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GENERAL OVERVIEW: ATOMISTICS  
OF ENVIRONMENTALLY-INDUCED FRACTURE

by

R.M. Latanision

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GENERAL OVERVIEW: ATOMISTICS OF ENVIRONMENTALLY-INDUCED FRACTURE

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INTRODUCTION

That the mechanical behavior of solids is affected by surface and environmental conditions is now well-known and was, in fact, the subject of an earlier NATO Advanced Study Institute on Surface Effects in Crystal Plasticity.<sup>1</sup> While the plastics properties (yield strength, work hardening rate, etc.) are sometimes substantially affected by the presence of surface films, solvent environments and the like, it is the remarkable effect of environments on the fracture of solids that is of most consequence in a technological sense. Generally the latter interactions are considered to be adverse, and this is often a reputation that is well deserved. Stress corrosion cracking<sup>2,3</sup>, hydrogen embrittlement<sup>4</sup>, liquid metal embrittlement<sup>5,6</sup> and other such failure phenomena take on catastrophic consequences. As engineers, we are of course typically concerned with the prevention and or control of such failures. On the other hand, we should not forget that there are entire industries based upon the fragmentation of solids: materials removal operations such as metal cutting and ceramic machining, grinding, comminution, rapid excavation of hard rock, and others. Is it possible that in these circumstances one might use controlled embrittlement to advantage in order to reduce the work of fracture or fragmentation? While this approach is not typical of current practice in industry, it seems clear that controlled embrittlement is not only feasible but may well prove technologically attractive. This matter will be discussed in detail by Westwood and Pickens<sup>7</sup>, and I will not pursue the issue further here.

My objective in this presentation is to develop a sense of perspective regarding the kinds of embrittlement phenomena that are

of significance to us and some of the issues which this interdisciplinary gathering might treat. I will not attempt to review all of the important aspects of these embrittlement phenomena. This will be treated with more deliberation and detail by others at this conference. What I will attempt to do, however, is to present a cross section of the phenomenology, short descriptions of some aspects of the current state of mechanistic understanding and, finally, some of my views on how interdisciplinary interactions such as these may prove useful in the future in developing an understanding of the atomistics of environmentally-induced fracture.

#### PHENOMENOLOGY OF ENVIRONMENTALLY-INDUCED FRACTURE

Environmentally-induced fracture or embrittlement may be considered from many points of view, all of which in our context refer in essence to the premature failure of a metal or alloy in the simultaneous presence of (tensile) stress and some usually specific environment. For example, the stress corrosion cracking of aluminum alloy 7075 in aqueous chloride environments may be thought of or manifest in terms of a loss of load carrying capacity, a loss of ductility, or an apparent loss of toughness (subcritical crack growth) in a fracture mechanics sense. For the purpose of this discussion, I wish to consider only certain aspects of the embrittlement of metals and alloys\* in the presence of (a) (often only mildly corrosive) electrolytes, (b) hydrogen, and (c) liquid metals with the general purpose of then developing a case for studying the atomistics of fracture from an interdisciplinary point of view. It is not intended that this discussion will be comprehensive, and much of the detail will appear in the presentations of others at this conference. Brief, general treatments are found in the texts by Tetelman and McEvily<sup>8</sup> and Hertzberg<sup>9</sup>. Many of my own detailed views on these questions have been presented elsewhere<sup>1,5,10-11</sup>.

As is true of all of the phenomena mentioned above, susceptibility to embrittlement is a complicated function of the chemical environment which is present, the metallurgical history of the materials, and mechanical conditions. For example, there is a general tendency for susceptibility to environmentally-induced embrittlement to increase as the strength of an alloy or family of alloys is increased. Age hardenable aluminum alloy 7075 is most susceptible to stress corrosion cracking in aqueous chloride solutions in the peak hardened condition whereas the thermally overaged alloy is more resistant. Likewise, high strength, quench and tempered steels are particularly susceptible to hydrogen embrittlement, whereas low strength steels are relatively immune.

\* It should be appreciated that environmentally-induced failure occurs in virtually all classes of solids<sup>1,3</sup>. This treatment will consider only metals and alloys.

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Similar temperature, stress level, grain size, strain rate, slip mode, etc., dependencies have been reported with reference to various embrittlement phenomena<sup>6,10,12</sup>.

In what follows I have not particularly attempted to describe the specific and often exciting areas of controversy and overlap that have arisen in the multitude of studies of environmentally-induced embrittlement. These will surely be aired in the workshop sessions. What I have attempted to do, however, is to develop just enough of a perspective that in the spirit of this conference we might consider some relatively new, interdisciplinary approaches to understanding embrittlement phenomena.

#### A. Stress Corrosion Cracking

There are several characteristics of stress corrosion cracking - the premature failure of metallic alloys in the simultaneous presence of a tensile stress and an often only mildly corrosive electrolyte - that are intriguing:

- a. It is often the alloys which are most resistant to general or uniform corrosion that are most susceptible to stress corrosion cracking. Examples are Fe-Cr-Ni (austenitic) stainless steels, some aluminum and titanium alloys, etc., which resist corrosion because of the presence of protective surface (passive) films.
- b. While environmental specificity is not now considered to be so restrictive as once thought, there are some alloy-environment couples that are particularly susceptible to stress corrosion cracking. Some of the latter are summarized in Table I. It is interesting, for example, that while transgranular stress corrosion cracking has been observed when austenitic stainless steels are exposed to hot  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{F}^-$  solutions,  $\text{I}^-$  inhibits stress corrosion cracking. Likewise, nitrates crack mild steels but inhibit stress corrosion cracking in austenitic stainless steels.
- c. Pure, unalloyed metals are generally resistant to stress corrosion cracking.
- d. Normally ductile alloys fail in what appears to be a brittle manner in the presence of certain environments.

Over the years much has been proposed in a mechanistic sense regarding models for the stress corrosion cracking of alloys<sup>3,4</sup>. Short descriptions of views which enjoy some current popularity are listed below, leaving details to literature cited.

Table 1: Environments Which Cause  
Stress Corrosion Cracking of Certain Alloys

|                                  |                                                              |
|----------------------------------|--------------------------------------------------------------|
| Aluminum Alloys                  | Seawater ( $\text{Cl}^-$ and other halides)                  |
| Copper Alloys                    | Ammoniated aqueous solutions                                 |
| Nickel Alloys                    | $\text{OH}^-$ ( $\text{H}_2\text{S}$ , pure water)           |
| Mild Steels                      | $\text{OH}^-$ , $\text{NO}_3^-$                              |
| High Strength Steels             | (water, moist air, $\text{H}_2\text{S}$ )                    |
| Stainless Steels<br>(austenitic) | $\text{OH}^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{F}^-$ |
| Titanium Alloys                  | Seawater ( $\text{Cl}^-$ , and halides)                      |

Mechanisms of Stress Corrosion Cracking. The various models of stress corrosion cracking can be divided into two basic classes: those which consider that crack propagation proceeds by anodic dissolution at the crack tip (dissolution models) and those which consider that crack propagation is essentially mechanical.

- a. Crack propagation by the dissolution of film-free metal due to an increase in the number of active sites provided by plastic deformation at the crack tip. This mechano-chemical model was proposed by Hoar and Hines<sup>13</sup>.
- b. Crack propagation by the dissolution of metal at the crack tip as a consequence of the rupture of otherwise protective surface films by emergent dislocation. The film-rupture or slip step dissolution model has several variations, but is largely similar to that proposed initially by Champion<sup>14</sup> and Logan<sup>15</sup>.
- c. Propagation of cracks by the repeated formation and rupture of a brittle film growing into the metal at the crack tip as first described by Fortyl<sup>16</sup>.
- d. Adsorption (stress sorption) of surface active species, the consequence of which is a reduction in the surface energy required to form a crack and, therefore, reduced fracture stress. This adsorption model has been applied to various embrittlement phenomena since its proposal by Petch<sup>17</sup> and has been discussed with relation to stress corrosion cracking by Uhlig<sup>18</sup>.

While I do not wish to debate here which model is correct - indeed, the consensus would probably agree that there is no single mechanism of stress corrosion cracking which applies to all circumstances - let's just look at the film rupture model as a demonstration of one possible series of events. This may be done sche-

matically with the aid of Figure 1<sup>19</sup>. In effect it is proposed that the motion of dislocations, even at stresses below the macroscopic yield point, ruptures the otherwise stable passive film on the alloy surface thereby exposing clean, reactive metal which is subsequently attacked. The rate of repassivation, or reformation of the surface film, determines in this view the extent of dissolution. This event is repeated and the crack which has initiated as described above propagates discontinuously into the solid. While this model is appealing in many respects, it is also deficient in some: for example, slip step dissolution has been observed on alloys which are susceptible to stress corrosion cracking as well as on pure metals which are not. In effect, film rupture may be considered a necessary though not sufficient condition for stress corrosion cracking to occur. The same commentary could be developed with regard to all the mechanisms that have been proposed - none is totally capable of accounting for every aspect of stress corrosion cracking phenomenology, though some elements of each model seem quite clearly to be important. On this basis, a useful montage<sup>20</sup> showing chemical,

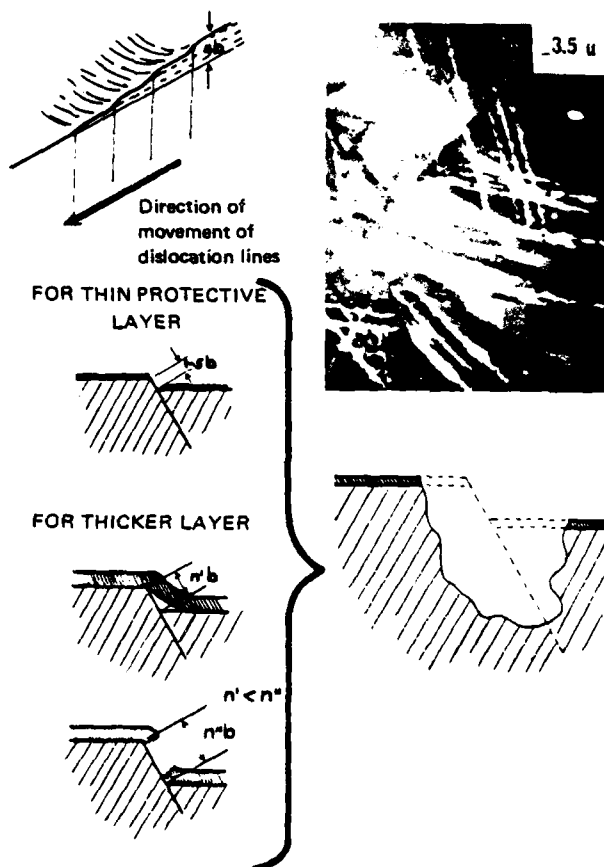


Figure 1: Schematic drawing illustrating the geometrical aspects of slip step dissolution (Smith and Staehle<sup>19</sup>).

metallurgical and mechanical processes thought to be important in stress corrosion cracking is given in Figure 2. It is difficult in my view to avoid the involvement of passive or protective surface films in the mechanism of stress corrosion cracking of austenitic stainless steels, aluminum alloys, etc. We'll return to this point later.

## B. Hydrogen Embrittlement

Hydrogen embrittlement is actually quite an old problem. Reynolds<sup>21</sup> and Hughes<sup>22</sup> in 1874 and 1880, respectively, were perhaps the first to associate certain detrimental affects on the ductility of iron with the presence of hydrogen. Not only is hydrogen embrittlement still a major industrial problem, but it is safe to say that in a mechanistic sense we still do not know what hydrogen (but not chlorine or nitrogen, etc.) does on an atomic scale to induce this degradation. I will return to this issue later.

Let's first consider the sources of hydrogen. Molecular hydrogen will, of course, induce embrittlement of susceptible metals and alloys (notice that hydrogen embrittlement is common to pure metals such as nickel<sup>23</sup> as well as complex alloys such as Hastelloy C-276<sup>24</sup>) provided that dissociation of  $H_2$  occurs thereby allowing for the absorption of atomic hydrogen into the metal lattice. Hydrogen embrittlement may also occur when the source of hydrogen is electrolytic, i.e., when hydrogen is produced by the discharge of protons in an electrolyte to form atomic hydrogen, provided in this case that surface recombination of adsorbed hydrogen to form molecular hydrogen is prohibited. If hydrogen adatoms are allowed to combine, then hydrogen will evolve from the surface in molecular form rather than being absorbed atomically. Once hydrogen enters a susceptible metal, the result is expected to be the same - i.e., embrittlement - but the entry process is clearly dependent upon the source of hydrogen and the catalytic properties of the surface exposed to the source. This has been discussed in detail by Berkowitz, et al.<sup>25</sup>.

Electrolytic hydrogen may be introduced into materials, for example, during cleaning (acid pickling) or electroplating operations or as a consequence of electrochemical corrosion itself. In the latter instance, the cathodic partial process which corresponds to anodic dissolution in a corrosion cell is likely to be proton reduction. Hence, it is quite possible that while a metal or alloy surface is anodically dissolving, hydrogen is being absorbed into that material. Awareness of this circumstance has, in fact, often presented something of a dilemma in the sense of distinguishing between stress corrosion cracking and hydrogen embrittlement in electrolytes. Indeed, while there are some incidences of embrittlement which appear to be clearly associated with hydrogen the

Figure 2. Montage showing important processes which affect stress corrosion cracking (after Staehle).

embrittlement of high strength steels in moist air or water) and others that appear to be anodically driven (the cracking of  $\alpha$ -brass in ammoniacal solutions) there are many other cases where the distinction is less clear. For example, whether the embrittlement of austenitic stainless steels and high strength aluminum alloys in chlorides should be attributed to stress corrosion cracking or hydrogen embrittlement is the subject of a considerable debate which I have considered in detail elsewhere<sup>10</sup>. The essence of this problem may be understood with the aid of Figure 3 which schematically shows (A) active path stress corrosion cracking wherein crack propagation is presumed to be anodically driven, the cathodic partial process serving only as a means of consuming electrons generated by the anodic process; and (B) hydrogen embrittlement in which case both reactions again occur, but crack initiation and propagation is driven this time by the absorption of cathodically produced hydrogen. It might seem conspicuous that one could distinguish between these two cases by examining the susceptibility of a given metal or alloy at applied anodic or cathodic currents. Unfortunately, for several reasons, this criterion is not unambiguous<sup>10</sup>. Some aspects of the crucial problem of crack tip chemistry at impressed anodic and cathodic potentials will be discussed at this conference by Pourbaix<sup>27</sup>.

As is true of stress corrosion cracking and liquid metal embrittlement, hydrogen embrittlement is affected by mechanical, environmental and metallurgical conditions<sup>12</sup>. For example, the susceptibility of high strength, quench and tempered steels to hydrogen embrittlement increases as the yield strength of the material is increased by thermal treatment. Indeed, above about 200 ksi yield strength, embrittlement occurs in moist air and water

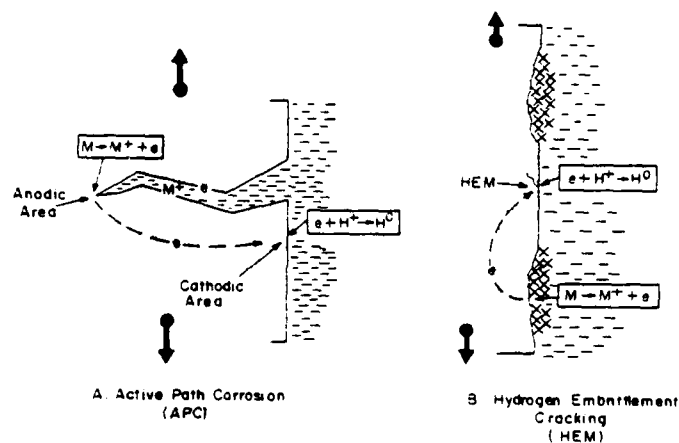


Figure 3. Schematic of cracking by active path corrosion (APC) and hydrogen embrittlement (HEM) mechanisms (after Wilde<sup>26</sup>).

vapor! On the other hand and with reference to environmental conditions, the presence of  $H_2S$  in aqueous environments limits the use of hardenable high strength steel in well drilling and oil and gas production equipment to a roughly 80-90 ksi yield strength. Sour gas (i.e.,  $H_2S$ -containing) presents substantial concern in terms of the materials for use as tubulars in deep wells<sup>24</sup>. One of the most striking demonstrations of hydrogen embrittlement and its control is shown in Figure 4<sup>28</sup> which illustrates the effect of oxygen, argon, hydrogen and water on the cracking behavior of a high strength steel. Note that dry hydrogen and moisture accelerate cracking whereas oxygen arrests crack extension. It is concluded that molecular hydrogen chemisorbs dissociatively on iron<sup>29</sup> allowing atomic hydrogen to be absorbed into the matrix. In moisture, it is expected that hydrogen is produced as a consequence of the corrosion of the iron surface as explained above. In effect, whatever the source, absorbed hydrogen leads to crack growth. By contrast, it is considered that oxygen inhibits embrittlement by producing an oxide barrier which suppresses subsequent absorption.

Mechanisms of Hydrogen Embrittlement. Hydrogen induced losses in strength or ductility have been attributed to several mechanisms. These have been succinctly described by Louthan and McNitt<sup>30</sup> and the list below is essentially an expanded version of that which appeared

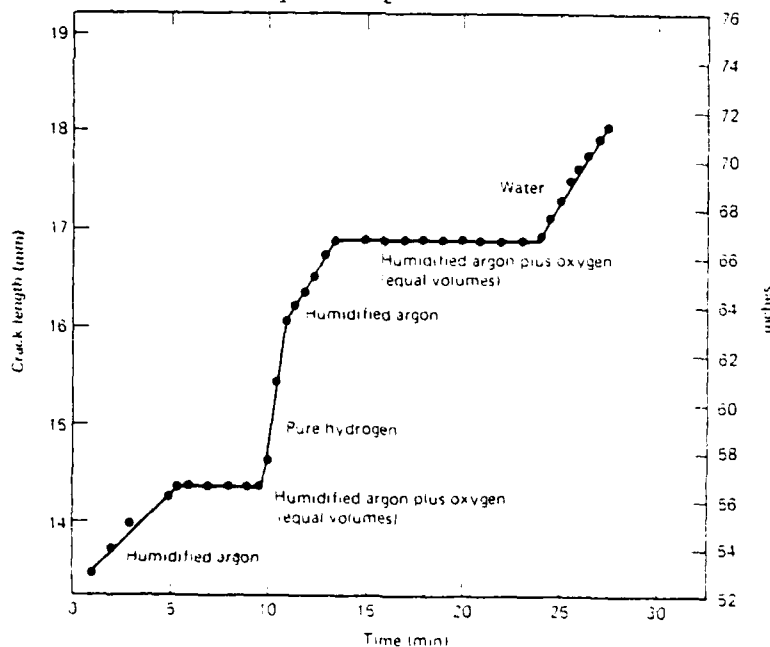


Figure 4: Fast crack growth of high-strength steel in water and hydrogen, but crack arrest in oxygen (after Hancock and Johnson<sup>28</sup>).

in their publication.

- a. The accumulation of molecular hydrogen in internal voids and cracks exerts a pressure which lowers the apparent fracture stress. This pressure model was originally proposed by Zapffe<sup>31</sup>.
- b. A hydrogen-induced decohesion of the lattice proposed by Troiano<sup>32</sup> and modified by Oriani<sup>33</sup>.
- c. Adsorption of hydrogen to reduce the surface energy as proposed by Petch, i.e., the hydrogen equivalent of stress sorption in stress corrosion cracking.
- d. Beachem's<sup>34</sup> suggestion that (absorbed) hydrogen-stimulated plastic deformation accelerates subsequent fracture. Though unspecific with regard to the means by which plasticity might be affected, recent field ion microscopy by Clum<sup>35</sup> suggests that hydrogen may reduce the work required to nucleate dislocations at the surface and, hence, induces plasticity. Lynch<sup>36</sup> has proposed similar behavior based on the view that chemisorption facilitates dislocation nucleation at crack tips, although, again, the mechanism by which this should occur is not well developed.
- e. Formation of a hydrogen-rich phase (e.g., hydride) which has mechanical properties different than those of the matrix<sup>37,38</sup>. This seems quite clearly to be the case for Ti and Zr and their alloys.
- f. Hydrogen-dislocation interactions which suppress glide and provide a means of producing locally large hydrogen accumulations that induce subsequent embrittlement<sup>38-40</sup>.

It is not my purpose in this instance to critically assess the above models. This has been done on many occasions by others and will surely be discussed elsewhere in these proceedings as well. It seems clear that there are circumstances where some models seem to apply better than others. Considering the volume of literature which has appeared on this subject, it should be no surprise that considerable support as well as contradiction may be found for each model.

As in the case of stress corrosion cracking, one may be led to conclude on the basis of the above that there is probably no one single mechanism of hydrogen embrittlement that applies universally. Of the suggestions listed above, perhaps the one that may most interest this interdisciplinary group is the electronic model of decohesion suggested by Troiano<sup>32</sup> for the hydrogen embrittlement of transition metals. I will return to this model

and its more modern successors which are just now developing, in a later section.

### C. Liquid Metal Embrittlement

Liquid metal embrittlement has been less studied than the industrially more common problems of hydrogen embrittlement and stress corrosion cracking. The proposed use of liquid metal (Li or Na) coolants in various nuclear systems has stimulated renewed concern.

The prerequisites for the embrittlement of an otherwise ductile solid metal by an active liquid metal appear to be as follows<sup>5,6</sup>:

- a. a tensile stress applied to the solid
- b. a pre-existing crack, or some measure of plastic deformation and the presence of a stable obstacle to dislocation motion in the lattice
- c. the presence of the embrittling species at this obstacle and, hence, at the propagating crack tip
- d. a usually specific solid metal-liquid metal couple, the characteristic of which is limited mutual solubility and little tendency to form intermetallic compounds. Table 2 indicates the susceptibility of some common liquid metal-solid metal couples.

As is the case of stress corrosion cracking, the specificity indicated in Table 2 is not now considered as restrictive as once thought. For example, Figure 5 shows that polycrystalline pure aluminum is only slightly embrittled by mercury at room temperature, but additions of as little as 1-3% of a number of elements to the mercury produces marked effects on the severity of embrittlement<sup>41</sup>. Liquid metal embrittlement is usually more severe in polycrystals than in single crystal solids. Grain boundaries, of course, serve as stable obstacles to dislocation motion, so the observation is not unexpected. Likewise, failure usually occurs in an intergranular manner although for highly anisotropic metals such as zinc, failure of polycrystalline specimens occurs predominantly by cleavage on basal planes.

In a mechanistic sense the most widely accepted view of liquid metal embrittlement may be understood with the aid of Figure 6<sup>42</sup>. This model, based on Kelly, et al.<sup>43</sup>, suggests that an equilibrium crack in a solid subjected to an increasing force will propagate by cleavage or grow slowly by shear depending on whether the tensile

Table 2 - Susceptibility of Liquid  
Metal-Solid Metal Couples

| Material         | Liquid Metal |    |    |    |    |
|------------------|--------------|----|----|----|----|
|                  | Hg           | Li | Bi | Ga | Zn |
| Steel            | NE           | E  | NE | NE | E  |
| Copper Alloys    | E            | E  | E  | -- | -- |
| Aluminum Alloys  | E            | NE | NE | E  | E  |
| Magnesium Alloys | NE           | NE | NE | NE | E  |
| Titanium Alloys  | E            | NE | NE | NE | NE |

NE - not embrittled

E - embrittled

fracture stress,  $\sigma$ , for the atom-atom bond or the shear stress,  $\tau$ , to cause dislocation motion on a favorable slip system is achieved first. Hence, as the ratio of  $\sigma/\tau$  decreases, cleavage becomes more likely and, conversely, shear failure becomes more probable as the ratio increases. Embrittlement is associated in the case of liquid metals with the reduction of the atom-atom bond strength due

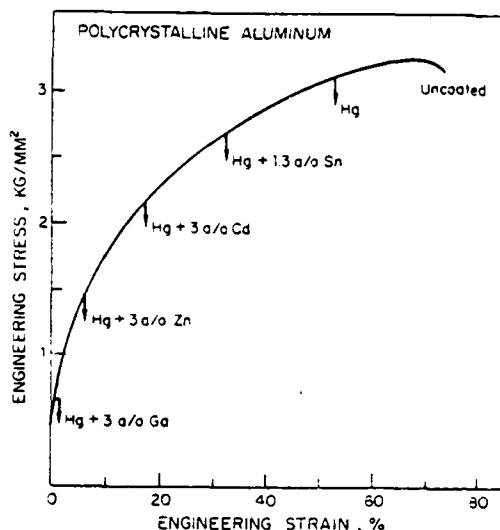


Figure 5. Embrittlement of polycrystalline pure aluminum by various mercury solutions (after Westwood et al.<sup>41</sup>).

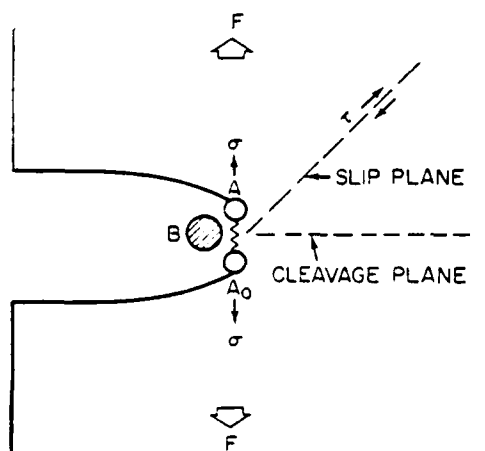


Figure 6. Schematic of a crack in a solid subjected to an increasing force  $F$ . The bond  $A-A_0$  constitutes the crack tip, and  $B$  is a surface-active liquid metal atom (after Westwood et al.<sup>42</sup>).

to the adsorption of the surface-active liquid metal atoms. Because of conduction electron screening in metals, it is expected that the yield stress or flow behavior of the solid should not be affected by the adsorbed species, whereas the stress and strain at fracture may well be influenced since the latter involves the consecutive rupture of surface bonds as the crack propagates. While it is in fact true that there are no measurable effects of liquid metals on bulk elastic or plastic properties, which adds support to the above model, Lynch<sup>36,44</sup> has recently argued that chemisorption may facilitate the nucleation of dislocations at crack tips, although the mechanism by which this might occur is unclear. The basis for Lynch's suggestion is the high resolution fractographic evidence for some crack tip plasticity (dimpling) even in the case of what appears otherwise to be a most brittle fracture surface. While the latter issue will surely be aired during the course of this workshop, there is analogous support for the suggestion of Lynch in the work of Clum<sup>35</sup>, mentioned earlier, which suggests enhanced dislocation injection in the presence of adsorbed hydrogen. It should be pointed out that while such analogs are often informative, it is important to develop such analogs with caution. For example, as pointed out by Stoloff<sup>6</sup>, while atomic hydrogen is quite mobile at ambient temperatures and may therefore be easily transported particularly into bcc solids, many embrittling liquid metal atoms are quite large and relatively immobile. It is, therefore, somewhat more difficult to account for the observed fractographic evidence of enhanced plasticity during the fracture process in the presence of liquid metals such as Hg than in the case of absorbed hydrogen.

#### SOME GENERAL OBSERVATIONS AND COMMENTS ON ATOMISTICS

As mentioned at the outset, my intention in the preceding section was not to attempt a comprehensive review of environmentally-induced embrittlement. Rather, my hope was to develop just enough of a perspective so that I might in this section describe areas where in my view subsequent interdisciplinary interaction might prove useful. As you will have recognized, there is considerable opinion that phenomena such as stress corrosion cracking, liquid metal embrittlement and hydrogen embrittlement have many similar characteristics. In this section even more common ground will appear, but I would caution the reader that common phenomenological characteristics do not necessarily imply that a unique mechanism (adsorption-induced decohesion, for example) is also common to these embrittlement processes. We do not have the atomistic basis yet to consider such a situation.

In the following sections I would like to consider what, if any, significance might be attached to (A) the solid/electrolyte interface, (B) grain boundary segregation phenomena, and (C) the experiences of organometallic and quantum chemists in understanding

environmentally-induced embrittlement.

### A. The Solid-Electrolyte Interface

In the sense that all of the embrittlement phenomena described to this point may occur in electrolytes - i.e., stress corrosion cracking occurs in aqueous environments, hydrogen may be generated as the cathodic partial process in a corrosion cell, and mercury may be deposited on zinc by a chemical replacement reaction from an aqueous mercuric nitrate solution - it may be worthwhile to consider the charge double layer which is characteristic of a metal-electrolyte interface. The schematic in Figure 7 shows the charge and potential distribution at a metal-dilute electrolyte interface. This has been described in detail elsewhere<sup>1</sup> and will not be repeated here. The point I wish to make at this stage is that, in the sense of the electrical analog shown in Figure 7, we have been typically more concerned with the Faradaic component - i.e., anodic dissolution or hydrogen evolution - than with the capacitive component. Should the charge double layer be of concern otherwise? Consider that the electric field across the double layer is likely to be of the order of  $10^7$  V/cm, typical of the field distribution present in a field ion microscope and capable of developing stresses approaching the theoretical cleavage and shear strengths<sup>45</sup>. In addition, it is known that the surface energy,  $\gamma$  (or surface stress in the case of a solid metal electrode<sup>46</sup>) is related to the surface

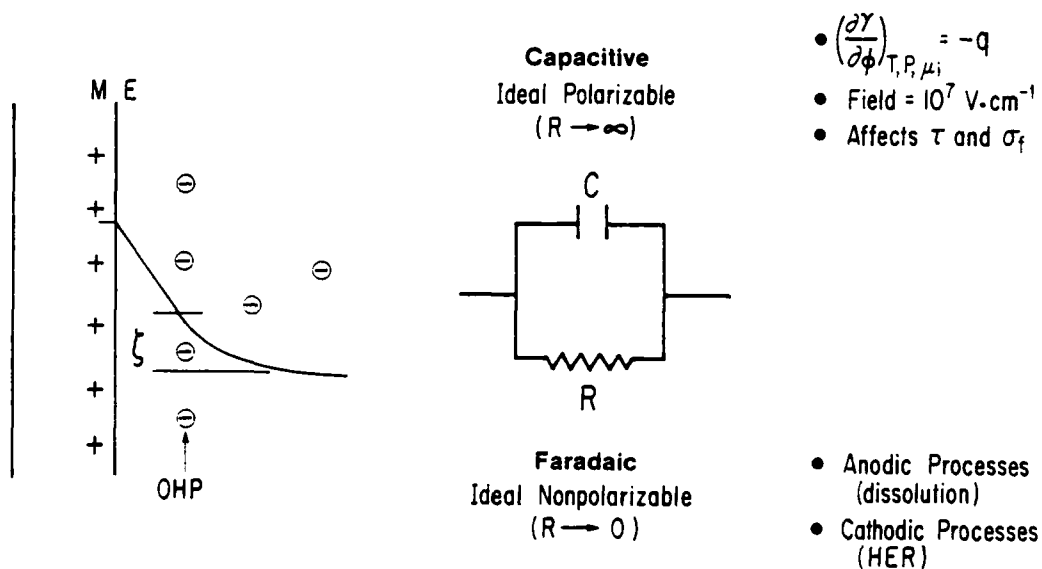


Figure 7. The charge and potential distribution at a metal-dilute electrolyte interface

charge density,  $q$ , and applied potential through the Lippmann equation<sup>47</sup>

$$\left(\frac{\partial \gamma}{\partial \phi}\right)_{T,P,\mu_i} = -q$$

At the potential of zero charge (pzc) the surface energy passes through a maximum. While there is considerable debate regarding the significance of changes in surface energy on the mechanical behavior of a variety of solids (see, for example, Macmillan<sup>48</sup> and Shchukin<sup>49</sup>), it does seem clear that changes in the surface charge density on metals can indeed affect the motion of dislocations which produce surface slip steps. In effect, the motion of such dislocations is resisted in part by the work required to produce the slip steps left in their trails and one expects that the pzc, where more work is required to create surfaces, the extent of glides of dislocations would be minimized. The net effect is that the creep rate of single crystals has been observed to pass through a minimum at the pzc<sup>50,51</sup> and the hardness passes through a maximum at the same potential<sup>52</sup>.

One expects that changes in the charge density on a metal electrode may affect its fracture behavior as well, and there is evidence to support this view<sup>52</sup>. With reference to Figure 8, it appears that crystal plasticity, hence  $\tau$ , may be affected by changes in the charge density, provided that glide dislocations produce surface steps. On this basis, one anticipates that the motion of such dislocations, Figure 8, away from sources near the crack tip may be inhibited (i.e., increasing  $\tau$ ) at the pzc encouraging cleavage. Likewise, because of the repulsion between like charges, the bond strength or cohesion between atoms in the surface layer of the crack tip, Figure 8, may also be affected by the charge density in the double layer. In this case one expects that at the pzc, where the surface charge is extinguished, cohesion of surface atoms would be maximized--i.e., cleavage would be discouraged.

It may be worth noting as well that the model proposed in Figure 8, would allow for the possibility that adsorbates may significantly affect the fracture of metals since the propagation of a surface-initiated crack involves the consecutive rupture of surface bonds, and chemisorption, which is likely to involve some change in the distribution of charges in the double layer, may thus affect the bond strength or cohesion (perhaps as described above) between the atoms constituting the crack tip. Liquid metal embrittlement is a classic example of this. Note that in liquid metal embrittlement, the embrittling species is considered to be adsorbed directly on the solid surface and, hence, strongly affects the strength of bonds between surface atoms. Thus, the consecutive rupture of surface atomic bonds, induced by reduction in the cohesive strength of

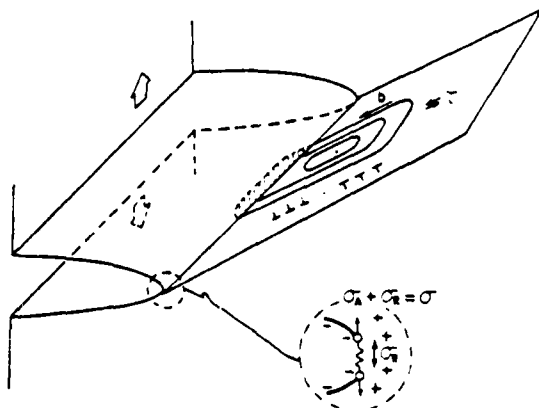


Figure 8. Crack tip showing the possible influence of double layer on  $\sigma$  and  $\tau$  (Latanision<sup>1</sup>).

surface atoms, leads to catastrophic fracture. In contrast, in aqueous electrolytes and in the absence of specific adsorption, ions present in the outer Helmholtz plane, are effectively shielded from the surface by water molecules, and are less likely to significantly influence cohesive strength (i.e., fracture). If it occurs, specific adsorption on the other hand (for example, of  $\text{Cl}^-$ ) may lead to a situation in an aqueous electrolyte approximately that of liquid metal embrittlement. Adsorption models based on this premise have been proposed for stress corrosion cracking. At any rate, it should be appreciated that  $\sigma$  and in some cases  $\tau$  may both be affected by variations in the charge density in the electrical double layer, regardless of whether the variations are due, for example, to the applications of external potential or to the chemisorption of surface-active species.

What is lacking in all of the above, of course, is the recognition that in phenomena such as stress corrosion cracking the metal electrode is likely to be film covered. Indeed, as mentioned earlier, the alloys which are most resistant to general corrosion, due to the presence of passive films, are also among the most susceptible to stress corrosion cracking. In effect, as shown in Figure 9, we are not dealing with a metal-electrolyte interface, but a metal/film/electrolyte interface. It is interesting that the mechanical behavior of semiconductors and insulator solids is environment sensitive as well. Such chemomechanical effects are described in detail elsewhere<sup>48,49</sup>.

In brief, there are two schools of thought regarding the mechanisms by which environments (particularly adsorbates) influence the mechanical behavior of such solids. The view developed by the discover of such effects, Rebinder, and his colleagues<sup>49</sup> is that adsorption-induced softening and strength reduction occur as a

result of the lowering of the specific free surface energy of the solid, i.e., the work of formation of new surfaces during deformation and fracture.

Alternatively, the view of Westwood and his co-workers is that many examples of such phenomena may be better understood from considerations of the influence of adsorption-dependent, surface potential induced, redistributions of the charge carriers in the solid, on the generation, motion and interaction of near-surface dislocations. Perhaps the most obvious demonstration of the dependence of the mechanical behavior of nonmetallic solids on surface potential is the correlation between  $\zeta$ -potential (a measure of the surface charge density), near-surface hardness and dislocation mobility indicated generally in Figure 9. This correlation, which shows that hardness passes through a maximum when  $\zeta=0$ , has been observed on solids such as  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and others. While an explanation for the symmetry observed in this correlation is a matter of discussion<sup>53,54</sup> the point of interest here is the suggestion by Westwood that chemomechanical effects (i.e., environmentally-induced changes in the charge distribution) on surface films may, in turn, affect the near-surface mechanical behavior of the underlying metal substrate, and, hence, may well play a role in embrittlement phenomena.

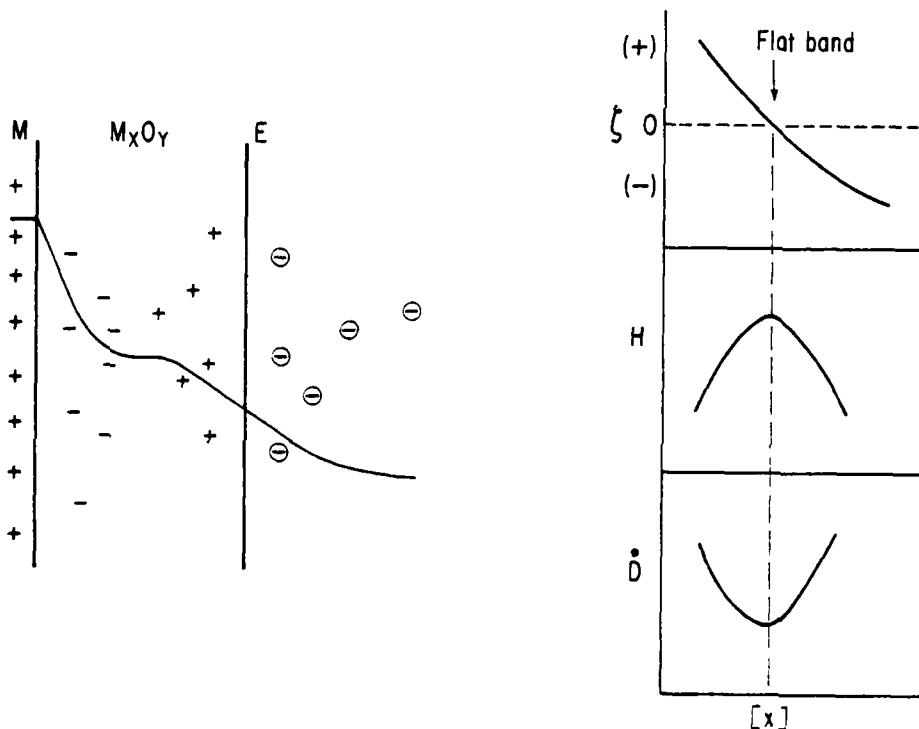


Figure 9. Charge and potential distribution at a metal/oxide/electrolyte interface and corresponding mechanical behavior effects.

## B. Grain Boundary Phenomena

The importance of impurity segregation at internal interfaces, particularly grain boundaries, has been discussed in terms of phenomenology of temper embrittlement<sup>55</sup>, stress corrosion cracking<sup>56</sup>, liquid metal embrittlement<sup>6</sup> and hydrogen embrittlement<sup>57</sup>. In each case, intergranular crack morphology is often, if not exclusively, observed. For example, temper embrittlement of steels appears related to the grain boundary accumulation of alloying elements such as Ni and Cr and impurity elements (metalloids) such as P, Sb, Sn, etc.<sup>59-62</sup>. Intergranular embrittlement of W<sup>63</sup>, Cu<sup>64</sup>, and phosphor bronze<sup>65</sup> have been associated with segregated P, Bi, and P, respectively. In many cases embrittlement has been attributed to a reduction in (grain boundary) surface energy, a consequence of the segregation of solutes to the grain boundary, or to galvanic effects in electrolytes arising out of chemical inhomogeneity between grain boundaries and contiguous grains<sup>56</sup>. Of course, depending upon the nature of the impurity element, increased or decreased reactivity may be expected to occur as a consequence of segregation. In the following, attention will be focussed on the part played by segregated impurities in the intergranular hydrogen embrittlement of polycrystalline metals and alloys. In addition, we will consider the effectiveness of grain boundary and lattice diffusion as well as of dislocation transport of hydrogen in the embrittlement process.

Impurity - Environment Interactions in Electrolytes. Impurities may play an important role in embrittlement induced by cathodically produced hydrogen, particularly if the segregated species happen to be metalloids such as those mentioned above which are known to be effective catalytic poisons for the hydrogen recombination reaction in electrolytes<sup>58</sup>. Perhaps the most effective way to examine the influence expected of metalloid elements on cathodic kinetics is to consider Figure 10 which shows the exchange current density for hydrogen evolution for some of the elements in the Periodic Chart. The exchange density may be considered a measure of the catalytic efficiency of a given element for the hydrogen evolution reaction at the reversible potential. Notice that the exchange current density for the hydrogen reaction is orders of magnitude higher on noble metals (typically  $\sim 10^{-3}$  A/cm<sup>2</sup>) or other transition metal surfaces ( $\sim 10^{-6}$  A/cm<sup>2</sup>) than on metalloid surfaces ( $\sim 10^{-13}$  A/cm<sup>2</sup>). The overall hydrogen evolution reaction may be broken down into, for example, a proton reduction step,  $H^+ + e = H_{ads}$ , and a hydrogen adatom - adatom combination step. Metalloid elements effectively poison the reaction  $H_{ads} + H_{ads} = H_2$  thereby increasing the population of adsorbed uncombined hydrogen on the electrode surface and, consequently, the probability that atomic hydrogen will be absorbed by the metal also increases. The influence of soluble metalloid salts in increasing the absorption of hydrogen from electrolytes at cathodic potentials is well documented<sup>67</sup>. Hence, as suggested by Latanision and

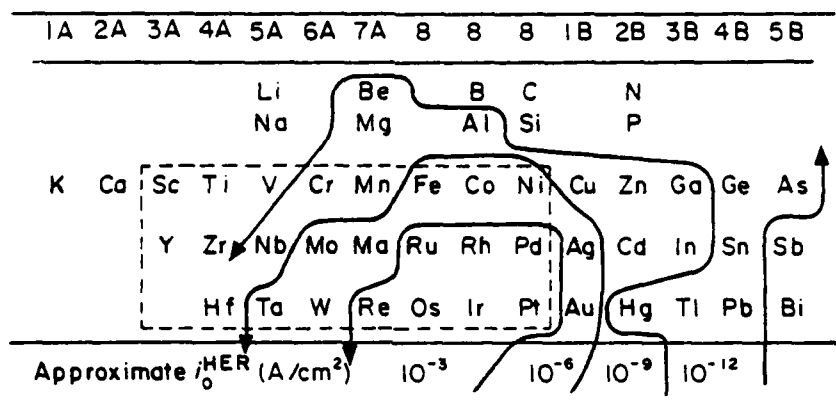


Figure 10. The exchange current density for the hydrogen evolution reaction,  $i_0^{\text{HER}}$ , for various elements in the Periodic Chart (from West<sup>66</sup>).

Oppenheimer<sup>57</sup>, one might expect metalloid-segregated grain boundaries to act as preferential sites for the absorption of cathodic hydrogen into polycrystalline metals, Figure 11. In essence, it was argued that the entry of hydrogen into nickel occurred preferentially in the proximity of the grain boundary intersections with the free surface due to the presence therein of segregates which act to poison the combination of hydrogen atoms formed by the discharge of protons from the electrolyte. At locations remote from the grain boundary, protons are reduced forming hydrogen adatoms which in the absence of a poison have a high probability of combining to form molecular hydrogen and are, thus, subsequently evolved. In the vicinity of a grain boundary, in contrast, rather than evolving from the electrode surface in molecular form, uncombined hydrogen adatoms increase in number at the interface and the probability of their absorption into the metal lattice increases. While metalloids may be expected to have the effect of increasing the rate of atomic hydrogen absorption, noble elements such as Ru, Pt, Pd, Rh, etc., would have the opposite influence with regard to cathodic charging. Hence, preferential segregation of noble metals to the grain boundaries of alloys otherwise embrittled intergranularly during cathodic charging may be beneficial. Indeed, the work reported by Pickering and coworkers<sup>68</sup> demonstrates very nicely that Pt introduced into the surface by ion implantation decreases the entry and permeation of electrolytic hydrogen into iron. Somewhat different but related considerations apply if the source of hydrogen is molecular as has been discussed by Berkowitz et al<sup>25</sup>. In this case, noble metals (hydrogen dissociation catalysts) segregated to the grain boundaries would be expected to stimulate hydrogen absorption and subsequent cracking. On the other hand, catalytic poisons should retard cracking as shown in the interesting work of Liu et al<sup>69</sup>.

It should be appreciated that the embrittlement of nickel described above<sup>57-58</sup> is not the result of segregation of metalloids alone as indicated by the fact that identical tensile specimens deformed in the absence of hydrogen were not embrittled. Indeed embrittlement is associated with the interaction between segregated species and the surrounding environment. Such impurity-microchemistry interactions may apply to other metals and alloys as well. Grain boundary segregation of phosphorus, for example, has been observed in thermally treated nickel-base alloys such as Inconel 600<sup>70,71</sup> and Hastelloy C-276<sup>24</sup>, both of which are subject to intergranular hydrogen embrittlement. Likewise, recent extensive work by Bruemmer, et al<sup>72</sup>, has shown a similar fracture mode transition in hydrogen charged iron as a function of grain boundary sulfur segregation. In addition, of course, it has been observed that the tempering temperature range producing shortest life in steels exposed to cathodic hydrogen corresponds also to the typical temper

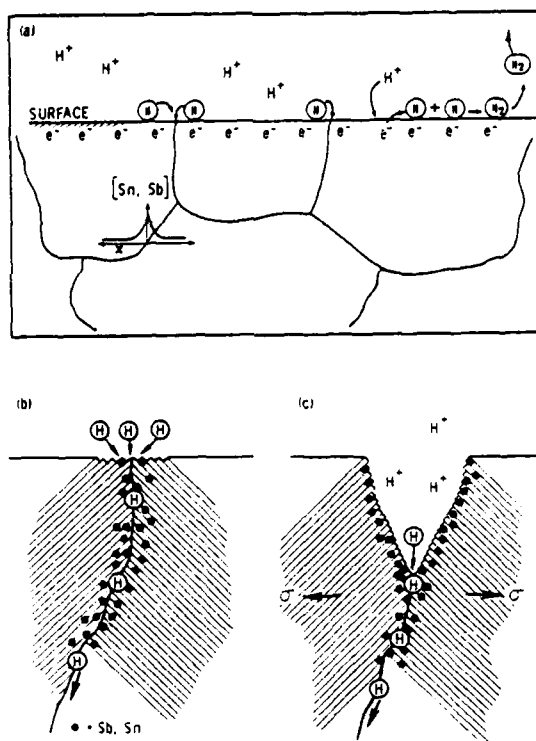


Figure 11. Schematic indicating the preferential absorption of atomic hydrogen along metalloid-segregated grain boundaries and subsequent intergranular embrittlement of polycrystalline metals and alloys (after Latanision and Oppenhaus<sup>57</sup>).

embrittlement range<sup>61</sup>. Moreover, it is known, as pointed out earlier, that temper embrittlement is associated with grain boundary accumulation of Sb, P, Sn, etc., all of which are very effective hydrogen recombination poisons. Recognizing that water and water vapor are damaging to high strength steels<sup>28</sup> -- presumably due to the presence of hydrogen produced as the cathodic equivalent of the oxidation or corrosion of iron -- it has been suggested<sup>58</sup> that temper embrittlement may be due not solely to the accumulation of impurities at the grain boundaries but, as in the case of nickel, in part as well to the local rate of absorption of hydrogen by the matrix. It should be mentioned that Yoshino and McMahon<sup>61</sup> attribute the increased hydrogen sensitivity of temper embrittled steels to the combined effects of impurities and hydrogen in reducing the intergranular cohesive strength. The point of the present discussion is to suggest that the accumulated impurities may be responsible as well for the presence of hydrogen in the grain boundaries.

Given all of the above, some of the elements which may be involved in the intergranular embrittlement of nickel are shown in the sequence in Figure 12. Recent studies (see reference 1 for a review) suggest that yielding begins in the surface grains of polycrystals through the action of dislocation sources near the free surface. The result is that one expects some hydrogen is dragged into the interior along with mobile dislocations which may then interact with grain boundaries, Figures 12(a) and (b). Some hydrogen is likely to enter the solid at other than poisoned grain boundaries, evidence for which is the fact that serrated yielding has been observed in large-grained polycrystals and in similar experiments with monocrystals<sup>73</sup> cathodically charged and deformed simultaneously. The latter suggests that dislocation-solute (hydrogen) interactions occur. There is evidence<sup>74</sup>, as well, to show that hydrogen induces softening of nickel under certain circumstances and this should, of course, be considered. Likewise, atomic hydrogen which presumably enters the solid preferentially at grain boundary intersections with the free surface may diffuse via the grain boundaries into the solid. In the later stages of deformation, internal dislocation sources become operational and the incidence of dislocations interactions with the grain boundaries increases. It is conceivable, for example, that dislocations generated by sources located at grain boundaries may sweep hydrogen into the bulk. The attendant stress and the presence of hydrogen in the vicinity of the grain boundaries may subsequently lead to embrittlement, Figure 12(c), perhaps as a result of the chemisorption-induced reduction in the cohesive strength of atomic bonds at regions of stress concentration.

While I do not wish to treat the question of hydrogen transport by dislocations as well as by grain boundary or lattice diffusion in detail here (our views in this regard have been presented else-

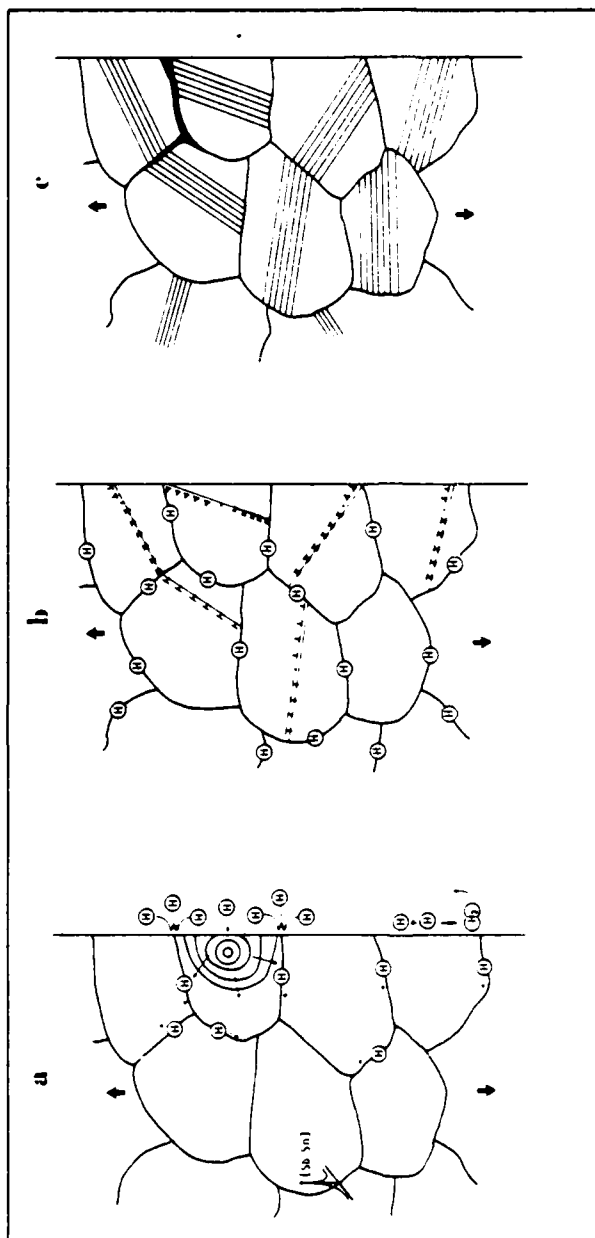


Figure 12. Schematic showing sequence perhaps involved in intergranular hydrogen embrittlement (after Latanision and Oppenhausser<sup>58</sup>).

where recently<sup>58</sup>), I do wish to make two points. Firstly, although one would like to examine the absorption and transport of electrolytic hydrogen in metalloid-segregated grain boundaries, this is experimentally difficult to do in situ. On the other hand, we have recently explored the use of metallic glasses as a structural and chemical analog of segregated grain boundaries in electrolytic hydrogen permeation studies<sup>75,76</sup>. Structurally, Ashby et al.<sup>77</sup> have pointed out that grain boundaries may be described on an atomic scale as a packing of polyhedra, a model which has been used as well to effectively characterize the structure of metallic glasses. In effect, both grain boundaries and metallic glasses may be considered to possess a certain short range order on an atomic scale, but not the long range periodicity typical of perfect crystals. Chemically, the transition metal-metalloid type glasses (typically 80 atomic per cent transition metals, 20 atomic per cent metalloid compositions) are of compositions that are good approximations of the chemistry of solute segregated grain boundaries in polycrystalline metals and alloys. As mentioned earlier, grain boundary segregation of phosphorus has been observed in thermally treated nickel-base alloys such as Inconel 600 and Hastelloy C-276. Hence, Ni-P binary glasses may be considered to be good structural and chemical analog of grain boundaries in thermally treated nickel-base alloys. Without elaborating in detail, using electrolytic hydrogen permeation techniques<sup>78</sup>, we find<sup>76</sup> that metalloid-containing glassy alloys do absorb considerable amounts of hydrogen, Figure 13, presumably catalytically stimulated as described earlier. On the other hand in a Ni<sub>81</sub>P<sub>19</sub> glassy alloy, which simulates P segregated grain boundaries in alloys such as Inconel 600 or Hastelloy C-276, the diffusivity of hydrogen is found to be  $\sim 10^{-10}$  cm<sup>2</sup>/sec, or roughly of the order of lattice diffusion in nickel. This is significant since it suggests, given the grain boundary-metallic glass analog, that fast grain boundary diffusion of hydrogen may be unlikely in nickel-base alloys. Still, considering that the permeation

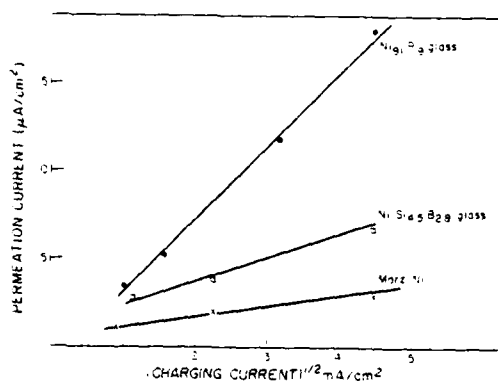


Figure 13. Steady state permeation flux as a function of charging current for various crystalline and glassy nickel-base materials (after Latanision, et al.<sup>76</sup>).

flux, if not the diffusivity, of hydrogen in metalloid-containing glasses is higher than in polycrystalline nickel, one may consider that the introduction of substantially more hydrogen occurs along segregated grain boundaries than via the bulk. Work is in progress now using means other than electrochemical to explore the possibility that considerable hydrogen transport may occur along grain boundaries (i.e., a large local flux) but not at significantly greater rates than by lattice diffusion.

The second point I wish to make concerns dislocation transport of hydrogen, which will receive considerably more discussion during the workshop sessions. Observations of dislocation transport have been reported in terms of tritium release measurements performed during deformation and by autoradiographic techniques<sup>79-81</sup> as well as in some recent electrolytic permeation studies by Kurkela and Latanision<sup>82</sup>. The latter work demonstrates that mobile dislocations transport hydrogen at rates much higher than lattice diffusion in polycrystalline nickel. Typical permeation build-up and decay transients under plastic deformation are shown in Figure 14. Hydrogen permeates through the 0.1mm specimen in less than 10 seconds and a steady state is reached in less than a minute. On switching off the charging current, the anodic current decays to the value observed prior to charging. When deformation is stopped the anodic current decays back to the original background value. Increasing strain rate increases the observed permeation flux. The largest strain rate ( $4.2 \times 10^{-4}/s$ ) was below the critical strain rate, given by  $\sim 10^{-11} \rho_H$  ( $\rho_H$  = density of hydrogen-carrying dislocations), above which hydrogen transport does not occur. The effective diffusivity of hydrogen in such experiments is found to be linearly dependent upon the strain rate and is of the order of  $10^{-5} \text{ cm}^2/\text{sec}$  in contrast to  $10^{-10} \text{ cm}^2/\text{sec}$  in unstrained nickel at room temperature. From these results, it is evident that in plastically deformed nickel dislocation transport of hydrogen is the predominant mechanism and that the transport rates are several orders of magnitude higher than in unstrained nickel where lattice diffusion is the predominant mechanism. It should be appreciated, however, that dislocation transport or any other rapid transport process does not guarantee in itself that the host material will be embrittled. Such transport mechanisms will only be important in materials that are sensitive to hydrogen. For example, hydrogen is very permeable in palladium, but embrittlement is not<sup>83</sup> anything like as serious as in nickel or some iron-base alloys.

In short, identification and/or control of the partitioning of solutes - alloying elements as well as metalloid impurities - may well provide a clue as to the nature of a particular intergranular embrittlement phenomenon (i.e., stress corrosion cracking vs. hydrogen embrittlement) as well as suggest means of reducing susceptibility by metallurgical treatment. Of course, we need at this stage to know much more about the details of such segregation

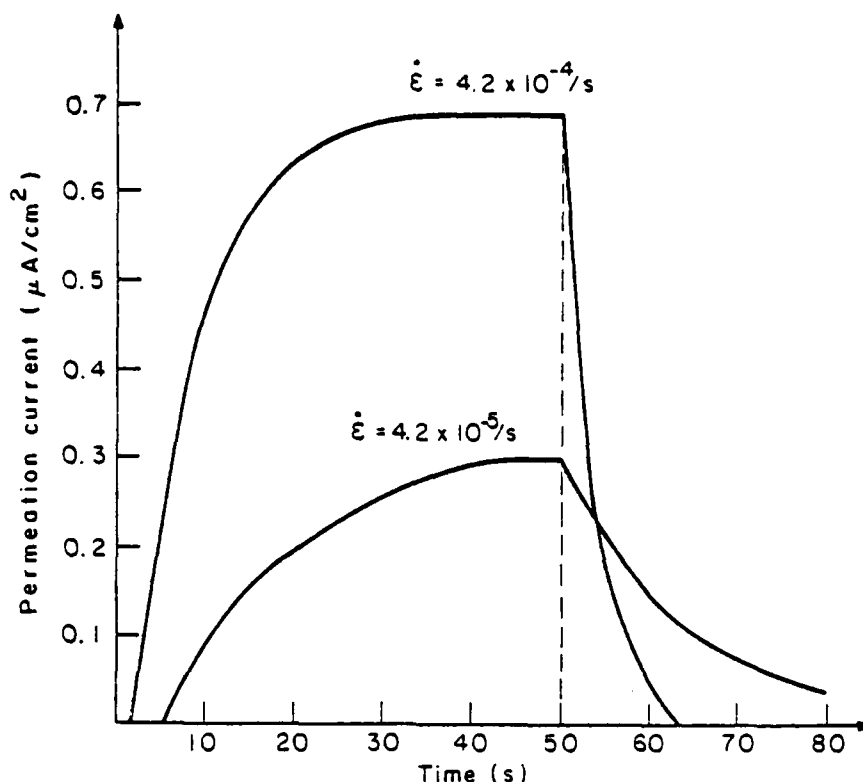


Figure 14. Effect of strain rate on the decay transient (after Kurkela and Latanision<sup>82</sup>).

phenomena - how might one treat an alloy to induce selective segregation; what interactions might one expect between segregated solutes; etc.? It is also clear that despite years of activity we still do not understand on an atomic scale how and what embrittling species (hydrogen atoms, chloride ions, liquid metal atoms, etc.) do to induce decohesion at a crack tip. This remains to be answered, I believe, by means other than traditional mechanical testing. Detailed studies of the surface structure, electronic structure, and bonding of adsorbed hydrogen, for example, on strained metal surfaces, are just beginning to proceed but are crucial, we believe, to understanding such phenomena. Here is an area where our coordination chemist and quantum chemist and other friends may begin to help us.

### C. Embrittlement Analogs in Chemistry and Physics

I believe it is clear that embrittlement phenomena such as stress corrosion cracking, hydrogen embrittlement, liquid metal

embrittlement and temper embrittlement are academically exciting and, even more clearly, technically important. These problems are also, I believe, poorly understood on an atomistic level. In short, we know quite a lot about the phenomenology and control of environmentally-induced embrittlement, but very little about atomistics. In some respects, this should not be surprising. As I have mentioned earlier, these are multidisciplinary problems involving not just materials science and mechanics but chemistry as well. The latter, it seems to me, is the area where we have been least effective in attempting to understand the atomistics of embrittlement, and probably, the area where some remarkably meaningful contributions may be made in the near future, provided that we properly cultivate the interest of this discipline. In the following I wish to present a short description of some aspects of chemistry which may be helpful. Many of these views are based on discussions with my colleagues Traugott Fischer, Keith Johnson, and George Whitesides, who are far more expert in these matters than I, and will fortunately follow me in the program with discussions of far greater depth. I hasten to add that the following is not intended to represent a complete or exhaustive indication of the input which might be forthcoming, but, rather, a starting point.

While it is possible to describe liquid metal embrittlement, hydrogen embrittlement, etc., on the basis of environmentally induced decohesion, the atomic scale interactions between the adsorbate (H<sub>2</sub>, H, etc.) and strained metal surfaces which cause decohesion are not well understood. In this context, one interesting electronic model of hydrogen embrittlement was proposed in 1960 by Troiano<sup>32</sup>. In this model, Troiano presumes that hydrogen behaves in an electropositive sense and donates its electron to the unfilled d-bands of the metallic cores as shown schematically in Figure 15. The increase in electron density leads to an increase in the repulsive force between adjacent metal cores or, in other words, a

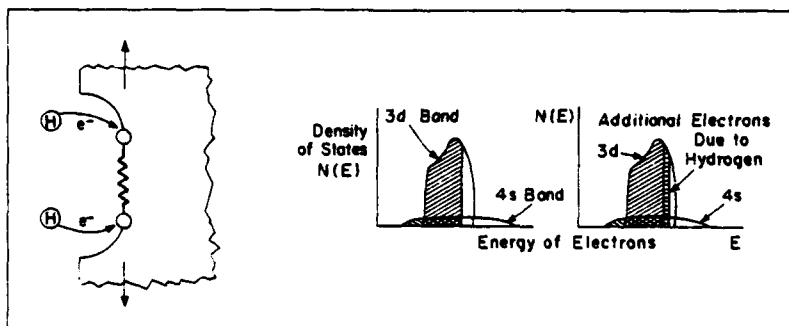


Figure 15. An electronic model for hydrogen embrittlement of transition metals (after Troiano<sup>32</sup>).

decrease in the cohesive strength of the lattice, i.e., in not unlike the manner described in Figure 8. Recognizing that the great cohesive strength of the transition metals may be associated with their band structures, particularly the filling of d-orbitals, the above model has a certain appeal.

Of course, there are alternate approaches to considering the nature and significance of the charge transfer processes which occur and which may be associated with the atomistics of hydrogen embrittlement as well as other (at least potentially) adsorption-induced embrittlement phenomena such as liquid metal embrittlement. For example, if we look into the literature of catalysis we find that there is considerable interest and understanding of one process which is of interest to us, namely the dissociative adsorption of molecular hydrogen. We can examine this problem in elementary terms with the aid of Figure 16 which shows the energetics involved when two hydrogen atoms are made to approach one another. When the spins of the electrons on the two atoms are opposed, attractive or bonding interactions occur between the atoms, with a pronounced minimum at  $r_0$ , whereas repulsive or antibonding interactions occur if the hydrogen 1s electrons have parallel spins. In effect, the two original hydrogen 1s orbitals are transformed into two new orbitals: one of these is a bonding molecular orbital and has a lower energy than the parent atomic orbitals while the

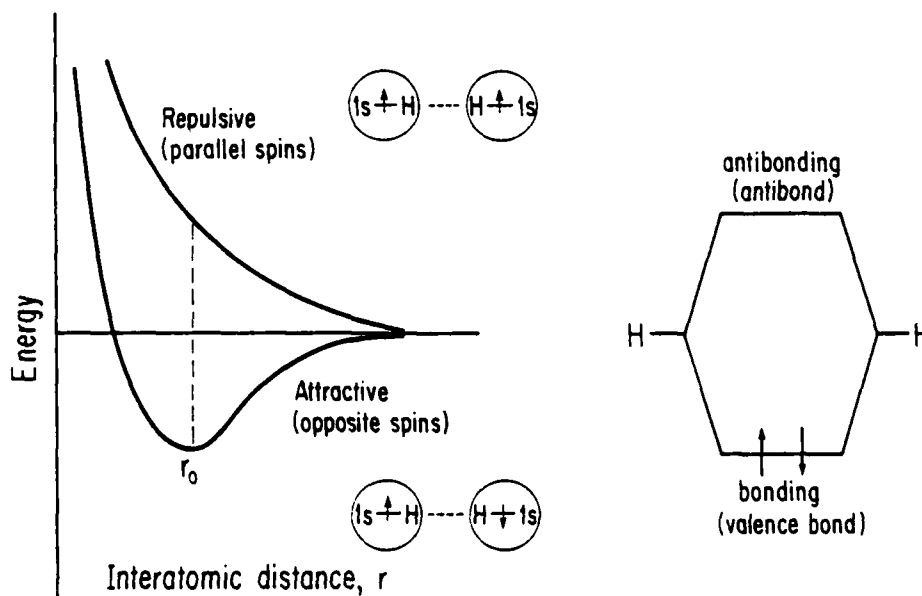


Figure 16. The hydrogen molecule.

other is an antibonding orbital and has a higher energy than the original atomic orbitals. A stable hydrogen molecule, at a separation  $r_0$ , would just fill the bonding orbital. Indeed, on this basis we can understand why a stable  $\text{He}_2$  molecule does not exist. In dissociative chemisorption, it is envisioned that electrons from the catalyst (for example, Fe, Ni, or other transition metals) are dumped into the antibonding orbitals of the hydrogen molecule. In such circumstances, the hydrogen molecule begins to dissociate. The efficiency of this dissociation depends on the amount of overlap between the metal orbital which is involved and the antibonding orbital of the hydrogen molecule. (See, for example, references 84 and 85.)

Of course, in the above description we have concerned ourselves with the dissociation of the adsorbate, hydrogen. What happens to the metal atoms in the surface of the transition metal catalyst? It is, of course, possible to identify bonding and antibonding orbitals in the density of state diagram for the metals involved, as described in Figure 17. On this basis it would seem that one might consider the stability of the metal surface in terms of the relative location and population of the bonding and antibonding orbitals in both the metal and adsorbate. Indeed, as pointed out by Fischer<sup>85-86</sup>, dissociative adsorption (catalysis) is the mirror image of chemisorption-induced embrittlement (and vice versa). On this basis one may consider that some metals, those which are embrittled by hydrogen, may transfer electrons from metal bonding orbitals to antibonding orbitals in the hydrogen molecule. While nonembrittled metals may dissociate hydrogen by transfer of charge from metal antibonding orbitals to hydrogen antibonding orbitals. In both cases hydrogen is dissociated.

Certainly, matters are more complicated than described above. There is, for instance, the issue of the mechanical stresses which are involved in the embrittlement situation. How does stress (or strain) affect the relation between orbitals in the metal and adsorbate. I do not believe that we have an answer at this stage, but some work along these lines is in progress<sup>87,88</sup>. The work of Eberhart et al.<sup>88</sup>, based on SCF-X $\alpha$ -SW molecular orbital cluster calculations, includes the influence of strain and is particularly exciting. Similar calculations have been performed recently by Briant and Messmer<sup>89</sup> in assessing the intergranular embrittlement of nickel by sulfur. Losch<sup>90</sup> has also recently considered a chemical model of temper embrittlement.

Although calculations which might demonstrate the above embrittlement of metals by hydrogen (or liquid metals, etc.), have not yet been performed, there is some experience in organometallic chemistry which by analogy with embrittlement phenomena is quite intriguing. For example, transition carbonyl molecules are known to

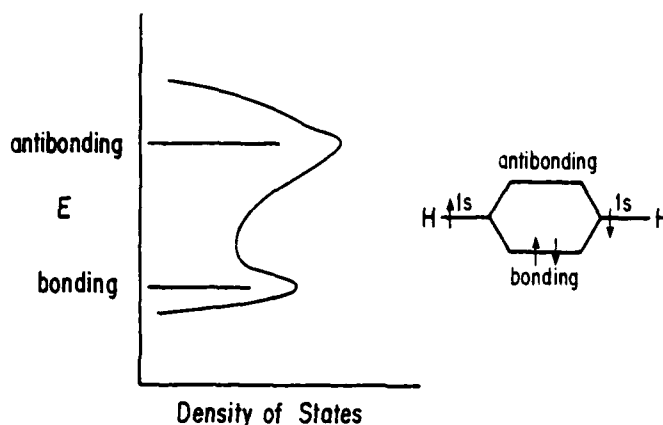
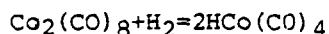


Figure 17. Adsorption of hydrogen on metal surfaces.

dissociate in the presence of molecular hydrogen; for example, as in the following<sup>91,92</sup>:



In effect the hydrogen molecule splits, but so too does the bond between the cobalt atoms in the carbonyl molecule. While the Co-Co bond in this carbonyl molecule may not be metallic in the usual sense, such reactions are, on an atomic scale, an interesting analog of the hydrogen embrittlement of transition metals.

At any rate, it seems to me that there is great potential for fruitful interactions between those involved in research in embrittlement phenomena and in catalysis.

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The objective is

#### CONCLUDING REMARKS

✓ In keeping with my initial objectives, I have attempted in this paper to provide a general overview of some of the phenomenology related to the atomistics of (particularly, environmentally-induced) fracture and of those areas where interdisciplinary activity involving materials science, mechanics, physical chemistry, surface physics and chemistry and atomic modeling might provide valuable insight. May of the details which I have omitted will, I suspect, appear in our workshops.

In all of the above phenomena, the action typically begins at the interface between the solid and the environment which surrounds it, and it should not be too surprising to find that many of the current mechanistic models for these phenomena involve film formation, adsorption of critical species from the environment, interfacial solute concentration gradients, etc. However, we know little about the possible influence of yielding initiation in the surface layer on the embrittlement of polycrystals. Nor, for example, do we seem to know very much about the influence of surface charge on crack propagation in metal electrodes, about the detailed atomic-order interactions between embrittling species and strained crystal surfaces, about the atomistics of decohesion or about the electron distribution at a crack tip. We have made some progress in recent years in these directions, and the potential for sizeable advances is enormous, provided, I believe, that the concerted activity of the disciplines represented here is stimulated.

We have learned quite a lot about the phenomenology of embrittlement, but it is safe to say that in an atomistic sense we still do not know in detail what hydrogen (but not nitrogen or oxygen, etc.) does on an atomic scale to induce this degradation. The same applies to other examples of environmentally-induced fracture; what is it about the ubiquitous chloride ion that induces premature catastrophic fracture (stress corrosion cracking) of ordinarily ductile austenitic stainless steels? Why, moreover, are chloride ions troublesome but chemically similar iodides inhibitors for SCC in such stainless steels? In short, despite all that we may know about the phenomenology of fracture on a macroscopic scale, we know precious little about the atomistics of embrittlement phenomena such as those described above.

On the other hand, it is interesting to note that physical chemists and surface chemists also have interest in the same kind of interactions that occur on an atomic scale when metals such as nickel or platinum, for example, are used as catalysts for chemical reactions. Such metals are very effective catalysts for the dissociation of molecular hydrogen. Indeed, considerable experimental study has been directed toward the surface chemistry of hydrogen adsorption, etc., on transition metal surfaces. But much

of the same uncertainty in terms of fundamental understanding pervades this area of science. Can we predict which metals will be effective catalysts and for which chemical reaction? It would seem that the development of fundamental understanding of the kind implicit in the above discussion of the catalytic dissociation of hydrogen (embrittlement of the hydrogen molecule!) would impact, as well, understanding of the fundamentals of the embrittlement of the metal surfaces (dissociation of metal atomic bonds). One might wonder in a converse sense if such interdisciplinary interaction might benefit the catalysis community as well. For example, is it possible that the effectiveness of a catalyst might be significantly increased if the catalyst were allowed to plastically deform while performing its chemical function?

At any rate, I believe that more direct and frequent communications must be stimulated between the kinds of disciplines described above. Indeed, it seems very clear now that much is known by physical chemists and quantum chemists that bears directly on problems of embrittlement and fracture of interest to materials scientists and those involved with the mechanics of solids. This information is often, however, not transferred. Development of the atomic scale understanding which is sought is not only of academic significance but may well lead to technological advances in chemistry and materials science ranging from catalysts for use in energy conversion and storage, for example, to the improved lifetime and reliability of complex and expensive structures in aggressive environments. In this context, in fact, it seems to me that the technological significance of the interactions of environments such as hydrogen, liquid metals, hot (perhaps molten) salts, etc., with materials will become increasingly more important in the decades to come. There is, for example, the issue of a hydrogen economy -- i.e., the use of hydrogen as an energy medium for this planet.<sup>93</sup> This is not unlikely, particularly if effective (semiconductor) photoelectrodes can be developed to split water, since water and sunlight are both plentiful and, at the moment, free! In addition, of course, questions such as materials for storage and transmission or distribution of hydrogen (perhaps in this case materials that are already in place) will become increasingly important. I suspect that if the previous decades of research and engineering on environmentally-induced embrittlement were considered exciting, the next decades will be even more so and the impact of this effort will be of even greater consequence.

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