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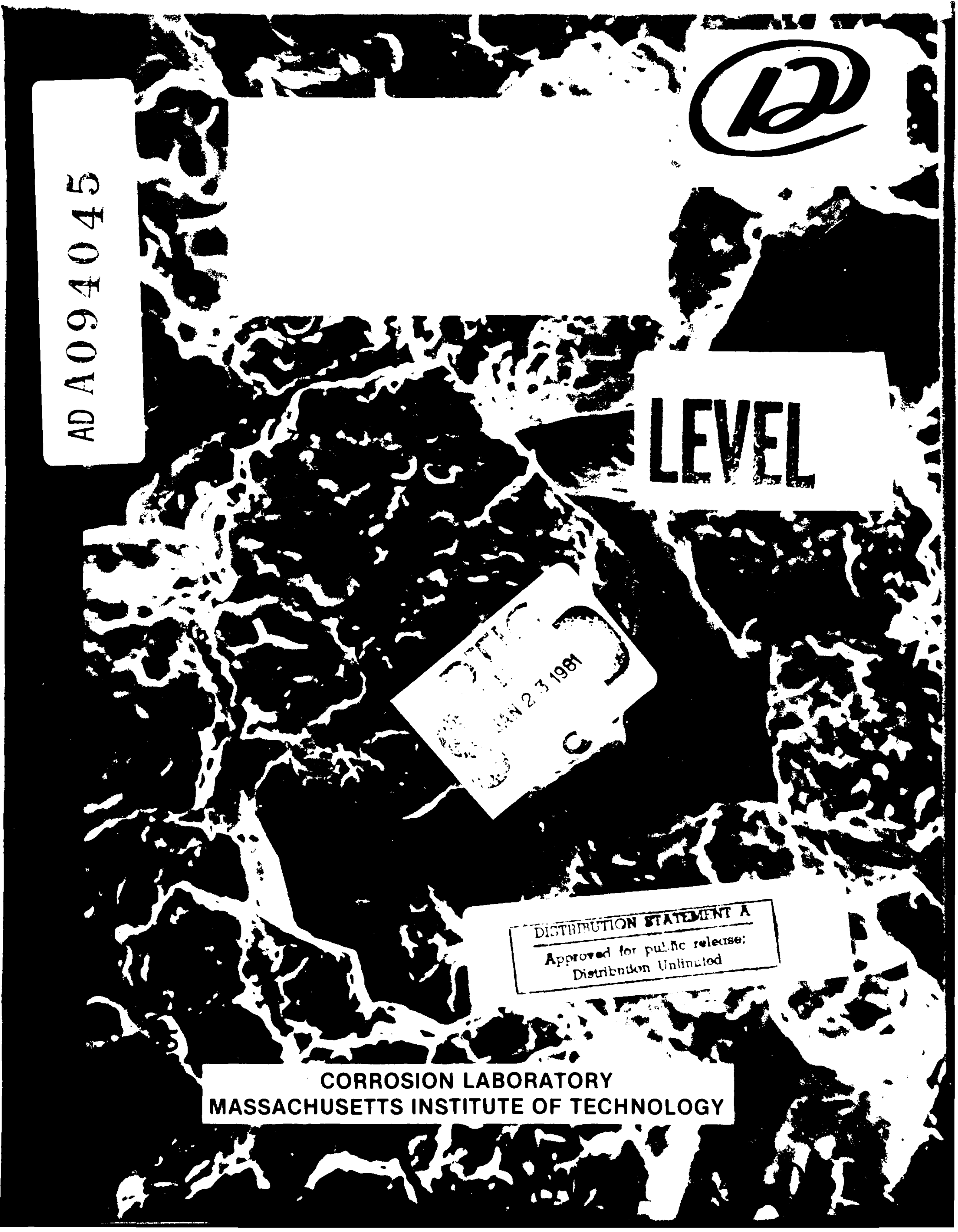

CORROSION LABORATORY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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# THE ROLE OF GRAIN BOUNDARY CHEMISTRY AND THE ENVIRONMENT ON INTERGRANULAR FRACTURE.

by

R.M. Latanision, M. Kurkela and F. Lee

Technical Report No. 5

to

Office of Naval Research

Contract No. N00014-78-C-0002, NR 036-127/8-24-77(471)

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October 1980

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| 1. REPORT NUMBER | 2. GOVT ACCESSION NO.<br>AD-A094 045 | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>THE ROLE OF GRAIN BOUNDARY CHEMISTRY AND THE ENVIRONMENT ON INTERGRANULAR FRACTURE | | 5. TYPE OF REPORT & PERIOD COVERED<br>Technical Report<br>6. PERFORMING ORG. REPORT NUMBER<br>Technical Report No. 5 |
| 7. AUTHOR(s)<br>R. M. Latanision, M. Kurkela and F. Lee | | 8. CONTRACT OR GRANT NUMBER(s)<br>N00014-78-C-0002<br>NR 036-127/8-24/77(471) |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Massachusetts Institute of Technology<br>Cambridge, Massachusetts 02139 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>Office of Naval Research<br>800 Quincy Street<br>Arlington, VA 22217 | | 12. REPORT DATE<br>October 1980<br>13. NUMBER OF PAGES<br>16 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | | 15. SECURITY CLASS. (of this report)<br>15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

hydrogen permeation, hydrogen embrittlement, solute segregation, metallic glasses, nickel-base alloys

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Block 20. Abstract - Continued -

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Proc. Third International Conference on EFFECT OF HYDROGEN ON BEHAVIOR OF MATERIALS, in press.

## Introduction

The importance of impurity segregation at internal interfaces, particularly grain boundaries, in the phenomenology of various forms of embrittlement -- temper embrittlement (1), stress corrosion cracking (2), etc., -- had been proposed some time ago. More recently, surface analytical tools such as Auger electron spectroscopy have made it possible to substantiate such proposals. 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. (3-6). Intergranular embrittlement of W (7), Cu (8), and phosphor bronze (9) 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 inhomogeniety between grain boundaries and contiguous grains (2). 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 present discussion, attention will be focussed on the part played by segregated impurities in the intergranular hydrogen embrittlement of polycrystalline metals and alloys. In particular, we will describe in this paper recent work performed in the Corrosion Laboratory at M.I.T. on the influence of solutes in the absorption of electrolytic hydrogen. In addition, we will assess 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. The significance of recombination poisons was first pointed out by Latanision and Opperhauser (10-13) in a study of the intergranular embrittlement of nickel by cathodically produced hydrogen. Perhaps the most effective way to examine the influence expected of metalloid elements on cathodic kinetics is to consider Figure 1, taken from West (14), 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$^2$) or other transition metal surfaces ($\sim 10^{-6}$ A/cm$^2$) than on metalloid surfaces ($\sim 10^{-13}$ A/cm$^2$). 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 (15-16). Hence, as suggested by Latanision and Opperhauser (10-13), one might expect metalloid-segregated grain boundaries to act as preferential sites for the absorption of cathodic hydrogen into polycrystalline metals, Figure 2. 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 Sn and Sb (and the absence of Cu) which act to poison the combination of hydrogen atoms formed by the discharge of protons from the electrolyte. At locations re-

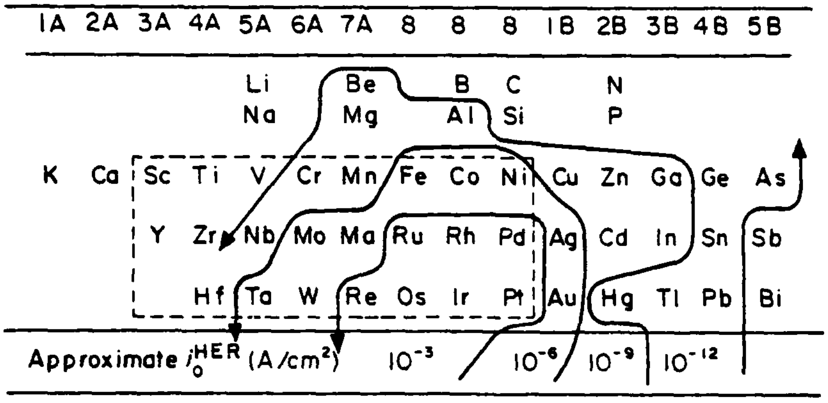

Fig. 1 - The exchange current density for the hydrogen evolution reaction, $i_o^{HER}$, for various elements in the Periodic Chart (after West (14)).

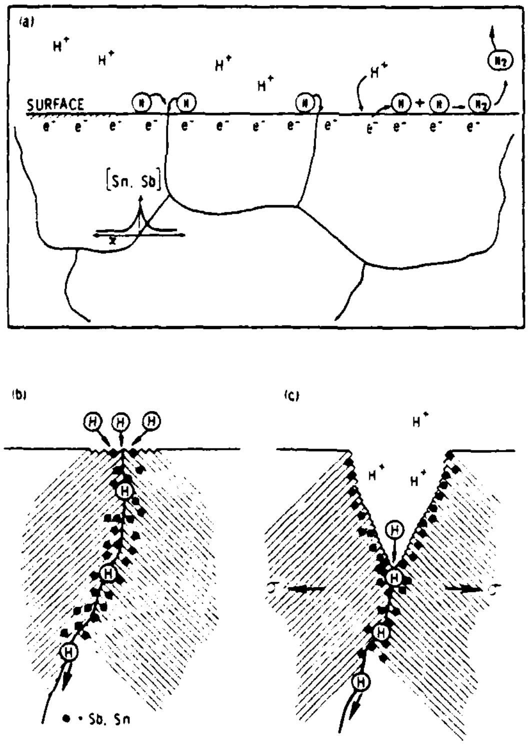

Fig. 2 - Schematic indicating the preferential absorption of atomic hydrogen along metalloid-segregated grain boundaries and subsequent intergranular embrittlement of polycrystalline metals and alloys (after Latanision and Opperhauser (12)).

mote 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. It should be noted that the observed absence of copper, which would otherwise stimulate the combination reaction, further increases the probability of atomic hydrogen absorption. Hence one must consider the influence of species which are deficient as well as in excess (relative to the unembrittled condition) on the grain boundaries.

While we have to this point discussed the importance of impurities largely from the point of view of their influence on cathodic hydrogen embrittlement, it might be well to notice that those impurities which increase the rate of hydrogen absorption from electrolytes (i.e., metalloids such as Sn, Sb, S, P, As, etc.) typically have the concurrent effect of reducing the corrosion rate. Since such elements have typically low exchange current densities for the hydrogen evolution reaction, one expects that in acid or deaerated electrolytes the open circuit corrosion rate will be decreased in those regions where the segregation of such metalloids occurs. In effect, in alloys that are not sensitive to hydrogen, susceptibility to stress corrosion cracking, presuming that cracking occurs by a dissolution related mechanism, may be reduced. Preferential selective segregation may therefore provide a means of stress corrosion cracking control.

In a similar context, control of susceptibility in alloys sensitive to cracking during cathodic charging requires quite different control. One would in this case hope to decrease the concentration of metalloids at grain boundaries by, for example, reducing grain size, purification of the alloy, or by providing alternate and non-continuous interfaces as opposed to grain boundaries at which solutes might accumulate. Conversely, while metalloids would 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, perferential segregation of noble metals to the grain boundaries of alloys typically embrittled intergranularly during cathodic charging may be beneficial. Indeed, the work reported by Pickering and Zamanzedeh (17) in the poster session at this conference 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. (18). 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. (19).

It should be appreciated that the embrittlement of nickel described above (10-13) 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 (20, 21) and Hastelloy C-276 (22), both of which are subject to intergranular hydrogen embrittlement. Likewise, recent extensive work by Bruemmer, et al. (23) 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 embrittlement range (5, 24). 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 (25) -- presumably due to the presence of hydrogen produced as the cathodic equivalent of the oxidation or corrosion of iron -- it has been suggested (13) 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 (5) 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.

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 embrittlement phenomenon (i.e., SCC 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 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 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 (26) but are crucial, we believe, to understanding such phenomena.

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 3. Recent studies (see reference 27 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 3(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 (12, 28) cathodically charged and deformed simultaneously. The latter suggests that dislocation-solute (hydrogen) interactions occur. 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 dislocation 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 3 (c), perhaps as a result of the chemisorption-induced reduction in the cohesive strength of atomic bonds at regions of stress concentration.

In the following sections we will examine the above views with regard to (a) the possibility of increased hydrogen absorption in the proximity of

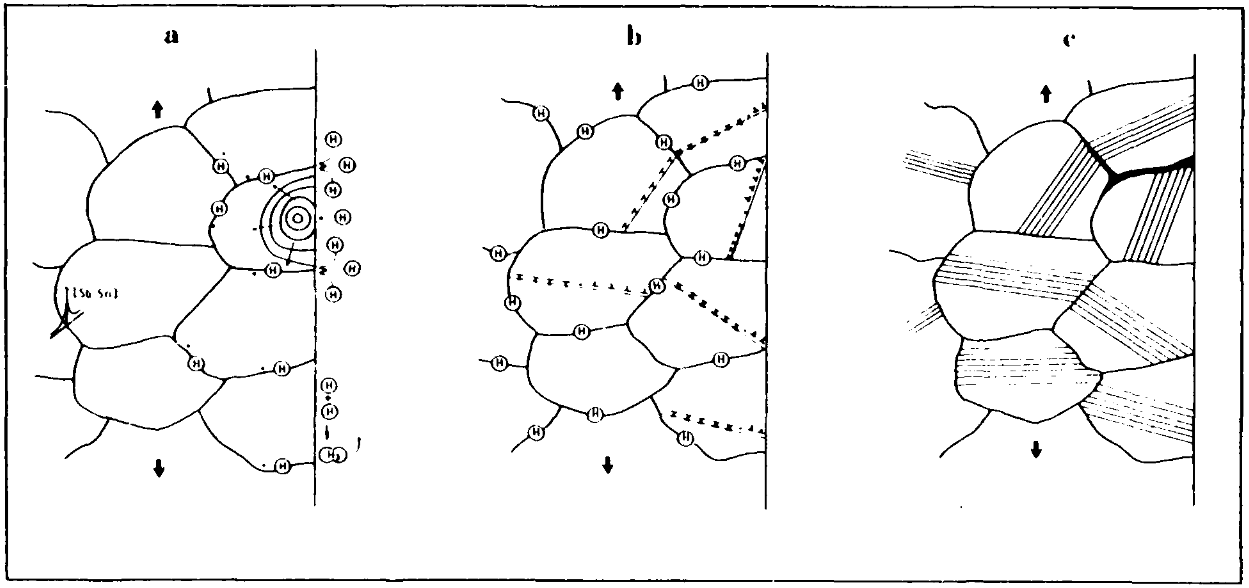

Fig. 3 - Schematic showing sequence perhaps involved in intergranular hydrogen embrittlement (after Latanision and Opperhauser (10)).

segregated grain boundaries; (b) the effectiveness of grain boundary diffusion; and (c) the likelihood of dislocation transport in nickel and nickel-base alloys.

## Hydrogen Absorption at Metalloid-Segregated Grain Boundaries in Nickel-Base Alloys

Ideally, one would like to explicitly examine the behavior of the grain boundary - electrolyte interface with regard to the hydrogen evolution/absorption processes. Obviously, this is 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 hydorgen permeation studies (29, 30). Structurally, Ashby et al. (31) 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 (32). 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. (For more detailed information on metallic glasses, see references 33 and 34.)

The studies of hydrogen absorption on metalloid containing glasses were pursued by means of hydrogen permeation measurements following the Devanathan technique (35). In this approach, a thin membrane is cathodically charged with hydrogen on one side while the other side is maintained at a constant potential sufficiently noble to oxidize all of the hydrogen diffusing out. The anodic current monitored between the membrane and a Pt counter electrode is a direct measure of the rate at which hydrogen permeates the membrane. Moreover, from permeation transients one may calculate both the diffusivity of hydrogen and the concentration of hydrogen just beneath the surface on the cathode side of the membrane. One expects, as explained earlier, that the presence of metalloids in some metallic glasses should increase the rate of absorption of atomic hydrogen into the membrane and, hence, affect the permeation flux. In effect, in a Fick's first law approximation, the flux of hydrogen at the anodic side of a membrane of thickness L expressed as a permeation current density is given by:

$$J = -nFD\left(\frac{\partial C}{\partial X}\right)$$

where C is the concentration of hydrogen, n the number of electrons involved in the hydrogen reaction, F, Faraday's constant and D the diffusion coefficient. Note that the measured current density is proportional to

$$-\left(\frac{\partial C}{\partial X}\right)_{X=L}$$

and this varies from zero to a steady state value of $\frac{C_o}{L}$. Hence, at steady state, the permeation flux is given by:

$$J_\infty = nFD\frac{C_o}{L}$$

Since Co is expected to increase in metalloid containing glasses, $J_\infty$ is correspondingly likely to increase. Work on Fe-base glassy alloys (29, 30) has shown $D_H$ to be of the order of $10^{-10}$ cm$^2$/sec and Co to be as high as 0.06 moles/cm$^3$. The latter is far higher than is typical of Ni or Pt ($1.4 \times 10^{-5}$ to $2.7 \times 10^{-4}$ moles/cm$^3$, respectively) and is more typical of the hydride forming elements Ti, Zr or Ta (~0.1 moles/cm$^3$). Likewise, it was observed that if the cathodic charging current (or, correspondingly, hydrogen overpotential) exceeded a certain limit, abnormalities would occur in the permeation transients. Indeed, rather than achieving a steady state, the permeation flux began to decrease with time despite the fact that the charging current was maintained constant throughout. Similar observations have been reported by Bockris and Subramanyan (36) and have been associated with trapping of hydrogen within the solid. In most instances, the nature and identity of traps in solids is relatively uncertain. In the present case, the traps seem quite clearly to be associated with micron-order diameter voids introduced during fabrication (29). Ultimately, glasses exhibiting such analogous transients were found to fail catastrophically, despite the absence of any externally applied stresses.

The results of permeation experiments on polycrystalline high purity nickel, a $Ni_{92.7}Si_{4.5}B_{2.8}$ glass, and $Ni_{81}P_{19}$ glass are given in Figure 4. The work on $Ni_{81}P_{19}$ was intended to address the case of the metallic glass analog of phorphorus-segregated grain boundaries in nickel-base alloys. In effect, as described earlier with reference to Figure 2, it has been proposed that the segregated grain boundaries might act as preferential paths for the entry of hydrogen into the polycrystalline matrix. Notice that as the charging current increases the steady state permeation current also increases, but far more rapidly for the metalloid-concentrated glass as expected. Figure 5 shows the dependence of the permeation transient on charging current or, correspondingly, overpotential. As in the case of Fe-based glasses evidence of trapping is present above a critical overpotential.

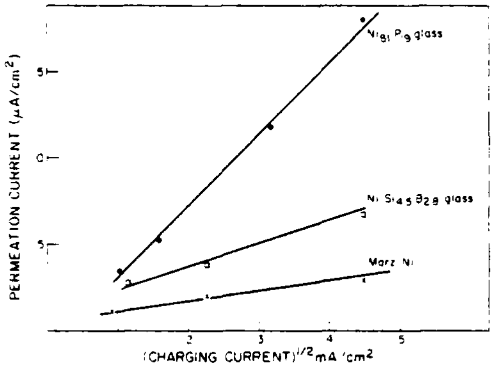

Fig. 4 - Steady state permeation flux as a function of charging current for various crystalline and glassy nickel-base materials (after Latanision, et al. (30)).

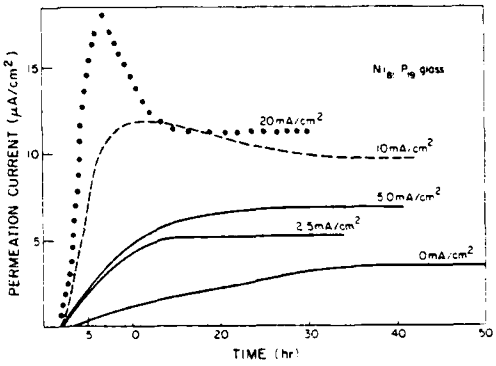

Fig. 5 - Permeation transients for $Ni_{81}P_{19}$ exhibiting trapping behavior at high charging current or, correspondingly, overpotential. (after Latanision, et. al. (30).)

Table I. summarizes the permeation information taken from this work.

Table I. Permeation Data

| Material | Ic(mA/cm$^2$) | D$_H$(cm$^2$/s) | Co(mol/cm$^3$) |
|---|---|---|---|
| $Ni_{81}P_{19}$ | 2.5 | $7.9x10^{-11}$ | $2.6x10^{-3}$ |
| $Ni_{81}P_{19}$ | 5.0 | $8.6x10^{-11}$ | $3.1x10^{-3}$ |
| $Ni_{81}P_{19}$ | 10.0 | $11.5x10^{-11}$ | $4.0x10^{-3}$ |
| $Ni_{81}P_{19}$ | 20.0 | $13.8x10^{-11}$ | $5.1x10^{-3}$ |
| $NiSi_{4.5}B_{2.8}$ | 1.25 | $7.0x10^{-11}$ | $1.5x10^{-3}$ |
| $NiSi_{4.5}B_{2.8}$ | 5.0 | $8.4x10^{-11}$ | $2.0x10^{-3}$ |
| $NiSi_{4.5}B_{2.8}$ | 20.0 | $10.0x10^{-11}$ | $3.0x10^{-3}$ |
| Polycrystalline Marz Ni | 0.8 | $1.9x10^{-10}$ | $2.3x10^{-4}$ |
| " " | 5.0 | $2.3x10^{-10}$ | $3.1x10^{-4}$ |
| " " | 20.0 | $3.1x10^{-10}$ | $3.8x10^{-4}$ |

In effect, the diffusivity of hydrogen in $Ni_{81}P_{19}$ is found to be $\sim10^{-10}$ cm$^2$/sec., or roughly on the order of lattice diffusion in nickel. This is significant since it suggests, given the grain boundary-metallic glass comparison, that grain boundary diffusion of hydrogen may be unlikely in the segregated grain boundaries of nickel-base alloys. Indeed, parallel efforts in our laboratory to detect grain boundary diffusion by electrolytic permeation experiments on polycrystalline nickel and nickel-base alloys have been unsuccessful (37). Despite the free volume available in glasses, perhaps metalloid-related or other trapping phenomena are overwhelmingly more effective than transport phenomena. Work is in progress using means other than electrochemical to explore the possibility that grain boundary diffusion may occur.

In summary, it appears that metalloid containing glassy alloys do absorb considerable amounts of hydrogen, presumably catalytically stimulated as described above. In both Fe-and Ni-base glasses, the diffusivity of hydrogen at ambient temperatures is of the order of the lattice diffusion coefficient in fcc metals. Evidence of internal trapping, which leads in some cases to catastrophic embrittlement, is also observed. In short, it does indeed appear that metallic glasses may serve very well as grain boundary analogs in certain circumstances. Work is in progress now to further explore their utility in this regard.

## Dislocation Transport of Hydrogen in Nickel-Base Alloys

As discussed with regard to Figure 3, the permeation of hydrogen into crystalline materials may occur in part by lattice diffusion, by grain boundary (or other short circuit) diffusion, or, in the case of specimens undergoing plastic deformation, by dislocation transport. In the latter instance, the transport of hydrogen occurs in the form of Cottrell atmospheres dragged by mobile dislocations. This was first suggested by Bastien and Azou (38, 39). Later, this concept was supported by observations of serrated yielding (28, 40-42), tritium release measurements during plastic deformation and autoradiographic techniques (43-45). Tien, et al. (46) and

Johnson and Hirth (47) have considered dislocation transport analytically. Recently, Kurkela and Latanision (48) have shown by more direct electrolytic permeation measurements that mobile dislocations transport hydrogen at rates much higher than lattice diffusion in nickel. The permeation of hydrogen was studied by the method developed by Devanathan and Stachurski (described earlier) modified to allow plastic deformation of the specimens during the introduction of hydrogen. Similar studies have been performed on $Ni_2Cr$ by Berkowitz, et al. (49) and are reported in this Proceeding.

Typical permeation build-up and decay transients under plastic deformation are shown in Figures 6 and 7. Hydrogen permeates through the 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. From Figures 6 and 7, it can be seen that increasing strain rate increases the observed permeation flux. Increasing charging current also gave higher permeation fluxes. 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. Figure 7 shows decay transients for two different strain rates observed after switching off the charging current. In the case of the higher strain rate, the decay is much faster.

The mathematics of hydrogen permeation has been dealt with elsewhere (35, 50). By applying Fick's second law with the appropriate initial and boundary conditions and using the half-rise time method, $D_H$ can be evaluated. In plastically deformed nickel, the "effective" $D_H$ was found to be of the order of $10^{-5} cm^2/s$ in contrast to $10^{-10} cm^2/s$ in unstrained nickel, the latter of which compares well with the findings of Robertson (51). Indeed, the effective diffusivity of hydrogen increases linearly with strain rate (37).

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 is interesting to note that according to the modeling of Tien, et al. (46), it should take about 5 seconds for hydrogen to travel through the specimens used in this work. Examination of Figure 6 shows that breakthrough times vary between 2.5 and 5.5 seconds and are functionally dependent on the strain rate. One should, in principle, be able to show that above a certain critical strain rate no dislocation transport occurs - i.e., dislocations outrun their atmospheres. In the case of nickel, the critical strain rate is about $10^{-1}$ $sec^{-1}$, far faster than is practical in our permeation experiments.

*Dislocations cannot travel from one grain to another* with their hydrogen atmospheres. When arriving at a grain boundary they are likely to "dump" the hydrogen there. Dislocation generated in the adjacent grain might then pick up the hydrogen and sweep it away. Based on this view, one might expect dislocation transport to be more difficult in a large grain size material where there are fewer obstacles to dislocation motion; i.e., dislocations have a larger mean free path. Figure 8 shows results for three different grain sizes. These results argee with the predictions - the larger the grain size the higher permeation flux.

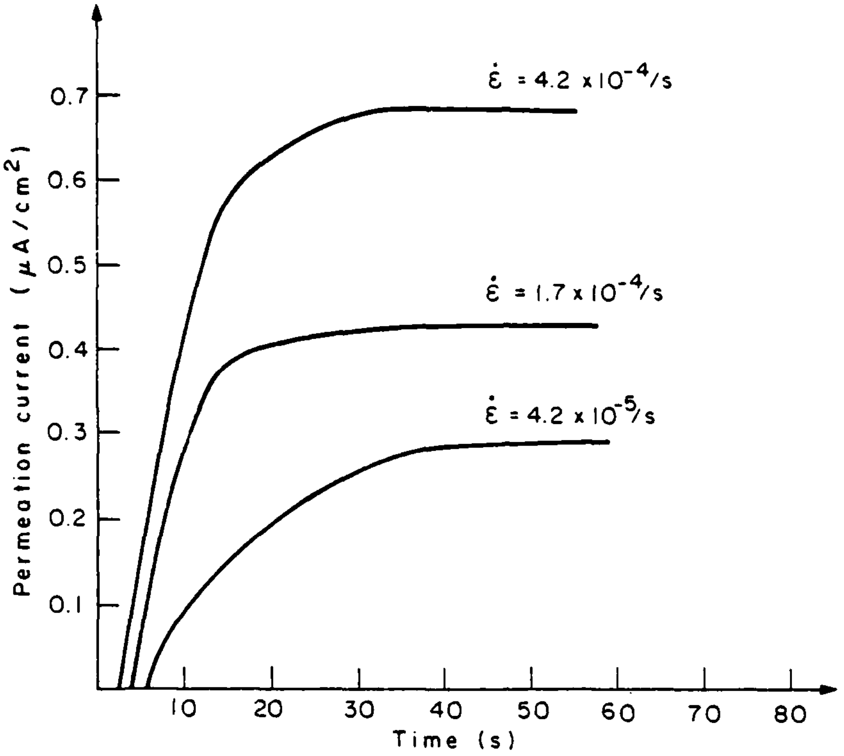

Fig. 6 - Effect of strain rate on permeation behavior (after Kurkela and Latanision (48)).

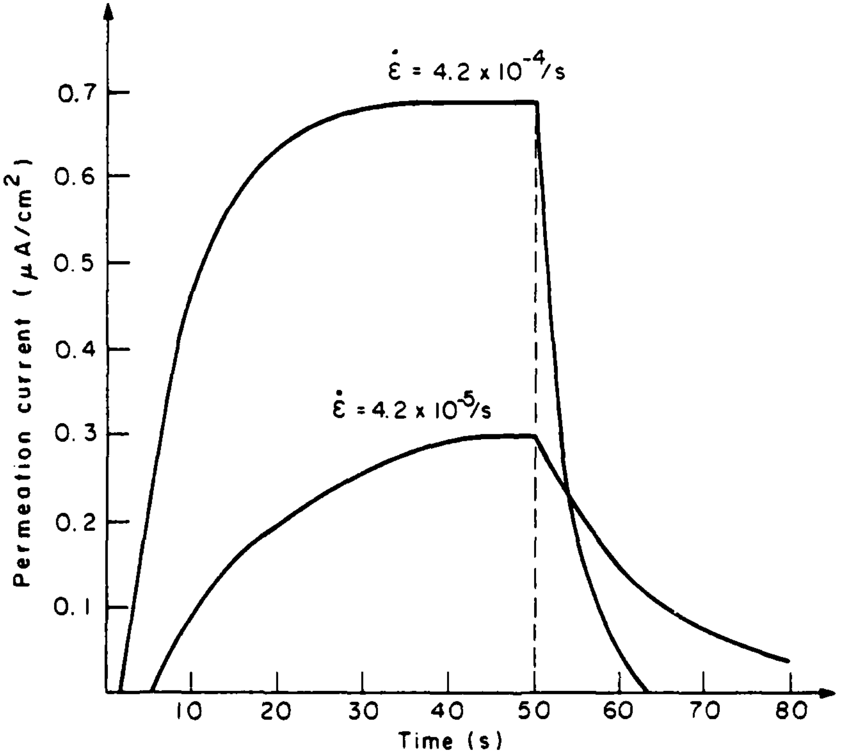

Fig. 7 - Effect of strain rate on the decay transient (after Kurkela and Latanision (48)).

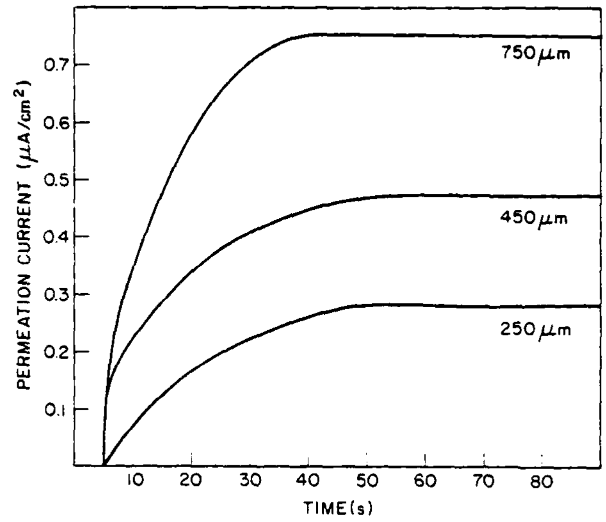

Fig. 8 - Effect of grain size on permeation behavior in Ni 270 undergoing plastic deformation .

## Closing Remarks

We have learned quite a lot about the phenomenology of hydrogen embrittlement. It is now more than 100 years, however, since Reynolds (52) and Hughes (53) and perhaps others first associated certain detrimental effects 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 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. In this regard one interesting electronic model for hydrogen embrittlement (decohesion) was proposed by Troiano in 1960 (54). More recent electronic structure calculations (55) involving the application of molecular orbital theory in modeling certain aspects of embrittlement phenomena seem promising.

On the other hand, it is interesting to note that physical chemists and surface chemists also have interests in the same kinds 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. Why is it that nickel and platinum are effective hydrogenation catalysts, but copper is not? And, why are other metals effective catalysts for other chemical reactions, but not for hydrogenation?

It seems likely that the development of fundamental understanding of the kind implicit in the above discussion of catalysis would impact, as well, understanding of the fundamentals of embrittlement, and vice versa. It is interesting, for example, that the dissociation of transition metal carbonyls such as cobalt carbonyl may be stimulated by the presence of hydrogen (56). Here is an example of a technology known to physical chemists, relatively unknown to materials scientists and solid state physicists, but of vital importance to both in the sense of atomic scale understanding of catalysis and embrittlement (the latter, in this case, the dissociation of atomic bonds between cobalt atoms in the cobalt carbonyl molecule). One wonders in a converse sense if the effectiveness of a catalyst might not be significantly increased if the catalyst were allowed to plastically deform while performing its chemical function.

At any rate, we 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 appreciated. 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 us that the technological significance of the interactions of hydrogen 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. This is not unlikely, particularly if effective (semiconductor) photoelectrodes can be developed to split water (57) 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. We suspect that if the previous decades of research and engineering on hydrogen were considered exciting, the next decades will be even more so and the impact of this effort will be of even greater consequence.

## Acknowledgments

The support of the Office of Naval Research Contract No. N00014-78 - C-0002, NR 036-127 is gratefully acknowledged. Special thanks are due to Dr. P. A. Clarkin of ONR for his continuing encouragement. Likewise, we are happy to acknowledge many exciting discussions over several years with Dr. T. E. Fischer of Exxon Research and Engineering Company regarding the atomistics of hydrogen embrittlement.

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