

## The dynamic nature of hydrogen assisting crack extension

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### Materials

#### ABSTRACT

**Purpose:** Purpose of this paper to develop new avenues into the understanding of hydrogen/deformation interactions

**Design/methodology/approach:** Metastable stainless steel mainly polycrystalline FCC system was selected. The interactive fracture problems enjoyed the assistance of fracture mechanics theory and methodology. Regarding hydrogen embrittlement the study leans towards generic hydrogen enhanced decohesion model allowing quantitative engagement with experiments. Mechanical response was tracked by contact mechanics methodology. Nano indentation beside continues scratch tests have been supplemented by visualization and measurements utilizing Scanning Probe Microscopy (SPM).

**Findings:** It was shown that hydrogen increased the load onsets for dislocations nucleation in metastable austenitic stainless steel by at least a factor of two, whereupon the yield point recovered after hydrogen outgases. Plasticity localization due to hydrogen was also substantiated.

**Research limitations/implications:** The nano mechanical approach allowed additional critical experiment of hydrogen/deformation affects to be programmed.

**Originality/value:** Fracture is a localized phenomenon and the fine scale features information on high resolution observations opened potential contribution by exploring small volume research activities.

**Keywords:** Metallic alloys; Crack resistance; Hydrogen/deformation interaction; Nano testing

### 1. Introduction

Hydrogen/metal interactive effects have significant implications on structural integrity aspects due to crack stability transition. Generally, susceptibility to aggressive environment requires special awareness regardless the structural scale. The current study intends to explore alternative experimental avenues for additional insights into hydrogen/deformation interactive effects. In fact, a local approach via experimental methodology was mainly focused. Although 316L metastable austenitic steel is categorized under intermediate degree of phase stability, the role of austenitic decomposition is always important. Phase stability aspects in austenitic stainless steel are either enhanced by solely mechanical driving force or by hydrogen interactive effects. In

this context, hydrogen can be provided externally, internally or both. Beside hydrogen availability due to residuals at micro structural trapping sites, hydrogen interaction intentionally utilizes electrolytic cathodic charging or by high temperature/pressure gasous charging. Previous studies have established already that regardless of the exact process of hydrogen charging the basic fundamental findings regarding phase transformation still prevails [1-4]. Major differences are more related to the damage evolution due to a more aggressive high fugacity charging [5-7]. Under the aforementioned circumstances the sequential events caused by hydrogenation indicated striking dynamic behavior. First, typical micro plasticity localization phenomena occurred and secondly micro crack onset and propagation developed. Here to emphasize that the present study is centered only on free hydrogen effects in contrast to

hydride formation that provides other phase influential origins. As known, hydrogen/deformation interaction has many facets with broad implications. Thus, extensive efforts have been invested in the understanding of this complex type of interaction.

## 2. Material and work methodology

It seems in order to review some of the experimental procedures as related to preliminary studies of 316L stainless steel namely, bulk interactions with hydrogen.

### 2.1. Bulk experiments

High fugacity electrolytic cathodic charging was performed. As such, post charging effects have been studied by quantitative x-ray diffraction and Mossbauer spectroscopy. These activities intrigued 316L stainless steel beside other austenitic steels were aimed to explore the austenite decomposed products. For the sake of comparative study, part of the experimental procedure was conducted on materials with no hydrogen interaction [4,5].

### 2.2. Nano scale procedures

Samples were cut from as received AISI 316L stainless steel sheet of 1.6mm in thickness. Surface preparation included mechanical followed by electro chemical polishing. The selected material consisted of 50-100  $\mu\text{m}$  grain size. Mechanical response with or with no hydrogen was characterized by contact mechanic methodology. For the case of post charging vs. elapsed times behavior was tracked during hydrogen out gasses. Cathodic charging was carried out by 1M NaOH under current densities in the range of 10 to 500  $\text{mA}/\text{cm}^2$ . The mentioned grain size enabled at least 10 consecutive tests to be conducted within the same grain. The prescribe load of 1000  $\mu\text{N}$  was used. Beside indentation tests, continuous nano scratch tests were performed. Visualization of the scratch traces enabled to add more insights on the possible issue of hydrogen affecting localized plasticity. Fine scale features were result by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The nano scratch test was performed by Micro Mechanic Tester (MMT) with 90° conical indenter of 1 $\mu\text{m}$  tip radius. The scratch as such was imposed by gradually increasing load with driving tip rates between 1-7  $\text{nm}/\text{s}$ . for a trace of about 200  $\mu\text{m}$  and penetration depth of 1.5  $\mu\text{m}$ , the normal load increased up to 50 mN.

## 3. Description of achieved results

### 3.1. Bulk results

With regard to the phase stability issue, quantitative findings by x-ray diffraction and Mossbauer spectroscopy analysis remained consistent [4]. Differences between the two techniques were expected, mainly attributed to the hydrogen affected layer

thickness factors. The transformation reaction by either imposed mechanical driving force or by hydrogen interaction resulted in austenite ( $\gamma$ ) decomposition according to the following reaction.



Where  $\varepsilon'$  and  $\alpha'$  are the hexagonal closed packed and the body centered-tetragonal martensitic phases respectively. During the transient time, hydrogen expanded phases  $\gamma^*$  and  $\varepsilon^*$  were formed. These were identified as pseudo phases by x-ray diffraction and internal friction studies. As mentioned, hydrogen in AISI 316L stainless steel induced phase transformation at ambient temperature. Accordingly It was found that at very short elapsed time the following transformation content actually resulted (all in volume fraction),  $\gamma$ -0.604,  $\alpha'$ -0.044, and  $\varepsilon'$ -0.352. In contrast, a plastic strain of 23% at 77K with no hydrogen indicated a volume fraction of the three phases almost in the same order, namely about 33%.

### 3.2. Nano scale results

Nano indentation indicated values for the Young's modulus and the yield strength of 195GPa and 190 MPa respectively. Typical results have been determined from load-displacement curves for hydrogen free case that indicated displacement excursions at a load of 200 $\mu\text{N}$ . The reversible nature of the metal-free hydrogen interaction was substantiated for relatively long time. At the same time yield initiation after charging could reach values up to 700 $\mu\text{N}$ . The load-depth dependency indicated also differences that were caused by the hydrogen interaction. For example, with hydrogen the load increased with increasing depth during the yield excursion. With respect to the continuous scratch tests hydrogen revealed major differences as well. Here, only two elements are mentioned. First, hydrogen caused enhances plastic localization. Second, the slip upset with hydrogen was associated with higher local plastic strain values. In fact, localized plasticity was revealed by fine scale features resolution with measurable potential. This quantitative evidence is highly important with substantial progress in designing critical experiments. Based on recorded load vs. horizontal distances, loads corresponding to selected segments could be established. In order to stress the hydrogen effects scratch segments corresponding to nearly equal normal loads were selected. Quantitative measurements of localized plastic deformation were assisted by the AFM. Some measurements regarding this content are summarized in Table 1.

Table 1.  
Hydrogen charging effects on plasticity characteristic – nano data activated by continuous scratch

Surface features	Non charged	Charged
Along the pile up		
Slip step spacing (s) (nm)	101	291
Slip step height (h) (nm)	15	94
Perpendicular to the pile up		
Slip step spacing (s) (nm)	106	261
Slip step height (h) (nm)	13	16

Overview regarding HE proposed mechanisms is briefly described. In fact, two major mechanisms seem to be viable beyond some ad hoc attempts for experimental interpretation. The aforementioned viable mechanisms suggested Hydrogen Enhanced Decohesion (HEDE) and Hydrogen Enhanced Localized Plasticity (HELP). The first model is characterized by hydrogen decreasing either grain boundary or cleavage plane cohesion, goes back to the original study by Troiano [8]. Following a comprehensive series of research activities as related to brittle fracture concepts, further developments supported also the HEDE HE model. Basically, the connection between the local tip stress intensity factors and the far/field stress intensity has been clarified. This connectivity has been modeled by a discretized dislocation simulation with single dislocations representing the near tip distribution and a super dislocation represents the far/field plasticity (see Figure 1).

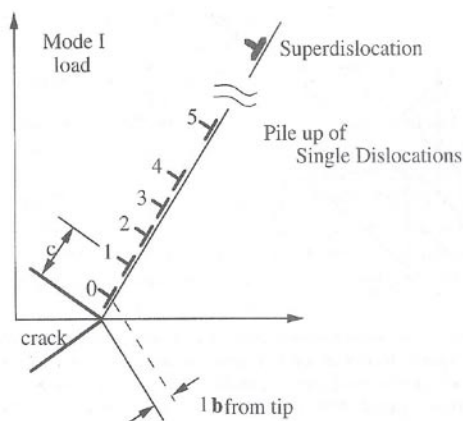


Fig. 1. Shielding dislocations at a mode I crack tip under a far – field K

This approach turned out to be very consistent experimentally with the ability to accommodate the principle common features as related to the threshold decrease and the substantial increase of the crack extension rate [9]. Increasing susceptibility to embrittlement in general, was also confirmed in most of hydrogen deformation interactions, typically accentuated by;

- Multi axial conditions (plain stress vs. plain strain)
- Opening crack mode dominance
- Increasing yield strength
- Increasing hydrogen pressure or internal concentration
- Increasing grain boundary segregation of metalloids
- Decreasing elastic modules

The HELP model suggests that solid solution free hydrogen causes dislocation unpinning from barriers that increase their mobility and allows higher localized deformation. Moreover, such enhanced plasticity might result in localized softening which enhances plastic failure, in contrast to the usual sense of embrittlement. Enhanced ductile processes due to hydrogen interactions have first been suggested by Beachem, joint later by others [10,11]. It appears important to emphasize the intensive experimental and theoretical efforts that have been invested in the

understanding of HE. The importance to crack stability issues and to structural integrity provided continuous incentives and challenges to explore the complex nature of the aforementioned interaction. Some of the information and assessment is given in Table 1. The present study is mainly engaged with AISI 316L metastable austenitic stainless steel. It seems advisable to distinguish between micro structurally stable material in which the solute free hydrogen interacts, in contrast, to unstable elastic-plastic solid. Thus, the phase stability degree is important and further elaboration has been addressed in previous studies [1-4]. The emphasis on dynamic aspects has been investigated not only in stainless steel but also in the case of ausformed steel. In principal, the phase stability issue includes also the role of hydride formation which affected the local mechanical field. However, the case of hydride formation or the role of non metallic inclusions deserves different considerations concerning other micro mechanism base, for possible mechanical damage origins [12,13]. Nevertheless, in the case of free hydrogen, the sequence of events and the dynamic nature of hydrogen interaction processes become more involved particularly in an unstable micro structure. The present experimental approach indicated that nano indentation or nano scratch test even accentuated the hydrogen role in terms of localization insights. The role of internal stresses beside plasticity behavior led to crack onset invoked as such important arguments as related to hydrogen/deformation metal degradation. Load displacement information based on nano mechanical probe methodology and supplemented by visualization, revealed significant elements concerning various events, from hydrogen-dislocation interaction up to micro crack initiation. The latter alluded already to the complexity of the HE process. Thus, the motivation for continuous research efforts in this field is also the notion regarding the interwoven nature of plasticity enhancing brittle fracture. This has been established in semi brittle materials even in the absence of hydrogen. In this context it appears that this is exacerbated with the role of hydrogen interaction. The nature of such interactive problems normally calls for "critical experiments". Experiments that can approach the basic building blocks as actually have been attempted in the current investigation.

First, by using in situ spectroscopy and microscopy that enabled to probe ultra small volumes, namely, by recognizing again the building blocks themselves. Here to mention, that other attempts involving TEM with environmental stages was clearly recognized [10]. Second, there are computational materials science modeling efforts that can either be calibrated against or incorporate those building blocks in embrittlement predictions [14,15]. Table 1, beside nano indentation findings stresses the major intentions of the current investigations. The ultimate goal remains in the developments of quantitative approach. In this case beyond evidences that hydrogen increase localized plasticity along a given slip band more was revealed quantitatively. In fact, the meaning of a local strain is defined associating a factor of three to the hydrogen interaction. The local plasticity argument is actually based on slip height  $h$  and slip spacing  $s$  as mentioned in Table 1.

To the author opinion at this stage, the current demonstration is the first estimate of the localized strain by AFM as enhanced by hydrogen uptake. Accordingly, such attempts might provide interpretation of interface stress failure (e.g. pile-up considerations) or plastic collapse via slip band or void instabilities.

## 4. Conclusions

1. In AISI 316L metastable austenitic stainless steel, phase stability aspect study revealed austenite decomposition by solely mechanical driving force at ambient temperature.
2. With hydrogen interaction, during a transient time pseudo phases are formed associated with a dynamic behavior directly related to hydrogen outgassing.
3. Nano mechanical test combined with surface probe visualization might assist in resolving local information in order to support hydrogen embrittlement viable mechanism.
4. In the investigated materials, the effect of hydrogen on dislocation nucleation becomes apparent with a tendency to raise the load with hydrogen concentration.
5. The localization accompanied by significant strain gradient provides condition for changes in the local load bearing capacity. This argumentation is highly relevant to hydrogen embrittlement model.

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## References

- [1] M.L. Holzworth and M.R. Louthan, Hydrogen induced phase transformation in type 304L stainless steels, Corrosion NACE 24 (1968), 110-124.
- [2] M.L. Holzworth, Hydrogen embrittlement of type 304L stainless steel, Corrosion NACE 25 (1969) 107-115.
- [3] H.Mathias and Y.Katz, 2<sup>nd</sup> Int. Cong. Hydrogen in Metals, Pergamon Press, Paris (1977), 6-11.
- [4] H.Mathias, Y.Katz and S.Nadiv, Metal-Hydrogen Systems, T. Nejat Veziroglu Ed.. Pergamon Press, Oxford (1982) 225-249.
- [5] H.Mathias, Y.Katz and S.Nadiv, Hydrogen effects in austenitic steels with different stability characteristic, Metal Science 12, (1978) 129-137.
- [6] E.Horenbogen, Martensitic transformation at propagating crack, Acta Metall, 26 (1978) 147-152.
- [7] Y.Katz, H.Mathias and S.Nadiv, Direct observation at a sharp crack tip vicinity in hydrogenated austenitic stainless steel, Fracture and Fatigue, ECF 3, Pergamon Press, Oxford (1989) 449-464.
- [8] A.Troiano, The role of hydrogen and other interstitials in the mechanical behavior of metals, Trans. ASM 52, 54-59.
- [9] W.W Gerberich, P.Marsh, J.Hoehn. S.Venkataraman and H.Huang, Hydrogen/plasticity interactions in stress corrosion cracking, Corrosion-deformation interactions, T.Magnin and J.M.Gras Eds. Les editions de physique (1993) 325-349.
- [10] H.K.Birenbaum, Mechanisms of hydrogen related to fractures of metals in environment induce cracking of metals, R.P.Gangloff and M.B.Ives Eds. NACE Houston (1988) 21-30.
- [11] H.K.Birenbaum, I.M.Robertson, P.Sofronis and D.Teter, Mechanisms of hydrogen related fracture, Corrosion Deformation Interactions, CDI 96, T.Magnin Ed. The institute of materials, (1997) 172-195.
- [12] J.P.Lufrano, P.Sofronis and H.K.Birenbaum, Modelling of hydrogen transport and elastically accommodated hydride formation near a crack tip, Phys. Mech. Solids (1996) 179-205.
- [13] J.Sojka, P.petakova, L.Hyspecka, L.Cizek, M.Sozanska and A.Hernas, Role of non-metallic inclusion shape in hydrogen embrittlement tested using slow rate test, 12<sup>th</sup> AMME (2003), 812-824.
- [14] P.Sofronis and R.M.McMeeking, Numerical analysis of hydrogen transport near a blunting crack tip, Mech. Phys. Solids. 37 (1989), 317-350.
- [15] J.Lufrano and P.Sofronis, Numerical analysis of interaction of solute hydrogen atoms with the stress field of a crack tip, Int. Solids. Struct. 33 (1996), 1709-1722.