal on each part. The following system (9) has to be solved in order to determine the unique solution for displacement and stress:

$$\begin{cases} U_{r\alpha}(0) = 0 & \text{Boundary condition} \\ U_{r\alpha}(a) = U_{r\beta}(a) & \text{Continuity condition} \\ \sigma_{rr\alpha}(a) = \sigma_{rr\beta}(a) & \text{Continuity condition} \\ \sigma_{rr\beta}(r_0) = 0 & \text{Boundary condition} \end{cases} \quad 9)$$

Those equations allow computing displacement and stress on a single particle submitted to hydrogenation. The considered concentration profile  $C(r)$  of hydrogen at time  $t$  into the particle came from Mathematics of Diffusion [16, Ch. 6]. This profile, expressed in equation (10), depends on the radius of considered sphere  $r_0$ , the diffusion coefficient  $\kappa$  and the time. We assume hydrogen concentration onto surface particle to be  $C_0$ .

$$\frac{C(r)}{C_0} = 1 + \frac{2r_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\left(\frac{n\pi r}{r_0}\right) \exp\left(-\kappa \frac{\pi^2 n^2 t}{r_0^2}\right) \quad 10)$$

## Results

The above model is implemented in Matlab software. After some optimized calculations, based on the depending on time hydrogen concentration, one can first obtain the displacement (Equation (8)) along the radius of the particle according to time. Other observables quantities are then computed from this displacement: radial stress, orthoradial stress, radial strain and orthoradial strain. The following particle radii are considered: 10, 50, 100 and 500  $\mu\text{m}$ . Due to size discrepancies, for a given concentration of hydrogen on the outer surface, the phase transformation at the core is reached at times that are all the longer as the particle is large. In order to compare the results from one particle size to another, the observable quantities are plotted as a function of the percentage of time with respect to the time necessary to reach the maximum stress in the 500 $\mu\text{m}$  particle.

Fig 3 shows the concentration profiles of hydrogen inside the particle (Equation (10)) for a simulating time of 4. At this time, the smallest particle is full of hydrogen, the ratio  $C_r/C_0$  is equal to 1, what also means the particle is fully in the  $\beta$ -phase. Arbitrarily, the threshold of phase transformation is fixed for the ratio  $C_r/C_0$  equal to 0.5. That means for a ratio lower than 0.5 the material is in the  $\alpha$ -phase whereas for a higher ratio it is in the  $\beta$ -phase. Thus the phase transformation interface is here clearly punctual creating a strong discontinuity. This choice is not trivial and is discussed in the "discussion" section. At this time, the two smallest particles are all  $\beta$ -phase while the two phases are present for the other.

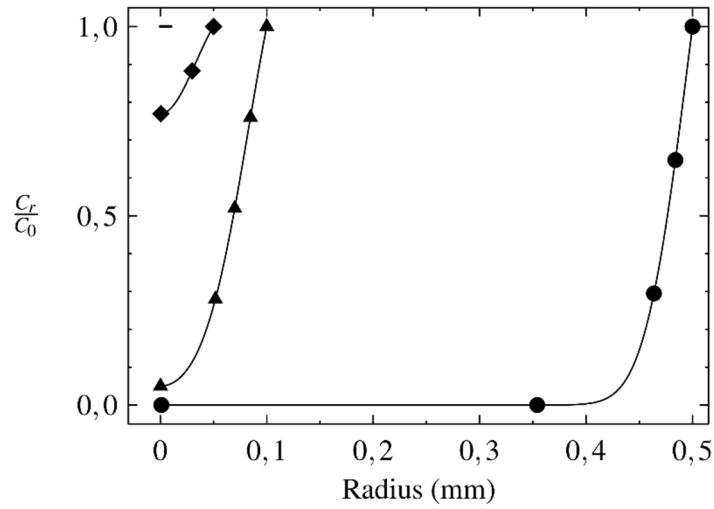


Fig 3: Hydrogen concentration profiles along the radial direction for 4 different particle diameters, 10 (-), 50 (◆), 100 (▲) and 500  $\mu\text{m}$  (●)

Collecting material mechanical properties for this study proved to be challenging, more specifically for the hydrided material, i.e. the  $\beta$ -phase. Once the material has absorbed hydrogen practically, it is no more a solid material, because decrepitation has occurred. Then particle size is very thin and mechanical characterization becomes tricky. For the non-hydrided material, some characterization using nano-indentation was performed to assess in a reasonable way its Young modulus. This value has been chosen to carry out the numerical simulation ( $\alpha$ -phase Young modulus: 300 GPa), where regarding the Young modulus of  $\beta$ -phase we tested two scenarios,  $\beta$ -phase is more or less rigid than  $\alpha$ -phase. Table 1 gives the numerical parameters introduced in the simulation to obtain the below results.

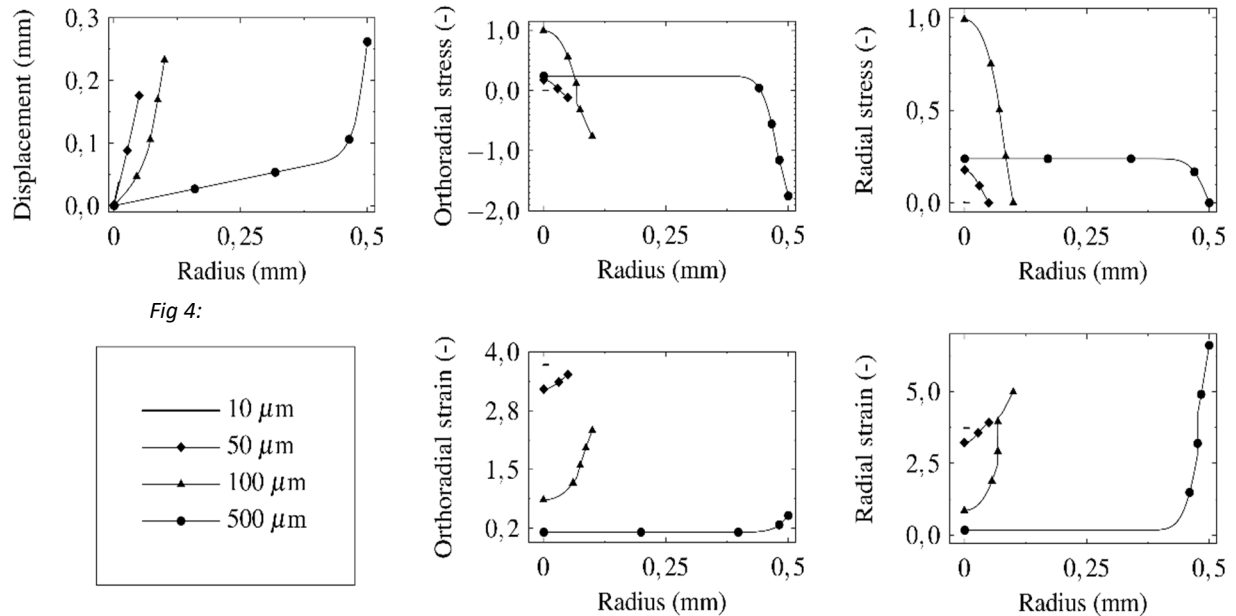
Parameters	Numerical value	Unit
$E_{\alpha}$	300	GPa
$E_{\beta}$	200 or 400	GPa
$\nu_{\alpha}$	0.3	-
$\nu_{\beta}$	0.3	-
$\kappa_{\alpha}$	3	%
$\kappa_{\beta}$	3	%
$\Delta V$	20	%

“Table 1 : Numerical parameters used for the calculation. Two cases are considered: either a stiffening of the material during hydriding, or a softening.”

First, it is noteworthy that the calculations of both softening and stiffening hydride, compared to the initial alloy, give very similar variations in stress and strain as a function of time or radius in the particle. Only the magnitude of the observables quantities differs.



Fig 4 illustrates the numerical results obtained for a  $\beta$ -phase more rigid than  $\alpha$ -phase. In Fig 4, displacement, orthoradial and radial stresses, orthoradial and radial strains are plotted at time 4 % for the different particle radius 10, 50, 100 and 500  $\mu\text{m}$ . It is worth notice stresses have been normalized using the maximum stress value considering the four particles.



Displacement, orthoradial stress, radial stress, orthoradial strain and radial strain along the particle radius for particle size of 10, 50, 100 and 500  $\mu\text{m}$  at 4 % of time compare to the time of maximum stress for the 500  $\mu\text{m}$  particle. Radial and orthoradial stress are also normalized by the maximum stress of the 500  $\mu\text{m}$  particle.

The mechanical state computation (Equation (3,4,6,8)) shows that the orthoradial and radial stresses are zero when the particle is fully saturated (see r 10 $\mu\text{m}$  particle on Fig 4). On the contrary, particle with an interface (see r 500 $\mu\text{m}$  particle on Fig 4) undergoes a core tensile stress, and within the transformed layer, a compressive orthoradial stress combined to a drop of the tensile radial component to reach a zero radial stress on the free surface (in accordance to Equation (9)).

The induced strain is a strong and increasing expansion from the center to the free surface (both radially and orthoradially) when the particle is fully transformed. Two phase particles present two deformation regimes: close to the center the deformation is weak and constant. Still in the alpha phase, when approaching the interface, an elbow is visible: the radial and orthoradial deformations accommodate the change in volume in the beta phase, transmitted by the conditions of continuity at the interface. Only a certain thickness seems affected. At the exact radius where the transformation interface is located, a jump in radial strain can be observed (see particle 100 $\mu\text{m}$  and 500 $\mu\text{m}$ ). It is not present on the orthoradial strains which are prevented by the integrity of the layer, but this induces a stress jump of stress on the orthoradial direction (visible on particle r 100 $\mu\text{m}$ ). Whatever the radius of the particle, the radial and orthoradial stresses reach jointly their maximum. This moment is different from one particle to another, but corresponds to the moment when the interface is close to the center but the particle is still in two phases.

# Discussion

Considering the studied hypothesis, our expectation was to identify a variation of the model response according to the size of particles. Assuming fracture and induced decrepitation are driven by stresses concentration, one can conclude smaller particles are more inclined to accommodate deformation if their maximum stresses are lower. It is worth notice the above results are consistent with general hypothesis, that are boundary and continuous conditions; involving for instance displacements and radial stresses are continuous between phases, outer radial stress is zero etc. According continuum mechanics, when continuity is fixed for the radial stress, orthoradial stress and radial strain show a bound at the frontier of phase transition. This matter of fact is peculiarly remarkable on the radial strains of 100 and 500  $\mu\text{m}$  radius particles, but also visible on the orthoradial stress, mainly for the 100  $\mu\text{m}$  radius particle. Smaller particles reveal a complete phase transformation in  $\beta$ -phase at 4 % of the full computation time, corresponding to the maximum stress in the 500  $\mu\text{m}$  radius particle. Consequently, such bounds are not observed for small particles at this simulating time. These discontinuities are directly linked to the way the transformation interface position is described in our model by a sharp threshold: ratio  $C_r/C_0$  equal to 0.5. Ulven *et al.* [13, 14], in their multi-modal numerical study of a two-phase particle of serpentinized olivine, have shown that the sharpness of reaction front and the magnitude of the volume expansion induced by the reaction are of primary importance on the stress state and consequently on the fracture type forms. Their approach uses the quite phenomenological 1D reaction front propagation model introduced by Rudge *et al.* [17] that allow to pilot the front sharpness with only two non-dimensional parameters. Zhang, Nasika, Donzé *et al.* [15] use a modified Avrami type reaction kinetics law to describe the reaction completion and round off the sharpness of the interface.

Looking at the full computation time, the magnitude of stresses and strains for all particles look like identical. The only discrepancy could lie on the time when the maximum of stress is reached, and finally according this model and these simulations all curves are apparently stackable if normalized according the moment of occurrence of maximum stress for each particle. To confirm this qualitative analysis the maximum magnitude of orthoradial and radial stresses normalized by the maximum stress of the 500  $\mu\text{m}$  radius particle have been plotted for all particles. Fig 5 presents both maximum orthoradial and radial normalized stresses according to time, for particle radius of 10, 50, 100 and 500  $\mu\text{m}$ . After normalization, radial and orthoradial stress overlap. Fig 5 confirms previous qualitative analysis; that is the particle mechanical response during hydrogen absorption is not particle size dependent according to the here developed model. We thus demonstrate continuum mechanics does not permit to describe the fracture phenomenon of particles, even in a qualitative way, and is enable to help at predicting a final and minimum size of these particles, size that is experimentally witnessed [9, 10]. To our knowledge, the impact of the particle size on the mechanical state induced by a phase transformation interface is not a main identified objective. Yeremeyev *et al.* [18], in his mathematical investigations of the stability of centisymmetric equilibrium two-phase deformations in an elastic solid, or Freidin *et al.* [12], in its work on the 1D propagation of the stress-assisted reaction front, the considered spherical solid is taken as a dimension less example, the sphere size influence is not considered. In the DEM numerical model of the two-phase spherical solid proposed by Ulven *et al.* [13, 14], they state that for a given particle geometry, the magnitude of volume change and the sharpness of the front reaction, are the two parameters that modify the fracture mode *ie* between the fracture of a multitude of small domains

or spalling of pieces of outer layers. Still, it is not clear if the influence of the magnitude of the volume change at front is inversely, or directly influential with respect to particle size.”

In light of this conclusion, we resume our experimental and numerical investigations on this topic, aiming to better understand the decrepitation at different scales, from the particle to allow then a description of a bed of particles, considered in a final step in closed environment which is the storage tank. In forthcoming papers, our first intention will be addressed by describing methodology to identify mechanical parameters of the raw material and by using dedicated numerical tool to overcome limitations of simple mechanical analysis. Mechanical parameters are then absolutely required to describe the mechanical response of the particle, and also collect relevant input data for numerical simulations. Forthcoming numerical investigations are based on the usage of a particularly well adapted tool when microcracking or powder media is involved, that is Discrete Element Method.

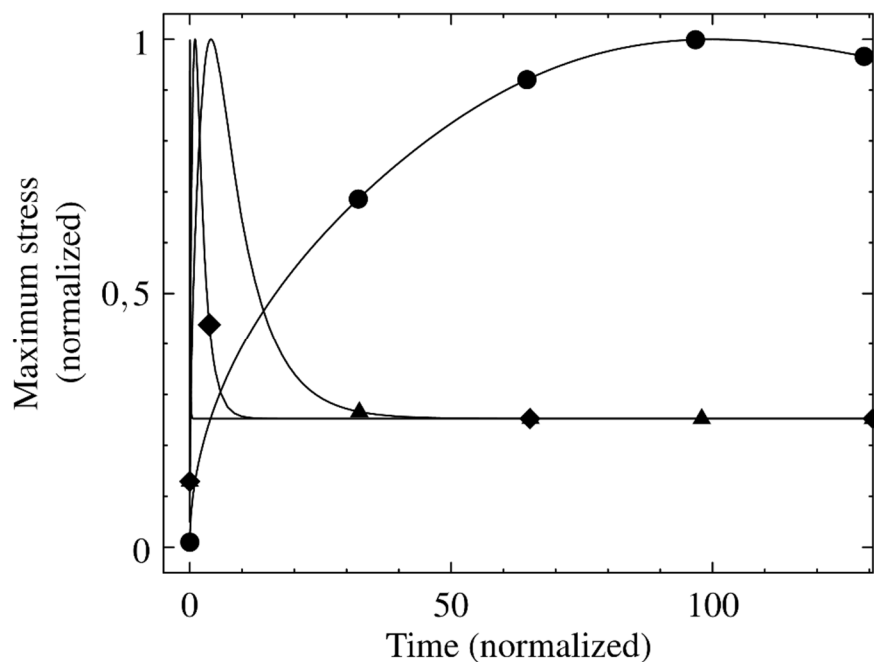


Fig 5 : Maximum radial and orthoradial normalized stress function of time for 10 (-), 50 (◆), 100 (▲) and 500  $\mu\text{m}$  (●) particles. Both overlap after the normalization. Time is normalized by the time of maximum stress for the 500  $\mu\text{m}$  radius particle.

## Conclusions

Hydrogen as an energy vector needs a storage facility to deploy. One way to store hydrogen is to make it react with intermetallic alloys but the reaction induces a phase transformation with an important volume change coupled with fracture phenomena. Experimentations show that the decrepitation phenomenon tends to interrupt leading to a stable granularity. We tested the hypothesis that the minimum size of particles is determined by the ability of the particle to deal with strain and stress induced by hydrogen absorption and phase transformation. We modeled a particle

as a sphere defined by its radius and we considered the classical continuum mechanics framework with a brittle, isotropic material. The absorption of hydrogen is assumed to happen layer by layer from outside according to Crank profile diffusion. The phase transformation is triggered after a certain concentration of hydrogen is overpassed, and volume change to the new phase is then added. After development, displacement, strain and stress along the radius of any particle are computed, we compare for different radius the maximum values of stress during time. To confirm the hypothesis, a smaller maximum stress for a tinier particle was expected. As the material is considered brittle, higher stress implies the rupture. Contrarily to this expectation, results reveal the same maximum of stress whatever the size of the particle is, only time of occurrence is shifting, what invalidates the first hypothesis. Consequently, a model based on the continuum mechanics seems not sufficient to explain the limit particle size of the intermetallic alloys subject to hydrogen absorption. To add complexity and variability in the particle, in geometry and in material, we will use other numerical methods like the Discrete Element Method. Helpful of this numerical tool, we expect a better understanding of the decrepitation phenomenon. Such progress should lead to improve the hydrogen tank design with better ability to sustain loading and unloading cycles.

## References

- [1] K. Mazloomi and C. Gomes, Hydrogen as an energy carrier: Prospects and challenges, *Renew. Sustain. Energy Rev.*, vol. 16, no. 5, pp. 3024–3033, Jun. 2012
- [2] A. Züttel, Materials for hydrogen storage, *Mater. Today*, vol. 6, no. 9, pp. 24–33, Sep. 2003
- [3] Y. Asakuma, S. Miyauchi, T. Yamamoto, H. Aoki, T. Miura, Numerical analysis of absorbing and desorbing mechanism for the metal hydride by homogenization method, *Int. J. Hydrog. Energy*, vol. 28, no. 5, pp. 529–536, May 2003
- [4] M. Martin, C. Gommel, C. Borkhart, E. Fromm, Absorption and desorption kinetics of hydrogen storage alloys, *J. Alloys Compd.*, vol. 238, no. 1, pp. 193–201, May 1996
- [5] S. Challet, M. Latroche, F. Heurtaux, Hydrogenation properties and crystal structure of the single BCC (Ti<sub>0.35</sub>V<sub>0.645</sub>)<sub>100-x</sub>M<sub>x</sub> alloys with M=Mn, Fe, Co, Ni (x=7, 14 and 21), *J. Alloys Compd.*, vol. 439, no. 1–2, pp. 294–301, Jul. 2007
- [6] B. Charlas, A. Chaise, O. Gillia, P. Doremus, D. Imbault, Investigation of hydride powder bed swelling and shrinking during hydrogen absorption/desorption cycles under different compressive stresses, *J. Alloys Compd.*, vol. 580, pp. S149–S152, Dec. 2013
- [7] M. Latroche, Structural and thermodynamic properties of metallic hydrides used for energy storage, *J. Phys. Chem. Solids*, vol. 65, no. 2, pp. 517–522, Mar. 2004
- [8] M. Okumura, K. Terui, A. Ikado, Y. Saito, M. Shoji, Investigation of wall stress development and packing ratio distribution in the metal hydride reactor, *Int. J. Hydrog. Energy*, vol. 37, no. 8, pp. 6686–6693, Apr. 2012
- [9] F. Qin, L.H. Guo, J.P. Chen, Z.J. Chen, Pulverization, expansion of La<sub>0.6</sub>Y<sub>0.4</sub>Ni<sub>4.8</sub>Mn<sub>0.2</sub> during hydrogen absorption–desorption cycles and their influences in thin-wall reactors, *Int. J. Hydrog. Energy*, vol. 33, no. 2, pp. 709–717, Jan. 2008

- [10] H. C. Lin, K. M. Lin, K. C. Wu, H. H. Hsiung, H. K. Tsai, Cyclic hydrogen absorption–desorption characteristics of TiCrV and Ti<sub>0.8</sub>Cr<sub>1.2</sub>V alloys, *Int. J. Hydrog. Energy*, vol. 32, no. 18, pp. 4966–4972, Dec. 2007
- [11] A. K. Nasako, Y. Ito, N. Hiro, M. Osumi, Stress on a reaction vessel by the swelling of a hydrogen absorbing alloy, *J. Alloys Compd.*, vol. 264, no. 1, pp. 271–276, Jan. 1998
- [12] A. Freidin, · N. Morozov, · S. Petrenko, · E. Vilchevskaya, Chemical reactions in spherically symmetric problems of mechanochemistry, *Acta Mech*, 227, pp. 43–56, 2016
- [13] O. I. Ulven, H. Storheim, H. Austrheim, A. Malthe-Sørenssen, Fracture initiation during volume increasing reactions in rocks and applications for CO<sub>2</sub> sequestration, *Earth and Planetary Science Letters*, 389, pp. 132–142, 2014
- [14] O. I. Ulven, B. Jamtveit, A. Malthe-Sørenssen, Reaction-driven fracturing of porous rock. *Journal of Geophysical Research: Solid Earth*, 119(10), pp. 7473–7486, 2014
- [15] L. Zhang, C. Nasika, F.-V. Donzé, X. Zheng, F. Renard, L. Scholtès, Modeling porosity evolution throughout reaction-induced fracturing in rocks with implications for serpentinization, *Journal of Geophysical Research: Solid Earth*, 124, pp. 5708–5733, 2019
- [16] J. Crank, *The Mathematics of diffusion*, Second edition. London: Oxford University Press, 1975
- [17] J.F. Rudge, P.B. Kelemen, M. Spiegelman, A simple model of reaction-induced cracking applied to serpentinization and carbonation of peridotite, *Earth and Planetary Science Letters*, 291 (1-4), pp. 215-227, 2010
- [18] V. Yeremeyev, A. Freidin, L. Sharipova, The stability of the equilibrium of two-phase elastic solids, *Journal of Applied Mathematics and Mechanics*, 71 (1), pp. 61-84, 2007

