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ASSOCIAZIONE PER LA PROTEZIONE DALLE CORROSIONI ELETTROLITICHE

Technical focus on “Electrochemical charging and hydrogen embrittlement of carbon and low alloy steels for Oil & Gas applications”

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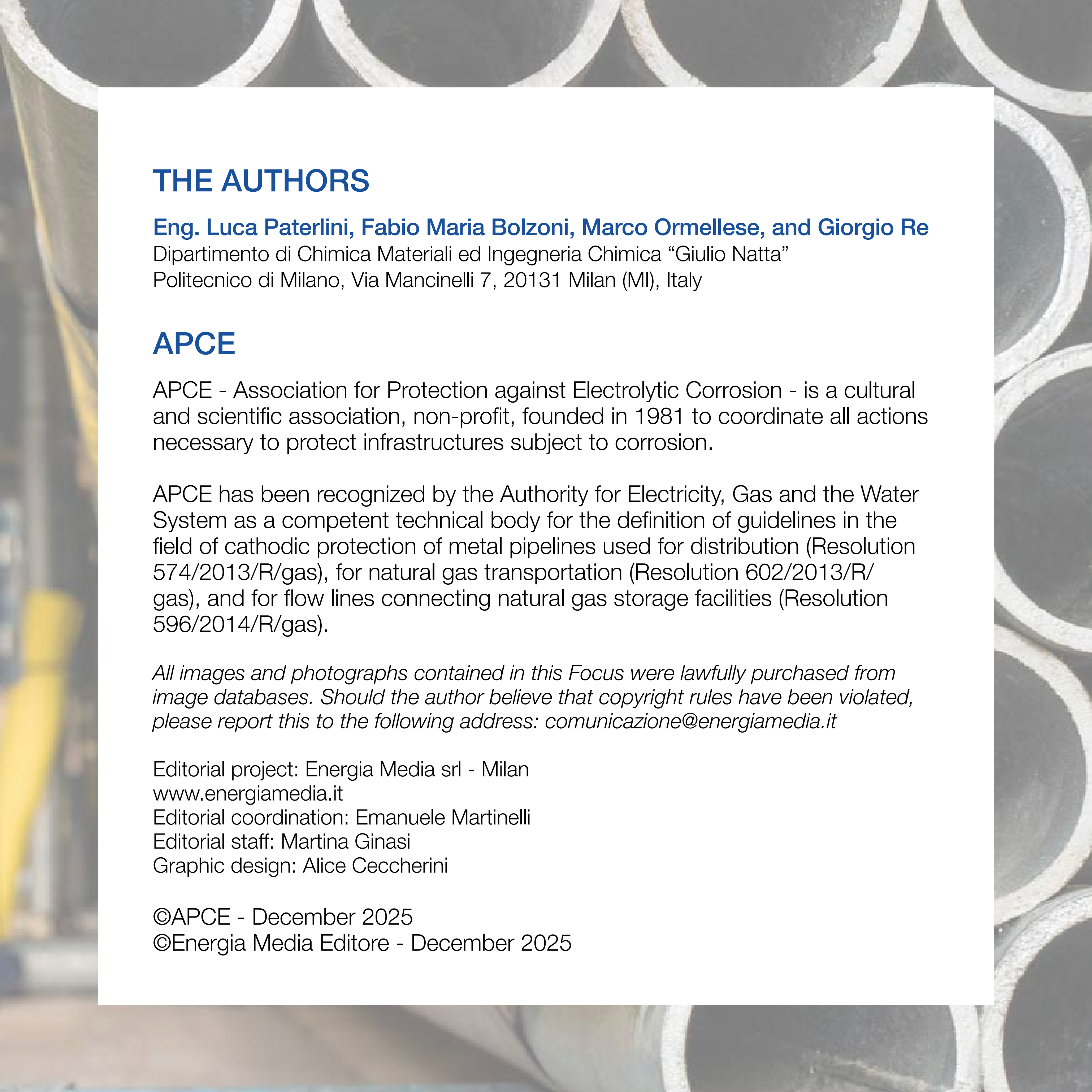

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APCE

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APCE has been recognized by the Authority for Electricity, Gas and the Water System as a competent technical body for the definition of guidelines in the field of cathodic protection of metal pipelines used for distribution (Resolution 574/2013/R/gas), for natural gas transportation (Resolution 602/2013/R/gas), and for flow lines connecting natural gas storage facilities (Resolution 596/2014/R/gas).

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FOCUS TEMATICO SU “CARICA ELETTROCHIMICA ED INFRAGILIMENTO DA IDROGENO DI ACCIAI AL CARBONIO E BASSO LEGATI PER APPLICAZIONI OIL & GAS”

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INTRODUCTION

The decarbonization of the energy sector has brought hydrogen to the spotlight as a strategic energy carrier. Its versatility as a clean fuel and storage medium positions it as a key element in future energy networks.

Yet, its chemical and physical properties introduce few challenges for materials engineers. Hydrogen embrittlement, the degradation of mechanical performance due to hydrogen absorption into metallic structures, remains one of the most critical barriers to the safe and widespread distribution of hydrogen.

Pipeline steels, predominantly carbon and low-alloy grades standardized under API specifications, are central to the Oil & Gas industry and are currently being considered for hydrogen transport and storage. Their mechanical strength, cost-effectiveness, and manufacturing scalability make them attractive candidates.

However, their susceptibility to hydrogen embrittlement can significantly compromise the reliability of pipelines and storage vessels. The phenomenon has been studied for decades and is known to reduce ductility, toughness, and resistance to crack propagation.

The mechanisms are multiple (Hydrogen Enhanced Local Plasticity "HELP", Adsorption-induced Dislocation Emission "AIDE" and Hydrogen Enhanced Decohesion Emission "HEDE") and often interdependent: hydrogen can weaken atomic bonds in the lattice, promote localized plasticity, or trigger dislocation emission at crack tips.

In all cases, the final effect is a reduction in the stress or energy required for crack initiation and growth *(Figure 1)*.

For the industry, the challenge is worsened by the cost and complexity of conventional hydrogen service qualification methods. In-situ testing in high-pressure hydrogen is the standard approach but requires specialized autoclaves, stringent safety measures, and long experimental times. These limitations hinder systematic screening of materials and further complicate the design of a new hydrogen-oriented infrastructure. To address this, the study presented in the thesis explores electrochemical hydrogen pre-charging as a complementary approach.

This technique introduces atomic hydrogen into steels in a controlled manner, enabling conventional mechanical tests to be performed in air while still reflecting the influence of absorbed hydrogen on the mechanical performances of the studied alloys.

The work couples this testing methodology with finite element method diffusion modelling and fracture analysis, to help in understanding and quantifying hydrogen embrittlement in steels of industrial relevance.

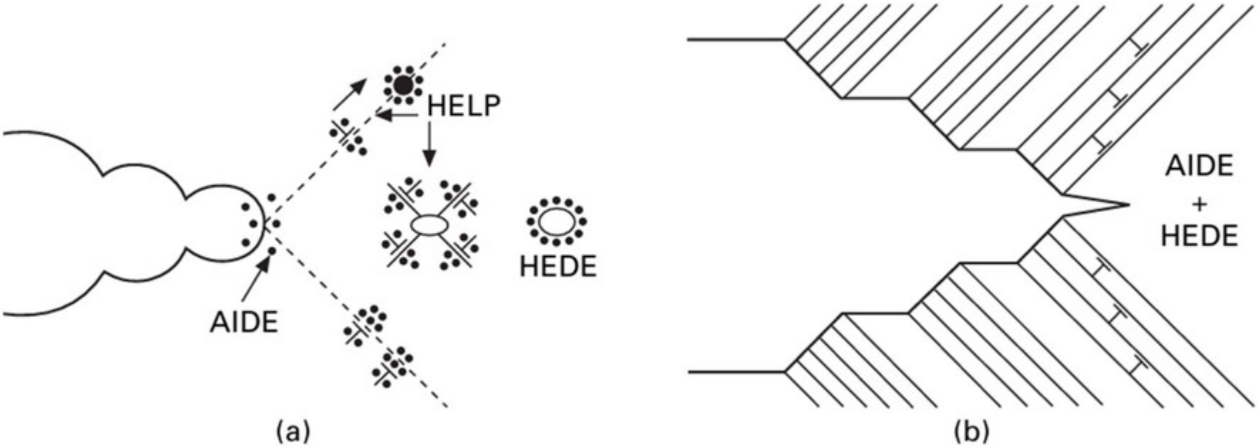

Figure 1 – Schematic representation of hybrid HE mechanisms.

a) AIDE with the contribution of HELP and HEDE ahead of crack-tip.

b) AIDE and HEDE alternance

MATERIALS AND METHODS

The steels investigated in the thesis cover a wide spectrum of Oil & Gas applications. Among them are pipeline grades such as API 5L X60, studied both in a vintage production (from now on X60 Vintage) and in a modern thermomechanically controlled processed variant (from now on X60 TMCP), as well as steels used for fittings and flanges, including A694 F65 (from now on F65) and A350 LF2 (from now on LF2).

Quenched and tempered 4140 steel (from now on 4140 Q&T), along with its annealed counterpart (from now on 4140 annealed), was considered to represent tubing and higher-strength applications, while API 5CT T95 (from now on T95) was selected for its relevance in casing materials for sour service. The set therefore spans from low-strength ferritic-pearlitic microstructures to high-strength tempered martensite, covering the range of steels currently deployed in pipeline and oil well applications.

Hydrogen was introduced in the alloys through electrochemical charging, exploiting the hydrogen evolution reaction, similarly to cathodic overprotection; a schematic representation of the electrochemical hydrogen charging set-up employed in this study is reported in *Figure 2*. Specimens were immersed in acidic electrolytes and polarized cathodically to favour the formation of atomic hydrogen and promote its absorption into the steel lattice.

Arsenic trioxide was introduced in the electrolyte as a recombination poison to

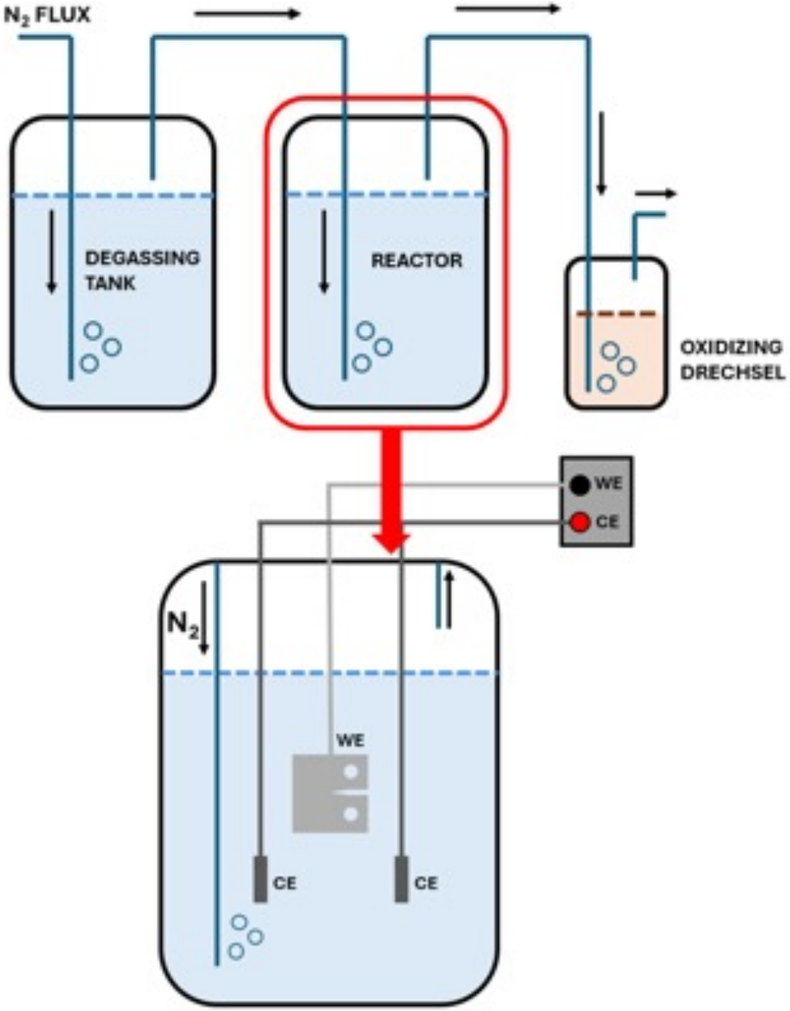

Figure 2 – Schematic representation of the electrochemical hydrogen charging setup on the top, zoom on the reactor cell on the bottom.

extend the residence time of hydrogen atoms at the surface, by hindering their recombination to molecular hydrogen, and therefore enhance uptake.

By controlling current density and charging duration, the absorbed hydrogen concentration could be tuned to mimic different high pressure or even sour service conditions. To ensure uniform hydrogen distribution, finite element methods analysis were conducted using the diffusion coefficients obtained by electrochemical permeation tests.

These tests, carried out in Devanathan–Stachurski double cells according to ISO 17081 Standard, provided a measure of the hydrogen apparent diffusion coefficients in the various alloys, which include the effects of microstructural traps in addition to plain lattice diffusion. A schematic representation of the hydrogen permeation tests set-up is reported in *Figure 3*.

Mechanical testing was then performed on hydrogen-charged specimens. Hydrogen concentrations were quantified before testing by hot glycerol extraction. Tensile tests were used to evaluate yield strength, ultimate tensile strength, elongation, and reduction of area, while fracture toughness was measured through J-integral methods on compact tension (CT) and single-edge notched bending (SENB) specimens.

Fractographic analysis was performed on of the same specimens. This latter step, carried out by scanning electron microscopy (SEM), offered direct insight into the fracture processes activated by hydrogen.

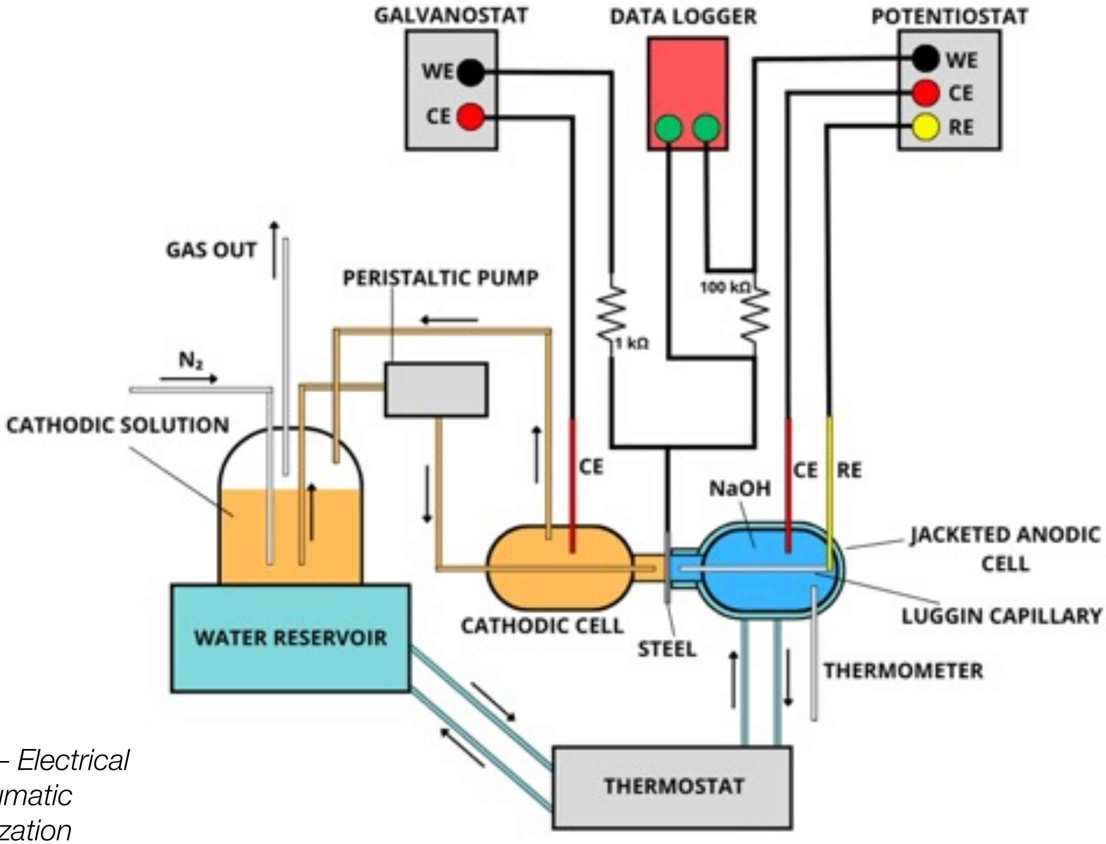

Figura 3 – Electrical and pneumatic schematization of the employed Devanathan-Stachurski permeation setup.

RESULTS

Mechanical testing on hydrogen-charged specimens highlighted the relevance of hydrogen exposure. Tensile properties confirmed that strength indicators such as yield strength and ultimate tensile strength were essentially unaffected by hydrogen absorption. In contrast, ductility related parameters suffered mild reductions. Both elongation at break and reduction of area decreased once hydrogen was introduced in the alloys. Nevertheless, no clear trend capable of explaining the data scatter of these parameters was found during this research.

On the other hand, the most critical outcome was observed in fracture toughness testing. In air, several of the investigated steels displayed high toughness, with J-integral derived values well above 400 MPa√m. After electrochemical hydrogen-charging, however, the fracture toughness collapsed to a narrow band between 120-150 MPa√m, largely independent of the alloy type or its initial toughness, as highlighted in *Figura 4*.

This convergence suggests, according to the authors, that once hydrogen is absorbed, the differences in initial toughness among the alloys are no longer decisive. For design purposes, this means that steels traditionally considered tougher in natural gas service cannot necessarily be expected to outperform others under hydrogen exposure conditions.

Furthermore, a consistent fracture toughness reduction was also observed when lighter hydrogen charging conditions were applied.

This suggests that even a small concentrations of hydrogen can impact fracture toughness and that there exist no minimal hydrogen content threshold, in the tested conditions *(Figure 4)*.

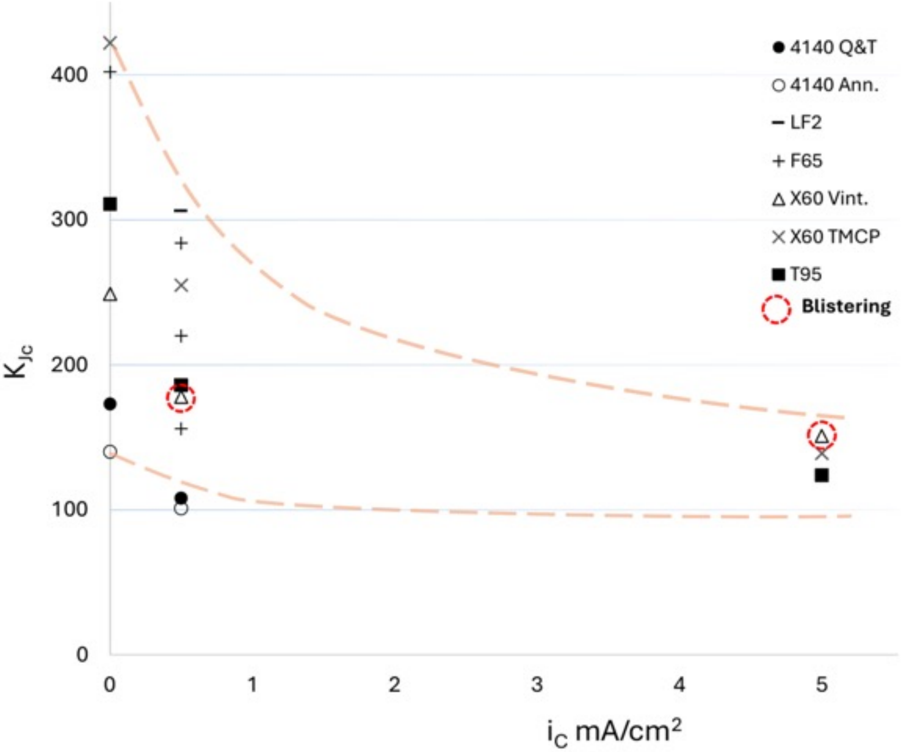

Figure 4 – Critical stress intensity factor (KJc) Vs applied electrochemical charging current density (ic). Higher ic identifies increasingly severe hydrogen exposure conditions.

These observations underline the fact that hydrogen embrittlement is not primarily a question of strength loss but of reduced ability to accommodate deformation before failure.

The obtained results and trends strongly aligns with in-situ J-integral tests performed in literature by other authors, suggesting good affinity between electrochemical and gaseous hydrogen testing, despite the difference between the two environments.

Fractographic analysis provided visual confirmation of these trends. In specimens tested without hydrogen, failure surfaces were characterized by ductile dimple rupture, with clear evidence of microvoid coalescence.

By contrast, hydrogen-charged specimens showed mixed morphologies: shallow dimples, quasi-cleavage facets, and secondary brittle cracks were consistently observed *(Table 1)*.

Tougher alloys, such as X60 TMCP and T95 *(Table 1, central and right columns)*, displayed a marked transition from ductile to brittle fracture morphology, demonstrating their sensitivity to hydrogen.

On the other hand, despite its initial lower fracture toughness, the X60 Vintage mostly conserved its ductile fracture features even when exposed to the harsher electrochemical hydrogen-charging conditions *(Table 1, left column)*.

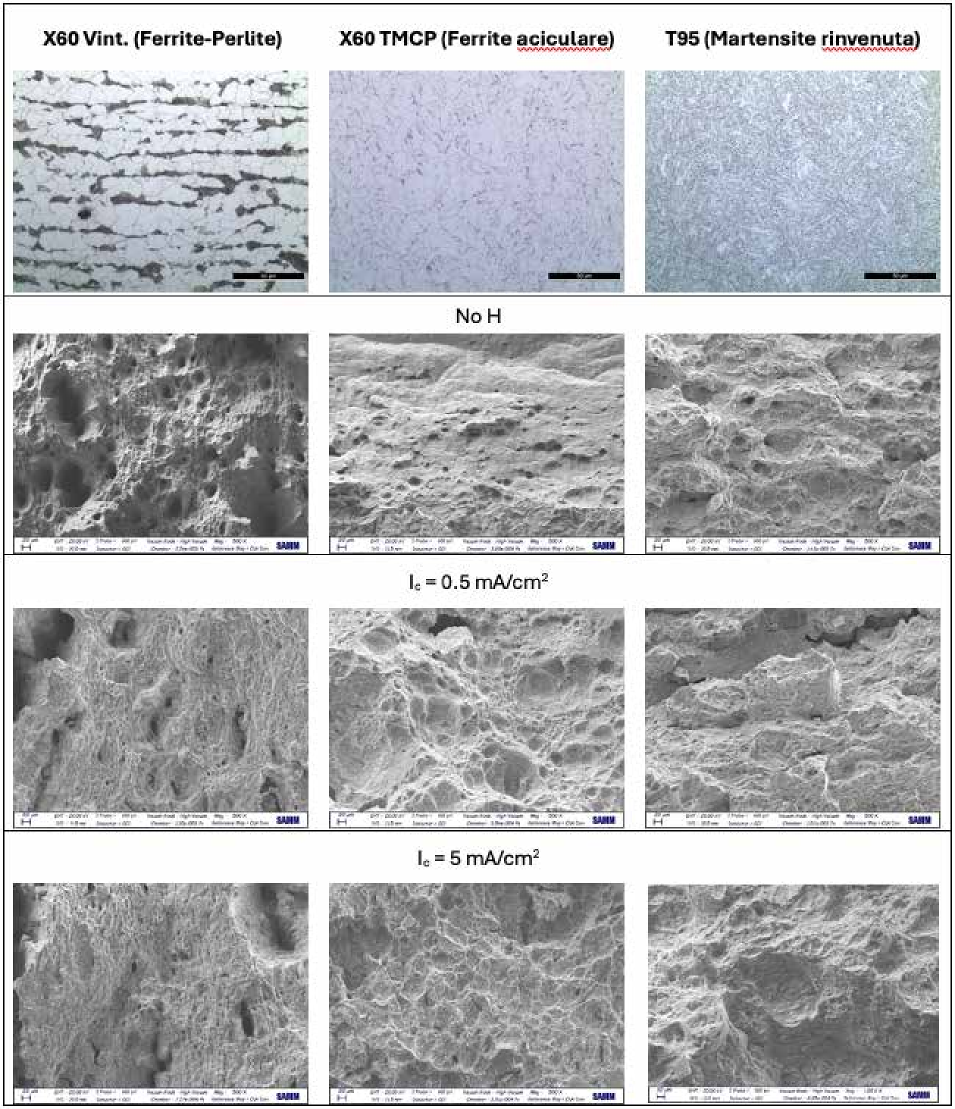

Table 1 – Microstructure and fracture morphology of X60 Vint., X60 TMCP and T95. Toughness tests samples, tests performed in increasingly severe hydrogen exposure conditions, from top to bottom.

DISCUSSION AND CONCLUSIONS

The results confirm that hydrogen embrittlement acts primarily through degradation of toughness and ductility, rather than strength.

This distinction is crucial for industrial applications. Pipelines and storage vessels are designed not only to sustain Hoop stress, but also to resist crack initiation and propagation. The sharp reduction in fracture toughness under hydrogen exposure directly affects defect tolerance and fatigue life, both essential parameters in the integrity management of large-scale infrastructure.

The convergence of toughness values across steels suggests that traditional distinctions between grades, based on their air-tested mechanical properties, tends to lose relevance in hydrogen service.

For instance, modern TMCP steels with excellent toughness in conventional environments showed similar degraded values as older, less refined materials once exposed to hydrogen. This finding indicates that hydrogen establishes a lower bound of fracture resistance that overrides microstructural improvements designed for conventional service, at least concerning the tested alloys.

Electrochemical pre-charging, coupled with hydrogen diffusion modelling, proved capable of reproducing embrittlement levels comparable to those obtained in costly high-pressure autoclave tests.

While it cannot fully replicate the dynamics of hydrogen access at an advancing crack tip in gaseous hydrogen, the method provides an effective and scalable tool for screening materials and generating comparative data.

This offers a valuable compromise: reliable insight into hydrogen effects can be obtained without the prohibitive cost and time associated with large-scale autoclave campaigns.

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