

## Hydrogen-induced intergranular failure in nickel revisited

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### Abstract

Using a combination of high-resolution scanning and transmission electron microscopy, the basic mechanisms of hydrogen-induced intergranular fracture in nickel have been revisited. Focused-ion beam machining was employed to extract samples from the fracture surface to enable the examination of the microstructure immediately beneath it. Evidence for slip on multiple slip systems was evident on the fracture surface; immediately beneath it, an extensive dislocation substructure exists. These observations raise interesting questions about the role of plasticity in establishing the conditions for hydrogen-induced crack initiation and propagation along a grain boundary. The mechanisms of hydrogen embrittlement are re-examined in light of these new results. Published by Elsevier Ltd. on behalf of Acta Materialia Inc.

**Keywords:** Hydrogen embrittlement; Intergranular cracking; Transmission electron microscopy; Scanning electron microscopy; Nickel

### 1. Introduction

The degradation in the mechanical properties of metals due to the presence of hydrogen is often accompanied by a change in fracture mode from ductile transgranular to intergranular [1–11]. The former has been described as strain-controlled with plasticity concentrated at the macro-scale, and the latter as stress-induced decohesion in which plasticity is blocked at the microscale and is incidental to the propagation of intergranular cracks [8]. The role of hydrogen was assumed solely to be to reduce the cohesive strength of the grain boundary such that crack initiation and propagation along the boundary was favored over slip transmission and ductile failure processes. The transition in failure mode in steels has also been attributed commonly to the presence of other segregants in addition to hydrogen at

the grain boundary [8], although more recent studies using high-purity steels have suggested hydrogen alone can cause intergranular embrittlement [12]. This result is consistent with studies using relatively pure polycrystalline metals.

For example, Lassila and Birnbaum showed that the degree of intergranular failure in nickel was dependent on the concentration of sulfur and of hydrogen, with the combination of the two being more potent than either individually [6,13], i.e. 100% intergranular fracture was possible if sufficient time was allowed to segregate a critical, but unknown and undetermined, concentration of hydrogen to the grain boundaries. Similarly, with sufficient sulfur segregated to the grain boundary, the fracture was completely intergranular, whereas with low sulfur coverage on the grain boundary, complete intergranular failure occurred only in the presence of hydrogen; again, the combined effect of the two segregants was more damaging than the individual contributions of each species.

To examine this further, Heubaum conducted in situ deformation experiments in a scanning electron microscope

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(SEM) of a hydrogen-charged nickel sample which, to retain the hydrogen, was stored at 77 K before testing [14]. Prior to intergranular failure, extensive surface rumpling and slip band formation was evident on the free surface. Additionally, slip traces were in evidence on the intergranular fracture surfaces. More recently Bechtel et al. demonstrated that the susceptibility of Ni-201 to hydrogen embrittlement could be reduced by thermomechanical processing to generate a high fraction of special grain boundaries, which were predominantly twins [15]. The reduced hydrogen susceptibility induced by the high special boundary fraction was rationalized by invoking one of two arguments. The first required more hydrogen segregating to, and accumulating at, random grain boundaries than special boundaries such that the magnitude of the reduction in cohesive strength would be less at the special boundaries. The second argument assumed the segregated concentration was independent of grain boundary character and as special grain boundaries are stronger than random ones, higher hydrogen concentrations would be needed to achieve a sufficient and necessary reduction in the cohesive strength to cause failure on special grain boundaries.

Although there is abundant evidence supporting transport of hydrogen by dislocations [16–18], there is a lack of information regarding the enhanced diffusion of hydrogen (or deuterium) along grain boundaries as well as its dependence on grain boundary type. Tsuru and Latanision measured the diffusivities of hydrogen in polycrystalline nickel and reported diffusion to be faster along grain boundaries ( $D_{\text{latt}} = 3.52 \pm 1.02 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{\text{gb}} = 2.05 \pm 1.50 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ) [19]. One of the few studies to consider the dependence of diffusion on grain boundary character is that of Ladna and Birnbaum, who compared diffusion along  $\Sigma = 9$  and  $\Sigma = 11$ ; only along the  $\Sigma = 9$  boundaries was the diffusion enhanced [20]. In addition to the lack of data on diffusion in the grain boundary, there is still a lack of data on the concentration of hydrogen that can exist in grain boundaries, as well as the effect that this hydrogen concentration will have on the cohesive strength of the boundary.

Electronic structure calculations have shown that the presence of impurities at grain boundaries changes the local bonding, such that the segregants decrease the cohesive strength of the boundary [21–23]. However, the magnitude of the reduction in the cohesive energy as a function of hydrogen on a particular type of grain boundary is not well documented. For example, using density functional theory, Dadfarnia et al. calculated that the reduction on a  $\Sigma 3$  grain boundary in iron was not significant and did not vary linearly with concentration [24].

Robertson and Birnbaum reported that cracks in nickel deformed in situ in a hydrogen environment in a transmission electron microscope (TEM) followed the contour of the grain boundary but did not necessarily propagate along the grain boundary [25]; Tabata and Birnbaum reported similar observations in iron [26,27]. Specifically, the crack path followed the slip planes, which paralleled, rather than

propagated in, the grain boundary. These observations raised the question about the actual crack path for intergranular fracture in these instances. However, based on results since these studies [28,29], including those presented herein, it is likely that the crack path observed in some, but not all, in situ TEM deformation studies may be special as it occurs when the dislocations approaching the grain boundary are not accommodated in it, but rather cross-slip to follow a path that parallels the boundary. Furthermore, intergranular fracture will not occur if the hydrogen content segregated and accumulated at the grain boundary is below some critical concentration. The failure to reach the critical hydrogen concentration at the grain boundaries is reasonable given these straining experiments were performed in a gaseous hydrogen environment using electron-transparent samples. That is not to say that intergranular failure has never been observed in this type of experiment as intergranular fracture was reported to occur in Ni-S [30] and in Ni<sub>3</sub>Al [31] deformed in the TEM in a hydrogen environment.

In an effort to relate the intergranular failure observed in macroscopically tested hydrogen-charged nickel [15] to the microstructure produced during the deformation that proceeded failure, the focused-ion beam (FIB) lift-out technique has been used to produce electron-transparent samples from the volume immediately beneath the fracture surface. The results from this investigation are reported and discussed in terms of known hydrogen embrittlement mechanisms. A new mechanism for hydrogen-induced intergranular failure of nickel emerges from this discussion.

## 2. Experimental procedures

Investigations were conducted on Ni-201 (yield strength 55 MPa [15]), a commercially pure nickel supplied by ThyssenKrupp VDM USA, Inc. Atomic hydrogen was dissolved into the specimens by thermally charging the specimens in high-pressure hydrogen gas; the lattice hydrogen content was approximately 2000 appm. The specimens for uniaxial tensile testing were 4 mm in diameter and had a gauge length of 25 mm; they were loaded on a servohydraulic MTS 810 mechanical testing machine (MTS Corporation, Eden Prairie, MN), operating in displacement control mode at a displacement rate of  $0.01 \text{ mm s}^{-1}$ , which corresponds to a strain rate of  $4 \times 10^{-4} \text{ s}^{-1}$ . Details on the effects of hydrogen on the mechanical properties have been reported by Bechtel et al. [15]. Specifically, hydrogen concentrations between 1200 and 3400 appm caused the reduction in area to decrease from 74–86% in the uncharged material to 6–29% in the hydrogen-charged material. This loss in ductility was accompanied by a change in the failure mode from ductile microvoid coalescence to intergranular fracture [15]. For the particular sample examined here, the strain-to-failure was 13%; corresponding to a test time of around 325 s.

The morphology of the fracture surface was examined by using a JEOL JSM-6060LV SEM, and the secondary

electron mode of a FEI 235 FIB microscope. Samples from selected regions were machined out and thinned to electron transparency using the FIB lift-out technique [32]. The resulting microstructure was determined using a JEOL 2010 LaB<sub>6</sub> TEM operated at 200 kV.

### 3. Results

An overview of the fracture surface morphologies in Ni-201 charged with hydrogen before testing, shown in Fig. 1, clearly indicates a predominantly intergranular fracture mode. On inspection of these surfaces at higher spatial resolution, evidence of slip lines on individual facets is abundant. On some facets, it is apparent that more than one slip system is active; on others, the slip traces are densely packed, as shown in Fig. 2. The fractographs presented in Fig. 3 indicate the continuity, albeit with a change in direction, as the traces intersect and cross a grain boundary. Note, however, that in Fig. 3a, the upper grain has two slip systems active, yet only one is transmitted to the lower grain. Given the two changes in the direction of the slip lines, indicated by the arrows in Fig. 3b, it would seem reasonable to suggest that the interior boundaries, marked by arrowheads labeled A and B, are twin boundaries. Although twin boundaries present stronger barriers to dislocation motion, slip transmission occurs with a corresponding change in slip direction [33]. The observations presented in Figs. 1–3 do not directly address the question of the precise role of plasticity in the intergranular fracture, but they do suggest that it is extensive.

To determine how the slip traces relate to the intergranular fracture, samples were extracted normal to the fracture surface using FIB machining. Examples of the microstructures that exist immediately beneath and 4–5 μm from it are presented in Figs. 4 and 5, respectively. In Fig. 4a, a FIB image with the Pt strip deposited to protect the area of interest during the lift-out process is shown. Clearly, the strip covers several parallel slip traces spaced about 1 μm apart. On this facet, only one slip system is visible.

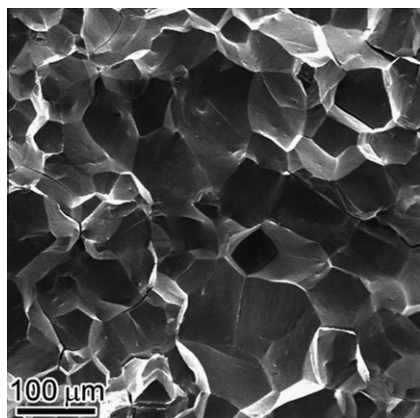


Fig. 1. Overview of the nickel fracture surface showing fully intergranular failure.

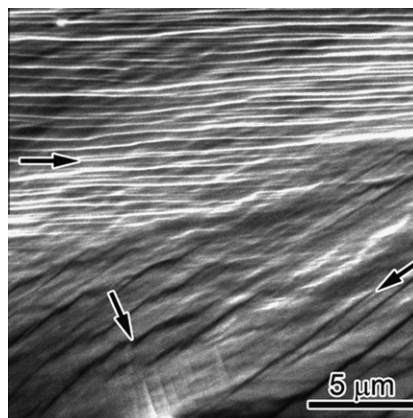


Fig. 2. High-resolution fractograph from one intergranular feature. The arrows indicate different slip traces on the surface.

Previously, this observation would have been interpreted as evidence that dislocation activity was occurring in one system only. However, as evidenced by the microstructure immediately beneath the fracture surface, Fig. 4b, this interpretation is incorrect. Note that the arrows in Fig. 4b mark steps or ledges on the fracture surface; the fact that these exist supports the premise that the fracture surface is protected by the Pt strip and features on it are preserved during the process of extraction and thinning. The form of these steps suggests that they are not simply protrusions on the facet surface due to the emergence of dislocations, which would be expected if they were generated by dislocations emitted in relation to the advancing intergranular crack. Rather these features represent periodic extensive shearing of the grain boundary that occurs by significant slip across the grain boundary. The underlying microstructure consists of a high density of dislocations that have self-organized into a cell structure, with the average cell size being on the order of 200–400 nm. From this micrograph, it appears that junctions of cell walls coincide with the surface steps, but steps do not exist at all cell wall junction intersections with the surface and several cells can exist between steps. For the surfaces examined, there was no evidence for the existence of a grain boundary immediately beneath the surface although for practical reasons only one side of the fracture surface was examined. Nevertheless, more than one sample was extracted from different locations, and, therefore, different grains, and in each case there was no evidence for a grain boundary existing immediately below the fracture surface. From this it is concluded that the crack is propagating in and not adjacent to the grain boundary.

Fig. 5 shows the microstructure 4–5 μm from the fracture surface. Again, the dislocation density is high and arranged into a cell structure (200–400 nm in size) that is consistent with that of a severely deformed material. Taken together with the results presented in Fig. 4, it is clear that there is no significant gradient in the dislocation structure with depth from the fracture surface.

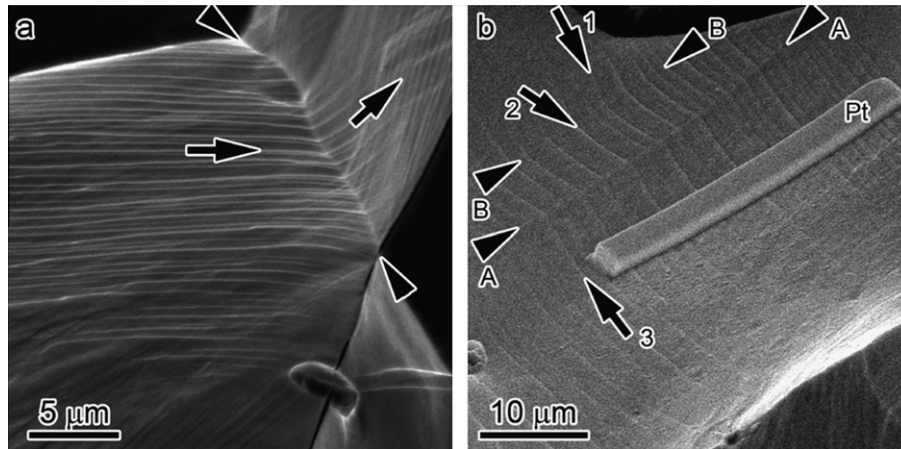


Fig. 3. High-resolution fractographs of intergranular surfaces showing interactions of traces with grain boundaries. Arrowheads delineate the location of grain boundaries; the arrows show direction of different traces. (a) Grain boundary here is marked by a distinct change of facet direction. Note how only one set of slip traces continues from the upper grain into the lower. (b) Slip traces passing through twin boundaries (marked by A and B). Traces show a change of direction, e.g. from direction 1 to 2, as they pass through boundary B, but otherwise appear to pass through both boundaries unimpeded.

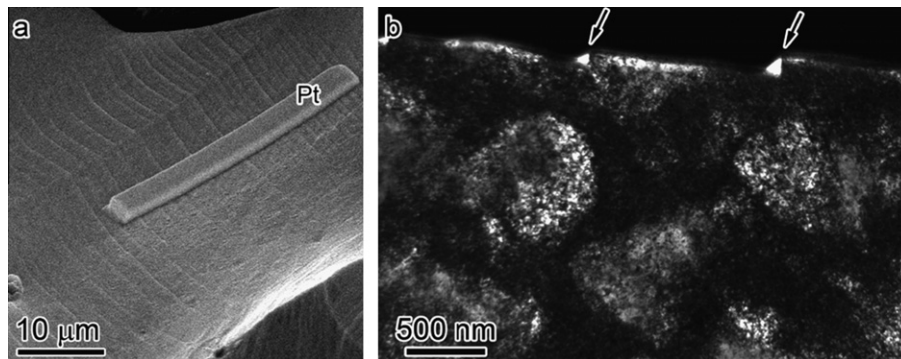


Fig. 4. (a) FIB electron mode micrograph showing location from which TEM sample was extracted. Pt strip shown indicates the top of the sample, and was deposited to protect the fracture surface underneath. (b) TEM micrograph showing microstructure beneath the region identified in (a). The arrows mark steps or ledges on the fracture surface. A dislocation cell size of 200–400 nm can be observed.

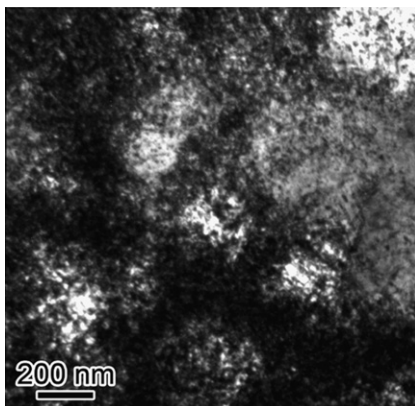


Fig. 5. TEM bright-field image of the microstructure well beneath the fracture surface. Dislocation cells approximately 200 nm in size can be seen.

#### 4. Discussion

The key finding reported in this work is that a distinct and fine dislocation cell structure exists immediately

beneath and well beyond the intergranular facets, including beneath those with only one step evident on it. At first sight, this latter comment might appear inconsistent with the formation of a dislocation cell structure, but is explained by appreciating that, in an interior grain, multiple slip systems are likely to be activated, not all dislocations intersect the grain boundary at the location that failed, and slip transmission process can cause ejection of dislocations into both grains [29,34]. Other facets show evidence of dislocation activity on multiple systems, Fig. 2, which can be easily envisioned to generate a cell structure beneath it. However, it is noteworthy that a one-to-one correspondence does not exist between the cell size and the slip traces, which reinforces the difficulty of interpreting dislocation processes from features on fracture surfaces. The observation of a fine dislocation cell structure suggests that dislocation activity plays a significant role in establishing the conditions necessary to cause intergranular fracture. What needs to be understood is the role of this plasticity in causing the hydrogen-induced intergranular fracture mode and how the evolution of the dislocation

structure is influenced by hydrogen. In the following discussion, various possible roles are considered and are discussed in terms of the likely mechanisms of hydrogen embrittlement.

As noted above, the central issue here is the role of this plasticity in generating the intergranular fracture and contributing to the embrittlement. One possibility, which might be particularly relevant in the case of Ni-201 with its yield strength of 55 MPa, is that the plasticity is significant in the sense that the associated work hardening raises the stresses locally on the grain boundaries to sufficient levels to exceed the grain boundary fracture strength (cohesion). Indeed, in this respect, intergranular fracture occurs in exactly the same fashion as transgranular cleavage fracture in low-strength steels as both are locally stress-controlled fracture modes [35,36] (invariably initiated by a dislocation pile-up at a grain-boundary particle), where local work hardening inside the plastic zone at the crack tip is essential to enhance the local stresses (as the yield strength is low). However, this argument does not take into account the role of hydrogen in reducing the cohesive strength of grain boundaries [21–23]; nor does it account for the need to establish a critical hydrogen concentration at the grain boundaries to cause the transition from hydrogen-induced transgranular to intergranular fracture.

The need for a critical hydrogen concentration was established by Lassila and Birnbaum [6,13], who demonstrated that the percentage of intergranular fracture in nickel specimens strained in uniaxial tension depended on the amount of hydrogen accumulated on the grain boundaries. The level of hydrogen at the grain boundaries was controlled either by using longer aging times before testing or a higher solute concentration in the bulk; the former provided sufficient time for a critical but unknown level of hydrogen to accumulate at the grain boundary. Taken together, the hydrogen-induced decrease in ductility, without a fracture mode transition, and the need to attain a critical hydrogen concentration at a grain boundary before a fracture mode transition can occur, would imply that the argument that strain hardening alone causes intergranular failure is too simple. As intergranular fracture is observed, this raises the question as to how the critical concentration of hydrogen is achieved. It could be achievable entirely by diffusive processes or, as the material is under an applied load, it could be augmented by dislocations transporting hydrogen to, and depositing it at, grain boundaries. The latter action is supported by the argument that dislocations are weak traps and consequently hydrogen will be deposited at the grain boundary during the action of slip transfer through grain boundaries. This is a dynamic process, but as multiple dislocations enter and are accommodated in a grain boundary before it responds by ejecting a dislocation, there is the potential for more hydrogen to be deposited than removed. Here, the role of plasticity is to enhance hydrogen accumulation at the boundary.

Support for hydrogen influencing the behavior of dislocations comes from the in situ electron microscope

deformation studies conducted in gaseous environments, both hydrogen and argon, which demonstrated that the dislocation velocity was enhanced by the presence of hydrogen gas only [25,30]. These observations, made in numerous pure metals and alloys, provide the basis for the hydrogen-shielding model of hydrogen embrittlement, which forms the basis for the “hydrogen-enhanced localized plasticity” or HELP mechanism [37]. Additional support for hydrogen-enhanced dislocation velocities come from analysis of stress relaxation data of bulk tests in terms of activation energy and area analysis [38]. Accepting that such a hydrogen effect is feasible, it is prudent to ask how it might modify the resultant dislocation structure. Prior attempts to find differences in dislocation density and distribution in Ni were inconclusive as no statistically significant differences were found between behavior in a hydrogen vs. an inert gas environment [39,40], i.e. similar dislocation densities and distributions were found in samples loaded in either environment, despite the difference in overall ductility. This result is unexpected as the dislocation structure is known to depend on the level of strain. For example, Keller et al. reported that in nickel at small strains, dislocations arrange in dipoles, tangles and walls; with increasing strain, dislocations begin to arrange in walls and cells, with the cell size decreasing with increasing strain [41]. In comparing the dimensions of the cell structure observed beneath the intergranular facets (13% strain) formed in the presence of hydrogen, it appears to be the same as that formed in face-centered cubic metals deformed to much larger strains. In fact, in high-purity nickel at 13% strain, Keller et al. measured a cell size of 1.2  $\mu\text{m}$ , whereas at the same strain in this study, the cell size observed is 200–500 nm. Interpolation of the measurement of cell size as a function of strain from the data provided by Keller et al. suggest that a strain of 40% is needed to achieve this small cell size in the absence of hydrogen. This difference in strain needed to produce similar cell dimensions suggests that the dislocation processes and interactions are accelerated and enhanced by the presence of hydrogen. This result, consistent with the principal tenet of the HELP mechanism [37,42], demonstrates one of the critical roles plasticity processes play in hydrogen-induced intergranular fracture.

Further support for the importance of the dislocation processes accelerated by hydrogen is in the appearance of steps on the intergranular fracture surfaces (Fig. 4b). These could:

- (i) reflect the natural faceted form of a particular grain boundary;
- (ii) be created by surface image forces pulling near surface dislocations to the surface;
- (iii) be formed by emission of dislocations from sources at or near a crack tip and by extension to the crack advance, arrest, advance mechanism associated with slow or intermittent crack growth [43–45]; or

- (iv) be associated with transmission of slip across the grain boundary prior to intergranular failure.

The first possibility can be dismissed as these features occurred on all grain boundaries and, on some facets, there was evidence for such features existing in multiple orientations (Figs. 2 and 3). The second possibility also can be dismissed as the dislocations exist in dense tangles and dissolution would require significant stresses, as there was no region free or with a reduced dislocation density at the fracture surface, and as there was continuity of steps across grain boundaries. This continuity would be unlikely if the features were simply due to dislocation rearrangements and loss from a particular grain.

The third possibility, based on dislocation configurations associated with cracks that result in crack advance through the process of microcleavage in Mo [43] and Fe–Si [45], generates surface steps on the fracture surface by means of the dislocations trailing behind the intermittent crack advance. Although surface features similar in appearance to those shown on the nickel intergranular facets have been reported in Mo [43] and Fe–Si [45], these features have not been correlated directly with the underlying microstructure. Furthermore, the sample geometry for the slow crack growth tests on Mo and Fe–Si contained a pre-crack and the dislocation density was low apart from immediately ahead of the crack. In contrast, in this case, the crack growth is not intermittent; the crack is propagating between grains containing a highly developed dislocation cell structure that is typical of material strained 40% and it extends significant distances from the fracture surface; there was no evidence for departure of the crack from the grain boundary plane, which would require an improbable symmetry in the dislocation sources on both sides of the grain boundary to prevent; and the steps are not consistent with the simple egress of dislocations at a free surface. Lastly, in situ TEM deformation experiments with Ni–S [30] and Ni<sub>3</sub>Al [31] in a gaseous hydrogen environment provided insight to the dislocation generation associated with an advancing crack. There was no evidence for these dislocations generating steps on the newly generated free surface. Therefore, the surface features are not associated with the emission of dislocations from sources near or at the crack tip.

The level of deformation at, and well beneath, the fracture surface supports the fourth mechanism involving slip transmission across the grain boundary. Moreover, it is important to appreciate that, with few exceptions, the dislocations that interact with the grain boundary are accommodated in it with new dislocations generated and emitted into the abutting grain: it is not the same dislocation in both grains [29,33,34]. However, the process is not necessarily one-to-one with many dislocations being accommodated prior to emission initiating. If the dislocation arrival and accommodation rate in the grain boundary is high, the transmission process can occur suddenly with a rapid ejection of dislocations from a grain boundary with the consequence that, locally, the boundary is displaced, rotated or

destroyed [46–48]. It is posited that it is this shearing of the grain boundary plane by the extensive slip transmission events that give rise to the features observed on the facets. The transmission of strain across the grain boundary has two additional possible influences that promote intergranular failure. Specifically, the transport of hydrogen by the dislocations to the grain boundaries can increase the hydrogen concentration on the grain boundary, which helps achieve the critical hydrogen concentration, and the accommodation and emission of dislocations from the grain boundary increases the strain energy density, or the disorder, of the grain boundary, which would weaken it.

The importance of the development of the underlying dislocation structure on the fracture mode and path is not unique to this system; the same concept has been introduced by Martin and coworkers to account for the presence of “quasi-cleavage” and “flat” fracture surface features in a hydrogen-failed pipeline steel with strength levels of 550–650 MPa [49,50]. In both cases, the dislocation structure was well developed and distinctly different from that normally assumed to exist beneath such features. Furthermore, Martin et al. showed that beneath a cleavage surface in a pipeline steel, produced by low-temperature fracture, the dislocation density was low and typical of the undeformed state, i.e. the sample preparation process does not introduce the observed dislocation structure [32]. These results provide new insight regarding the link between the deformation and failure processes and suggest the evolved microstructure plays an important and perhaps crucial role in determining the local hydrogen concentration and the fracture path. As the microstructure is different from that anticipated, Martin et al. [32] suggested that interpretation of fracture surface features based on a posteriori knowledge of deformation processes should be made with caution.

Therefore, based on the evolved microstructure immediately beneath the intergranular fracture surface (Fig. 4), the multiplicity of slip systems in evidence on intergranular facets (Fig. 2), and the need to establish a critical hydrogen concentration at the grain boundary to cause intergranular fracture, an alternate model is posited to explain hydrogen-induced intergranular fracture in nickel. It is proposed that hydrogen drives the development of the complex dislocation cell structure, which increases the stress level locally, and deposits hydrogen on the grain boundary, which then assists in achieving the critical hydrogen concentration at the grain boundary. It is this combination of processes that establishes the conditions for hydrogen-induced intergranular fracture by decohesion; the cohesive strength of the grain boundary being reduced below that of the work-hardened matrix by hydrogen. This is a radical departure from conventional thoughts about the role of plasticity in hydrogen-induced intergranular fracture.

## 5. Conclusions

The role hydrogen-enhanced plasticity processes play in establishing the local conditions favoring hydrogen-induced

intergranular failure has been discussed. In contrast to previous assertions that some plasticity occurs and aids the process to a limited extent, the present results show that plasticity plays a significant role and is not confined to the vicinity of the grain boundary. In addition to its necessary role in raising the local stress through work hardening, the deformation processes are essential for establishing a significant and sufficient hydrogen concentration at the grain boundary. This combination results in a reduction of the cohesive strength of the boundary such that intergranular failure is favored over failure in a dislocation-hardened matrix. Furthermore, intergranular failure may be promoted by the change in the strain energy density in the grain boundary that is associated with the process of slip transmission.

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