Multi scale insights into deformation/environment interaction affecting the mechanical behavior

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1. Abstract

Significant efforts have been invested into deformation/hydrogen interaction affecting the mechanical response. By adopting a material approach, elastic-plastic polycrystalline and single crystal systems were selected accompanied by comprehensive mechanical characterization. In the current study, a major activity section is centered on metastable austenitic stainless steel interacting with external/internal low fugacity hydrogen. Subsequent events due to free hydrogen interaction have been tracked, enjoying the assistance of experimental advances to match improved computational capabilities. In order to define better the crack-tip mechanical environment, fracture mechanics methodology was supplemented, namely, important step to reduce ambiguity, so typical to multi-parameter and complex problems. The engagement with phase on top of crack stability aspects provided further powerful views regarding time dependent processes. Global/local findings established integrated approach based on crack-tip dislocations emission model that enabled beneficial resolutions. Small volume information by nano tests, micro probe measurements and fine features visualization facilitated comprehensive and consistent developments. Simulations assisted by findings confirmation on relevant scales contributed to brighten important facets as related to micro mechanism analysis, including assessment of a complex highly localized material degradation process.

2. Introduction and background

Generally, it is a well-accepted perception that fracture or fatigue is localized processes that require as such critical experiments. The meaning is continuous search for information that is founded on ultra-fine features resolution, confined to small volume mechanical response. Nevertheless, technological needs associated with highly vital structural integrity problems enhanced intensive activities along global avenues that have been later stretched to basic concepts. The aforementioned notion describes briefly the historical background as related to deformation/hydrogen interaction effect activities in elastic-plastic metallic systems. Even by narrowing the current scope only to the interaction of free hydrogen, the issue of Hydrogen Embrittlement (HE) was still raised following the engagement with proposed fundamentals up to even suggestions or declaration of viable micro-mechanisms. Engineering wise, the intensive studies by the available global tests and observation have been highly important, revealing gradually the problem complexity beside continuous technological progress. Thus, highly localized physical origins on one hand have been tackled by argumentations based on macro findings. Notice, confronted difficult questions that have been pointed out in the case of deformation/hydrogen interaction are basic dilemma in fracture physics understanding even with no environment. The above arguments distinguish between the continuous search for strongly founded mechanism dominating the phenomena of HE in contrast to the urgent activities guided by the practical demands to established model that promise predictive capabilities that can explore design criteria development. The importance of a better resolution has been recognized but the gain of macroscopic observations was essential and even beneficial. Nowadays, localized information requirement became even more demanding in order to explore small volume mechanical response. The current investigation is constructed by describing briefly HE global findings and some of the efforts associated with the phenomena in various systems. The study follows experimental/simulation/theoretical interfaces toward small volume interactive behaviour. In this context novel techniques and visualisation were utilized. Beside the incentive to demonstrate the experimental and computational feasibility and the nano-contact mechanics potential contribution to small volume in mechanical studies in general, critical experiments as related to HE have been particularly attempted as well. Ultra fine resolution has been recognized at relatively early stages by the Illinois school [1-10] emphasized the scale issue or the essential requirements needed in order to explore the HE mechanism. For this purpose "in situ" TEM and HVEM observations and measurements have been conducted. Dedicated hydrogen cell enabled to follow dislocation activity including velocities measurements that were affected by hydrogen. The search for viable mechanism has been addressed also by Lynch [11,12] suggesting the mechanism of adsorbed hydrogen in contrast to solute hydrogen enhancing failure by plasticity. The later is closely related to the suggested liquid metal embrittlement mechanism in which environment adsorption might generate dislocations causing to crack instability. Thus, the consistent studies by the Illinois school proposed the Hydrogen Enhanced Local Plasticity (HELP) and Lynch model represented the Adsorption Induced Dislocation Emission (AIDE) mechanism. The aforementioned mechanisms recognize the critical role of dislocations activity that might lead even to brittle fracture. For example, the enhanced cleavage or shear localisation by hydrogen interaction considered the ramification of the transition in dislocation dynamics. Nevertheless, the problem of brittle fracture including cleavage requires special elaboration. It is important to mention that the essential role of plasticity to be frequently the main triggering agents in enhancing the brittle fracture mode has been established already [13,14]. By alluding previously to the continuous striving for better understanding of the low energy fracture mode process, emphasised the concept that brittle fracture is a first of all topics, regardless with or with no environmental effects. This appears certain in the brittle/ductile (B/D) transition phenomena so typical to specific crystal structures, fracture mode transition that is thermally and strain-rate dependent. This appropriate example served as a prior background. In addition the engagement with B/D transition might reveal conditions for enhanced cleavage mode transition reflecting as such immanent connection to the "embrittlement" issue [15,16]. With this in mind the Minnesota school developed a broad theoretical/experimental numerical simulation program resulting in the development of crack-tip dislocation model. Along these avenues, iron-based single crystals have been included, later extended to the deformation /hydrogen interaction problem. In the aforementioned program, crystal plasticity considerations were added with coherent information as related to the crack-tip dislocation emission assisted by observations that confirmed the dislocation model to be physically based. Following a comprehensive series of research activities as related to brittle fracture concepts in general, further developments resulted also in the Hydrogen Enhanced Decohesion (HEDE) - HE model [17-21]. The major concern in developing the HEDE model has been a desire for predictive model capacity still in the framework of the fracture process as related to deformation/hydrogen interactive effects. Generally, it has been easier to embrace a generic decohesion model with emphasis on the fracture stress as the end result of sequential micro-mechanisms in an elastic-plastic solid. As such, HEDE is directly related to enhanced "embrittlement" in contrast to the HELP model that refers (in our perception) more to hydrogen-induced material degradation. Only for the sake of briefness the current study describes mainly activities in meta-stable austenitic steel. In AISI 316L, global and local experiments have been performed; however the localized mechanical efforts are mainly elaborated. At this stage it seems important to stress the achievements that have been obtained by global tests regarding monotonic or cyclic remote load circumstances. Degradation at mechanical properties due to hydrogen interaction included elements like reduction in fracture resistance, changes in threshold values and dramatic efforts on phase and crack stability. The refinement to nano mechanic and scratch techniques beside micro probe visualization and measurements provided different level of resolution. The prior established dislocation model was challenged by imposed local-mechanical based tests, with dramatic information as related to crystal plasticity, dislocation dynamic affected by hydrogen interaction. This approach opened interesting insights into the already proposed micro-mechanisms. Thus a certain progress in a comprehensive evaluation in which localized plasticity beside the traditional decohesion model actually supplement each other

3. Materials and experimental procedures – Global/local

Although centering on meta-stable austenitic steels, the established background has been remarkably broad. Materials selections included structural classes of steels, Al-alloys and Ti-alloys-polycrystalline systems. In addition, iron based single crystals and the AISI300 austenitic stainless steels 304L, 316L, 310 that covered a wide range of phase stability degrees in which second phase aspects became interesting. Hydrogen has been provided either by electrolytic cathoding charging or by high temperature/pressure gaseous charging. Austenite decomposition products were determined by X-ray diffraction and Mossbauer spectroscopy analysis. Mechanical properties were established including fracture toughness parameters affected by hydrogen. Cyclic behaviour including sub-critical crack extension rates or single overload effects were also supplemented. Local tests in AISI316L utilized contact mechanics methodology, namely nano-probing and scratch tests, beside visualization and measurements. In this case, electrochemically hydrogen charging in 1M NaOH was conducted for 4-6 h prior to testing. Here, current densities ranged from 10-500 mA/cm^2. Experimentally, various techniques were used including, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) assisting also to provide Selected Area Channelling Pattern (SACP) images. In addition, for ultra fine features visualisation and measurements, Atomic Force Microscopy (AFM) and Acoustic Emission (AE) spectroscopy were supplemented. As mentioned, for the 316L austenitic stainless steel a comparative global/local study was performed. Following electrochemically polishing and hydrogen charging, nano-indentation by Hysitron was conducted. For a prescribed load of 1000μN a 90^O intender with 400 nm radius of curvature was utilized. Tests were performed at different stages namely, prior to hydrogen charging, instantly after charging and after long elapsed time of one day. In addition nano-scratch tests were conducted with gradually increased load during the moving intender across the tested surface. Here again, 90^O conical intender was used with 1μm radius of curvature. A typical scratch consisted of horizontal and vertical displacements at rates of 1μm/sec and 7nm/Sec. With a prescribed scratch length of 200 μM the normal force increased to 40-50 mN depending on the local surface inclination. The maximum penetration depth sealed up to 1.5 μm. SEM and AFM visualisation measurements enabled to achieve quantitative results of localised strain enhanced by hydrogen uptake.

4. Experimental results and analysis - global/local

4.1 Experimental results

Hydrogen fugacity and other factors as related to the hydrogen source might be significant in the detail of mechanical properties degradation, initial damage formation sites or in affecting the sub-critical crack extension kinetics. However, in the 316L austenitic steel, phase stability and enhanced brittle fracture mode transition prevailed regardless the exact hydrogen source (see Fig.1).

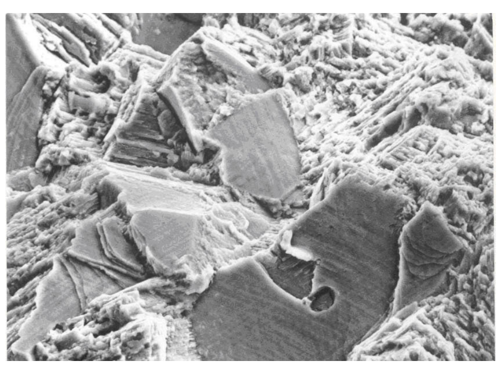

Fig. 1 Fractography, fracture mode transition 316L stainless steel

The transformation reaction caused by hydrogen consisted according to (Eq.1):

$$\gamma \rightarrow \varepsilon' + \alpha'$$

Where γ is the austenitic phase transformed to έ and ά that are the hexagonal close-packed and the body-centered tetragonal martensitic phases respectively. Mechanical degradation was manifested by ductility reduction, enhanced brittle fracture mode transition delayed cracking initiation/propagation and fracture resistance reduction in threshold wise behavior. Cyclic behavior was affected by hydrogen interaction resulting in higher crack extension rates and typical process zone behavior due to multi phases of a single overload behavior. Generally expended transformed phases were formed with hydrogen indicating during transient time of gas release identified pseudo phases by X-ray diffraction and internal friction studies [22,23]. The transformed phases fractions established by X-ray and Mossbauer spectroscopy analysis were highly consistent. In addition the martensitic phases were characterized by Mossbauer spectroscopy to be identical to the thermal/mechanical transformation below the M_d with no hydrogen.

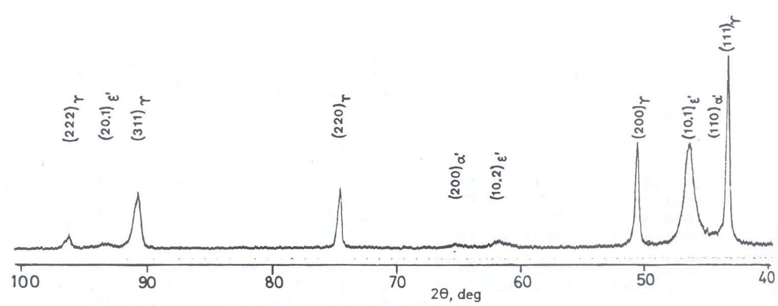

Fig. 2 x-ray diffraction of H charged 316L stainless steel, scanning after 16h

Referring back to the nano-probing findings, the contact load-displacement curves indicated dramatic changes as related to yield excursions. For example, reproducible excursions at an average load of 200μN were observed in non-charged surfaces compared to about 700μN caused by hydrogen interaction. Based on the recorded load vs. horizontal distance, loads corresponding to selected scratch segments could be estimated. For better comparison of the hydrogen effects, scratch segments corresponding to nearly equal normal loads were selected. For the non-charged surfaces, numerous closely spaced slip lines were observed. In contrast, charged surfaces, slip lines were widely spaced with higher-surface upset. Thus, quantitative measurements indicated enhanced localized slip with hydrogen, with typical local plastic strain.

4.2 Additional insights into analysis/simulation attempts.

Higher resolution findings resulted in the HELP proposed mechanism, namely, the notion that solid solution free hydrogen causes dislocation unpinning. Thus, dislocations increase their mobility and allow highly localized deformation. The "in situ" TEM observations during step-wise hydrogen addition/removal stages were performed in ultra-thin sections with no plastic constraint (attracted controversial remarks). Although the microscopic findings appear to be the strongest experimental conformation other supportive arguments have been supplemented as overviewed thoroughly by Birnbaum et al [4]. High-resolution Electron Micro Auto Radiology (EMARS) should also be mentioned as related particularly to ß-Ti polycrystalline alloy.

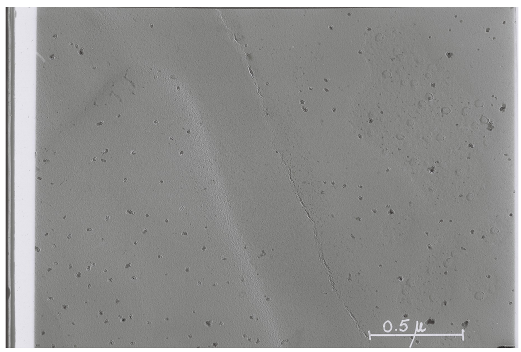

Fig. 3 EMARS of ß-Ti indicating variations in local concentrations

Indicating for example the depleted zone at grain boundaries or local hydrogen concentration variations in the multi-phases matrix. Intentionally the ß-Ti system is mentioned, a system that despite the fact of hydrogen enhanced dislocation velocity the HELP mechanism could not explain easily the embrittlement occurrence [4]. The nano-probe methodology provides clearly ultra high resolution information resulting by utilizing mechanical technique. Nano contact tests open wider range of information regarding environmental effect on dislocation nucleation and dynamic provided from load-displacement curves with attention to load excursions. Probe visualization and measurement contributed to comparative investigation regarding slip features or local quantitative plasticity measurements in terms of local strain. Regarding HE the local conditions of hydrogen concentration and stress remained a critical factor. Thus, the efforts to define the crack-tip mechanical environment became essential. Moreover, the connection between the local crack-tip and the far-field stress intensify required also further clarification. This connectivity as depicted in Fig. 4 has been modeled by discretized dislocation simulation with single dislocations representing the near-tip distribution and a super-dislocation representing the far field plasticity.

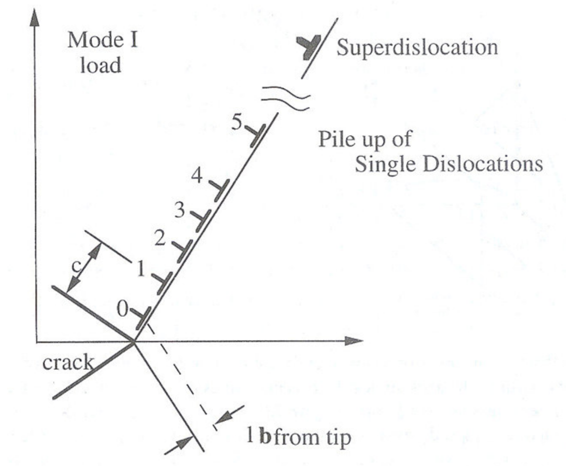

Fig 4. Crack tip dislocation emission model

With all the pair interaction between crack tip, dislocations and the applied stress a summation of forces using the anisotropic elasticity theory of Atkinson and Clements [23] provides the equilibrium positions of all dislocations. For a given dislocation, emission positions local and far intensity values were all interconnected by numerical simulations. Also the crack shielding aspects could be better explained, i.e. each added dislocation increased the local shielding. The important contribution however remained in defining the stress field distribution (See Fig. 5).

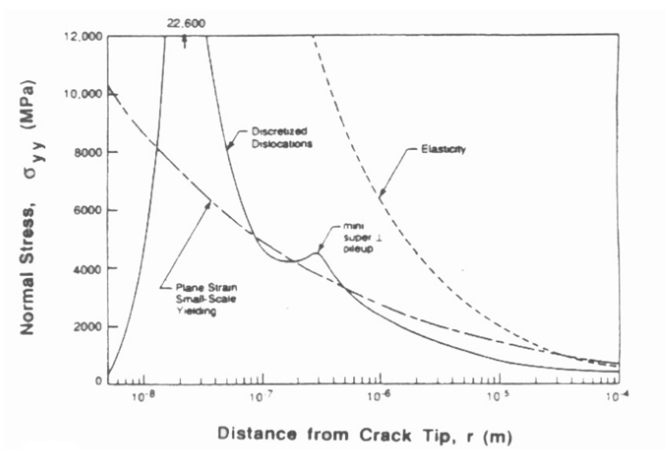

Fig. 5 crack tip mechanical environment-numerical results

5. Discussion

Deformation/environment interaction with complexity heightened by hydrogen enjoyed already ample of proposed models with hierarchy of experimental confirmation. The striking effects of hydrogen enhancing brittleness opened in general critical questions regarding low energy fracture transition. It becomes apparent that mechanical behavior exacerbated with the presence of hydrogen.

The current global/local approach demonstrated in meta-stable austenitic stainless steel provides insights that might facilitate the understanding of the fracture physics. At the same time the present study remains reluctant to add more model to the already existing models pile-up. Micro-structural aspects join the extremely wide range of circumstances affecting in various ways the exact mechanical responses. For example, some trap binding sites such as grain boundaries vs. precipitate interface may compete differently by considering dependency on the relative boundary coherency. Prior to emphasizing the present local findings it seems appropriate to add findings obtained in iron based single crystals. In particular, the deformation/hydrogen interaction in single edge notched specimens enhanced discontinuous slow crack extension under sustained load condition. The dislocation emission model enabled to explain the crack stability, B/D alternate transition assisted by the numerical simulation in comprehensive views of crystal plasticity and macroscopic cleavage [24]. On the nano-scale in near surface austenitic stainless steel, hydrogen increased the yield point by a factor of three. On this scale, hydrogen outgassing and softening or the return to almost the initial state could be followed. Previously hydrogen charging of 5 μm thickness of 316L strips have been affected vigorously by internal stresses sufficiently large to form delayed micro-cracking during the transient time of gas-release. Long elapsed out-gassing time reverted brittle to ductile behavior clearly not perfect reversible cycle by considering the damage formation. Beside the nano indentation results, plastic deformation features near the scratch trace with and with no hydrogen were striking. Deformation/hydrogen interaction indicated consistently wider slip step spacing (more than a factor of two) and higher slips steps (by a factor of 2 o 6) with hydrogen. The fine features results remained consistent by measurements along ore perpendicular to the scratch pile-up. Still on the background of global information in austenitic stainless steel, it seems that hydrogen affect the flow stress surface energy, decohesion energy, local stress intensity also the localized behavior of the slip morphology. The connectivity to the fracture process requires further activities. More has been addressed elsewhere [25,26].

5. Summary

The multi-parameter deformation/hydrogen interaction problem leaves always enough unresolved issues. The lack of consistency is frequently demonstrated resulting from over expectations even in a case that remarkable research has been invested. These efforts achieved continuous progress in evolutional fashion. For example, can fundamental expectations be translated to practical fracture criteria so essential in engineering methodology? In this respect the proposed decohesion mechanism seems useful with more of predictive potential. The impact of small volume response information beside global findings opened essential avenues regarding dislocation dynamics, critical information, as revealed by localized contact mechanics tests. Beside high-resolution visualization nano-indentation, load-displacement curves revealed load excursions that were attributed to the onset of dislocation nucleation. Still in terms of a comparative study, namely with and with no environmental interaction, even in terms of localized analysis, more

of direct evidences become possible. The earlier contributions regarding hydrogen effects on dislocation velocities and localized plasticity are supplemented by additional small volume mechanical tests with further powerful analysis.

6. Conclusions

Multi-scale comprehensive studies became in an evolutional fashion highly deductive, in the understanding of deformation/environment interaction processes. Localized approach remains essential, beside current requirements to explore engineering abilities towards nano-structures design and applications. Thus the following is concluded;

(a) Nano-mechanical testing assisted by surface probe microscopy suggest already several critical experiments for resolving scaling relationships involving hydrogen embrittlement mechanism.

(b) Crack-tip dislocation interactive model provide predictive abilities regarding the role of hydrogen on the threshold stress intensity factor, sub-critical crack extension behavior and the introduction of an intrinsic length scale dominating in fact the crack-tip mechanical environment.

(c) Experimentally based, the effectiveness of dislocation shielding in a slip plane associated with this length scale can be changed by hydrogen.

(d) Hydrogen interaction affect not only the flow strength, decohesion energy or the local Griffith stress intensity but also the character of slip bands up to enhanced localised plasticity.

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