Investigation of hydrogen embrittlement of 316L steel by in-situ synchrotron tomography under hydrogen gas pressure.

Gianpaolo Pillon[1], Henry Proudhon[1], Yazid Madi[1], Victor Okumko[1,2], Andrew King[2], Laura Henry[2], James Ball[3], Jonathan Wright[3], Thilo F. Morgeneyer[1]

[1] Centre des Matériaux, MINES Paris, Université PSL, CNRS UMR, 7633, Versailles, France
[2] Synchrotron SOLEIL, Saint-Aubin, France
[3] European Synchrotron Radiation Facility, 38000 Grenoble, France

Corresponding author: gianpaolo.pillon@minesparis.psl.eu

Keywords: 316L, in-situ synchrotron tomography, delta-ferrite, hydrogen embrittlement, martensitic transformation.

Austenitic stainless steels are widely used in the energy industry for their corrosion resistance and their low susceptibility to H_2 embrittlement (HE). However, industrial processes such as welding can induce δ-ferrite (BCC structure) inside the austenite matrix (FCC structure). For 316L welds, the presence of the δ-ferrite (up to 10%) is well known to be the crack initiation site under H_2 as hydrogen segregates at the δ-ferrite/austenite interphase [1]. Moreover, this δ-ferrite represents an easy path for hydrogen diffusion inside the steel as its rate is up to an order of magnitude of 5 higher in this BCC phase than in the parent FCC austenite phase [2]. Another microstructural phenomenon affecting HE resistance is the fact that austenitic stainless-steel alloys may experience martensitic transformation [3]. Since Nickel is an austenite stabilizator, Nickel content reduction increases the probability for martensite to be formed under strain or stress. In terms of damage mechanisms, these microstructural features are also of extreme importance as BCC phases are more prone to fail by quasi cleavage than BCC phases.

The 4 mm hot-rolled sheet of 316L used in this study is provided by APERAM and presents relatively low Nickel content in the aim of resource optimization. The microstructure presents austenite grains with an equivalent grain size of 5.4 µm and δ-ferrite in form of layers of 1 µm thickness and width of tens of micrometers, which has brought less attention to the research community. Lab and in-situ synchrotron micro-tomography tensile tests are carried out to investigate the effect of δ-ferrite on tensile mechanical behavior and in particular HE. All tests were conducted at room temperature, at a strain rate of 10^{-4} s^{-1} under air, hydrogen gas pressure (from 200 to 240 bar) and thermally pre-charged hydrogen (12-25 days at 200-250 bar and 300°C). Tomography data for samples tested under hydrogen gas pressure reveal significant surface damage propagating toward the sample center. Correlative scanning X-Ray Diffraction-Computed Tomography (sXRD-CT) measurement reveals FCC (austenite) and BCC (ferrite and martensite) phases on a 2D slice and confirms that delamination occurs at the δ-ferrite/austenite phase interphase.

Coalescence cracks between the delamination cracks follow two scenarios:

- slant and related to martensitic transformation;
- necking of austenite phase leading to coalescence of delamination crack.

Results are similar for hydrogen thermally pre-charged sample in terms of bulk damage, and both samples reveal surface cracks through quasi cleavage that is likely related to martensitic transformation [4], as shown by sXRD-CT.

References:

[1] M. i Luppo, A. Hazarabedian, et J. Ovejero-García, « Effects of delta ferrite on hydrogen embrittlement of austenitic stainless steel welds », *Corros. Sci.*, vol. 41, nº 1, p. 87-103, janv. 1999, doi: 10.1016/S0010-938X(98)00083-3.

[2] M. Lin *et al.*, « A microstructure informed and mixed-mode cohesive zone approach to simulating hydrogen embrittlement », *Int. J. Hydrog. Energy*, vol. 47, nº 39, p. 17479-17493, mai 2022, doi: 10.1016/j.ijhydene.2022.03.226.

[3] C. Sanmarchi, « Effects of alloy composition and strain hardening on tensile fracture of hydrogen-precharged type 316 stainless steels », *Int. J. Hydrog. Energy*, vol. 33, nº 2, p. 889-904, janv. 2008, doi: 10.1016/j.ijhydene.2007.10.046.

[4] M. Kawamori *et al.*, « Dual effects of deformation on hydrogen embrittlement of austenitic stainless steels revealed by hydrogen visualization combined with microstructural analysis », *Int. J. Hydrog. Energy*, vol. 145, p. 559-577, juill. 2025, doi: 10.1016/j.ijhydene.2025.05.426.

Relever les défis du stockage cryogénique de l'hydrogène.

<u>Dr. Pierre-Emmanuel LEGER[1]</u>, Dr Dorian HACHET[1], Dr Pauline Huguenin[1]

[1] Aperam Research, BP 15, 62330 Isbergues

Dans le cadre de la transition vers la neutralité carbone, l'hydrogène liquide, maintenu à une température de -253°C à pression atmosphérique, constitue une solution stratégique pour la logistique énergétique. Aperam, spécialiste des aciers inoxydables et alliages de nickel, mène des recherches approfondies pour répondre aux contraintes extrêmes de ce mode de stockage. Ce dernier impose l'usage de matériaux hautement performants avec une faible perméabilité, d'excellentes propriétés mécaniques aux températures cryogéniques et une bonne résistance à la fragilisation par hydrogène. La famille 316L sera mise en lumière dans cette présentation car elle rassemble les qualités métallurgiques requises et constitue le matériau de référence pour la construction de tubes ou de réservoirs destinés à l'hydrogène liquide.

Effect of triaxiality and strain rate in the hydrogen embrittlement and damage development as well as the impact of maximum principal stress on surface crack growth for mini-specimen tested in a H_2 gas environment for a X70 steel

E.B. Campos[1*], V. Okumko[1,2], Y. Madi[1] , A. King[2], T.M. Morgeneyer[1]

[1] Centre de Materiaux – Mines Paris, [2] SOLEIL - synchrotron
*eduardo.ballmann_de_campos@minesparis.psl.eu

For this work, the effect of a hydrogen atmosphere is studied for a modern X70 pipeline steel. The effect of stress triaxiality and strain rate on hydrogen embrittlement (HE) are measured for mini-specimens. The specimens are charged with hydrogen gas of 6.0 quality inside a pressure chamber. The extensometry measures are made with Edge Tracing (ET) techniques to ensure accurate measurements without the need for mechanical measuring devices inside the gas chamber [1]

The mechanical testing is done with H_2 gas pressures of 80, 160 and 240 bar and compared to tests in air. Two different geometries are used, what allows comprehending the effect of stress triaxiality on HE. Different strain rates (10^{-4} and 10^{-5} s^{-1}) were applied and compared to see the effect of time and diffusion on HE.

The strain rates not only have an effect on the loss of ductility but also on the reproducibility of the experiments. For both geometries, the strain rate of 10^{-4} s^{-1} results show a significant scatter in the radial contraction data, going from 26 to 32%, while for the tests in air the radial contraction surpasses 60%. For the strain rate of 10^{-5} s^{-1} the tensile tests were more repeatable, ranging from 23 to 27% radial reduction before failure.

The specimens were analyzed with SEM microscopy and synchrotron microtomography of stopped test samples to better understand the fracture. Whilst the material tested under air showed classical ductile damage, hydrogen charged samples showed embrittlement and the appearance of surface cracks. Also, there is a difference in the damage at the center comparing the two different strain rates. At 10^{-4} s^{-1} most of the hydrogen embrittlement (HE) is found near the surface while the center remains ductile. At 10−5 s−1 hydrogen induced surface cracks are less prevalent and more bulk damage in form of cracks is found for the smooth tensile samples. Correlative EBSD shows that the cracks are transgranular and contained in single grains. The dominant crack of the notched tensile samples at 10−5 s−1 initiates by quasi cleavage cracking from the sample centre normal to the tensile axis. Inclined surface cracks in mNT samples are also present

Through an elasto-plastic FE simulation of the mNT samples, the observed damage zones are compared tothe fields of magnitude and orientation of the maximum principal stress. It is shown for the test at a strain rate of 10^{-4} s^{-1} that the crack location is consistent with the highest maximum principal stress location in the notch root and that their orientation is normal to the maximum principal stress direction. This highlight the importance of the maximum principal stress in the quasi cleavage damage development.
Because different strain rates change the total duration of the test, they also affect the total amount of hydrogen that diffuses into the sample. At a strain rate of 10^{-4} s^{-1}, the difference in hydrogen concentration between the surface and the center is greater than at 10^{-5} s^{-1}. Since embrittlement depends on the local hydrogen concentration, failure may remain ductile in the sample center at a strain rate of 10^{-4} s^{-1} .

As the material becomes more brittle, the normal stress required to initiate a crack decreases. Consequently, fracture does not necessarily occur at the location of maximum principal stress. Instead, it occurs where the principal stress exceeds the locally reduced critical stress for crack initiation, which has been lowered by the local hydrogen concentration. The interaction between the stress gradient and the hydrogen concentration gradient leads to the observed behavior.

References

[1] Y. Madi *et al.*, "Mechanical characterization of hydrogen embrittlement in a gaseous environment: An innovative test setup using sub-size specimens," *Engineering Failure Analysis*, 2024, vol. 162, p. 108362

Influence de l’hydrogène de volume sur le comportement mécanique d’aciers faiblement alliés exposés à l'hydrogène gazeux

Luciano MEIRELLES SANTANA[1], Florian THEBAULT[2], Michel PIETTE[2],Jacques BESSON[1], Yazid MADI[1]

[1]MINES Paris - PSL, Centre des Matériaux, CNRS UMR 7633, 21 Allée des Marronniers, 78000 Versailles France

[2]Vallourec OneR&D, 60 route de Leval 59 620 Aulnoye-Aymeries, France

Le développement des infrastructures de transport et de stockage de l’hydrogène impose une qualification rigoureuse des matériaux métalliques, en particulier face aux risques de fragilisation induite par l’hydrogène. Cette étude porte sur l’impact de l’hydrogène de volume sur le comportement mécanique d’un acier faiblement allié à haute résistance, envisagé pour des applications de stockage sous haute pression.

À température ambiante, l’absorption d’hydrogène gazeux par ces aciers reste très limitée, notamment en présence de couches d’oxyde natives en surface. Pour pallier cette barrière, une couche mince de palladium est déposée afin de catalyser l’absorption d’hydrogène et de simuler des conditions d’exposition prolongée. L’approche proposée se distingue par la combinaison d’un traitement de surface et d’une sollicitation mécanique, permettant de reproduire plus fidèlement les conditions d’usage industriel, tout en contournant les limites du chargement électrolytique souvent peu représentatif.

Des essais de traction menés sous atmosphère contrôlée d’hydrogène gazeux, couplés à une caractérisation in situ par tomographie 3D aux rayons X, permettent d’observer l’évolution de l’endommagement interne et d’évaluer les effets de l’hydrogène sur la ductilité et la résistance du matériau. Ce travail pose les bases d’une méthodologie de qualification plus représentative pour les aciers utilisés dans les infrastructures hydrogène. Des campagnes complémentaires en ténacité et en fatigue sont également prévues pour compléter l’analyse.