Rapport sur le mémoire de thèse en

Science et génie des matériaux

Intitulé :

Modèles éléments finis pour l'étude de la fragilisation par l'hydrogène des structures en acier

Présenté par

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The PhD thesis, presented by Daniel Lopes-Pinto, is dedicated to the modelling of Hydrogen-material interactions, in term of transport and modification of the materials properties.

It is a dense document, based on the philosophy of experience-simulation dialogue. Experiments are claimed to have been done by other people, but have been presented for the sake of clarity, indicating a good understanding of the ins and outs of these tests.

Writing is pleasant, and supported by numerous bibliographic references, from several fields: a mark of the variety of issues addressed by the candidate. Some references related to Hydrogen are however not well placed or misinterpreted:

$$N_T = 23.26 - 2.33\exp(-5.5p)$$

has not been proposed by Kumnick & Johnson (1980) but by Sofronis & McMeeking (1989). This function is only valid for iron (although it is widely used by everyone, including me, for any other material)[1].

A lot a repetition of information at the beginning of each chapter/section (already said in the bibliographic part) and in the text. This gives the reading a feeling of déjà vu and constant flashback that is a little disturbing. References to the doctoral student's published

[1] Please refers to Colombo et al (2020). *Theoretical and Applied Fracture Mechanics*, *110*, 102810 for a non-comprehensive review of these kinds of models.

articles are not, in my view, relevant in a doctoral thesis, especially when it is stated that the doctoral results confirm or are confirmed by these articles.

Please note the constant switch of notation p-κ for the equivalent plastic strain, p is used also for the pressure (and average stress p. 31).

The document is made of 5 chapters, plus a conclusion

1. A bibliography for hydrogen-metal interactions & modeling, failure models, and mechanical tests for fracture mechanics. A section is dedicated on the locking issue: 38 pages;
2. Experiment and modeling of the Disk Pressure Test (DPT): 26 pages;
3. Experiment and modeling of the H transport and trapping by dislocation in tensile samples: 23 pages;
4. Numerical modeling of Hydrogen Embrittlement (HE); application on tensile samples and DPT: 15 pages
5. Application on CT samples: 30 pages.

Chapter 2

This chapter is divided into 3 main parts: modeling of ductile fracture; material-hydrogen interactions (and associated models); fracture toughness testing (norm and size effects). A digression is made on the volume locking problems, which is of importance in plasticity of ductile damage finite element modeling. This last point motivated the implementation strategy, the latter being also very practical for integrating the effects of hydrostatic pressure into the diffusion.

Chapter 3

Chapter 3 is devoted to the Disk Pressure Test (DPT): it is first presented, as well as the material studied, then, modified geometries are introduced to localize the plastic deformation. Anisotropy is neglected for the sake of efficiency, while strain rate effects are taken into account.

It would have been interesting to start the study on the modification of the geometries of the DPT at the point where it was stopped by Moro 2009.

What criteria were used for the location of the notch? We note that the minimum thickness was kept constant (0.75 mm): for the same loading rate and the same exposure time, we

therefore expect the same penetration of H. Elements of choice on the geometries could have been indicated here.

p.54: "it was then reasoned that to obtained an optimal HE sensitivity, the most effective approach is to induce the maximum plastic strain in a region exposed to H2". This sentence deserves further explanation. If plasticity is so important, does this mean that dislocation trapping drives the HE?

p. 55: "although the displacement at the disk's center is greater when pressure is applied to the notched side". From what I understand from Figure 3.16, the experimental curves clearly show that the displacement at failure is the same, but not the failure pressure. The numerical curves stop at more than 10 MPa after the experimental failure.

Section 3.4.3: "effect of the pressurization rate"

As mentioned earlier in the paper, DPT results show several regimes under H2 with decreasing pressure rate: rapid decrease, then plateau, slight increase then for very low pressure rates. It is also observed a dependence of the pressure rupture under Helium (decreasing with decreasing pressure rate): the embrittlement index evolves accordingly from 1 (low pressure rate to a minimum value at intermediate rates, back to 1 for high pressure rates). Of course, "high" and "low" depend on all the kinetics involved: adsorption/absorption, passivation, H transport and the range can be wide: How can we be sure that the tests were carried out in the zone of maximum embrittlement?

E.g., on fig 3.19:

- a decrease in failure pressure under He can be observed, especially for X52

- for E55, a slight increase in the rupture pressure under H_2 can also be detected (no embrittlement at all for the cup disc)

Are there experimental dispersions on each point?

3.5 FEM modelling

p. 67, fig 3.29: the conclusion on the more relevant model is based on dimensionless Ctot maps, in which it can be seen that H is diffusing through the whole sample with the 'low N_T', i.e., "Therefore, the model that aligns most closely with experimental observations".

However, due to the chosen scale representation, it is not possible to know if there has been diffusion or not in the sample with the "high N_T" (max values x100!), noting that the boundary condition seems to close to 0.3-0.4 appm. Last, the cause of HE is here not indicated, leading to possible misinterpretation of the numerical results: is C_T or CL is responsible of the embrittlement process? Depending of the answer, the maps who must be looked at could leads to very different conclusions.

p. 67, fig 3.29: Conclusions on the relevance of the N_T models are based on scaled C-maps, in which it can be seen that H diffuses throughout the sample with the "low N_T", i.e. Therefore, the model that aligns most closely with experimental observations". However, due to the chosen scaling representation, it is not possible to know whether or not diffusion has occurred in the sample with the "high N_T" (max values x100!), noting that the boundary condition seems close to 0.3-0.4 appm. Finally, the cause of HE is not indicated here, leading to a possible misinterpretation of the numerical results: is C_T or CL responsible for the embrittlement process? Depending on the answer, the maps that need to be examined could lead to very different conclusions. This must also be connected to the previous assertion: "it was then reasoned that to obtained an optimal HE sensitivity, the most effective approach is to induce the maximum plastic strain in a region exposed to H2".

Fig 3.32: How is the relationship between C and the maximum principal stress calculated? At a given integration point (if yes: where?)

This chapter lacks a conclusion on the interest of having different shapes: is it useful? What information does it bring? Can they be used to qualify materials for hydrogen storage? This is also related to the reasons that led to the choice of geometry.

Chapter 4

This section deals with the comparison between experimental data and numerical model: tensile tests were carried out under H_2 at several strain rates up to different strains, with or without a step. The experimental results are first presented, then interpreted by the numerical model. This section could have gained clarity by comparing the experimental and numerical results directly.

Table 4.4 is not clear: test under air have no strain rate nor maximal strain + strain rate are sometime displaced in s (!).

Fig 4.9 (– 4.11 - 4.13): the impact of H on tensile test cannot be seen as F/S_0 is plotted versus time.

TDS calibration (fig 4.5): It is not clear what the uncharged sample represents. Could it be initial residual hydrogen? This could be investigated by performing TDS twice on the same sample: if the results are identical, it is a TDS artifact. Otherwise, there is residual H in the samples. This can significantly change the conclusion for K.

The same question arises for fig 4.6: "The three additional peaks observed at temperatures above 300°C are attributed to contamination from specimen engraving or other sources not investigated". The dislocation trap can be located at the new peak, but we can also imagine that, if the other 3 peaks designate 3 irreversible traps, a part of the diffusible H has also been trapped in the latter (because the characteristics seem to have slightly evolved). This is admitted p. 80-81: "Two additional peaks appear at temperatures above 250°C, particularly in the case at 1×10^{-4} s^{-1}. These peaks may originate from other trap sites with higher binding energies than the first peak." (it can be seen that at 1×10^{-3} s^{-1}, the contribution of these two additional traps is as important as that of the dislocation).

This section lacks a conclusion: what can be said about the influence of the strain rate? The penetration of hydrogen into the sample is an element that needs to be studied. Especially, the points in Figure 4.10b seem to be aligned. The impact of retention (section 4.4.3) tends to support the impact of the penetration depth, because the higher the plasticity, the lower the apparent diffusion coefficient.

Section 4.5-4.6:

The identification procedure is not that clear:

- Why 40 kJ/mol have been chosen for trapping by dislocation? TDS with different $\dot{T}$ could have been made to identify this parameter.
- The identification of N_T needs an estimation of θ_L which is not given?
- How the N_T has been identified ("Various functions were tested, and the one that provided the most accurate results is described below"), and based on which experimental data (least square method….)?

Moreover, the question of D_L can be raised, since the one for iron was used (and perhaps not relevant for the materials studied): there are cases in which the modeling is far from the numerical results (but since we do not know what data were used to define N_T, it is difficult to say something for the configurations for which the experimental and numerical results match). Choosing another D_L and performing the N_T identification again will lead to a different $N_T(p)$ that is able to consistently model the point used for identification but not the other configurations.

In all the experiments, there is only one critical kinetic term, assuming instantaneous trapping: the diffusion of hydrogen through the sample. Using all the data in this chapter could have been very useful to, at the same time, identify D_L and $N_T(p)$,, being able to minimize any distance between the exp. and numerical points.

The proposed N_T validates the proposition of Moro; what consequences could this conclusion have on the DPT simulation and its results?

Section 5

This chapter presents the nonlocal GTN model and its modification to include the impact of hydrogen on the growth and nucleation term (plus HEDE, by included by a term in $\dot{f}_n$). A detailed presentation of the implementation is presented. The model is then applied to several configurations: GTN parameters were identified on a test without H_2.

designed

H is considered to influence only the nucleation of voids (brittle failure), through a critical stress that is set to an exponential decrease (2 parameters to be identified). How this function was designed?

Once again, no distinction is made between diffusive and trapped hydrogen as the cause of HE.

The model is applied to a tensile test and convincingly reproduces the experimental data up to $5x10^{-3}$ s-1 (macroscopically and locally, in terms of crack initiation), when there is no HE numerically (contrary to experiment). What ingredient of the model needs to be modified/added to be able to better match the experimental results at high strain rates?

The model was then applied to DPT and CT samples: for both, it allows to efficiently reproduce the results of the papers published under He or H_2.

The use of flux (Kagayama 2021) is not straightforward, especially since he used a heat transfer analogy, without any reference to the oxide layers that might be broken. How can this flux be related to partially free adsorption surfaces?

Section 6

The CT modeling is reconsidered, as well as the mDCT samples, and applied to the two materials of section 3 (X52 and E355). The GTN parameters are identified on the tensile test.

Particular attention has been paid to the modeling of crack propagation. Hydrogen is not included here, as far as I know, and this chapter should therefore be understood as the first step in modeling the effect of hydrogen on the mDCT samples.

Simulations and experiments have been extensively compared: good agreement is observed for X52 but not for E355, indicating that size effects are more pronounced for the latter.

In conclusion, Daniel Pinto Lopes has produced an impressive amount of results, and, if it is difficult to know exactly which part was carried out by the doctoral student (implementation, calculation, etc.), shows a great mastery of coupled finite element calculation, including non-standard aspects. This work, carried out in close collaboration with other doctoral students, may have suffered from the time constraints induced by these collaborations. Chapter 4 would thus have been a very good study upstream of the one on the disk test (chapter 3).

For the hydrogen community, a non-local GTN model is proposed for the first time, at a time when there is a stir around ductile damage models assisted/modified by H. A reflection, not very common, is also conducted on the type of elements to use in the calculations, in a community that often does not pay attention to these points, yet important when we want to make the finite element calculation more reliable.

Finally, D. Pinto Lopes paves the way for studies of small-scale fracture specimens in H environment, which will certainly be done in a future doctorate.

J'estime donc que D. Pinto Lopes a toutes les qualités requises pour présenter son travail en vue de l'obtention d'un doctorat de l'Université PSL préparée à Mines Paris-PSL.

Fait à Villetaneuse, le 28 février 2025.