# Modeling hydrogen transport by dislocations

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## ABSTRACT

Recent experimental studies of the microstructure beneath fracture surfaces of specimens fractured in the presence of high concentrations of hydrogen suggest that the dislocation structure and hydrogen transported by mobile dislocations play important roles in establishing the local conditions that promote failure. The experiments demonstrate that hydrogen is responsible for the copious plasticity in large volumes of material before the onset of fracture and further afield from a crack tip. A revised model for hydrogen transport that accounts for hydrogen carried by dislocations along with stress driven diffusion and trapping at other microstructural defects is proposed. With the use of this new model, numerical simulation results for transient hydrogen profiles in the neighborhood of a crack tip are presented. Based on hydrogen-enhanced dislocation mobility and density, the results indicate that dislocation transport can contribute to the elevation of the local hydrogen concentrations ahead of the crack to levels above those predicted by the classical diffusion model and to distributions that extend farther afield.

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## 1. Introduction

Recent experimental observations of the evolved microstructure in metals containing high concentrations (a few thousands at. ppm) of solute hydrogen suggest that hydrogen not only accelerates the evolution of the microstructure but also stabilizes it in unanticipated configurations (Martin et al., 2011a, 2011b, 2012a, 2013, 2012b, 2014; Nagao et al., 2012; Wang et al., 2014). In every case the evolved microstructure was found to be more complex than would be envisioned based on prior assumed knowledge of dislocation behavior in the presence or absence of hydrogen. Key features in these studies are that the evolved microstructure is indicative of very high strains and in some situations exists in configurations that do not conform to the accepted evolution pathway. The enhanced evolution was explained in terms of the hydrogen-enhanced

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dislocation activity, which is motivated by the hydrogen-enhanced localized plasticity (HELP) mechanism (Sofronis and Birnbaum, 1995; Robertson, 2001). In addition, since hydrogen must travel with the dislocations, a requisite for the continued operation of the HELP mechanism, the hydrogen concentration must be increased in the regions of the evolved microstructure.

Hydrogen transport by mobile dislocations is not a new concept; it was first suggested by Bastien and Azou (1951) and is supported by numerous experimental observations (Kurkela and Latanision, 1979; Hwang and Bernstein, 1986; Windle and Smith, 1968; Itoh et al., 1997; Nagao et al., 1998; Frankel and Latanision, 1986). Models for hydrogen transport by dislocations have been proposed by Tien et al. (1975, 1976) and Tien (1976). These dislocation transport models yield much faster diffusion rates than lattice diffusion and support the idea that dislocations can carry hydrogen deep into a specimen gage section or plastic zone even at ambient temperatures. Associated with these models by Tien is the proposition that local hydrogen supersaturations develop through stripping of the solutes off the moving dislocations by traps. On the other hand, theoretical analysis by Hirth and Johnson (1983) points out that transport of hydrogen by dislocations in iron or steel at room temperature produces only small supersaturations at internal trap sites; larger supersaturations by dislocation transport are predicted to be possible in metals with much smaller diffusivities for hydrogen, e.g. nickel. A secondary but important consequence of the attendant hydrogen concentration associated with the dislocations is that it reduces the interaction energy between dislocations allowing them to pack more densely. It will also stabilize the microstructure preventing reorganization since an additional driving force would have to be provided to first remove hydrogen from the dislocations to permit reorganization (Ferreira et al., 1998).

This hydrogen-induced acceleration of the evolved microstructure is not confined to the volume of the crack tip plastic zone but extends, as it must, throughout the deforming volume. In addition, it must occur from the onset of plastic deformation. A consequence of this is that the microstructure into which a crack must propagate is evolved and characterized as being highly strained with a high hydrogen content. Indeed the local hydrogen content is likely to be higher than the enhancement achievable in the hydrostatic stress peak location ahead of a crack tip as predicted by the classic diffusion model. The mechanism for such widespread hydrogen accumulation is transport by mobile dislocations whose mobility is further accentuated by the HELP mechanism – a distribution and accumulation mechanism that has yet to be considered fully.

For example, in considering hydrogen-induced intergranular failure, it is known that a critical level of hydrogen must be established on the grain boundaries before the failure mode will transition from transgranular to intergranular (Lassila and Birnbaum, 1986, 1987, 1988). It was assumed that this critical concentration was achieved by diffusion, which may be enhanced by diffusion along grain boundaries. For example, Ladna and Birnbaum (1987) determined the diffusion of deuterium along grain boundaries in nickel and found it to be enhanced along high energy 39° ⟨110⟩ symmetrical tilt boundaries ($\Sigma=9$) but not along low energy 129° ⟨110⟩ symmetric tilt boundaries ($\Sigma=11$). However, based on experimental observations of the evolved microstructure immediately beneath hydrogen-induced intergranular facets in Ni (Martin et al., 2012a), a martensitic alloy (Nagao et al., 2012) and Fe (Wang et al., 2014), Sofronis, Robertson and coworkers suggested that the interaction of hydrogen-carrying dislocations with grain boundaries played an important role in establishing the conditions for promoting transition of the failure mode from transgranular to intergranular. They proposed that as transfer of strain across an interface does not necessarily involve equal numbers of dislocations absorbed and ejected by the interface (Lee et al., 1990a, 1990b; Clark et al., 1992), there will be an increase in the accumulated hydrogen at some interfaces. In addition, the process of slip transfer causes a change in the grain boundary energy as there will be a net difference in the Burgers vectors of the absorbed and ejected dislocations that remains in the grain boundary (Lee et al., 1990b; Clark et al., 1992). This effect will be magnified in the presence of hydrogen because of the attendant enhancement of the dislocation velocity. The increased strain energy density due to the residual grain boundary dislocations created by the act of slip transfer and the increase in hydrogen concentration on the grain boundary along with the elevated stress due to the evolved microstructure around the grain boundaries all contribute to promote intergranular failure. Of course, this mechanism is not restricted to hydrogen-induced intergranular failure, it must operate even if the failure mode remains ductile. Indeed, the evolved microstructure has been seen to be enhanced in other failure modes (Martin et al., 2011a, 2011b, 2013). Sofronis, Robertson and coworkers suggested that hydrogen-induced failure be more appropriately termed hydrogen-accelerated plasticity mediated failure. The specific final failure may be by a particular mechanism but the conditions for determining the failure mode and path is determined by the preceding plasticity, the local stress state, and hydrogen concentration established by these two factors.

The experimental evidence for dislocation assisted transport combined with the evidence of extensive plasticity prior to hydrogen-assisted failure suggests dislocation transport of hydrogen may be a critical component of the failure mechanism. For, in addition to the extent of the plasticity, the degree of plasticity is observed to be remarkably more advanced than predicted or observed in the absence of hydrogen. In other words, there is sufficient hydrogen to affect dislocation behavior further from the crack tip than expected by current transport models. The transport by dislocations seems best suited as a candidate to account for this disparity in hydrogen concentration.

To date, in simulations of hydrogen transport in elastoplastically deforming materials, hydrogen trapping and stress-driven hydrogen diffusion were accounted for, but, the effect of transport of hydrogen by moving dislocations was neglected as was the accelerated generation, recombination and annihilation of dislocations due to the presence of hydrogen (Sofronis and McMeeking, 1989; Taha and Sofronis, 2001; Dadfarnia et al., 2009; Novak et al., 2010). In this work, the model by Taha and Sofronis (2001) and Dadfarnia et al. (2009) to determine hydrogen profiles ahead of a crack tip is extended to take into