doi:10.1017/S1431927622006419
Microsc. Microanal. 28 (Suppl 1), 2022

Insight on High Temperature Hydrogen Attack Initiation and Morphology on Case Studies - 3D FIB-SEM and TEM Analyses for Fine Microstructural Characterization of Attacked Low Carbon Steels

Camille Flament[1*], Olivier Gillia[1], Thomas David[1], Romain Soulas[1], Laure Guetaz[1], Charles Le Nevé[2], Raphaël Goti[2]

[1.] Université Grenoble Alpes, CEA - LITEN, Grenoble, France
[2.] TotalEnergies, Total Research and Technology Gonfreville, Harfleur, France
* Corresponding author: camille.flament@cea.fr

High temperature hydrogen attack (HTHA) is a phenomenon which affects low carbon ferrito-pearlitic steels constituting pressure vessels under temperature (T>250°C) and hydrogen pressure [1–3]. It is characterized by the formation of methane bubbles at grain boundaries due to the reaction between hydrogen and carbon atoms present in solid solution and in carbides. It leads to a surface decarburization of the steel. As ageing in hydrogen atmosphere progresses the bubbles grow and coalesce until cracking occurs leading to mechanical properties loss. A special attention is paid to this well-known phenomenon in petroleum refining and petrochemistry but it will also have to be predicted in the new power-to-gas reactors and in biomass energy recovery processes. The identification of the elements at the origin of bubbles creation is a key parameter to prevent irreversible deterioration of pressure vessel steels.

The objective of this work is thus to investigate the origin of HTHA in low carbon ferrito-pearlitic steels still used in petroleum facilities. To this purpose different pieces of steels, i.e. base metal and weld, coming from several petroleum refineries and which were submitted to high temperature (between 250 and 400 °C) and hydrogen pressure (ranging from 18 to 136 bars) after tens of years in powerplant have been studied. Their observation allows to describe HTHA after different stages of attack. Advanced characterizations of the steel damage microstructure have been performed by means of optical and electron microscopy as well as X-ray tomography. More specifically a focused ion beam - scanning electron microscopy (FIB-SEM) allowing 3D reconstruction of about 10 μm^3 volume of materials and transmission electron microscopy (TEM) have been used to examine the microstructure of the hydrogen attacked steels from micron to nanometer scale.

A careful attention has been paid to the location of initiation and the morphology evolution of defects (bubbles/voids, cracks) on the different case studies of this work. On a much-attacked C-steel vessel coming from a CO-methanation tube, observations at micron scale by optical microscopy and SEM reveal a particular attack profile with orthoradial intergranular cracks near the inner surface submitted to hydrogen atmosphere and radial near the outer surface. Pearlite grains, which are constituted of packets of cementite carbides plates distributed in a same ferrite grain, are preferentially attacked since their amount decreases approaching inner surface (Figure 1). This induces a surface decarburization and a weakening of the steel from the inner surface. On a much less attacked vessel coming from a hydrofinishing reactor, SEM observations from inner surface show that voids decorate some pearlite grains. They are located at the interface between cementite and ferrite as well as at grain boundaries. No crack has been noted for this stage of attack in this microstructure. 3D FIB-SEM technique has allowed to visualize in three dimensions the link between voids, carbon phases and inclusions distributed along particular planes which can cross several ferrite and pearlite grains (Figure 2). When a plane rich in inclusions intercepts a grain of pearlite or a grain boundary, voids are detected. Associated to TEM observations, it has been shown that the small inclusions observed both close to voids and carbon phases are mainly nanometric AlN precipitates. They could be a catalyst of voids nucleation. It shows that the advanced characterization techniques used in this study are very powerful for understanding the early hydrogen attack stage and as far as our knowledge, only very few articles [4] describe such combination of fine characterizations in order to highlight the trigger of HTHA.

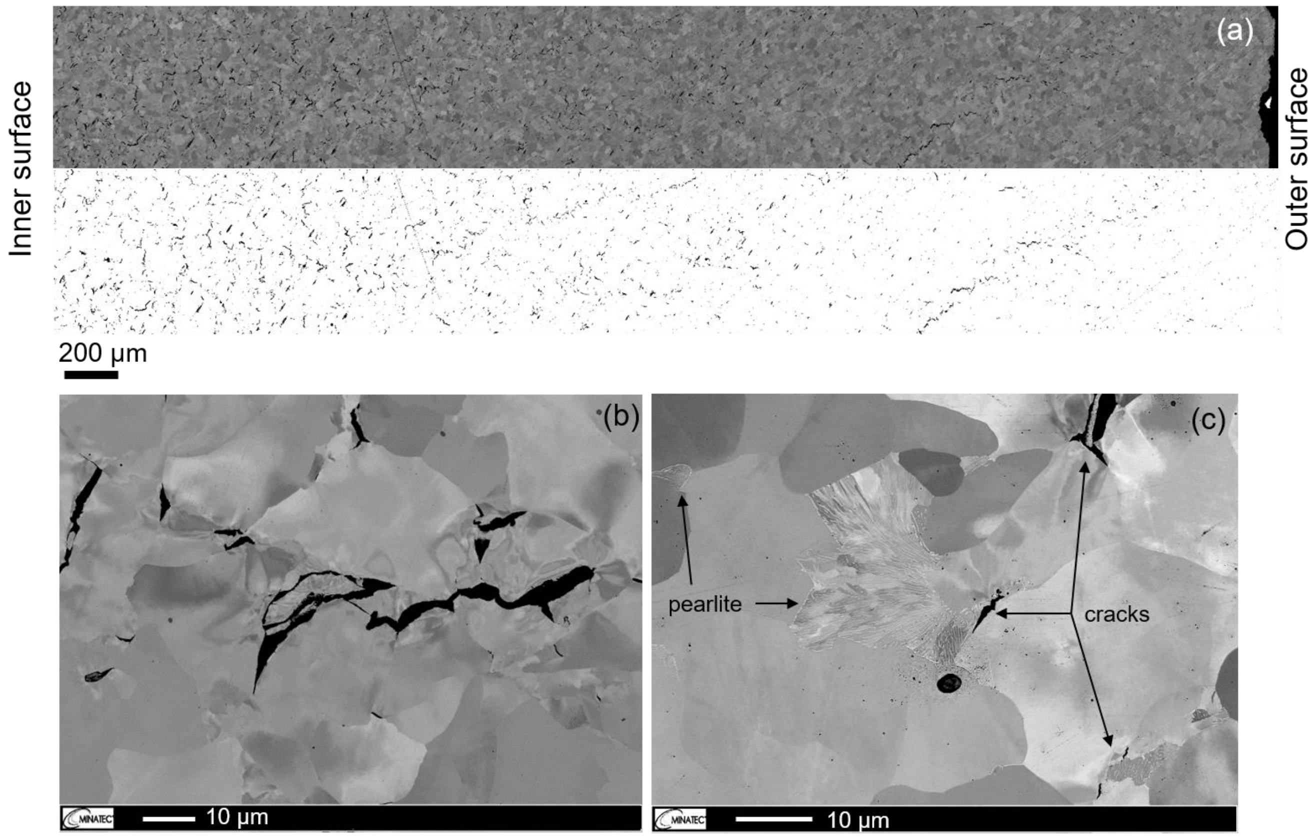

Figure 1. Characterization of much-attacked steel microstructure. (a) SEM observations from the inner (left) to the outer (right) surface of a piece of attacked tube as well as the image analysis by Image J showing cracks in black. (c,d) SEM observations of intergranular cracks at different magnifications showing their relation with pearlite grains.

https://doi.org/10.1017/S1431927622006419 Published online by Cambridge University Press

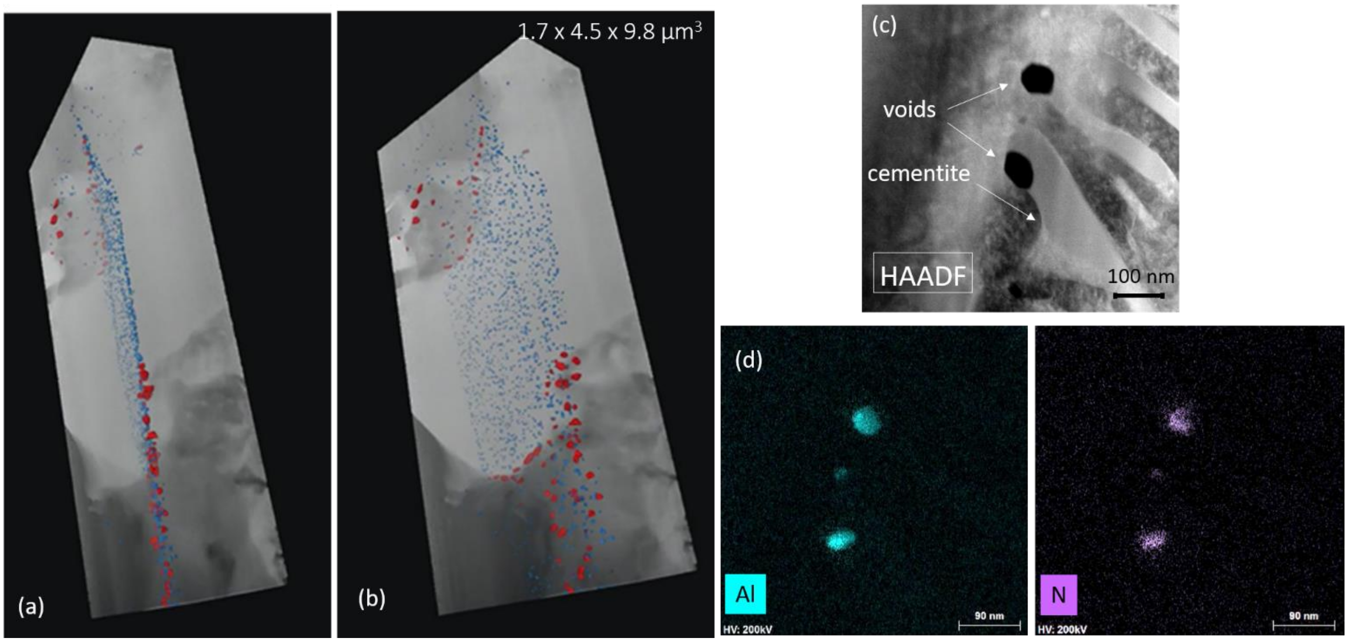

Figure 2. Characterization of less-attacked steel microstructure. (a,b) 3D view of an alignment of small inclusions (blue objects) in ferrite (light grey) linked to voids nucleation (red objects) when the inclusion plane interferes with the carbon phase - cementite (dark grey) (volume dimension : 1.7 x 4.5 x 9.8 μm^3). (c) STEM-HAADF (high angle annular dark field) image showing voids at carbides interface with the matrix. (d) Al and N EDX maps suggesting inclusions in voids can be AlN precipitates.

References:

[1] G. A. Nelson, Present. Proc. API Div. Refin., **29M (III)** (1949), p. 163.
[2] API Recommended Practice 941, « Steels for Hydrogen Service at Elevated Temperature and Pressures in Petroleum Refineries and Petrochemical Plants », 8th edition (2016).
[3] J. E. Cantwel, Mater. Perform., **33** (1994), p. 58- 61.
[4] M. L. Martin, M. Dadfarnia, S. Orwig, D. Moore, P. Sofronis, Acta Materialia, **140** (2017), p.300-304. doi:10.1016/j.actamat.2017.08.051.