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TESTING FOR HYDROGEN EMBRITTLEMENT: PRIMARY AND SECONDARY INFLUENCES

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Abstract

The deleterious consequences of hydrogen on an engineering structure come about through an influence on either the crack initiation or the slow crack growth stage of fracture. Whether or not these two stages of fracture are affected by hydrogen will depend on a number of primary and secondary influences which severely complicate the embrittlement process. In this review we present a somewhat phenomonological overview of the hydrogen embrittlement process, both internal as well as external, in an effort to make more clear the type of parameters which must be considered in the selection of a test method and test procedure such that the resulting data may be meaningfully applied to real engineering structures. We consider what are believed to be the three primary influences on the embrittlement process: (1) the original location and form of the hydrogen, (2) the transport reactions involved in the transport of hydrogen from its origin to some point where it can interact with the metal to cause embrittlement, and (3) the embrittlement interaction itself. Additionally, a few of the large number of secondary influences on the embrittlement process are discussed, for example, the influence of impurity species in the environment, surface hydride films, and surface oxide films. Finally, specific test procedures are discussed in order to further elucidate the parameters which must be considered in the development of a standardized test method.

Key Words: Internal hydrogen, External hydrogen, Hydrogen transport, Fracture.

INTRODUCTION

The capacity of an engineering structure to withstand an applied load is often severely degraded by the presence of hydrogen originating from its equilibrium position within the metal lattice, from a gaseous hydrogen environment in contact with the structure, or as the product of a heterogeneous reaction between a hydrogen-containing molecule and the metal surface. The oldest and most extensively studied form of hydrogen embrittlement is that due to hydrogen within the metal lattice.[1-5] Hydrogen can enter a metal during production processes, such as pickling and electrolytic plating operations, where the hydrogen concentration at the metal surface can be very large.[6] The most recent form of hydrogen embrittlement to be recognized results from the direct exposure of a clean metal surface during deformation to a gaseous hydrogen environment. This form of embrittlement was first studied in detail in 1961[7] and has since been regarded with increasing concern. Because of the usefulness of the hydrogen-oxygen reaction as a fuel cell to produce electric current[8] and as a source of energy for propulsion,[9] this form of embrittlement will become more and more important and may, in the future if not today, control one phase of our technological growth.

The deleterious consequences of hydrogen on an engineering structure come about through an influence on its fracture behavior.[10] Under conditions of static loading, fracture in an inert environment occurs in two stages — crack initiation and rapid, unstable crack growth. An additional stage of fracture can be present in a structure under conditions of cyclic loading or in the presence of an active species such as hydrogen. This stage of fracture is termed the subcritical or slow crack growth stage and occurs following crack initiation but prior to rapid fracture. Under cyclic loading this stage of fracture is the result of the mechanical action of opening and closing the crack. When hydrogen is present, either internally or externally, this stage of fracture occurs because hydrogen embrittlement is a time-dependent process — time-dependent because time is required to transport hydrogen from its original location and form to some point on or within the metal where hydrogen can interact with the metal lattice.[11]

The interaction between hydrogen and the metal may result in the formation of a solid solution of hydrogen in the metal, second-phase hydride precipitates, molecular hydrogen within the metal lattice, products of the reaction between hydrogen and impurities, and others. From the numerous studies conducted on hydrogen embrittlement, the phenomenon can be classified into two distinct types according to its strain rate dependence. The first type of embrittlement is aggravated by increasing strain rate, while embrittlement of the second type decreases with an increase in strain rate. From an engineering standpoint, both forms of embrittlement are important. The first type is due to the presence of a product of a completed reaction within the metal lattice and involves fracture theory as related to the crack initiation and crack growth processes within the second-phase precipitate and through the metal lattice. In the second type, a kinetically controlled reaction occurs concurrently with embrittlement and, in fact, controls the degree of observed embrittlement. This form of embrittlement must then involve reaction kinetics as related to the transport of hydrogen or its interaction with the metal lattice, or both, as well as the mechanics of the fracture process itself. Additionally, the second type of embrittlement, unlike the first, need not involve a second phase reaction product.

In general, hydrogen embrittlement is a very complex phenomenon and many times can be further complicated by what can appear to be unimportant secondary considerations. It is the purpose of this paper to present a somewhat phenomonological overview of the processes of hydrogen embrittlement, both internal as well as external, in order to make more clear the type of parameters which must be considered in the selection of a test method and test procedure such that the resulting data may be meaningfully applied to real engineering structures. We will discuss what I believe to be the three common, primary influences on the embrittlement process, that is: (1) the original location and form of the hydrogen, (2) the transport reactions involved in the transport of hydrogen from its origin to some point where it can interact with the metal lattice to cause embrittlement, and (3) the embrittlement interaction itself. The implications of each and the potential influence of secondary considerations on each will be considered in some detail in an effort to elucidate the parameters which must be considered in the development of a standardized test method.

THE ORIGIN OF HYDROGEN

After an engineering structure is processed, assembled, and in use, hydrogen can be present either externally (in contact with the metal structure) or internally (within the metal lattice). When it is present externally, hydrogen can exist as a molecule, as a dissociated molecule or atom, or as a component of a complex molecule such as hydrogen sulfide, water, or methanol. Internally, its form may be as an atom or screened proton within the metal lattice, as a molecule precipitated at a lattice defect, or as a precipitated metal hydride phase. The original location and form of hydrogen are of primary importance in that they establish the starting point and thus, the complexity of the overall transport process involved in embrittlement. For an example, if we are dealing with a metal that readily forms hydrides, such as alpha-titanium, and hydrogen is originally present in the form of massive hydrides within the metal lattice, the metal may be brittle because of the hydrides and additional hydrogen transport is not required. This type of embrittlement is termed fast-strain-rate embrittlement, as previously discussed.

In this example it is the original location and form of the hydrogen within the metal structure that is the cause of embrittlement. If, however, hydrogen is originally present in solution within the metal lattice, hydrogen must be transported through the metal lattice under an activity gradient by lattice diffusion to a location where a sufficient concentration is developed to form a hydride and embrittle the metal. This process is time-dependent because hydrogen transport is involved. Likewise, if hydrogen is originally present in the external environment, hydrogen transport will also be involved; however, the overall hydrogen transport reactions will be much more complex.

In the design of a standardized test method, it is imperative that the original location and form of hydrogen simulates that which will exist in or around the engineering structure. If tests are being conducted to qualify a plating procedure or to determine the hydrogen pickup in an engineering structure which potentially could be embrittled by the presence of hydrogen, tests are conducted on coupons processed along with the structure made of identical material to that of the structure or of material known to be more susceptible to embrittlement. If tests are being conducted to establish the influence of a working environment on an engineering structure, it is equally important that the form and contaminant level in the environment, the condition of the metal surface, and other such variables be duplicated in the greatest detail.

THE TRANSPORT OF HYDROGEN

If hydrogen is observed to influence the fracture behavior of a structure, hydrogen must have been at some critical location before the metal was stressed or have been transported to this location during deformation. As previously discussed, an example of the former is the embrittlement of a metal by the presence of massive precipitates in the metal lattice; examples of the latter are forms of embrittlement identified by an inverse strain rate dependence. This inverse strain rate dependence is a result of an overall kinetic reaction involved in the transport of hydrogen from its equilibrium or quasiequilibrium position in the system to some critical location where it can influence fracture. The rate in which a metal becomes embrittled, then, will depend on the reaction kinetics of the overall transport reaction.

The overall transport reaction involved in the embrittlement process will be very different depending on whether hydrogen originates in the environment surrounding the metal or is present within the metal lattice. When hydrogen originates in the metal lattice, lattice diffusion will be the primary transport reaction;[12] however, other reactions such as phase formation, dissolution onto an internal surface (of a void perhaps), and desorption into the void cavity may also be involved, depending on where and how hydrogen influences fracture. Even though these transport processes are relatively simple, they can still be influenced by a number of secondary considerations. For example, alloy microstructure and grain size can have a significant influence on hydrogen diffusivity.[13] Additionally, the presence of plane strain as contrasted to plane stress or the existence of a notch can have a significant influence on the activity gradient for lattice diffusion.[14]

When hydrogen originates in the environment, the overall transport reaction will be much more complex, reflecting the form of the species in the environment, the purity of the environment, and the nature of the metal surface.

For the simple case of embrittlement caused by a very high purity gaseous hydrogen environment where the interaction influencing fracture occurs well within the metal and does not involve a phase precipitation, the elementary reactions may be as shown schematically in Fig. 1 and are:

1. Gas-phase diffusion of molecular hydrogen to the crack surface

$$r_1 = k_1 P \tag{1}$$

where

k_1 = rate constant,

P = molecular hydrogen pressure.

2. Molecular hydrogen strikes the metal surface, dissociates, and is adsorbed as atoms

$$r_2 = k_2 P^{1/2} (1 - \theta) \tag{2}$$

where

θ = hydrogen surface coverage.

3. An adsorbed atom migrates across the metal surface and chemisorbs

$$r_3 = k_3 \text{ grad } u \tag{3}$$

where

grad u = gradient in surface hydrogen concentration.

4. An adsorbed atom passes into the metal

$$r_4 = k_4 \theta [1 - (u/u_s)] \tag{4}$$

where

u = hydrogen concentration just inside the metal surface,

u_s = saturation concentration of hydrogen in the metal.

5. A hydrogen atom near the metal surface diffuses to the critical location to cause embrittlement

$$r_7 = D[(u - u_\ell)/\ell] \qquad (5)$$

where

D = diffusion coefficient,

u_ℓ = hydrogen concentration at the critical location ℓ distance from the metal surface.

The overall transport reaction will be the sum of the individual reaction and can involve reactions occurring in opposite directions, consecutively, and in parallel.[11]

The exact form of the overall transport reaction will be very complex, reflecting the original location and form of the hydrogen, the pressure and temperature of the test, as well as secondary considerations such as impurities present in the environment. For example, hydrogen-induced slow crack growth of hardened AISI-SAE 4130 steel in high purity molecular hydrogen has been observed to exhibit the temperature dependence shown by the dashed curve in Fig. 2 and obeys the equation:[15]

$$\mathring{R} = C_1 \frac{C_2 P T^{-1/2} \exp[-\Delta H/RT]}{C_3 + C_2 P T^{-1/2} \exp[-\Delta H/RT]} P^{1/2} \exp(-E_m/RT) \qquad (6)$$

where

C_1, C_2 and C_3 = constants,

P = molecular hydrogen pressure,

T = absolute temperature,

$(-\Delta H)$ = heat of adsorption,

E_m = energy for surface migration of hydrogen on steel.

When atomic hydrogen is present in the environment, the temperature dependence obeys a simple exponential relation and crack growth rate is increased orders of magnitude as shown by the solid curve in Fig. 2.[16] The interpretation of these observations is that the process involved in the dissociation of the molecule on the steel surface is the slowest transport process and controls crack growth in molecular hydrogen. In atomic hydrogen the dissociation reaction is no longer required in the overall transport process, the transport of hydrogen is more rapid, and the rate of slow crack growth is increased.

The importance of transport reactions to embrittlement, particularly external hydrogen embrittlement, cannot be overemphasized. If any one of the reaction steps is hindered or eliminated, the structure will be less susceptible to embrittlement and, in fact, may not exhibit embrittlement at all. The influence of hydrogen pressure and test temperature on embrittlement comes about primarily through their involvement in the overall transport process. In general, there is no real difference between high pressure hydrogen embrittlement[17] and low pressure hydrogen embrittlement[18] except that the higher is the hydrogen pressure, the more rapid will be the rate of hydrogen transport.[11]

Secondary influences are of extreme importance to external hydrogen embrittlement in that they can have significant effects on the reaction steps involved in transport. For example, contaminants in the external environment such as small amounts of oxygen[19] can slow down or can even eliminate the adsorption reaction (Eq (2)). The presence of oxide films on the metal surface many times will not permit the dissociation of molecular hydrogen[20] (Eq (2)). Hydride films present on metal surfaces can slow down hydrogen entry into the metal lattice[21] (Eq (3)). Because there are so many required transport steps, each of which is capable of being influenced by so many secondary considerations, it is somewhat amazing that environmental hydrogen embrittlement is ever observed. Likewise, it is easily understood how selective embrittlement occurs in seemingly compatible systems after years of successful operation. For example, the classic gaseous hydrogen-steel storage tank failures of the 1960s,[22] the N_2O_4[23] and methanol[24] embrittlement of titanium, and the hydrazine embrittlement of stainless steel.[25] In each of these examples embrittlement occurred because of what was originally thought to be unimportant, secondary changes made to the originally compatible system.

Some metals such as aluminum, copper, and others do not adsorb molecular hydrogen at room temperature[26] and thus hydrogen cannot be transported to the metal lattice. Under normal conditions, these metals and some of their alloys would never be expected to exhibit environmental hydrogen embrittlement. This is not to say that environmental hydrogen embrittlement may not some day be observed in these systems. Presently we cannot be assured that these systems, too, will not be embrittled if a catalytic adsorption reaction develops from some unforeseen circumstance and permits hydrogen transport.

THE HYDROGEN EMBRITTLEMENT INTERACTION

A number of theories have been proposed to described the potential interaction of hydrogen with metals. In general, they fall into one or more of the following categories: pressure formation,[27-30] surface interaction,[31-33] lattice decohesion,[34-36] dislocation interaction,[37-41] and hydride precipitation.[42-43] Each category has a strong experimental base and the occurrence of each really cannot be denied under some specific set of conditions. Which of these interaction mechanisms results in the embrittlement of a structure depends on the conditions which exist in that structure.

Under some condition or another, hydrogen has been observed to influence the fracture behavior of all metals investigated to date. In a few metals, however, these effects are seen only when the lattice contains a supersaturated concentration of hydrogen with respect to the lattice equilibrium solubility or terminal solubility. Under this condition, hydride-forming metals such as titanium, zirconium, and vanadium will precipitate a brittle hydride phase; metals such as iron, copper, and aluminum will precipitate molecular hydrogen; while metals such as nickel, magnesium, and palladium can precipitate either molecular hydrogen or a hydride phase depending on the degree of supersaturation.[37, 44-46] If second phase precipitation is extensive, all metals can fail, even without an applied load because of pressure buildup of molecular hydrogen at internal defects[10] or the stresses developed around the less dense hydride precipitate.[37]

Precipitation of a hydrogen-rich second phase in metals need not be associated only with precipitation from a supersaturated *bulk* lattice. It can also occur as the result of a *localized* supersaturation. The conditions for localized precipitation are: (1) if a localized saturation originally exists, transport within the metal lattice must be sufficiently slow to maintain the localized saturation during precipitation; or (2) if saturation is not originally present, transport must be sufficiently rapid to develop this saturation. An example of the former is the formation of titanium hydride on the surface of alpha-titanium when exposed to a gaseous hydrogen,[47] and of the latter, is the formation of hydride at the alpha-beta titanium boundaries by rapid transport of hydrogen in the non-hydride-forming beta-titanium phase.[48-50]

Second-phase precipitation is a sufficient but not a necessary condition for the occurrence of hydrogen embrittlement. Embrittlement is observed in many metals under conditions where a supersaturation probably could not exist. Most notably is, of course, the failure of many metals in a low pressure gaseous hydrogen environment. Under these conditions, applied load acts to concentrate the hydrogen at areas of lattice distortion; for example, at areas of triaxial stress ahead of a crack tip or at a grain boundary. Hydrogen in these areas may deleteriously affect lattice cohesion to the extent that crack nucleation and propagation are possible. For steel in a hydrogen environment, the hydrogen-lattice interaction appears to occur on or just below the crack tip[15,16] and can be considered the limiting case of lattice decohesion, that is, surface decohesion. Embrittlement as the result of a hydrogen-lattice interaction, unlike embrittlement by second-phase precipitation, is always associated with a brittle mode of failure; whether this mode is transgranular or intergranular apparently depends on the site of crack initiation and the relative strength of the grain boundaries.

The contribution of the hydrogen-dislocation interaction to the embrittlement of metals appears, in most cases, to be of secondary importance; however, under the right conditions, this mechanism could conceivably play an important role.[40] Hydrogen can combine with dislocations and influence their motion in iron,[51,52] molybdenum,[53] vanadium,[54] columbium,[55] and nickel.[56,57] The rate of hydrogen transport within the lattice can be increased by its association with dislocation movement.[41] In general, however, these effects require large hydrogen concentrations. Such hydrogen concentrations are not normally obtainable, say from a gaseous hydrogen environment at room temperature. Additionally, the effects of fatigue crack growth and gaseous hydrogen-induced crack growth in titanium appear to be independent processes; the former, of course, associated with deformation (dislocation motion), thus eliminating any significant contribution of dislocation motion to the latter.[58]

From the above discussion it should be obvious that the hydrogen-metal embrittlement interaction is a specific interaction depending on many secondary influences. If conditions are not correct for a precipitation-type interaction, they may be correct for a decohesion or a dislocation interaction. The relative importance of each depends on the original location and form of the hydrogen, the transport reactions, as well as the stage of fracture most important to the failure of the particular structure.

TESTING FOR HYDROGEN EMBRITTLEMENT

The deleterious effects of hydrogen on the failure of an engineering structure comes about through its influence on either the crack initiation stage or the subcritical, slow crack growth stage of fracture. Most engineering structures contain preexisting cracks because of various processing procedures so the crack initiation stage of fracture is of little or no importance to the failure process. This may not be the case, however, for some structures and more importantly for many test specimen configurations such as the tensile bar[17] and rupture disc,[59] particularly when evaluating environmental hydrogen embrittlement. In these, the crack initiation stage can dominate the failure process.

When hydrogen is originally present within a structure, the crack initiation stage of fracture can be readily influenced. All engineering metals contain internal defects which can act as internal surfaces for molecular hydrogen precipitation or contain locally strained regions which can induce hydride precipitation. These areas are sites for crack initiation. The propensity of a metal to "precipitate" a crack is dependent on the degree of hydrogen saturation, or in other words, the amount of hydrogen and the distance hydrogen must be transported to the site of nucleation. If the level of hydrogen is high and the metal lattice is supersaturated, crack initiation will be virtually spontaneous;[60] if it is low, however, crack initiation will be time-dependent with its rate controlled by the rate of hydrogen transport.[61] When hydrogen is present in the environment, the influence of hydrogen on this stage of fracture becomes more random and is dependent on the development of a surface site for crack nucleation where the environment can interact. In metals which do not form hydrides, crack initiation is more or less random because of the probability of an initiation site occuring on the metal surface,[11] whereas in hydride-forming metals, such as alpha-titanium, crack initiation is more predictable because a surface hydride can form in which crack initiation can more easily occur.[11]

The subcritical crack growth stage of fracture occurs at values of stress intensity below some critical value for rapid fracture. In a very simple manner, crack growth will occur in a engineering structure at some level of applied stress when the applicable criteria are met, such as that proposed by Griffith for brittle materials.[62] Crack growth will occur at a lower applied stress, however, if hydrogen can influence the variables in the criteria in such a way as to reduce the stress intensity value determined by the criteria. If the influences of hydrogen on variables in the criteria were instantaneous and if hydrogen were originally present within the structure at sufficiently high concentrations and was homogeneous throughout, the new value of stress intensity would be the critical value, and unstable crack growth would immediately result. However, the influence of hydrogen is localized at or near the tip of a nucleated or existing crack and continued crack growth is dependent on the rate of hydrogen transport to this localized area. These conditions are easily understood for hydrogen-induced crack growth by the interaction with a crack propagating from a surface; however, the same conditions apply to the propagation of a crack from an internal surface (void) as the result of the interaction of hydrogen within the void. Under the latter condition the additional force applied to the crack tip by the hydrogen pressure within the void must be considered.[10] Other mechanical factors which influence hydrogen-induced crack growth include mode of loading, state of triaxial stress about the crack tip, amount and form of plastic deformation associated with the crack tip, etc.

As we have seen, the process of hydrogen embrittlement can be a very complicated phenomenon. Figure 3 is a montage meant to better illustrate this point. Underlined in this figure are what I consider to be the primary steps in the embrittlement process and include origin of the hydrogen, transport of the hydrogen, and the interaction processes of hydride formation, lattice decohesion, dislocation interaction, and pressure formation. Also shown are a few of the secondary considerations which can influence one or more of the primary steps; these include impurity species in the environment, surface hydride films, surface oxide films, plastic blunting of the crack tip, and the level of stress triaxiality. Let us next consider specific test procedures in order to further illustrate the parameters which must be understood in the design of a standardized specimen and test procedure, if their results are to have meaning when applied to an engineering structure.

Internal Hydrogen Embrittlement

Probably the most usual cause of hydrogen within an engineering structure is a production process such as pickling or electroplating. Hydrogen pickup is the result of a high hydrogen fugacity developed during processing and is dependent on process-variables of bath composition, current, time, temperature, etc. When a potentially susceptible structure is processed, it is imperative that the degrading effect of the process be established in order to ensure the integrity of the structure. This is done either by qualifying the process with the use of test coupons or by processing test coupons along with the structure, or both. All process variables must be duplicated on the test coupons, including such variables as material, surface condition, potential susceptibility, etc. Following processing, the coupons are tested to establish any degrading influences of hydrogen pickup during processing.

In the selection of coupon design and test method, consideration must be given to (1) the original location and form of the hydrogen picked up during processing, (2) the transport of the hydrogen from its original location to the site where it can interact with the metal to cause a degrading effect, and (3) the interaction process itself. Design parameters which can affect these variables include presence, location, and severity of a stress concentrator and level and form of loading. A test coupon should contain a stress concentrator such as a notch as near to the original location of hydrogen as possible to shorten the required transport path, as severe as possible to increase the rate of hydrogen transport by stress enhanced diffusion, and at the point of maximum tensile load to concentrate the hydrogen-metal interaction at the point of maximum stress. The coupon should be statically loaded to some level for some period of time reflecting the use condition of the engineering structure to permit the transport of hydrogen from its origin to the point where it can interact with the metal lattice to cause embrittlement. A number of current coupon designs fit these considerations.[63-65] Which one of these is optimum for the particular production process will depend on the particular metal tested as well as the suspected location and form of hydrogen within that metal.

External Hydrogen Embrittlement

Hydrogen in an external environment can degrade the properties of an engineering structure by interacting with the structure while it is being loaded or is under load. This form of embrittlement is much more complicated than internal hydrogen embrittlement because of the variety of external species which can supply hydrogen to the structure (molecular hydrogen, dissociated or ionized hydrogen, complex hydrogen containing gases such as hydrogen sulfide, and complex hydrogen containing liquids such as water and organics) and because of the large number of reaction steps required to transport the hydrogen from its equilibrium form in the environment to the metal lattice. Small amounts of contaminants can have a large influence on the transport process and thus on the potential embrittling effect of the particular environment. For example, small amounts of oxygen can eliminate the degrading effect of a hydrogen environment in some systems[18] whereas small amounts of carbon dioxide in a hydrazine environment can induce severe embrittlement in a normally passive system.[25] When testing for the potential embrittling effects of an environment, it is of extreme importance that either the influences of all species in the environment be understood or the environment be exactly duplicated.

Although both the initiation and growth stages of fracture can be influenced by hydrogen, in general the greatest influence will be on the crack growth stage of fracture. When testing for external hydrogen embrittlement, it is imperative that the relative influence of the initiation and growth stages of fracture in the failure of a structure be understood such that the selected specimen design will yield data which can be meaningfully applied to the engineering structure.

Test specimen configurations which do not contain a preexisting crack (the smooth and notched tensile bar, the smooth and notched bend bar, and the rupture disc) must involve the crack initiation stage in the fracture process. The extent of involvement will be dependent on specimen configuration and method of loading as well as on the sensitivity of this stage to the influence of hydrogen. If crack initiation occurs early in the deformation process, say because of its sensitivity to hydrogen, the crack growth stage may be the primary stage governing failure. However, if the material tested is extremely notch sensitive, failure may occur immediately upon the initiation of a crack.[11] In general, it is difficult if not impossible to separate the initiation stage and the crack growth stage in specimen configurations which do not contain preexisting cracks and thus data obtained from these types of specimens can only be applied to engineering structures with reservation. These problems are not always eliminated by the use of precracked specimens. Even in these types of specimens, the crack initiation stage may contribute to the failure process if the precrack is not sharp but is blunted by plastic deformation or if the precrack surface is contaminated.

The influence of hydrogen on the subcritical crack growth stage of fracture can be determined precisely in high strength materials by the use of the correct specimen design and test method. Specimen design should, whenever possible, conform to the guidelines put forth by ASTM for plane strain fracture toughness testing. Precracks should be introduced in the specimen by cyclic loading or other methods at stress intensity values below those expected to be required for hydrogen-induced, slow crack growth. Additionally, if precracking is done in air, the oxide film normally formed at the crack tip must be ruptured in the test environment before hydrogen-induced, slow crack growth will be observed. One of the many acceptable test techniques applicable to high strength materials will be outlined below.[49]

The following test procedure is presented to illustrate one of many acceptable techniques used to determine the rate of hydrogen-induced, slow crack growth in high strength materials. Specimens are wedge-opening-loaded, double-cantilever-beam (DCB) type originally discussed by Mostovoy,[66] Fig. 4. The side grooves are added to ensure that the crack will propagate in a direction normal to the applied stress. This fracture mechanics-type specimen has several features that are extremely useful when investigating hydrogen-induced cracking. For any fixed crack-opening displacement (COD), the stress-intensity level decreases as the crack grows, thus permitting a high degree of control of crack growth. Crack-growth rates can be easily determined by either opticalmeasurement methods[67] or by measurement of compliance changes.[49] The specimen is also easy to precrack by either fatigue or overload procedures.

Tests can be conducted in any test chamber that can be evacuated and then backfilled with hydrogen. The chamber should always be evacuated prior to backfilling with hydrogen to ensure that the total concentration of background gases will be lower than the concentration of active impurities in the test environment. Prior to testing, each specimen is precracked by fatiguing in the hydrogen environment. By this method, the original machined notches are extended and sharpened. After the desired environmental conditions (temperature, pressure, etc.) have been established, the specimen is rapidly loaded to a preselected COD value and held at that value while the corresponding load is continuously measured. As the crack grows, the continuously measured load (stress intensity) will decrease at a rate which is related to the crack-growth rate. Figure 5 shows typical results of tests conducted using the above procedure.[49] In this figure the rate of hydrogen-induced, slow crack growth is shown as a function of stress intensity, K , at a hydrogen pressure of 0.9 atm. and at five different temperatures. This data can now be applied to an engineering structure to estimate the life of that structure.[68,69]

SUMMARY

Hydrogen embrittlement has been shown to be a complex process which is many times further complicated by what could be termed secondary influences. Embrittlement, whether caused by internal or external hydrogen, involves three primary influences: (1) the original location and form of the hydrogen, (2) the transport reactions involved in the transport of hydrogen from its origin to some point where it can interact with the metal to cause embrittlement, and (3) the embrittlement interaction itself. Of these, probably the most important is the hydrogen transport process — it is this process which controls the rate of hydrogen arrival at some critical location on or within the metal and thus controls the rate or severity of embrittlement in the structure. Further, if any one of the reaction steps involved in the transport process is hindered or eliminated, the structure will be less susceptible to embrittlement and, in fact, may not exhibit embrittlement at all. Besides these primary influences, a large number of secondary influences can be involved in embrittlement through their effect on the primary factors. Some secondary influences are impurities in the environment or within the metal, surface films of hydride or oxide, and state of stress triaxiality within the specimen or structure. The above discussions are intended to clarify the type of parameters which must be considered in the selection of a test method and test procedure such that the resulting data may be meaningfully applied to real engineering structures.

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FIGURE TITLES

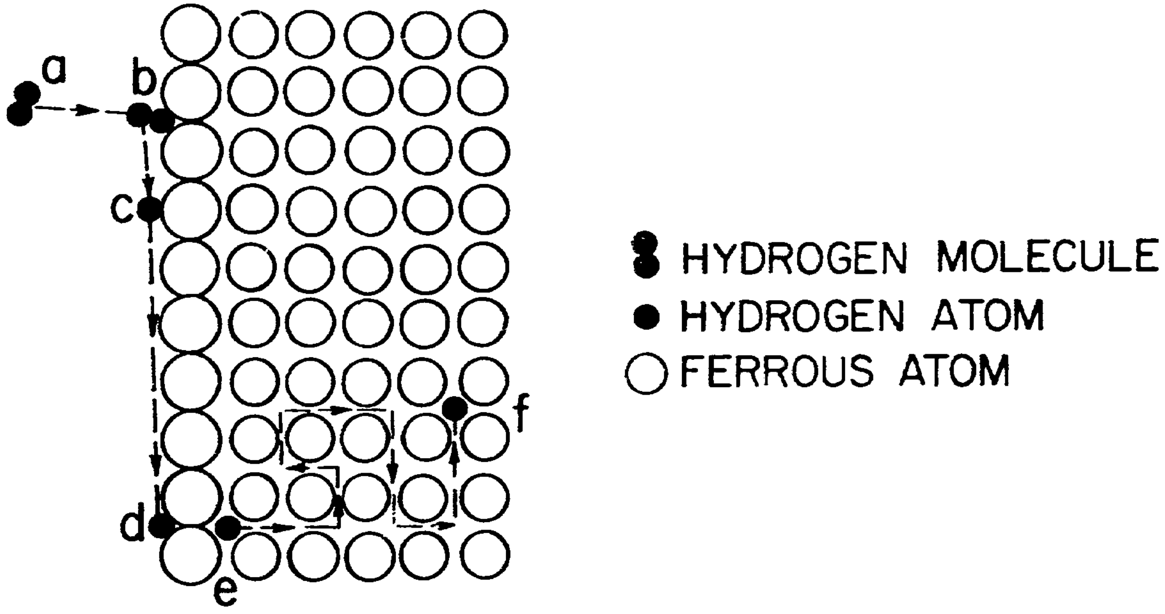
Fig. 1 — Schematic of possible elementary transport reactions involved in external hydrogen embrittlement.

Fig. 2 — Temperature dependence of slow crack growth in atomic-molecular hydrogen compared with that predicted for a molecular hydrogen environment at the same pressure.[15, 16]

Fig. 3 — Montage of primary and some secondary effects involved in the embrittlement of a metal by hydrogen.

Fig. 4 — Double-cantilever-beam (DCB) specimen.[49]

Fig. 5 — Experimentally determined relationship between hydrogen-induced crack growth and applied stress intensity in Ti-5Al-2.5Sn.[49]



REACTION STEPS

a → b GAS-PHASE DIFFUSION
b → c PHYSISORPTION AND DISSOCIATION
c → d ADATOM MIGRATION AND CHEMISORPTION
d → e SOLUTION
e → f LATTICE DIFFUSION

Fig. 1

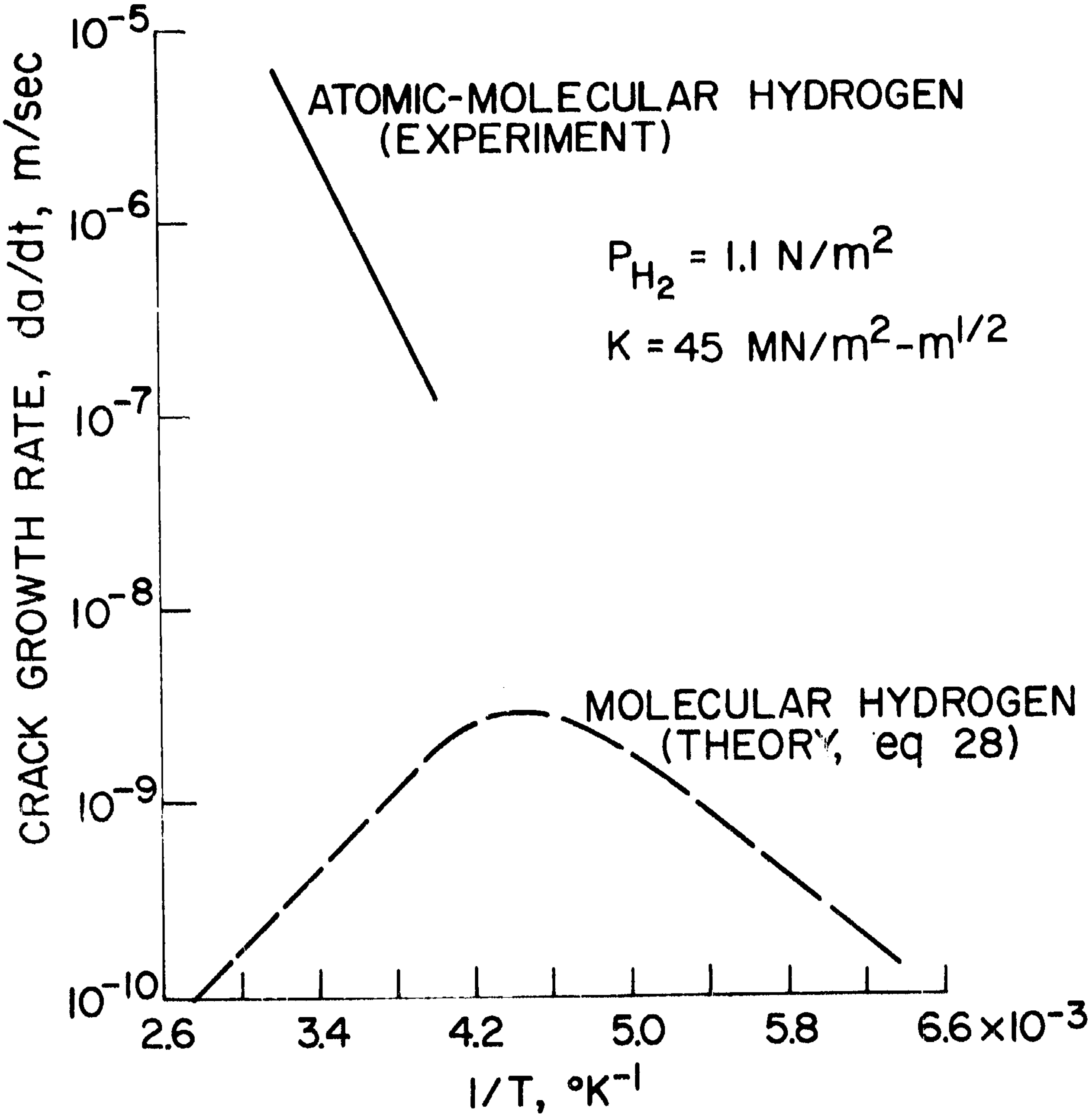

CRACK GROWTH RATE, da/dt, m/sec
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
ATOMIC-MOLECULAR HYDROGEN (EXPERIMENT)
P_{H_2} = 1.1 N/m^2
K = 45 MN/m^2-m$^{1/2}$
MOLECULAR HYDROGEN (THEORY, eq 28)
2.6
3.4
4.2
5.0
5.8
6.6×10^{-3}
1/T, °K^{-1}

Fig. 2

MONTAGE OF HYDROGEN CONSIDERATIONS

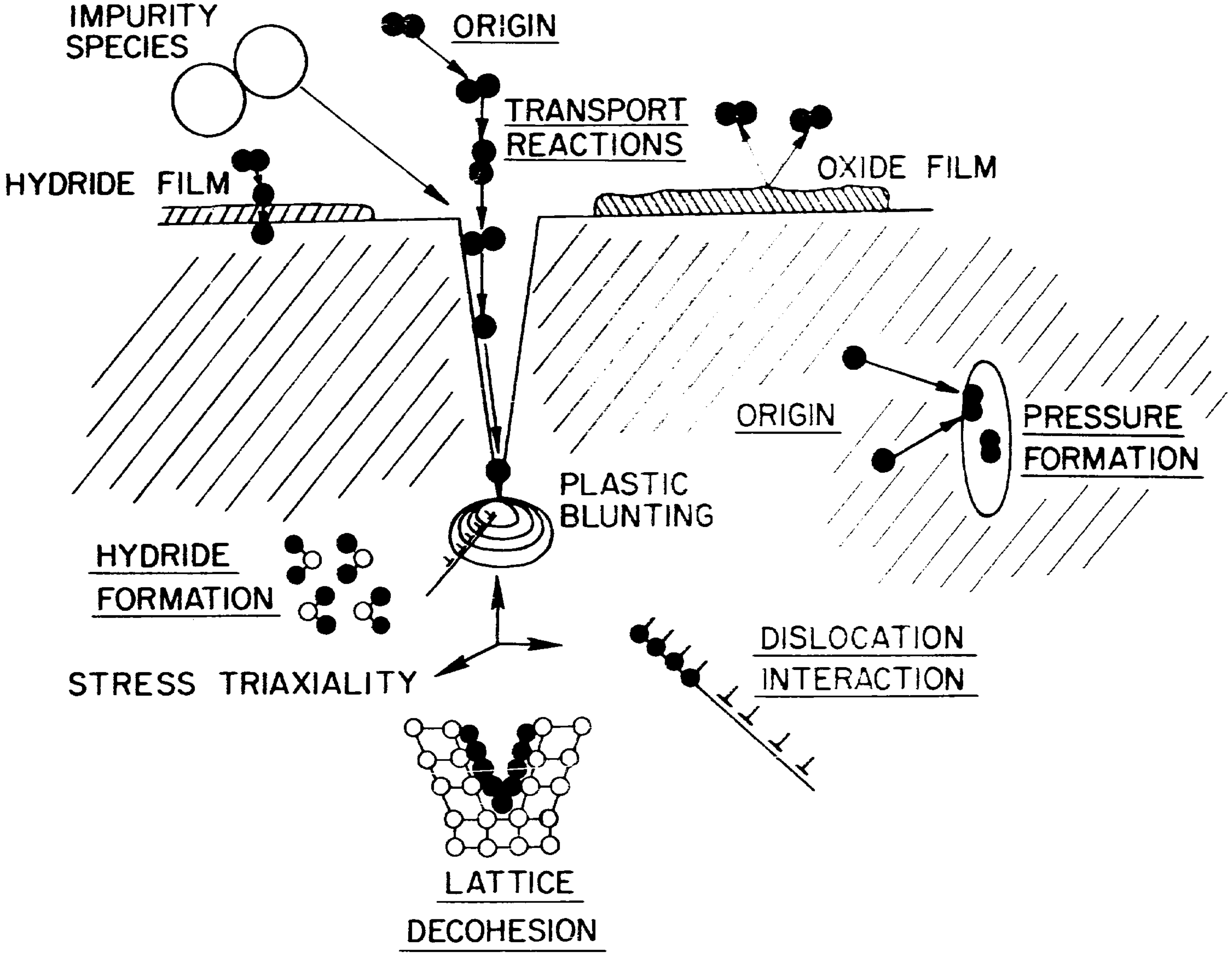


Fig. 3

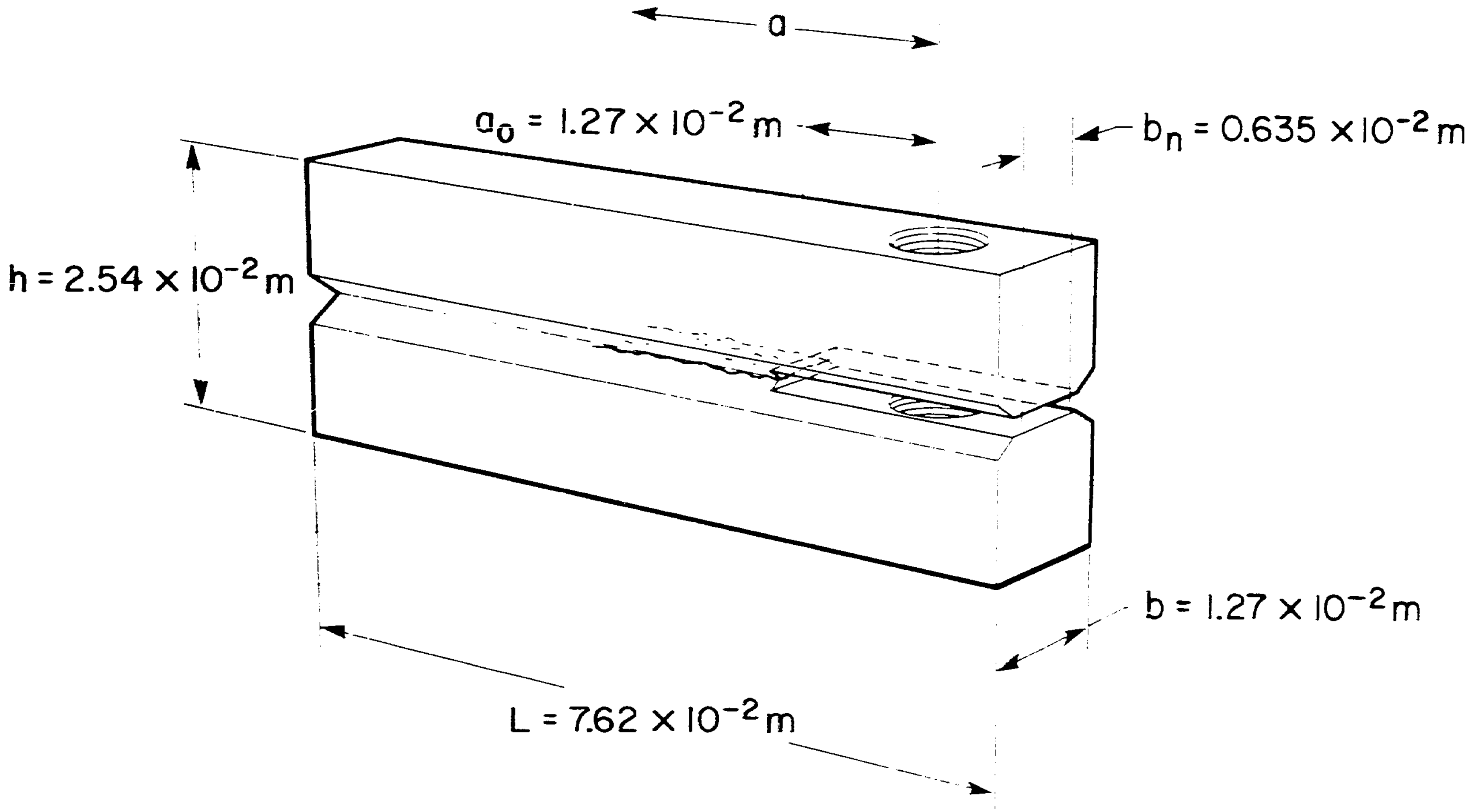

a
$a_0 = 1.27 \times 10^{-2}$ m
$b_n = 0.635 \times 10^{-2}$ m
$h = 2.54 \times 10^{-2}$ m
$b = 1.27 \times 10^{-2}$ m
$L = 7.62 \times 10^{-2}$ m

Fig. 4

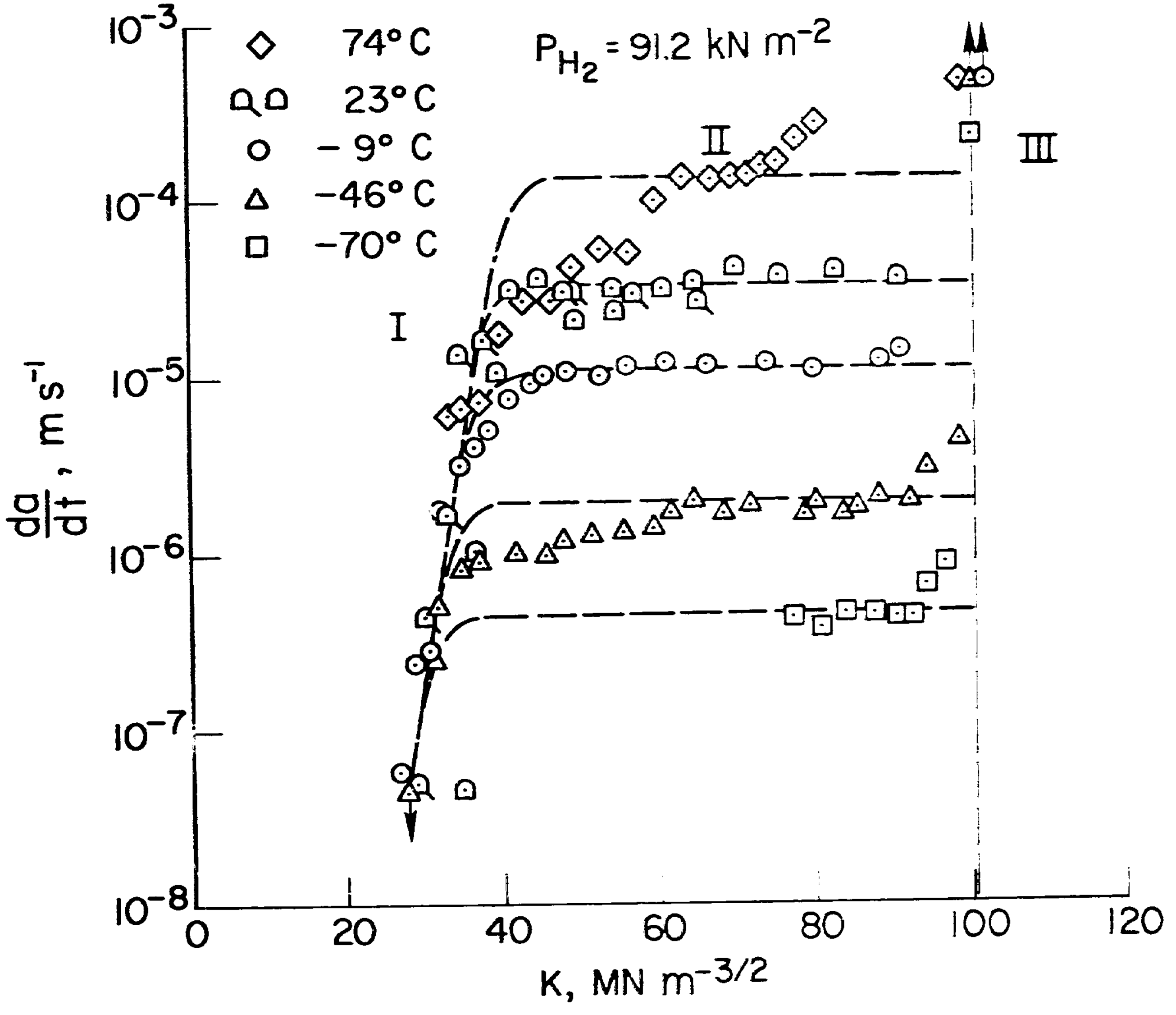
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
$\frac{da}{dt}$, m s^{-1}
0
20
40
60
80
100
120
K, MN $m^{-3/2}$
◇ 74° C
ᑫᗝ 23° C
○ − 9° C
△ −46° C
□ −70° C
P_{H_2} = 91.2 kN m^{-2}
I
II
III

Fig. 5