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MATERIALS ASPECTS OF THE ELECTROCHEMICAL INSERTION OF HYDROGEN AND DEUTERIUM INTO MIXED CONDUCTORS

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Abstract

A number of features of the presence of interstitial species in metals and alloys relevant to “solid state fusion” experiments are discussed. These include experimental evidence for very high virtual pressures under certain conditions, and the influence of promoters and surface blockers. Dislocation generation and motion can result from the large stresses accompanying composition gradients and phase transformations. Because of preferential segregation of interstitial species to dislocations, transport along dislocations can be much faster than through the bulk crystal, and dislocation motion can cause unusually rapid interstitial solute transport and both entry and emission from surfaces. Mechanical effects related to the presence of hydrogen often are sporadic and can have long delay times. It is possible that some of the same microstructural features and phenomena that are responsible for delayed mechanical behavior play an important role in the “solid state fusion” observations. Two dislocation mechanisms are presented that can produce transient local hyperloading.

Introduction

It is the purpose of this paper to discuss several of the materials aspects of the solution of hydrogen isotopes in metals and alloys. It will be seen that there are several features that are directly relevant to the efforts that are currently being undertaken to investigate “solid state fusion” phenomena. It will also be evident that some of the experimental observations that appear to be so vexing, and have raised serious doubts and questions, such as the sporadic nature and “materials dependence” of some of the observed effects, are not at all surprising in light of what is known about other features of the insertion of hydrogen isotopes and other interstitial species into metals.

An important feature of the behavior of such systems is the interplay between interfacial phenomena and bulk thermodynamic conditions. As a result, it is possible to obtain species distributions and related phenomena inside solids that are equivalent to those that would be present if there were a very high external pressure of one of the components.

Composition gradients and phase transformations with accompanying large changes in specific volume can generate very large internal stresses, leading to dislocation generation and motion. In addition, segregation to dislocations is commonly observed, with the possibility of greatly enhanced local concentrations.

There is good evidence for the enhanced transport of hydrogen isotopes by dislocation motion, and experiments have shown a definite correlation between gas evolution and plastic deformation that causes dislocation emission from the surface.

Changes in internal microstructure relating to some of these phenomena have often been observed to exhibit a time dependence, leading to sporadic behavior and delay times that are difficult to predict, similar to some of the “solid state fusion” observations.

General Comments

The relatively easy absorption of large amounts of hydrogen into metals was first reported by Graham over a hundred years ago [1]. The first examples that he studied were palladium and palladium-silver alloys. He also showed that hydrogen could be introduced into such materials by electrochemical charging [2,3].

Since that time there has been a large amount of work on various aspects of hydrogen in metals, leading to a rich scientific literature. This has led to the acquisition of much fundamental knowledge about thermodynamic, kinetic and structural aspects of interstitial solid solutions, as well as the development of a number of important experimental techniques. Hydrogen and its isotopes move rapidly in palladium, and this metal has served as the primary example for the study of these matters. Large concentrations of hydrogen isotopes can be readily absorbed under experimental conditions that are relatively easy to achieve, and experiments can be performed in both air and aqueous environments without the formation of a blocking surface oxide.

There is a considerable amount of practical interest in the use of hydrogen-permeable metallic membranes, primarily palladium-silver alloys, for the separation of gases. A good measure of research effort has also gone into the exploration of the use of hydrogen absorption in metals and alloys for the storage of hydrogen, and more recently, for the use of such materials as rechargeable electrodes in battery systems.

In addition to these essentially positive applications, hydrogen can have very significant, and generally deleterious, effects upon the behavior of metals in technological applications. One of the most important involves the influence of hydrogen on various mechanical properties. Hydrogen embrittlement and hydrogen-related stress corrosion cracking are very important practical problems with some metals and alloys.

We shall see that consideration of some of the knowledge generated in these other areas may be instructive in providing insight, and perhaps even understanding, concerning some of the recent observations in the “solid state fusion” arena.

The Imposition Of Very High Activities Of Solute Species Inside Solids

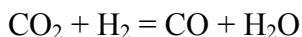
One of the features of the electrolytic experiments that seems the most foreign to many who are not conversant with the relevant thermodynamic and kinetic principles is the concept that a solid that is obviously sitting in an environment with a total pressure of one atmosphere can behave as though it were under an extremely high applied pressure of one of its constituents.

Equilibrium Between a Bulk Solid and Its Surface

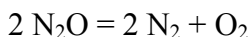
Many years ago Wagner and his co-workers pointed out that if a solid surface acting as a heterogeneous catalyst is exposed to a reacting gas mixture for a sufficiently long time under steady state conditions at elevated temperatures, thermodynamic equilibrium becomes established between the species in the surface region, i.e., adsorbed reactants, intermediates, and products, and atomic and electronic species in the bulk underlying solid.

They showed that if species transport across the interface and in the bulk solid to and from the surface is sufficiently fast, one can obtain information about the thermodynamic state of the surface species during the catalysis reaction by observation of some suitable physical property relating to the corresponding species in the bulk solid. Furthermore, this information, in conjunction with the macroscopic system and rate parameters, can be used to evaluate the activities of surface species, and to identify the rate-determining step in a typical sequential catalytic reaction.

This approach was used as a diagnostic tool to understand the mechanism of the heterogeneous reaction in a number of simple cases at elevated temperatures, where surface-bulk equilibrium could be readily established. Early examples by the Wagner group included studies of oxygen transfer reactions, such as



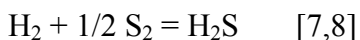
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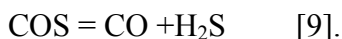
on the surface of oxide catalysts [4], and gaseous hydrogenation and dehydrogenation reactions, such as the hydrogenation of ethylene [5] and the decomposition of formic acid [6] on metals.

Use of Back-Side Solid State Electrochemical Cell as Sensor of Interfacial Parameters

In addition, Wagner showed that, under appropriate conditions, a properly designed solid state electrochemical cell on the back side of the catalyst material could also be used as a sensor to give information about interfacial conditions. Demonstrations included the use of an indirect silver ion-conducting solid electrolyte cell for the evaluation of the sulfur activity on the surface of Ag₂S when used as a catalyst for reactions such as



and



Again, an important criterion is rapid transport of atomic and electronic species in the solid, so that equilibrium can be attained between the bulk solid and its surface on one side, i.e., the front side, upon which the heterogeneous reaction takes place, and also on the back side between the solid and the adjacent electrolyte.

High Solute Activities Resulting From Heterogeneous Catalysis

A slightly different twist was given to the general proposition that the interior of a solid comes into equilibrium with its own surface in connection with observations that phenomena can occur within solids that seem to be very far from equilibrium, if certain reactions are taking place upon their surfaces.

At about the same time as the work of Wagner mentioned above, Temkin and Pyzhev introduced the concept of “virtual pressure” into the catalyst community in connection with their work on the rate expression for ammonia synthesis upon a heterogeneous catalyst [10,11]. This concept has subsequently been further pursued by others as well [12-14].

This concept arose in connection with the experimental observation that iron nitride Fe₄N has been found to form near the surface of iron during the catalytic synthesis of ammonia from hydrogen and nitrogen at 400 °C. On the other hand, it is known that at that temperature Fe₄N can be formed by the direct reaction of iron and nitrogen if the nitrogen pressure is higher than about 108 Pa, or about 103 atm. Nevertheless, if the nitrogen is replaced by NH₃, Fe₄N readily forms at about 1 atm pressure. This means that so far as species in the iron are concerned, NH₃ at 1 atm on the surface of iron in the presence of hydrogen behaves as though it has a virtual nitrogen pressure of 103 atm.

This type of behavior is interpreted in terms of the mechanism of the relevant heterogeneous reaction that is taking place on the surface of the iron. In a sequential reaction in which a number of elementary mechanistic steps operate in series, under steady state conditions the actual rates of all the steps must be the same. However, the different steps will normally have different virtual maximum rates, a concept introduced by Wagner in 1970 [15], and thus different impedances, so that the overall driving force for the reaction that is taking place at the interface is unevenly distributed between them. The concentrations of reactants, intermediates, and products on the surface must therefore adjust themselves in order to arrive at the same rates for all steps. The species that are involved in the step with the greatest impedance, i.e. the lowest virtual maximum rate, will therefore have the greatest concentration at the surface.

In the case of the very large virtual pressure of nitrogen when the ammonia decomposition reaction is taking place at 1 atm total pressure on the surface of iron, it is obvious that the concentrations of nitrogen-containing species at the interface must have the same magnitudes as they would be if nitrogen gas at a pressure of 103 atm were to be in contact with the solid.

Interfacial Reactions and Species Distributions During Electrolysis of Aqueous Electrolytes

An analogous situation exists in the case of reactions taking place at the liquid-solid, electrolyte-electrode interface in an electrochemical cell, although the terminology that is used to describe it may be somewhat different. Discussions of this matter may be found in a number of places [16-18].

In electrochemical reactions, the driving force is electrical, and under steady state conditions, the species populations at the surface have to adjust themselves so that the different elementary steps involved in the overall process have the same rates. If there is sufficiently rapid equilibration between the surface of the solid and its nearby interior, this interfacial population distribution thus will determine the virtual pressure, or activity, of the relevant species in the subsurface region of the solid.

Under conditions of steady state electrolysis of water at high currents, the electrical potential at the surface of the cathode, for example, must be significantly displaced from its equilibrium value. This can lead to very large values of virtual pressure, or activity, of hydrogen in the solid electrode just below the surface. With time, as diffusion of atomic species takes place, the thermodynamic conditions imposed in this surface region will gradually equilibrate throughout the bulk solid. The rate at which this takes place will be determined by the chemical diffusion kinetics of the mobile species, e.g. hydrogen isotopes, within the solid. This can occur by their transport through the bulk crystals, or along dislocations and grain boundaries, which act as rapid pathways.

The Use Of Permeation Experiments To Evaluate The Interfacial Composition

One of the techniques that has been used to study the transport properties of hydrogen isotopes in metals involves the measurement of the rate at which such species are transported through thin membranes under either pressure gradients or electrochemical driving forces. There are a number of variants on this general method, and they have been discussed in several reviews in this field [17-19].

Since in metals and alloys diffusion of species is driven only by concentration gradients, this method can be used to evaluate the concentration of hydrogen isotopes in the vicinity of the electrolyte-electrode surface in electrochemical cells. It can be used in cases in which that concentration corresponds to hydrogen pressures greater than one atmosphere [20], and recent work has involved experiments in which electrolysis is taking place at the hydrogen entry interface [21].

Stresses Resulting From The Insertion Of Interstitial Species

Because they have a positive partial molar volume, the presence of interstitial species such as the hydrogen isotopes causes expansion of the metal lattice. The partial molar volume of

hydrogen in the α phase of all fcc metals is approximately the same, about 1.65 cm³ per gm atom of H [22].

The presence of interstitial hydrogen deforms the host lattice and creates a long range elastic strain field. The interaction between the strain fields of two such interstitials is such that they are attracted to each other. Rather detailed discussions of this are available in the literature [23,24].

As the concentration of interstitial hydrogen species increases, so does the elastic strain energy. Above a certain critical value, palladium has a lower Gibbs free energy if it separates into two phases, forming a miscibility gap in the phase diagram. When the total concentration is above the solubility limit in the terminal solid solution α phase, additional hydrogen is accommodated in regions of much higher concentration, called the β phase, even though the basic structure of the palladium host is the same. The jump in partial molar volume change accompanying the $\alpha \rightarrow \beta$ phase transformation is 1.57 cm³ per gm atom of H, and in the β phase it is 1.30 cm³ per gm atom of H [19].

These values give rise to very significant changes in volume, and if this volume change does not take place simultaneously at all points within the solid, very large stresses can be generated. This leads to mechanical distortion by plastic flow, a large increase in the hardness, and often the nucleation and propagation of cracks.

The Non-Uniform Distribution Of Interstitial Species

It is well known that hydrogen isotopes occupy interstitial sites, primarily those with octahedral coordination, in face centered cubic metals, such as palladium. This has been found to be the case in both the α and β phases [25,26]. Because such interstitial solute species cause localized expansion of the crystal lattice, they are attracted to microstructural features where there is local lattice dilation. The preferential location of interstitials is along the dilation side of edge dislocations, and the segregation of hydrogen and nitrogen to the dilated regions around the edge components of dislocations in iron alloys is well established [27,28]. This has also been demonstrated for hydrogen in niobium [29].

Flanagan et al. [30] compared the hydrogen solubility of cold-rolled (12 - 80%) and well annealed samples of palladium in the α phase. They found that the presence of dislocations resulted in a substantial enhancement of the apparent solubility of both hydrogen and deuterium, with the magnitude of the enhancement ratio is dependent upon the amount of plastic strain, reaching values of about 1.35 at high strains. Very heavily deformed palladium chips gave an even greater enhancement ratio of 1.63 [31]. The enhancement ratio was about the same for hydrogen and deuterium, and was found to be independent of the hydrogen isotope content in the α phase. The general form of this behavior is the same as the dependence of the hardness upon plastic strain [32].

This solubility enhancement is due to a higher local concentration in the stress fields of the dislocations. That is, there is a solute “atmosphere” around dislocations. Contrary to the behavior of bcc metals, there is no experimental evidence for the presence of hydrogen isotopes in the core region of dislocations in palladium [31].

The effect of the local hydrostatic stress σ_h upon the chemical potential m_H of dissolved hydrogen can be written as

$$Dm_H = - \sigma_h / V_H$$

where V_H is the partial molar volume of the interstitial hydrogen. The experimentally determined value of V_H for hydrogen in all fcc metals and alloys is $1.65 \pm 0.05 \text{ cm}^3/\text{g atom H}$ at 298 K [22]. Since the solubility enhancement is about the same for hydrogen and deuterium, it was suggested [31] that one can assume that the values of V_H and V_D are about the same.

By comparison of the solubility enhancement and an estimate of the influence of the degree of deformation upon the dislocation density, Flanagan and Lynch [31] were able to show that above a dislocation density of about $10^{10}/\text{cm}^2$ the enhancement of the solubility by the presence of dislocations should be experimentally observable. To achieve this critical value of dislocation density in a previously annealed sample of palladium one would need to impose more than 5% deformation at room temperature. This explains why the data on the solubility of nominally “annealed” samples measured in various laboratories is so reproducible, despite the wide difference in actual treatments, whereas there is a lot of scatter in the data reported for deformed samples.

Direct evidence that hydrogen isotopes are preferentially located in dislocation atmospheres, internal interfaces, and grain boundaries was presented in 1974 by Lacombe's group by the use of tritium autoradiography [33] in samples into which a small amount of tritium was deliberately added.

Autoradiography has also been presented recently as evidence of the presence of tritium in samples that have been involved in electrolysis experiments related to “solid state fusion” [34,35]. The images that were obtained in these cases also indicated a very non-uniform distribution of tritium within the solid. It was assumed that there was not any tritium present in the materials prior to the electrolysis experiment, so that the autoradiographic results give an indication that tritium must have been formed during the electrolysis process.

Sicking [36,37] also used tritium as a radiochemical tracer in a study of the influence of plastic deformation on the apparent diffusion of hydrogen isotopes, as will be described later.

Microstructural Changes Related To Hydrogen Insertion

Very significant microstructural changes accompany the insertion and deletion of hydrogen isotopes in metals, as a result of the changes in specific volume that occur.

Because of the great practical importance of the deleterious influence of the insertion of hydrogen into iron and its alloys, much of the work in this area has involved these and other bcc materials. It is now well established that hydrogen charging (and discharging) of these materials causes the generation of large, and non-uniform, dislocation densities [38,39]. A similar phenomenon is well known in connection with the diffusion of dopants into semiconductors. The spatial inhomogeneity of these phenomena leads to non-uniformity in both time and position in the accompanying lattice parameter changes and solute compositional distribution. Deformation bands and dislocation pile-ups at grain boundaries, as well as the spontaneous initiation of internal fractures have been found by electron microscopy [39].

In the case of metals such as palladium, in which a phase transformation takes place, with the accompanying large discontinuous volume changes (about 9%), these effects are especially striking. Phase transformations in Nb, Ta and V, in which the products are crystallographically incoherent, were discussed by Schober and Wenzl [40]. Under various conditions, the β - α phase transformation in palladium can be either incoherent, partially coherent, or fully coherent.

Electron microscopy studies [41,42] have shown that the β - α transformation in palladium is discontinuous, and resulted in the generation of a high dislocation density in the α phase. The α phase nucleates in partly coherent form at the intersection of dislocations with the surface, and grows by the formation of large lenticular “dendrites” along the elastically soft $\langle 100 \rangle$ directions in the β matrix.

As these precipitates continue to grow, the local coherency strain field disappears and further dislocations are generated. It has been found [32] that further transformation involves both the growth of the dendritic α regions already nucleated and the nucleation of new α grains. As in the case of martensite reactions, growth of an individual “dendrite” plate is limited by both crystallographic constraints and intersections with other microstructural features. As a result, as the overall transformation proceeds the size of new α grains becomes ever smaller, as they must grow between previously formed ones.

Erratic phase transformation behavior on charging and discharging was found in the electron microscopy work when palladium from one source was used [41]. This was not the case with palladium from a different source was used. Likewise, some coherent precipitates were found in one case, but not in the other. It was concluded [42] that this was related to a difference in the presence of minor impurities in the palladium.

Variability in the time dependence of the start of the β - α transformation at room temperature was found in both cases. This was attributed to the probable presence of surface films when the samples were exposed to air [42].

Evidence for the generation of dislocations during cyclic β - α phase transformations was the observation [43] that the hydrogen solubility was enhanced by going through the phase change. This is similar to the observation of the influence of plastic deformation on this parameter [30], as discussed earlier. Additional evidence for the generation of large dislocation concentrations as a result of the β - α phase transformation was the observation of significant changes in mechanical properties, such as large increases in hardness [32].

The Influence Of Species Upon The Surface - Promoters

It has been known for a long time that the presence of even very small amounts of certain elements has a very marked effect in enhancing the entry of hydrogen isotopes into metals [44,45]. This occurs both in the case of absorption from the gas phase and upon electrochemical charging. Species that seem to be most effective in causing hydrogen to enter metals, apparently at considerably higher activities than those characteristic of the external environment include those containing P, As, Sb, Bi, S, Se, Te, cyanide, and I, as well as several organic species. Discussions of this can be found in several reviews [17,46,47]. Figure 1 shows the effect of the presence of small amounts of several promoters, as well as the applied current density upon the permeation rate of hydrogen through steel [48]. Since the permeation rate is proportional to the

concentration gradient, these data indicate the influence of these parameters upon the local concentration of hydrogen just under the entry surface.

The mechanism whereby this promoter effect influences absorption phenomena has been quite controversial, and the experimental results obtained by different investigators have been conflicting. One of the current hypotheses involves the observation that some of the most effective promoters are known to form hydrides [45], and experiments showing the influence of pH upon the promoter effect has been used to support the concept of the importance of the hydride-forming tendency of the most effective promoters [49].

The hydrides of a number of these materials are extremely toxic, and some (e.g. H₂S) can be readily detected at very small concentrations. Since there are no reports of the observation of the escape of such hydride species into the gas, and very small concentrations of the hydride formers in the electrolyte seem to act for a long time, rather than becoming consumed, it seems reasonable to assume that the formation of free molecular hydrides of the promoters is not a realistic expectation.

As pointed out earlier in this paper, when highly mobile species such as hydrogen isotopes are present, we can assume that the interior of a solid comes into equilibrium with its outer surface under steady state conditions. Therefore, one should think of the action of promoters in terms of how they might control or modify the hydrogen-related interfacial species distribution.

Thermodynamic data indicate that the hydrides of the active promoter species are actually not very stable with respect to their formation from molecular hydrogen. On the other hand, the Gibbs free energy change that would be involved if they were to form from atomic hydrogen is generally quite large and negative. A promoter species such as As might bond to adsorbed hydrogen atoms on the surface, thereby influencing the interfacial species distribution that is "seen" by the bulk solid. Such a simple model would be consistent with the molecular structures of some of the promoter hydrides.

It should be pointed out, however, that there are currently no data available on the influence of promoters under the extreme electrolytic conditions imposed in many of the "solid state fusion" experiments.

Evidence For the Electrolytic Production of High Hydrogen Activities in Other Face Centered Cubic Metals When a Promoter is Present

The work on the influence of promoters has primarily involved either materials such as palladium that absorb large amounts of hydrogen isotopes, or iron base alloys, where the influence of hydrogen at high activities can be very deleterious. However, the same phenomena can be found in other materials, such as fcc copper, which is generally thought to not be sensitive to hydrogen, and in which the equilibrium solubility at ambient temperatures is negligible.

Experiments on the cathodic charging of annealed copper foils at 10 mA/cm² in an acid solution have been performed recently [50]. When the electrolyte contained As₂O₃, known as a promoter in the cases of both iron alloys and palladium, they found that the ductility was drastically reduced, blisters and voids were formed both inside grains and in grain boundaries, and a high dislocation density, with dense tangles was observed by transmission electron

microscopy. In the absence of the promoter, there was no microscopic evidence of significant hydrogen absorption into the copper.

The Inhibiting Effect Of Some Surface Species

Whereas the discussion above centered upon the action of certain species to promote or enhance the absorption of hydrogen isotopes into metals, there are also a lot of examples in which either experimental conditions or specific species have just the opposite effect.

It is well known that the presence of oxygen results in the presence of blocking layers on the surface of metals that tend to form hydrides. This is a major problem limiting the cycle life of the otherwise very attractive magnesium hydrides.

The Influence Of Prior Plastic Deformation Upon Diffusion Of Hydrogen Isotopes

Compilations of data relating to the diffusion of hydrogen isotopes in palladium can be found in several places [51]. Whereas most experiments have been performed on annealed materials, it has been found that prior plastic deformation that results in the formation of large dislocation densities causes the observed macroscopic diffusion coefficient of hydrogen isotopes in palladium to be substantially reduced [19]. Similar recent results were reported by Hasegawa and Nakajima [52].

This is primarily due to the fact that previously generated dislocations act as traps. Data showing this effect in the case of the diffusion coefficient of tritium in palladium are shown in Figure 2. Recent measurements clearly showing the effect of prior plastic deformation upon the diffusion coefficient of hydrogen in palladium were presented by Falanga et al. [53].

This effect of dislocation trapping upon the transport of hydrogen and other interstitials is well known in other metals. For example, the large effect of quenched-in dislocations upon the apparent diffusion kinetics of hydrogen in niobium, as well as the influence of concurrently generated dislocations upon the permeation flux in Ti-Mo alloys, Ta and Nb was recently reported [39].

Sicking and co-workers developed an electrolytically driven permeation method to study the effect of prior cold work in which tritium was used as a sensitive tracer [36]. This technique was utilized to study the influence of prior deformation upon the diffusion of tritium in palladium, and the influence of the amount of deformation upon the trap concentration [37]. They found that the dislocation trap binding energy for tritium in palladium is about -18 kJ/mole (-187 meV/atom), and that the local vibrational modes for tritium in the trap positions are distinctly softer than they are in the normal octahedral interstitial positions in the crystal structure.

Their results, as well as the conclusions of Kirchheim [54-56], indicate that there is a considerable amount of lattice distortion near the dislocations, leading to the possibility of the accumulation of a very high local concentration in the dislocation atmospheres, as mentioned above.

The Transport Of Hydrogen Isotopes By Dislocation Motion

It was proposed by Bastien and Azou as early as 1951 that hydrogen may be transported in metals by being carried along by moving dislocations, and that this mechanism could produce more rapid hydrogen transport than that which is possible by conventional point defect diffusion in the crystal lattice in response to concentration gradients [57]. This concept has since been confirmed by a number of other authors [58-60].

The importance of the motion of hydrogen along with dislocations [61] to the serious problem of the hydrogen embrittlement of metals [60], [62-64] has received a lot of attention [16]. As a result, work at a number of laboratories has emphasized the importance of the coupling between dislocation motion and the transport of hydrogen [65].

A model for the ductile, as distinct from brittle, fracture of metals in a hydrogen atmosphere that is based upon hydrogen transport by dislocations has also been presented [66].

While much of the early attention was given to hydrogen transport via moving dislocations in bcc iron-based alloys, the same phenomenon was observed for fcc nickel as well [67]. It has been shown that serrated yielding, characteristic of dislocations with solute atmospheres, occurs in hydrogen-charged nickel [68,69], and also in an aluminum alloy [65].

It has been suggested that the enhancement of the release of hydrogen isotopes from a number of metals that were previously charged is caused by the egression of mobile dislocations from the surface [58,67]. This question was investigated by Donovan using tritium as a sensitive radioactive tracer [65]. His experiments included both bcc and fcc metals, and the results were comparable in all cases.

He demonstrated that the rate of gas evolution could be greatly enhanced relative to that due to normal crystalline point defect diffusion when plastic deformation is taking place. Observations at different values of strain clearly showed that the enhanced tritium evolution was not due to higher diffusivity in the presence of elastic strain, but definitely involved dislocation motion. The rate of evolution varied as the plastic strain increased, obviously being dependent upon the changes in dislocation behavior connected with strain hardening. Eventually fracture, which also involves dislocation generation and motion, caused an additional large sudden increase in the rate of gas evolution. These features are clearly seen in the data presented in Figure 3, which shows the rate of tritium release as a function of strain for an austenitic stainless steel [65]. The rate of tritium release was found to be a function of strain rate, increasing at higher rates. However, the volume of tritium released per unit strain decreased as the strain rate increased.

The tritium emission was found to be complicated in the case of an austenitic (fcc) stainless steel that undergoes a strain-related transformation to form a phase with a much lower hydrogen isotope solubility. The differences in solubility of the initial and product crystal structures caused additional tritium to be expelled as a result of the phase transformation.

In the case of an aluminum alloy that showed dynamic strain aging and repeated yielding tritium release was discontinuous, and there was a clear relation between jumps in the tritium release rate and the periodic plastic yielding. This is shown in Figure 4. The general model for

this type of mechanical behavior (called the Portevin-LeChatelier effect) involves the sudden generation of a high density of mobile dislocations when yielding occurs.

The amount of tritium released during plastic deformation and fracture should be related to several factors. These include the rate at which dislocations encounter the external surface, the amount of tritium associated with the Cottrell atmosphere of an average dislocation, and the ability of this tritium atmosphere to move with the dislocations.

Under equilibrium conditions, the excess concentration of tritium associated with the atmosphere of a dislocation C_d can be written as [70,71]:

$$C_d = C_l \exp(-G_b/RT)$$

where C_l is the nearby lattice concentration, and G_b is the binding energy of the tritium to the dislocation “trap”. R and T are the gas constant and the absolute temperature. The binding energy is negative, so the amount of local concentration enhancement is greater at lower temperatures. As an example, the value of G_b has been found to be -1.9 kcal/mol in the case of nickel.

Upon the application of a local shear stress large enough that it would normally cause dislocation motion, three things can happen if the dislocation has a solute atmosphere. Either the solute pins the dislocation in place, preventing its motion, the solute atmosphere moves along with the dislocation, or the dislocation breaks away from its atmosphere, leaving the excess solute behind in the lattice. What happens will depend upon the mobility of the solute, the dislocation velocity, and the magnitude of the solute-dislocation binding energy.

The velocity of a solute v_s moving in the elastic force field of a dislocation is [70]

$$v_s = D F / k T$$

where D is the diffusivity of the solute, F is the force due to the local gradient in hydrostatic strain, and k is the Boltzmann constant. For the case of an edge dislocation,

$$F = 0.56 G_b / b$$

where b is the Burgers vector of the dislocation.

Therefore, there will be a critical dislocation velocity v^* above which a dislocation will break away from its solute atmosphere, given by

$$v^* = D (0.56 G_b)/(b k T)$$

For any given macroscopic strain rate, there will be a range of dislocation velocities, depending upon the local stress distribution. As the strain rate increases, there will be more dislocations that break away from their atmospheres, and thus do not carry along any substantial excess solute concentration.

The rate at which solute will be carried to the surface by dislocations will be proportional to the product of the mobile dislocation density near the surface, the average excess solute concentration associated with the dislocation atmospheres, and the average dislocation velocity normal to the surface.

The plastic strain rate is related to the mobile dislocation density ρ_m and the average dislocation velocity v by

$$d\epsilon/dt = f b \rho_m v$$

where f is a geometric factor and b is again the Burgers vector.

Unfortunately, without experimental evidence, it is not easy to separate the effect of a change in the mobile dislocation density from a change in the average dislocation velocity, as they both have the same effect upon the strain rate.

As plastic strain takes place, dislocations are generated, and various interaction processes take place. This results in the following relation between the density of mobile dislocations and the amount of plastic strain ϵ_p [72]:

$$\rho_m = (\rho_0 + M \epsilon_p) \exp (H \epsilon_p/s)$$

where ρ_0 is the initial mobile dislocation density, M a multiplication coefficient, H the strain hardening coefficient, and s the applied stress.

This relationship leads to a maximum in the mobile dislocation density at relatively small values of strain, decreasing again at larger strains, as illustrated in Figure 5 [72]. This is the same kind of strain dependence that was found for tritium emission during plastic strain, as shown in Figure 3.

The strain rate dependence of the tritium emission rate was evaluated by Donovan in the case of iron, nickel and stainless steel at room temperature, and from this information he was able to extract the volume of tritium emitted per unit strain [65]. He found that this quantity decreased with increased strain rate. This is in accordance with expectations, for at higher strain rates a greater number of dislocations will have velocities greater than the critical value v^* , and will thus break away from their atmospheres and not drag solute species along.

The Sporadic Nature Of Mechanical Effects Related To Hydrogen Absorption In Metals

It has been known for a long time that the presence of hydrogen introduced during processing, as well as from the environment, can have an important, and generally deleterious, effect upon the mechanical properties of steels. A summary of much of the early work in this area was presented by Troiano [73].

One of the important characteristics of these phenomena is their sporadic and unpredictable nature. Delayed failure is commonly observed with hydrogen embrittlement and the related observations of stress-corrosion cracking. The term "static fatigue" has often been used to describe these hydrogen-related, time-dependent mechanical effects. Important early contributions to the study of the delayed failure phenomenon were made by Bastien and his co-workers [74], and a useful discussion of the state of knowledge in this area was presented in the review by Oriani [16].

One of the primary early goals of the work on these problems has been the establishment of methods with which one could obtain reproducible test results. This is quite similar to the current status of the “solid state fusion” area.

Especially important was the determination of the initiation time for the generation of cracks with the critical characteristics such that they would propagate. Highly variable incubation times of months, sometimes years, were often observed. An example of typical data is illustrated in Figure 6, in which the time to failure of a group of samples of AISI 4340 steel is shown for three different strength levels [75]. The tremendous scatter along the time scale is clearly evident.

Gradually, it became recognized that hydrogen entry causes time - dependent microstructural changes, and that the critical parameters involve not just the intensity of the applied stress and the environmental variables, but also the influence of the solute content and microstructural parameters upon the yield stress necessary for dislocation motion, as well as other aspects of the microstructure. An illustration of the importance of prior thermo-mechanical treatment that produces changes in microstructure upon the time delay prior to failure [76] is shown in Figure 7. The large influence of the chemical environment upon the relation between the stress intensity and the hydrogen-related crack velocity [77] is shown in Figure 8.

A thorough discussion of the various metallurgical parameters that are involved in the time delay and other features related to the influence of dissolved hydrogen upon the mechanical behavior of steels was presented by Kerns, et al. [45].

A Possible Explanation For The “Burst” Character Of Tritium Emission

A common observation in “solid state fusion” experiments is that tritium emission appears to occur as “bursts” in both gas loading [34] and electrochemical [78-81] experiments. Since the analytical methods generally used for the detection of tritium in the electrochemical experiments are not continuous, but involve periodic sampling, it has not been possible to determine the actual time scale of the reported appearance of tritium.

It is most probable that the tritium that was observed in these experiments was generated inside the palladium [82], but only was detected outside as a result of one or more emission events related to sporadic dislocation motion, as discussed above.

Dislocation Mechanisms That Can Produce Transient Local Hyperloading

It has now been well established that one of the conditions that is necessary in order to observe the generation of excess thermal power and energy in the electrolytic experiments with palladium cathodes is that the sample must have a high average deuterium concentration, i.e. high loading. Another feature that is also apparently useful is that the system be rather abruptly perturbed. Methods by which this is sometimes accomplished include a rapid temperature change, or a jump in the electrolytic current. It is to be expected that these methods also lead to appreciable dislocation motion.

There are two simple ways in which the motion of dislocations can produce transient local “hyperloading” of solute in the palladium. These are illustrated schematically in Figures 9 and 10. In one case, breakaway of a dislocation from its solute atmosphere leaves behind a volume of normal crystal that suddenly has a local solute concentration that is higher than the average loading. If the average loading is already near saturation, this produces a local region in the normal crystal structure that is “hyperloaded”. The extra solute atoms will, of course, gradually diffuse away with time to relieve this local supersaturation.

Local hyperloading can also occur if two dislocations dragging solute atmospheres that are moving on intersecting slip planes meet. When this occurs, there is also suddenly a local region in the solid that is hyperloaded, with a solute concentration that is essentially the sum of the two atmospheres.

Concluding Comments

Although the electrochemical “solid state fusion” experiments in which deuterium is inserted into palladium may appear to be very simple and unsophisticated, what actually takes place involves the complex interplay of a number of microscopic phenomena.

The details of the local composition and the imposed dynamic phenomena at interfaces can have great importance, because of the influence of the interfacial mechanism during electrolysis, and the presence of promoters or inhibitors can greatly affect the activity of solute species resident in the solid. Under some conditions this solute concentration may be comparable to that which would be present at very large external gas pressures.

The distribution of interstitial species such as hydrogen isotopes in polycrystalline metals is very non-uniform. The strain field around dislocations causes a significant local enhancement of their concentration. Large stresses can be generated as a result of composition gradients and phase changes, leading to plastic deformation, which involves the dynamics of dislocation generation and motion. Because of the preferred association of hydrogen isotopes with dislocations, this results not only in substantial changes in the microstructure but also in significant transport and rearrangement of the solute content within the solid.

It is well known that the presence of hydrogen isotopes produces large and time - dependent effects upon the dislocation-related mechanical properties of metals, and workers in that area have long been plagued with some of the same problems of sporadic behavior and apparent irreproducibility that are characteristic of many of the “solid state fusion” experiments at the present time.

Dislocation mechanisms can produce local regions of transient hyperloading, and may be related to the “burst” character of some of the phenomena that are often observed in “solid state fusion” experiments.

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FIGURES

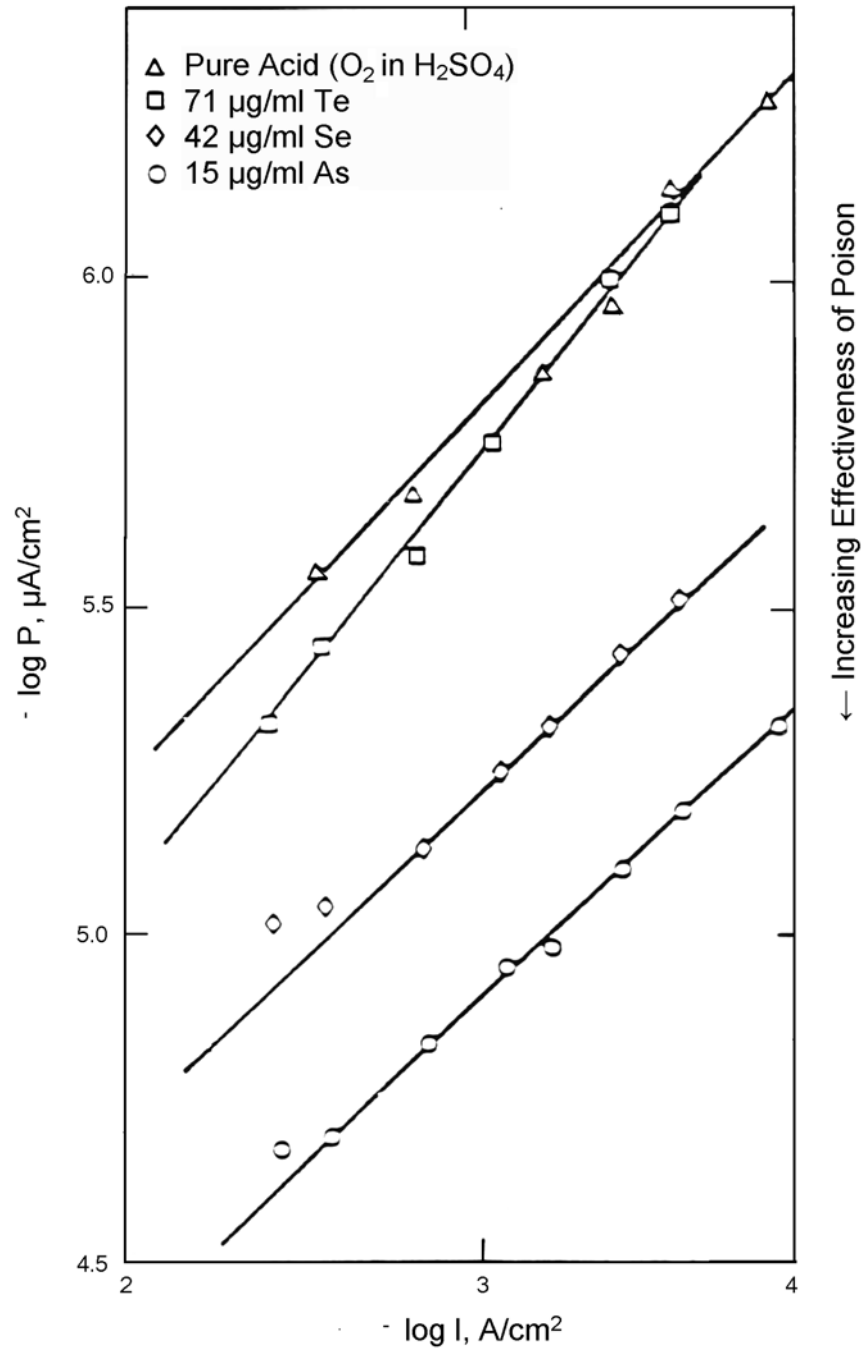


Figure 1. Effect of Several Poison Additions, as well as the Cathodic Current Density, on the Permeation Rate of Hydrogen Through Low Strength Steel [48].

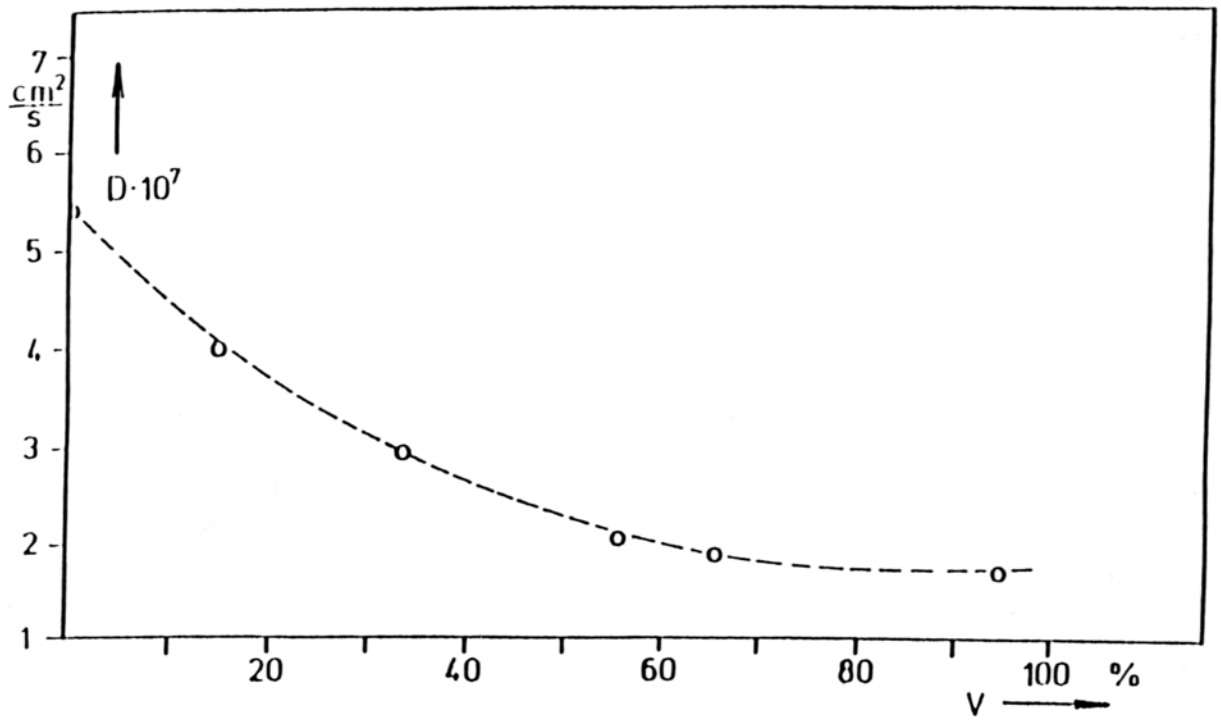


Figure 2. Influence of the Degree of Prior Plastic Deformation V Upon the Chemical Diffusion Coefficient of Tritium in Palladium [19].

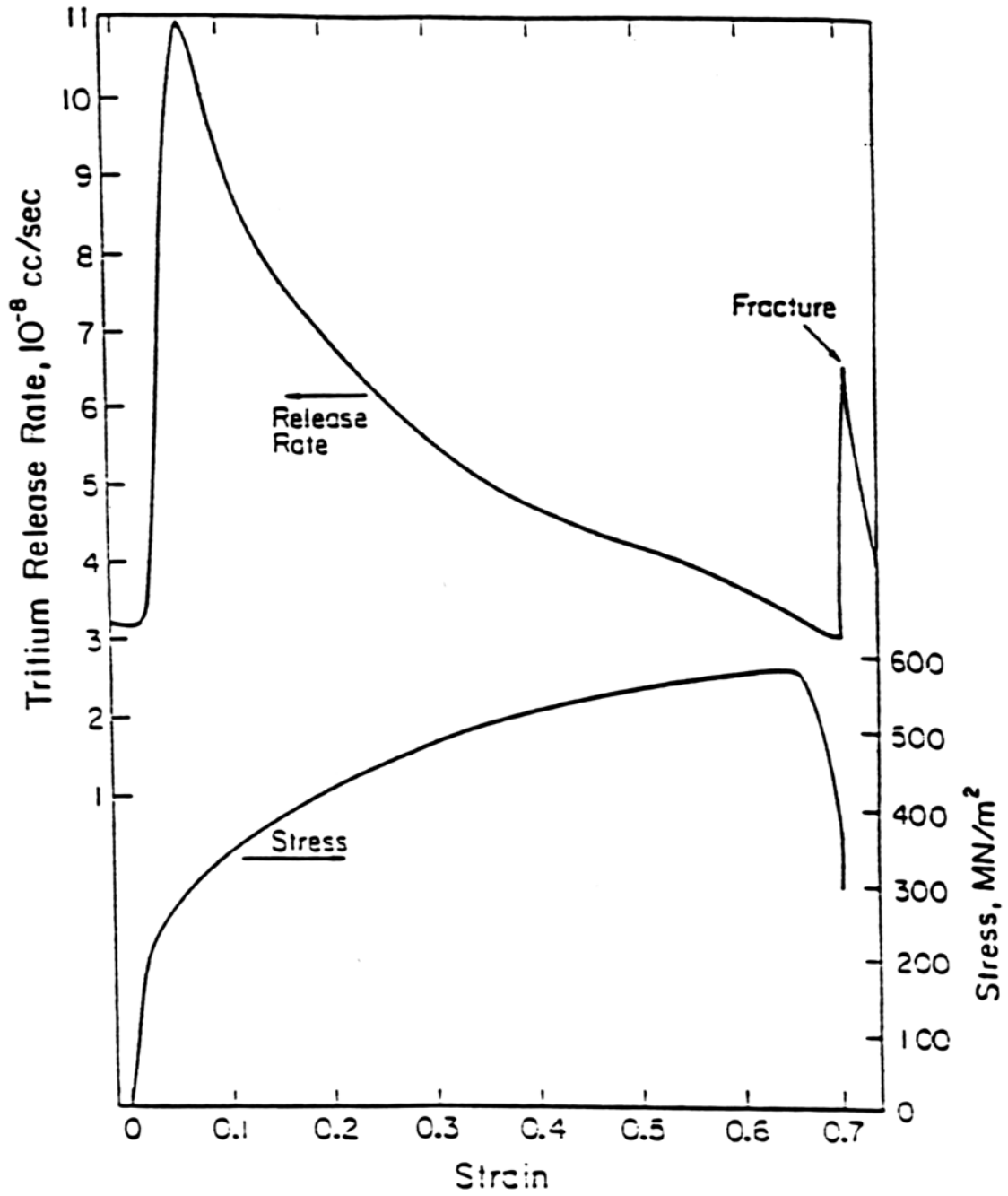


Figure 3. Rate of Tritium Release and Plastic Strain in a Type 304 Stainless Steel [65].

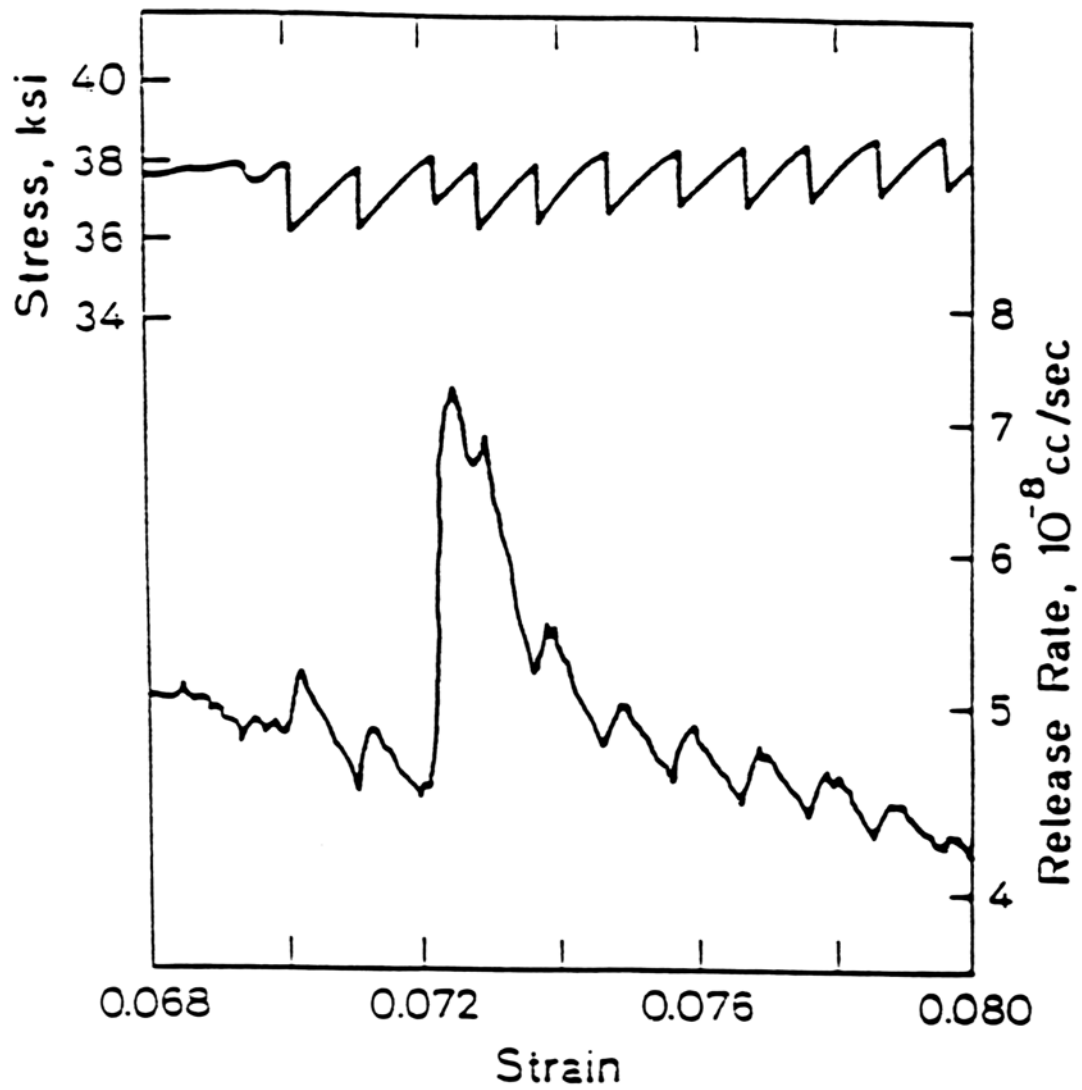


Figure 4. Correlation of the Rate of Tritium Release With Yielding in a 5086 Aluminum Alloy [65].

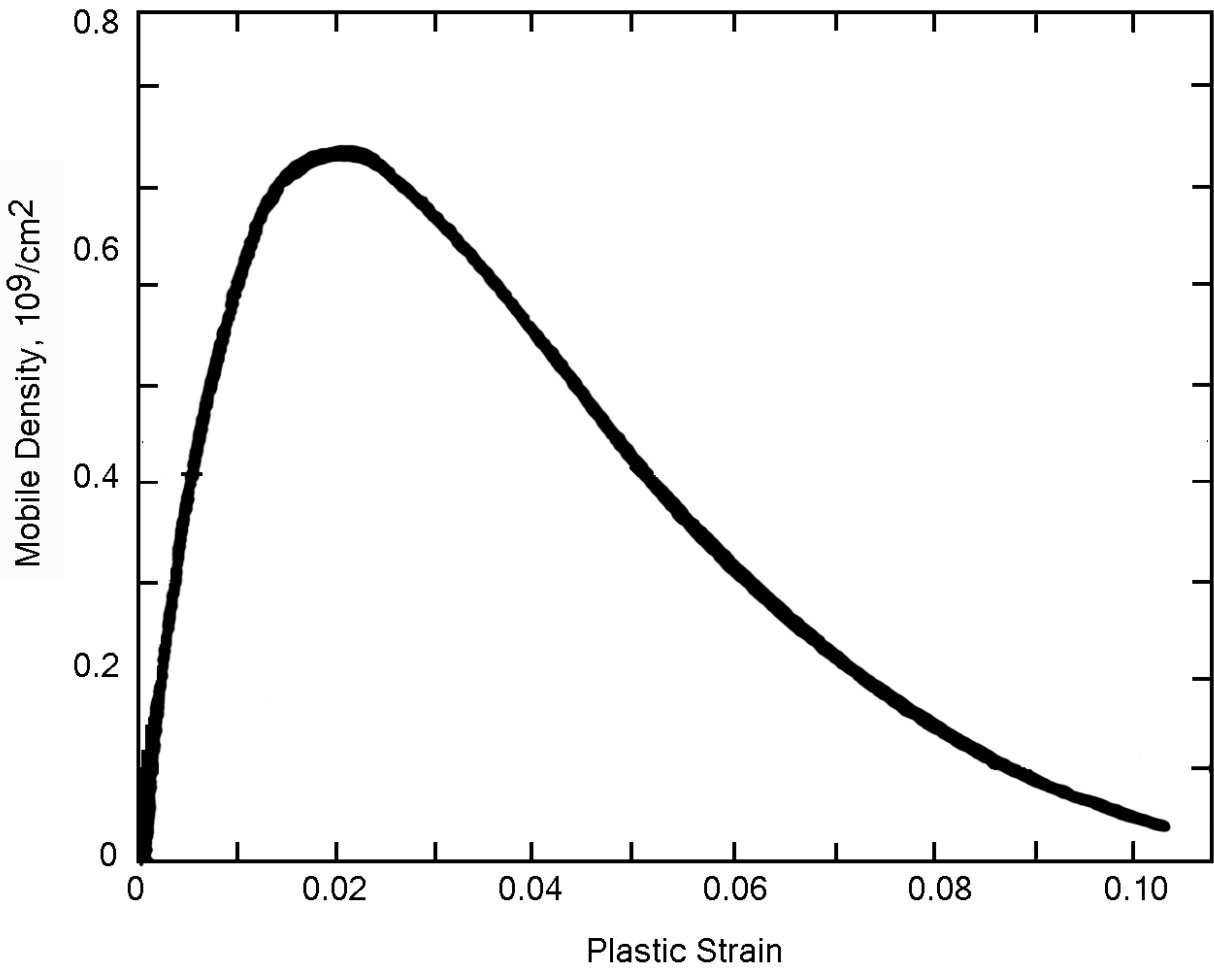


Figure 5. Influence of the Degree of Plastic Strain Upon the Mobile Dislocation Density [72].

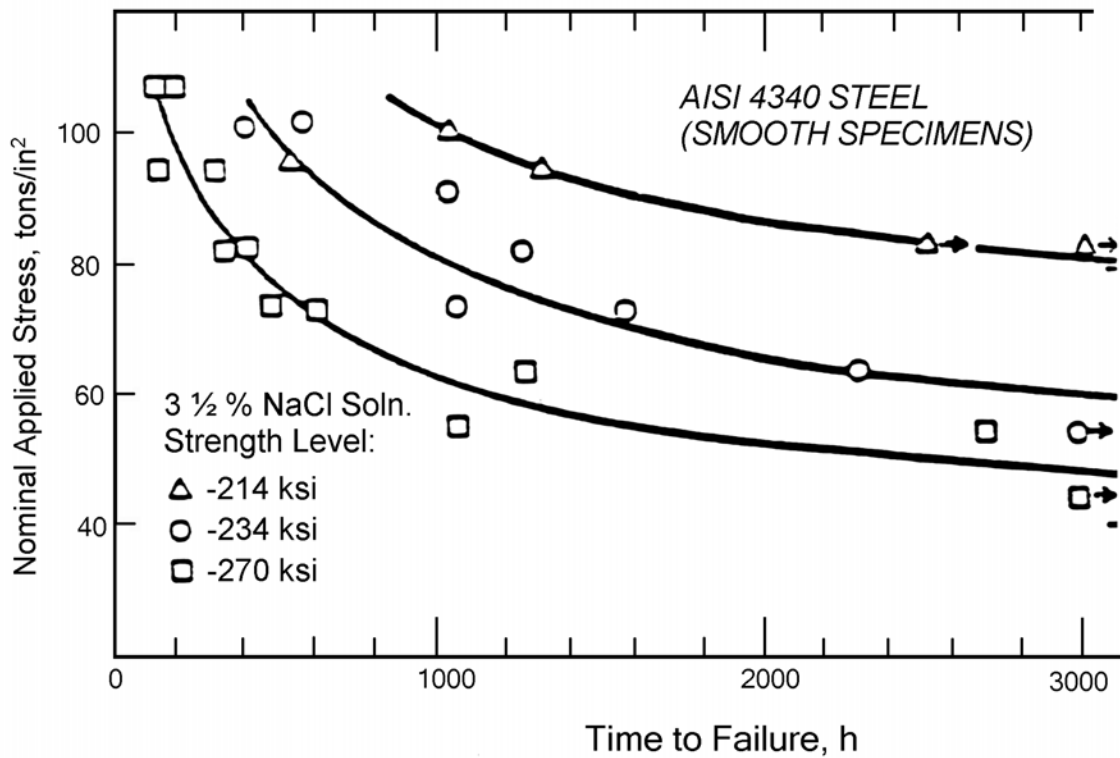


Figure 6. Data Showing the Tremendous Scatter in the Time at Which Delayed Failure Occurred in Different Samples of AISI 4340 Steel Under Applied Stress. The Deleterious Influence of Increased Strength Level is Also Clearly Evident [75].

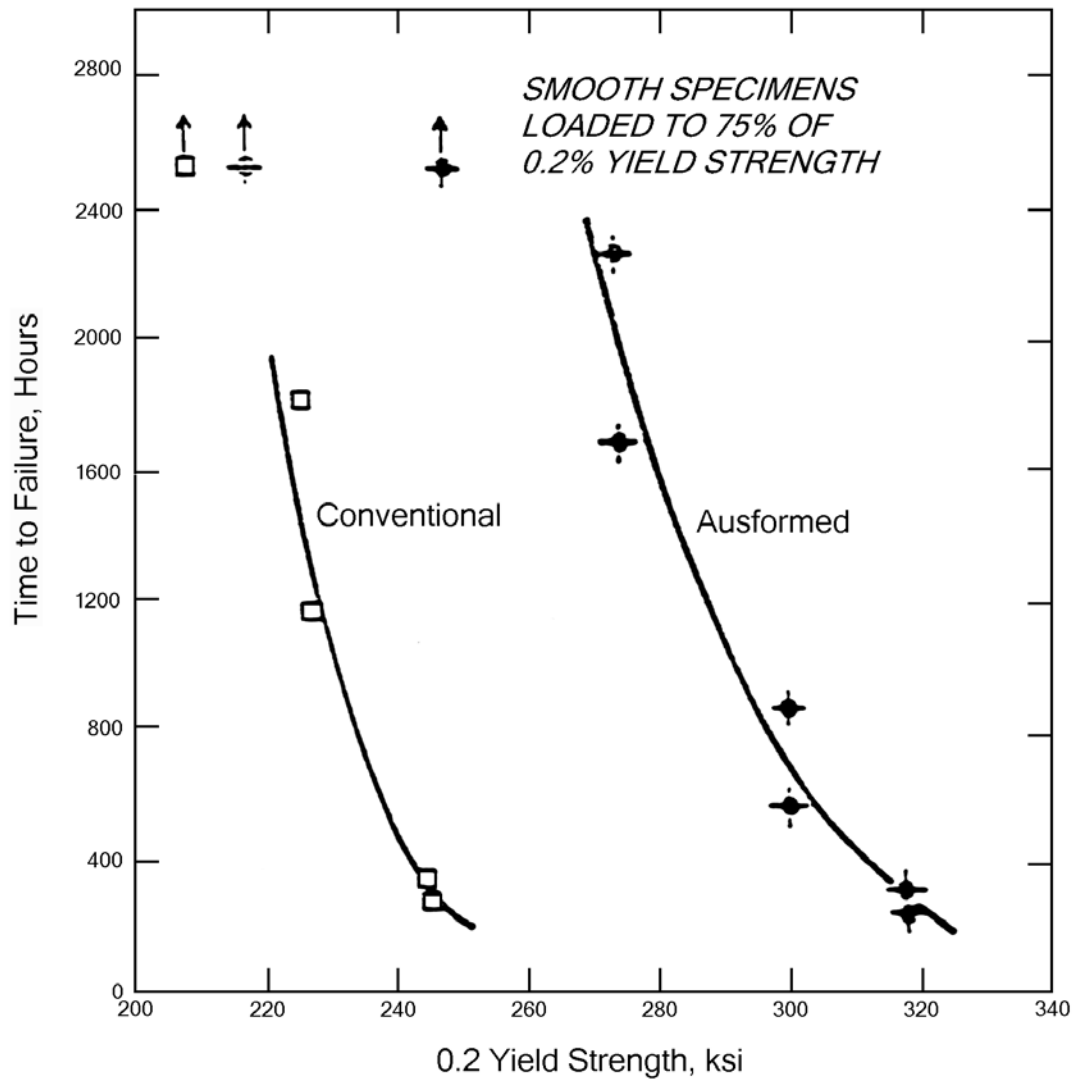


Figure 7. The Influence of Prior Thermo-Mechanical Treatment Upon the Time Delay Prior to Failure of D6AC Steel in Distilled Water Environment [76].

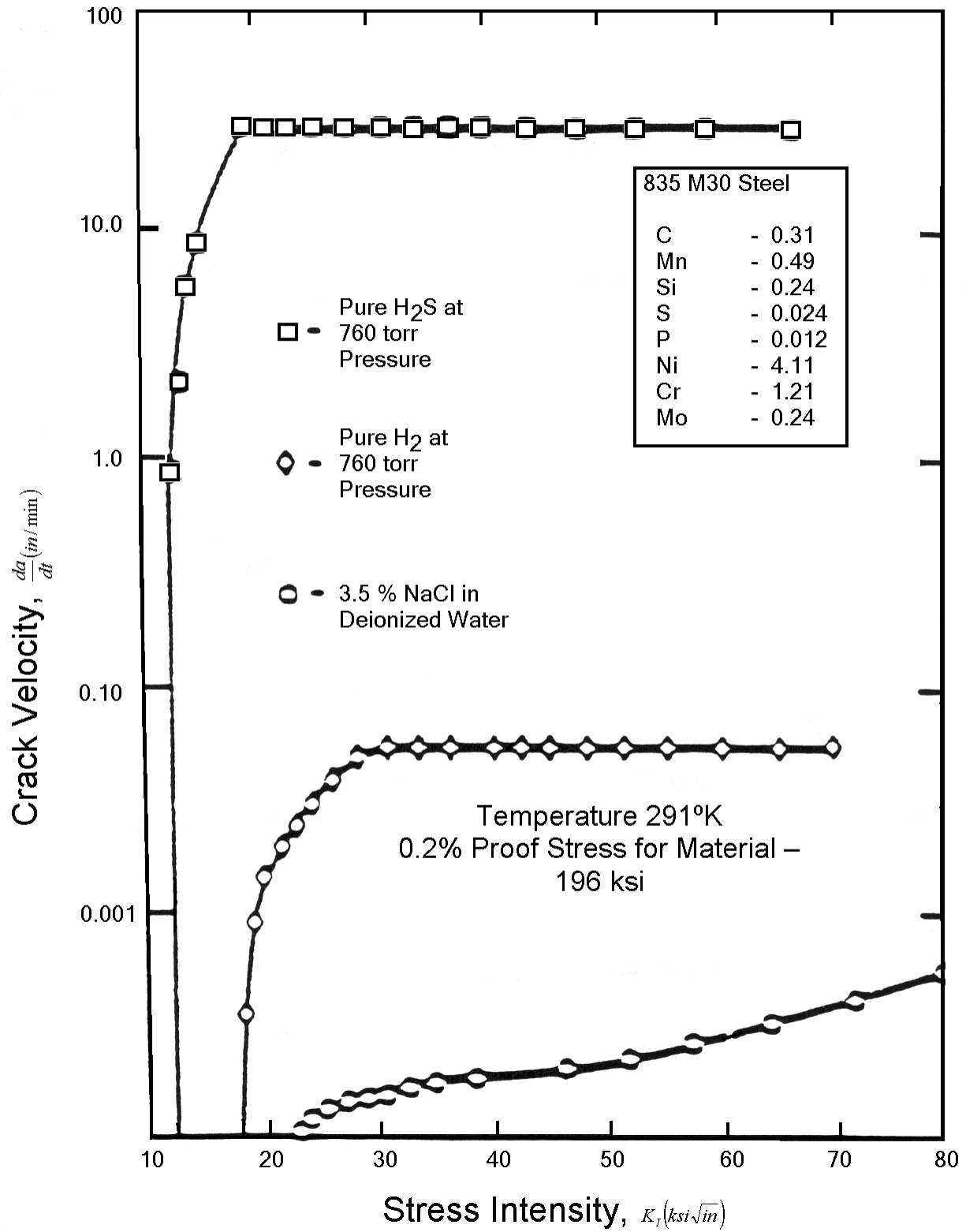


Figure 8. Data Showing the Large Influence of the Chemical Environment Upon the Relation Between the Stress Intensity and the Hydrogen - Related Crack Velocity of 835M30 Steel [77].

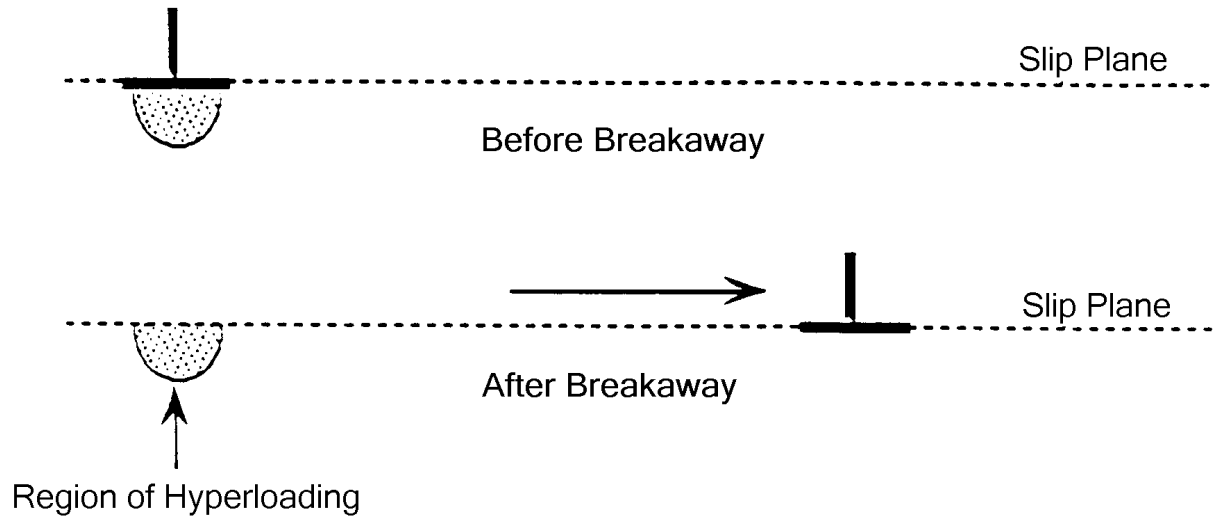


Figure 9. Dislocation Breakaway Mechanism That Could Produce Transient Local Hyperloading

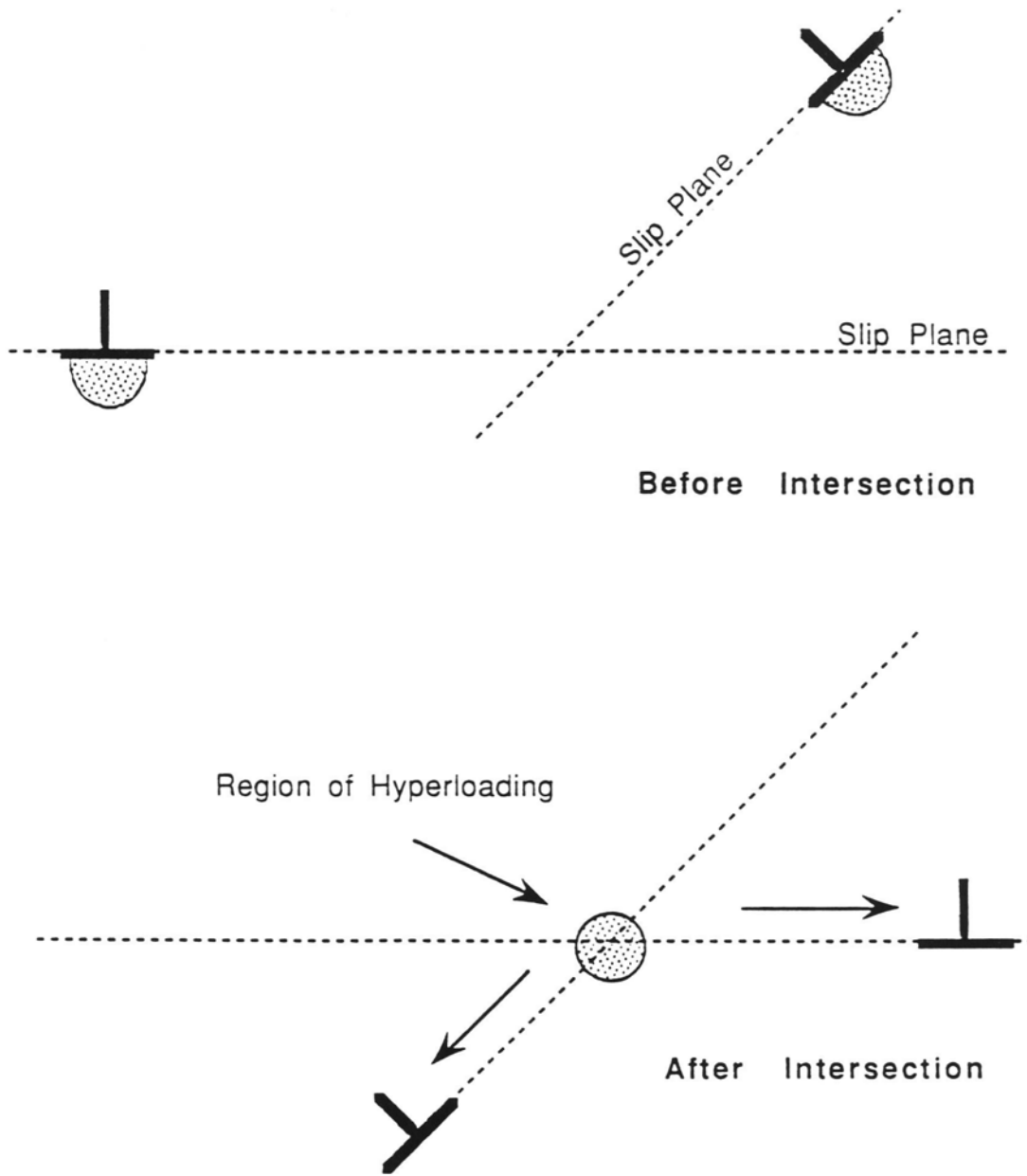


Figure 10. Dislocation Intersection Mechanism That Could Produce Transient Local Hyperloading