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EFFECTS OF ADSORPTION ON STRENGTH

By

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by

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ABSTRACT

Adsorbed surface-active species can influence the strength of materials by affecting cohesion and dislocation behavior at the surface, and possibly by affecting dissolution behavior in mildly corrosive environments. In this paper, these and other possibilities are discussed in connection with such phenomena as liquid metal embrittlement, stress-corrosion cracking, complex-ion embrittlement, Rebinder effects, the adsorption-locking of dislocations, and the photo- and electromechanical effects.

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1. INTRODUCTION

The materials scientist's approach to the problem of producing increasingly strong materials, or materials of improved strength-to-weight ratio, has been largely confined to manipulation of the metallurgical variables, composition and structure. However, the strength of a material also can be significantly affected by the chemical variable, environment[1]. This paper will be particularly concerned with some of the intriguing and important variations in mechanical behavior associated with the adsorption of certain surface-active species on stressed materials. In many instances the mechanisms involved are not fully understood, so that some of the hypotheses to be presented must be considered speculative in nature. In brief, however, there appear to be three ways in which an adsorbed surface-active species can affect strength (i) by reducing the surface free energy, or the cohesion of a solid locally (ii) by adsorbing at and affecting the behavior of dislocations at the surface, and (iii) by affecting dissolution behavior in a corrosive environment.

The first of these possibilities has received most attention in the past. In particular, several workers[2-4] have proposed that the phenomenon of liquid metal embrittlement* is associated with a reduction in the surface free energy of the solid metal by the adsorbing liquid metal species. Since surface free energy is defined as the work necessary to form unit area of

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* Throughout the text, the term embrittlement is used to denote a reduction in strength or ductility; it is not meant to imply that the fracture process necessarily occurs in a completely brittle manner.

surface by a process of division[5], such a proposition is undoubtedly correct, but it also is not particularly informative[6]. It does not provide any insight into the mechanism of embrittlement on an atomic or electronic scale, nor does it account for the specificity* of the observed phenomena.

In view of the limitations of the reduction-in-surface free energy hypothesis, it has been suggested that it might prove more worthwhile to consider that embrittlement is associated with a localized reduction in cohesion in the vicinity of certain chemisorbed species[6-8], and then to seek an understanding of the manner in which such an effect could come about. Cohesion could be reduced locally by inducing a redistribution of the bonding or valence electrons between nearby ions in the surface layers. Such a phenomenon might be expected to influence dislocation motion[1], and also the initiation[9,10] and propagation[6,8,11,12] of cracks. Some evidence for such effects will be presented below. However, the electronic interactions involved in the chemisorption of various species on metals are not at all understood[13], and only recently have attempts been made to understand such effects in the semiconductor materials[14].

The second possibility is based on the hypothesis that, since the mechanical behavior of most crystalline solids is governed by the generation and motion of dislocations, the most direct manner in which an adsorbed species could affect mechanical behavior would be by interacting with the dislocations where they meet the surface[15]. As a result, one might expect

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*For example, gallium embrittles cadmium but not magnesium; mercury embrittles zinc but not cadmium, etc.

the operation of surface sources[15,16], the core structure of dislocations at the surface[15,17], and the cross-gliding of screw dislocations near the surface[15,18] to be affected, with consequent variation in the yielding behavior of the material.

The third possibility is based on observations of the effects of adsorbed step-poisons on the dissolution behavior of solids in mildly corrosive environments, and in particular of their ability to cause tunnel corrosion, i.e., the formation of "etch-tunnels"[19,20], Fig. 1. This form of dissolution may be relevant to stress-corrosion cracking in certain metallic alloys[1], and the presence of such stress concentrators in notch-sensitive (high-strength) materials would certainly be deleterious.

These possibilities will now be considered in connection with recent experimental observations on environment-sensitive mechanical behavior.

2. EFFECTS OF ADSORPTION ON COHESION

Recent thinking on the mechanism of liquid metal embrittlement has been based on the hypothesis that embrittlement results from a localized reduction in cohesion of the solid metal due to chemisorption of the liquid metal at regions of strain in the lattice[6-8], e.g., at a stressed crack tip. While it is difficult to devise experiments to evaluate this reduction-in cohesion hypothesis directly, studies utilizing the double cantilever cleavage technique demonstrated that whereas some 90 ergs/cm^2 is required to propagate a cleavage crack in zinc immersed in liquid nitrogen, only some 50 ergs/cm^2 is

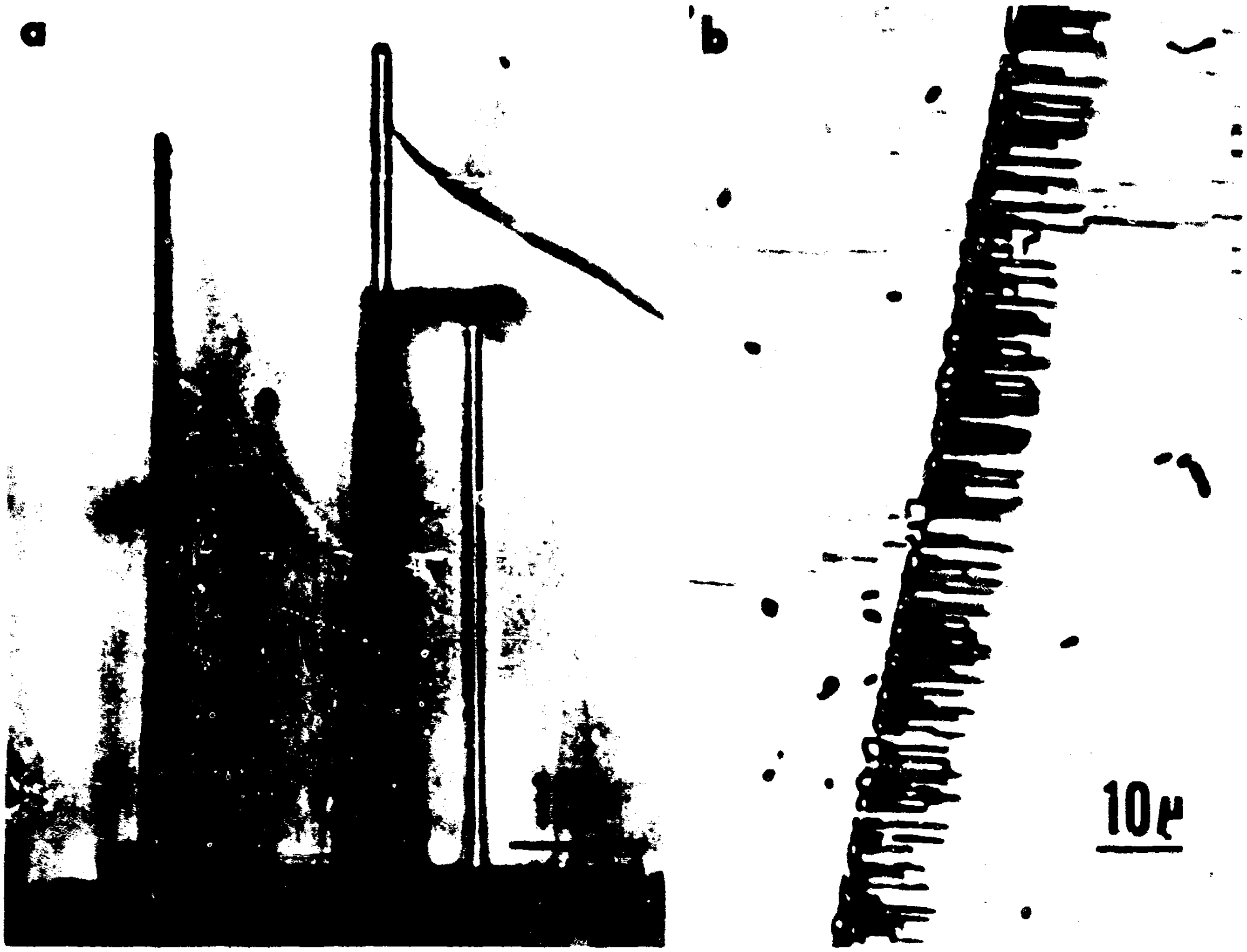

Fig. 1- Illustrating tunnel-corrosion in lithium fluoride. (a) Negative-platelets and a negative-whisker in cross-section (b) tunnels associated with a sub-boundary. Transmitted light. The etchant was 2-5 × 10^{-6}N stearic acid in water. (After Westwood and Rubin[19].)

required to propagate a similar crack at room temperature in the presence of mercury, Fig. 2[6]. Since the value of 90 ergs/cm^2 is considered to be the true surface free energy of the basal plane in zinc, this result suggests that a genuine reduction in cohesive strength of the "bonds" across the basal plane does occur in the presence of mercury*.

The same investigation[6] also provided evidence to support the view that in certain adsorption-induced embrittlement phenomena, the total energy involved in propagating a crack, Φ_p, can be represented as the product of the terms γ_o, ρ, and η ; γ_o being the true surface free energy of the fracture plane; ρ being defined as (a_p/a_o), a_p being the actual radius of the crack tip and a_o the interatomic distance across the fracture plane - thus ρ is a dimensionless variable dependent upon the degree of plastic relaxation in the vicinity of the crack tip; and η being termed a "coefficient of embrittlement", and defined as the ratio of the energies required to separate base-metal atoms at a crack tip in the presence and absence of the embrittling species. The significance of this relationship is that Φ_p is a multiple of

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*Recent studies of the variations in electrical conductance, ferromagnetic moment and ferromagnetic anisotropy of tungsten, iron and nickel with chemisorption of oxygen, carbon monoxide and nitrogen have indicated that these species weaken the binding of the metal surface atoms; hydrogen does not[13]. It is possible that such techniques could be advantageously applied to the problem of liquid metal embrittlement in certain systems. Incidentally, the observation that hydrogen did not reduce surface cohesion suggests that the adsorption of hydrogen may not be an important factor in the hydrogen embrittlement of steels.

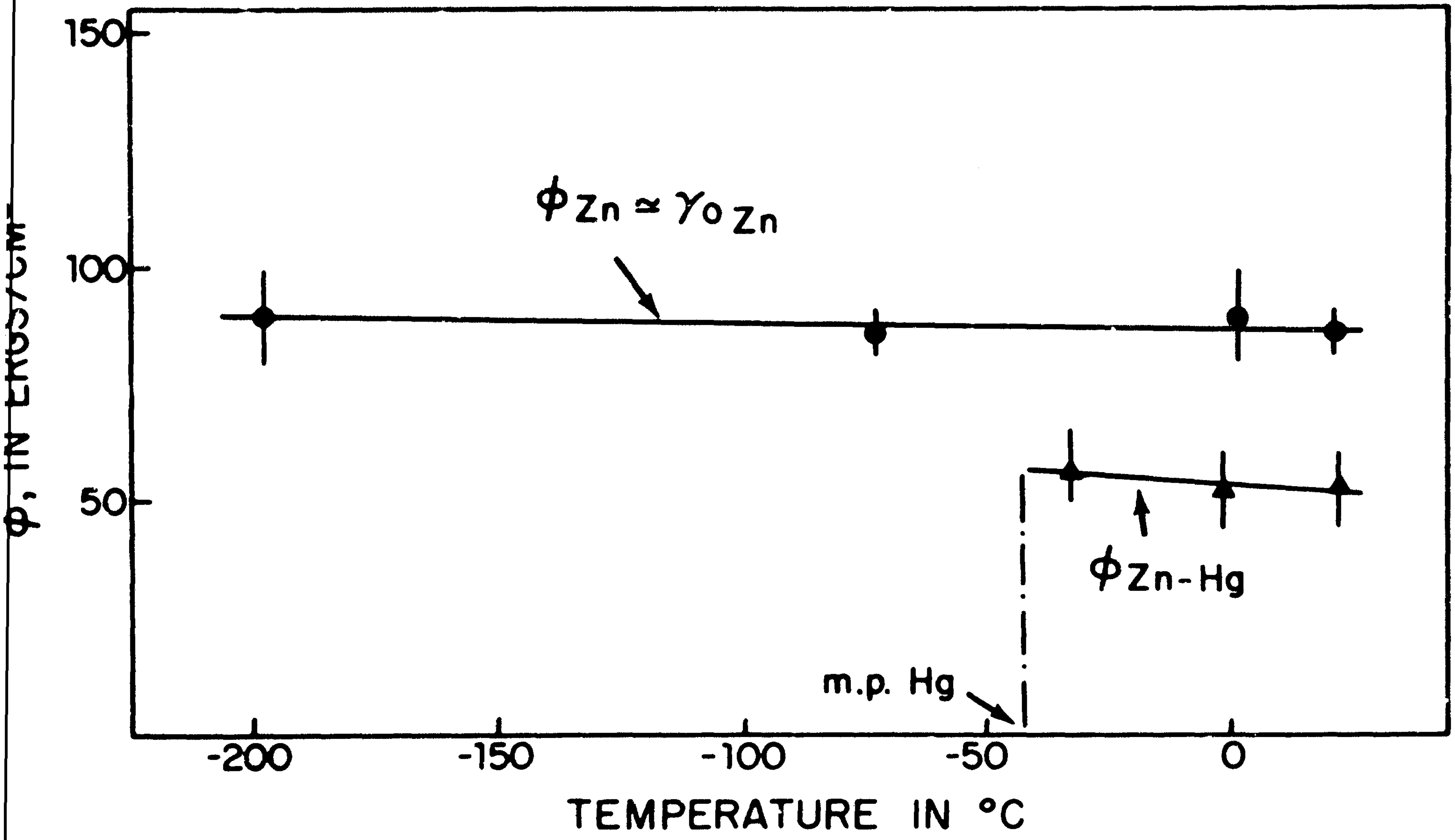

Fig. 2- Effects of temperature and mercury environment on the cleavage fracture energy, ϕ, for (0001) planes of zinc. (Westwood and Kamdar[6].)

γ_o, and not the sum of two independent terms of γ_o and p^2; ρ being the energy disipated by plastic relaxation in the vicinity of the crack. Thus if γ_o is reduced by the factor η (η being < 1 for an embrittling environment), then Φ_P is reduced in proportion. For the zinc-mercury couple at 298°K, η was determined to be ~ 0.6, and for the zinc-gallium couple at the same temperature, η was 0.48.

The value of the ratio η can also be estimated from crack initiation studies on liquid metal-coated, coarse grained specimens by means of the relationship $(\sigma_{F_{A-B}}/\sigma_{f_A})^2 = \eta$; where $\sigma_{F_{A-B}}$ is the brittle fracture stress of specimens of metal A when coated with liquid metal B, and σ_{f_A} is the flow stress of solid metal A [9]. From such studies, the value of η for the zinc-mercury couple at room temperature was again found to be ~ 0.60.

Recently Stoloff et al.[21] have estimated the value of η for the Fe-49%Co-2%V alloy-mercury couple by means of the relationship $\eta = (\sigma_F k)_{Hg}/(\sigma_F k)_{air}$; σ_F being the appropriate fracture stress, and κ the grain size dependence of the flow stress. For this system, η was $\simeq 0.77$.

Observations on several liquid metal embrittlement couples have established that the "mechanical" prerequisites for embrittlement are a tensile stress, and either a pre-existing crack, or some measure of plastic deformation and the presence of a stable obstacle to dislocation motion in the lattice[4,22]. In other words, a concentrated tensile stress resulting in highly strained bonds across the fracture plane. It is also known that metals which under equilibrium (unstressed) conditions exhibit very limited mutual affinity - e.g., little or no solid solubility and an absence of intermetallic compound formation - under stressed conditions often constitute embrittlement couples[23]. The cadmium-gallium and iron-cadmium systems provide examples of this behavior. Whether from this it may be inferred that the embrittlement mechanism involves a "strain-activated" chemisorption process[6] is as yet uncertain.

The empirical rule that systems which form stable intermetallic compounds tend not to exhibit embrittlement phenomena[23] also is in accord with the reduction-in-cohesion theory of embrittlement, for the adsorption of liquid metal atoms which were capable of forming strong intermetallic bonds with solid metal atoms at, for example, a crack tip, would be unlikely to reduce the energy required to propagate this crack and thereby induce brittle behavior. Indeed, the converse would appear more likely. This conclusion suggests a possible means of inhibiting liquid metal embrittlement in certain systems. Suppose that it were expedient to use a certain liquid metal B as a coolant for a component of solid metal A - but that under conditions of stress these two metals constituted an embrittlement couple. It is suggested that the addition of a soluble element C to the liquid metal B, element C being chosen because of its known tendencies to form high melting point (strongly-bonded) intermetallic compounds with solid metal A, might inhibit embrittlement in [illegible]stem. Inhibition could result either from the simple screening of A from B by C, caused by preferential adsorption of C on A; or as a result of the formation of "strong" A-C bonds at, for example, a crack tip, effectively reducing the ability of the crack to propagate under the applied stress.

Preliminary experiments to evaluate this possibility have been encouraging. For example, barium is slightly soluble in liquid mercury at room temperature, and is known to form stable intermetallic compounds with zinc, such as $Zn_{13}Ba$ [24]. Thus the addition of a small amount of barium to mercury might be expected to reduce or inhibit the embrittlement of zinc by mercury. Such an effect has been observed[25]. The fracture stress of polycrystalline zinc specimens amalgamated with pure mercury was 0.59 ± 0.15 Kg/mm^2; the fracture stress of similar specimens coated with mercury containing 0.3 a/o barium was 0.98 ± 0.32 Kg/mm^2 - about a 70% improvement.

Embrittlement phenomena apparently involving a localized reduction in cohesion associated with the adsorption of an active species also have been observed for non-metallic materials. For example, when polycrystalline silver chloride is exposed to environments containing highly charged complex ions, such as 6N sodium chloride containing $AgCl_4^{3-}$ ions or concentrated hydrochloric acid containing $CuCl_5^{3-}$ ions, its fracture mode changes from ductile and transcrystalline to brittle and intercrystalline[10-12, 26]. Both positively and negatively charged complexes can cause brittle behavior, and it has been found that the degree of embrittlement increases with concentration of the critical complex species present in the environment; increases with charge on the complex-ion; is a function of the distribution of charge on the complex; and for negatively charged complexes, is very sensitive to the applied stress, Fig. 3. Embrittlement by silver chlorocomplexes can be prevented by the addition to the environment of such inhibitor-ions as Cs^+ and K^+ (Fig. 4), Zn^{2+}, Cd^{2+} and Hg^{2+} etc. Such ions either interact with

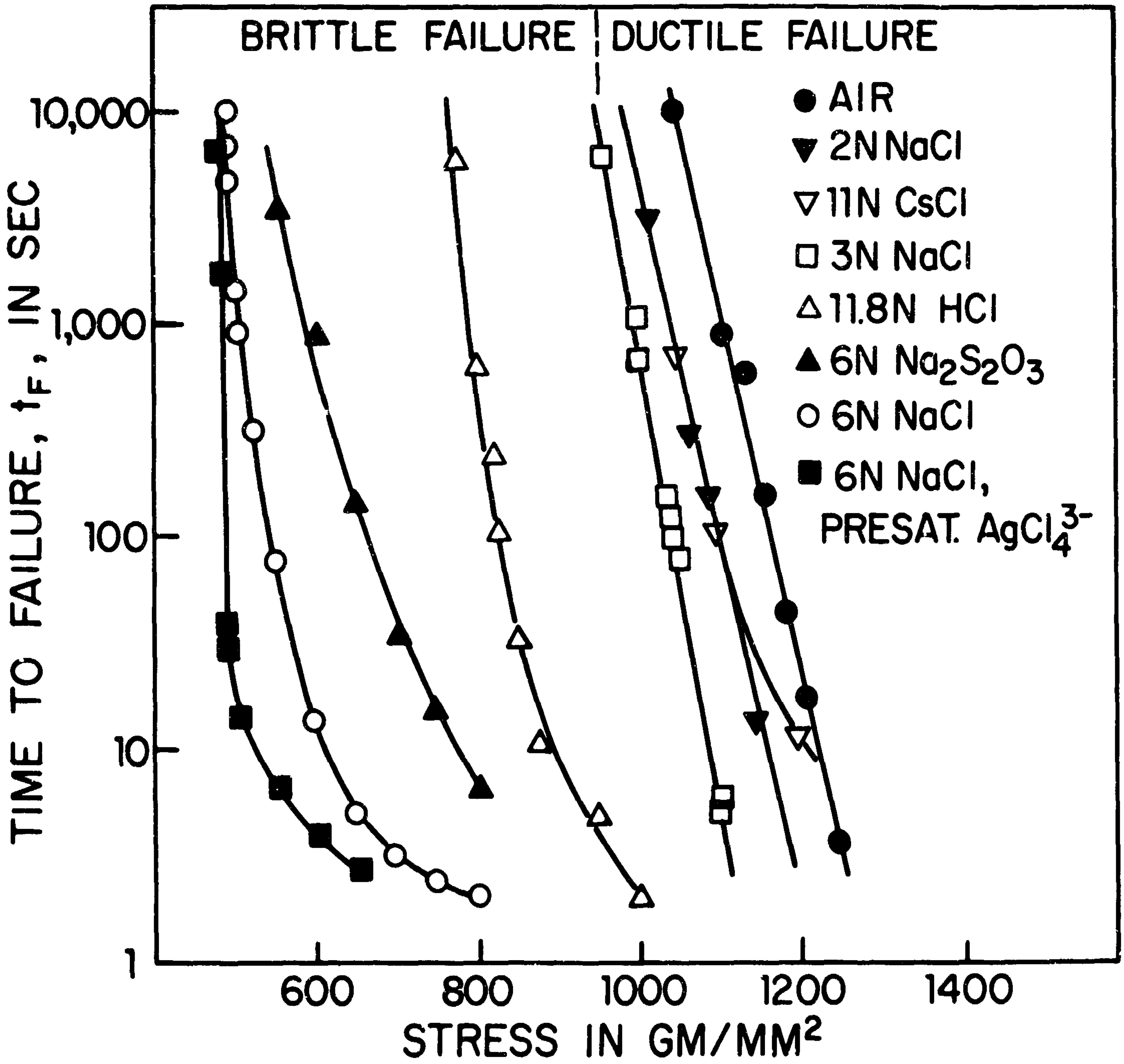

Fig. 3- Effects of applied stress and environment on the time to failure of polycrystalline silver chloride at room temperature. Note variation in degree of embrittlement with concentration of aqueous sodium chloride, the effect of presaturating 6N sodium chloride with $AgCl_4^{3-}$ complexes, and the stress sensitivity of the phenomenon in the latter environment. (Westwood, Goldheim and Pugh[12].)

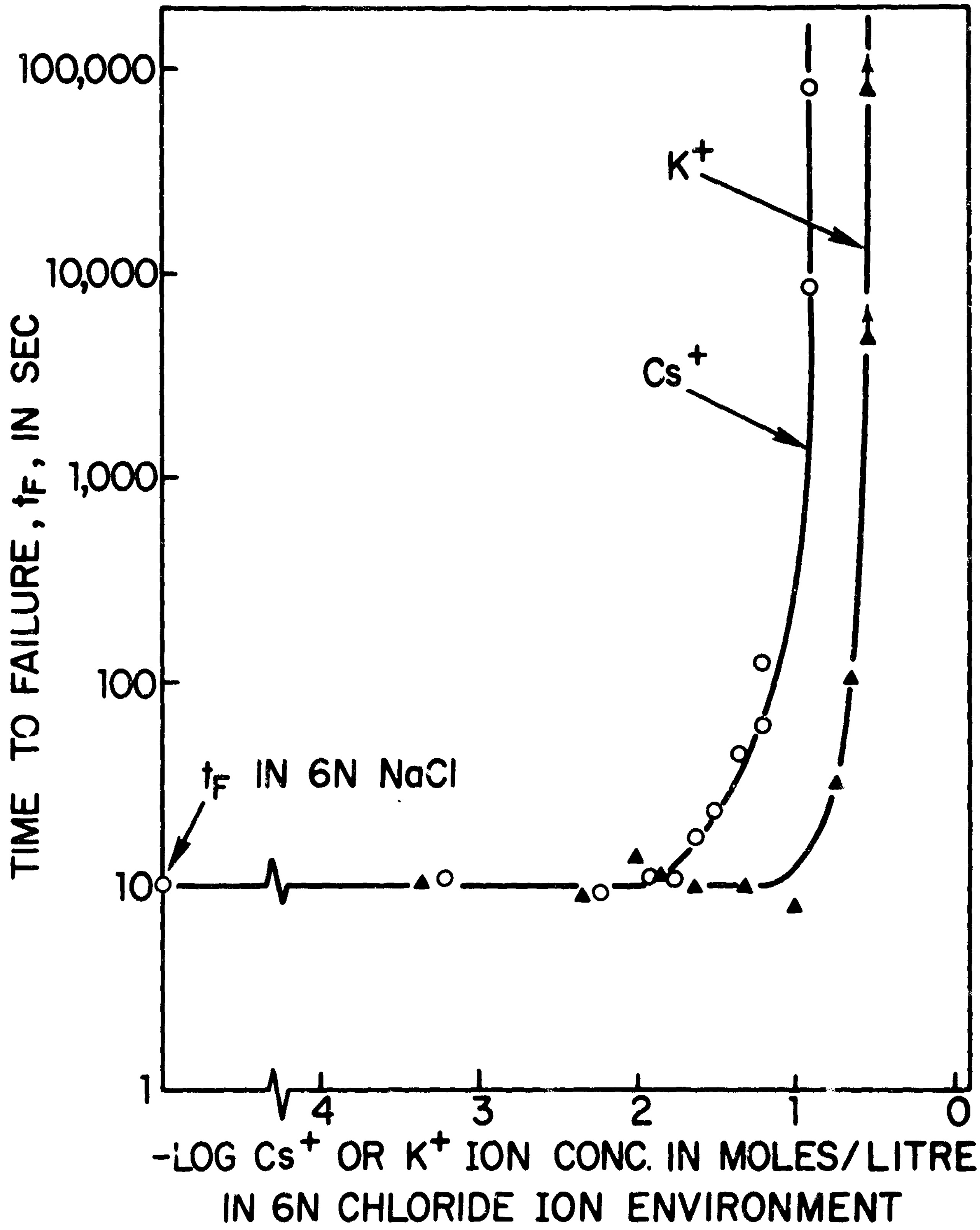

Fig. 4- Inhibition of embrittlement in a 6N chloride environment resulting from the replacement of Na^+ ions by K^+ or Cs^+ ions. The applied stress was 600 g/mm^2. (Westwood, Goldheim and Pugh[12].)

(screen) the negatively charged complex ions, effectively reducing their charge, or cause a chemical breakdown of the critical complexes, forming less embrittling species. Monocrystals also can be embrittled, providing that they contain a pre-existing crack[11].

The results of metallographic studies of this phenomenon are particularly interesting. Figure 5, for example, illustrates the observation that when a polycrystalline specimen is deformed in an embrittling environment, cracks are formed only where slip bands are arrested at a grain boundary, and that they then propagate in an intercrystalline and relatively brittle manner[10-12,26]. Other observations revealed that cracks were not formed when the stress field associated with an arrested slip band was relieved by slip in the neighboring grain[11,12].

On the basis of these and other observations, and bearing in mind that bonding in silver chloride is partially covalent[27,28], it has been proposed[10,12] that embrittlement is associated with the adsorption of complex-ions of high charge in the vicinity of strained surface bonds. More specifically, when a highly charged complex-ion adsorbs at the site of an ion of opposite charge, the distribution of shared or bonding electrons between this ion and its neighbors is likely to be considerably perturbed. If the perturbation is such that cohesion is reduced locally, as seems to be the usual case, then, in the presence of an applied tensile stress, embrittlement will result. This essentially simple hypothesis is consistent with all the experimental observations made so far, and also successfully predicted that complex-ion embrittlement phenomena would not be manifested by relatively "pure" ionics, such as sodium chloride[12], since there are no "shared" electrons to be affected.

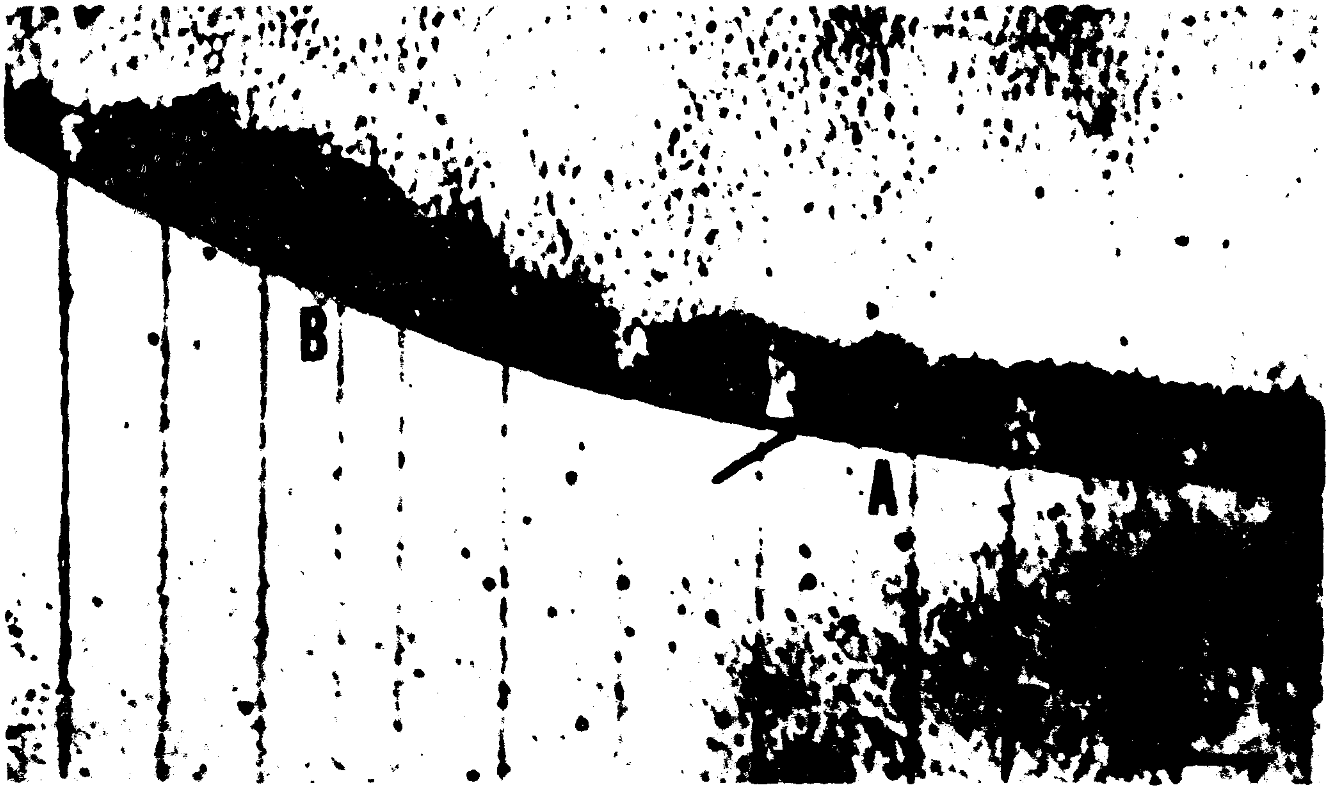

Fig. 5- Polycrystalline silver chloride stressed at 300 g/mm^2 in solution of 3.8N $CuCl_2$ in 11.8N HCl containing copper chlorocomplexes (probably $CuCl_5^{3-}$); demonstrating that cracks are initiated where slip bands are arrested at a grain boundary, as at A, and propagate in a brittle, intercrystalline manner, as at B. Transmitted light. (Westwood and Goldheim[26].)

Recent studies have also demonstrated that adsorbed water can play a more significant role in determining such surface-sensitive mechanical properties as microhardness and fatigue strength than hitherto credited. For example, Westbrook and Jorgensen[29,30] have studied the time dependent microhardness observed when such covalent or ionic materials as germanium (Fig. 6), alumina, titanium carbide, magnesium oxide and lithium fluoride are tested in (moist) air. They found that this dependence disappeared when the specimens were pre-heated to desorb water films and then tested under "dry" toluene. Metallic materials, such as copper, NiAl or tin, did not exhibit such effects.

Westbrook also has demonstrated that such phenomena as the photomechanical (Fig. 7(a)) and electromechanical (Fig. 7(b)) effects* in semiconductors are also related to the presence of adsorbed water films[30].

The mechanisms of these phenomena are not yet clear. Holt[17] has suggested that they involve an adsorption-induced change in the core structure of dislocations in the surface layers; this possibility will be discussed in section 3. Another possibility is that an adsorption-induced reduction in surface cohesion is involved. For semiconductor materials, the chemisorption process is considered to involve the localization of electrons or holes in chemisorption bonds at the surface[31]. Since either illumination by light of some characteristic frequency, the presence of an external field,

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*The photomechanical effect is the change in surface hardness of a material when it is subjected to illumination; the electromechanical effect is the change in surface hardness of a material when a small potential (< 0.1V) is impressed between the indenter and test surface, or a low current (< 100 MA) is passed through the specimen.

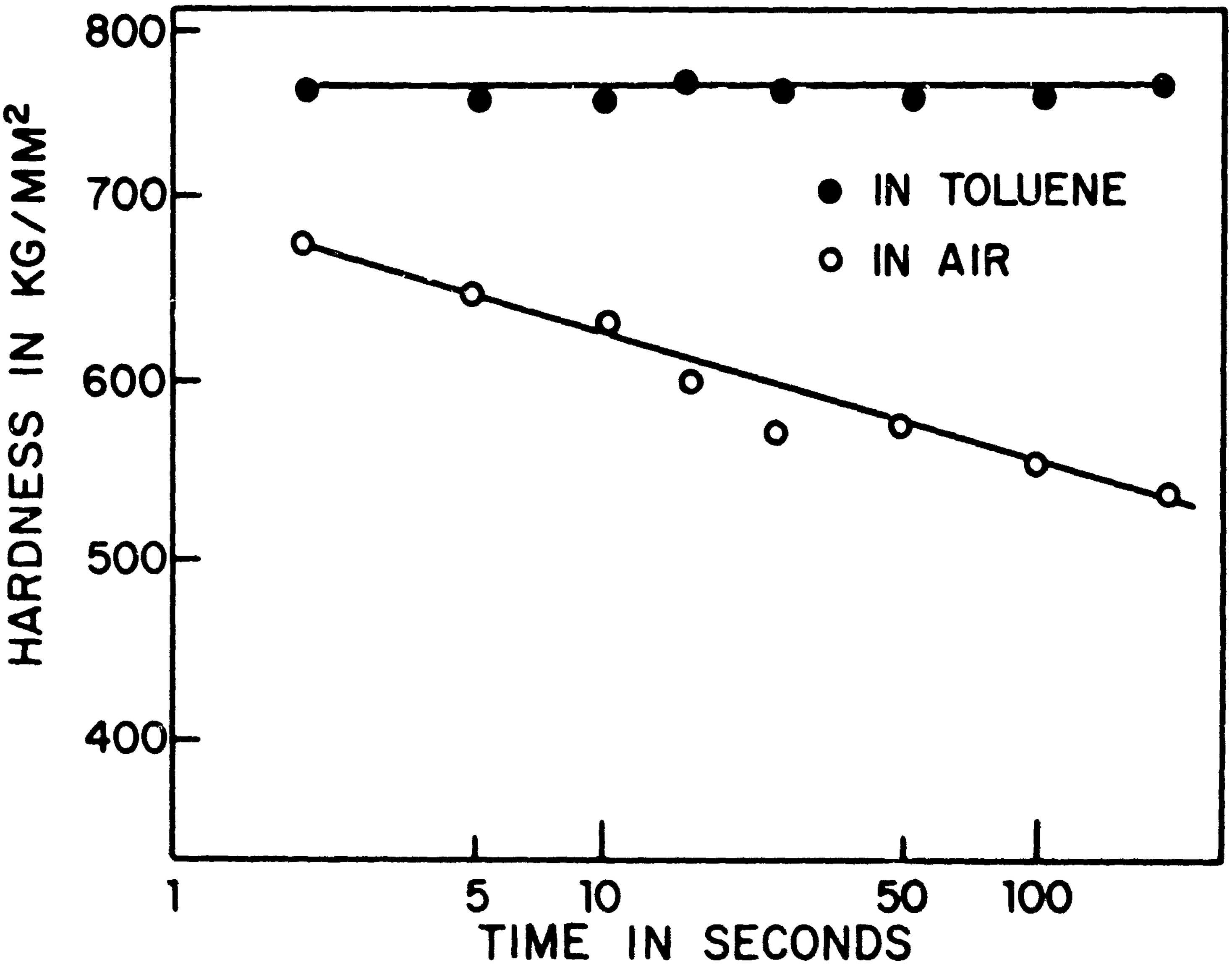

Fig. 6- Illustrating the time dependence of hardness (anomalous creep indentation effect) of germanium in (moist) air. (After Westbrook[30].)

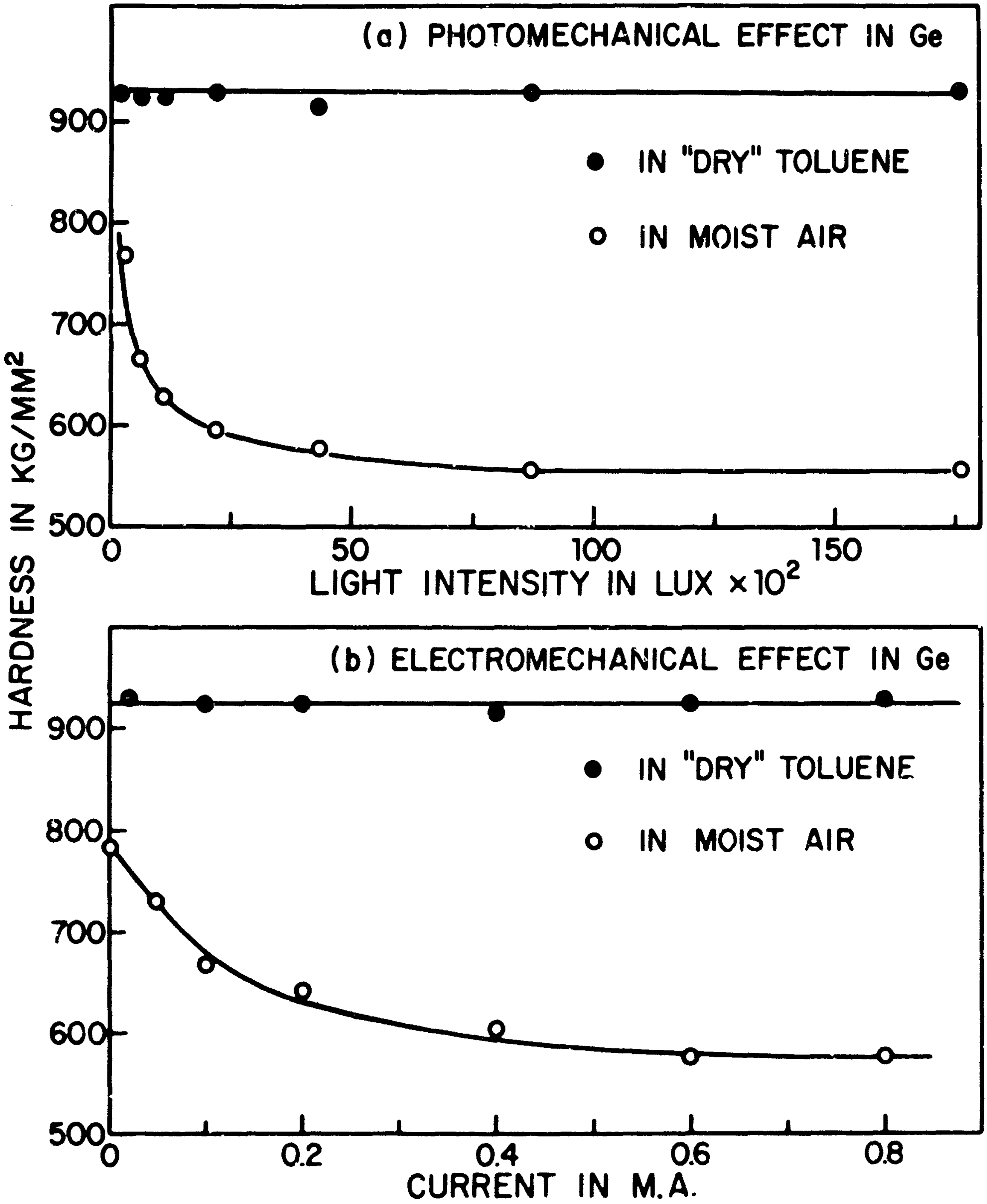

Fig. 7- Demonstrating the influence of adsorbed water on (a) the photomechanical effect, and (b) the electromechanical effect in a germanium crystal. The "moist" air was of 40% relative humidity. (After Westbrook[30].)

or the passage of a current is likely to affect the relative surface concentrations of these electron and holes, these factors also will affect the degree and type of chemisorption occurring. If, in turn, the chemisorption process affects cohesion, then it seems reasonable that in the presence of water vapor some variation in surface microhardness would occur with type of illumination or the passage of a current through the specimen.

Adsorbed water molecules also can affect the strength of metallic materials. For example, Nichols and Rostoker have recently investigated the effects of adsorbed organic liquids on the fatigue life of high strength steels[32]. A systematic variation in lifetime with chain length of the organic molecules was noted, Fig. 8, but water was found to be the most effective embrittling environment evaluated. Moreover, when a strong dehydrating agent ($CaSO_4$) was added to the organic environments, reductions in strength were no longer observed - compare the data for ethyl alcohol in Fig. 8. On the basis of these and other observations, it was concluded that the reductions in strength observed in the organic liquids were in fact related to the adsorption of water on the surface of the test specimens, and not to the adsorption of organic polar molecules as earlier proposed by Karpenko and coworkers[33]. The relationship between chain length of the alcohol and fatigue life illustrated in Fig. 8 can be interpreted in terms of the known decrease in solubility of water with increasing molecular weight of the alcohols.

The decreases in the mechanical properties of metals apparently associated with the adsorption of long chain fatty acids, amines and alcohols from organic solvents have long been a source of controversy among experimenters[15, 33-39]. Such phenomena are usually referred to as Rebinder effects,

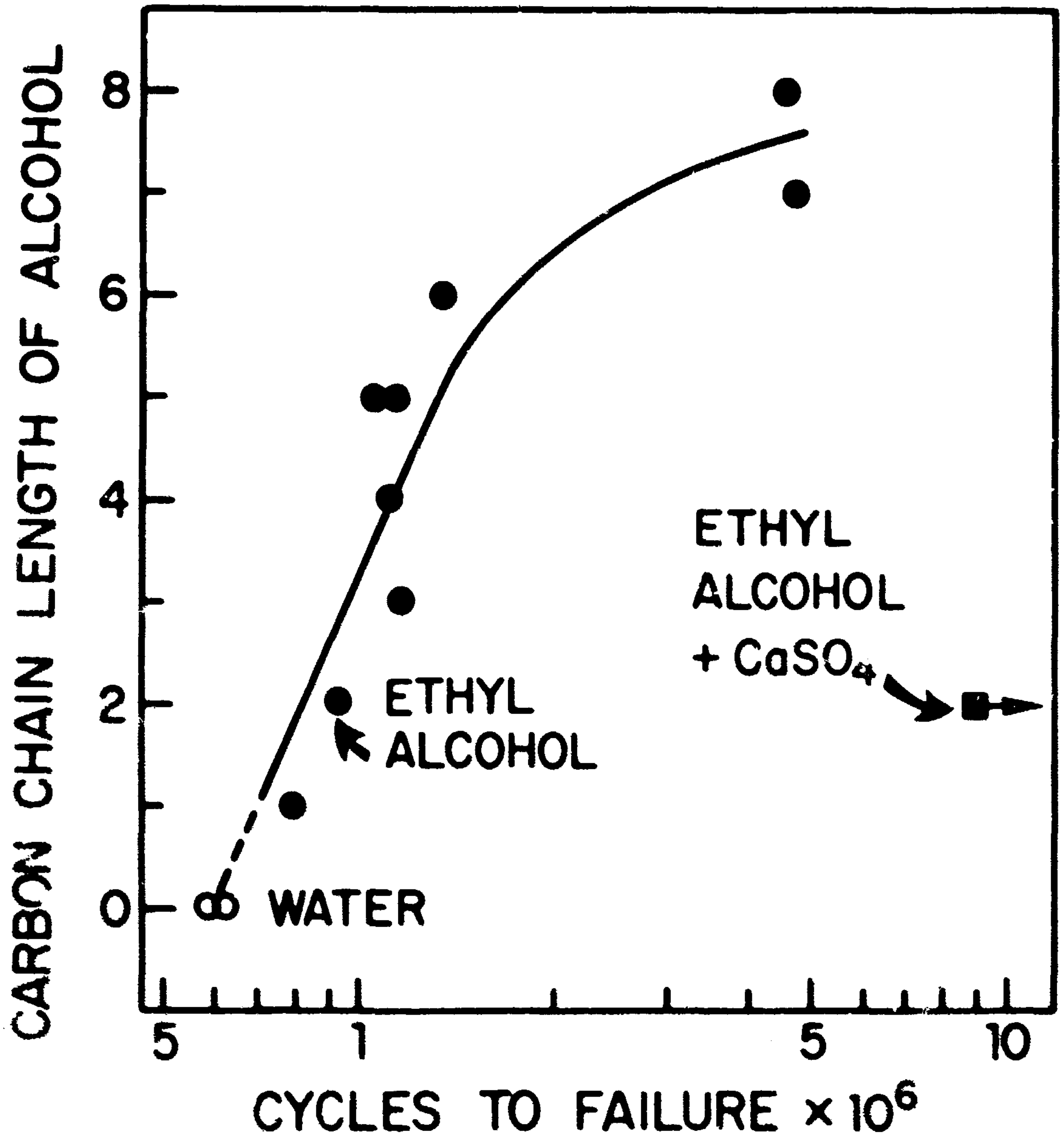

Fig. 8- Variation in fatigue life of a modified AISI-4340 steel when tested in several primary alcohols, and in water. Note effect of dehydration with $CaSO_4$ on fatigue life in ethyl alcohol. (After Nichols and Rostoker[32].)

and Rebinder and his co-workers have suggested that they are a consequence of the decrease in surface energy which accompanies adsorption[33, 34]. Several workers[35-37, 39] have unsuccessfully attempted to reproduce the decrease in yield stress reported to occur in a surface-active medium[33, 40]. However, some variations in the rate of work hardening of aluminum and copper crystals when tested in paraffin oil containing different concentrations of stearic acid have been observed[39]. These results exhibited marked similarities with others obtained in solvent environments, and thus it has been suggested[39] that fatty acid molecules react at the surface of the metal to form metal soap molecules, and that these then desorb into the environment. The rate of surface dissolution is thus a function of the concentration of fatty acid molecules in the environment, the rate of reaction at the surface, and the rate of desorption of the soap molecules. Significantly, no effects were observed when the paraffin oil was presaturated with the appropriate metal stearate, and no effects were observed with gold crystals. It is known that gold soaps are not normally formed because the free energy required is too large[41].

3. EFFECTS OF ADSORPTION ON DISLOCATION BEHAVIOR

A freshly-cleaved surface of lithium fluoride is clean, oxide-free, and contains the half-loop surface sources which are known to control subsequent yielding behavior. Thus it is an ideal material for examining the hypothesis that if adsorbed surface active molecules affect mechanical behavior, as suggested by Rebinder and co-workers[33, 34], they may do so by interacting with dislocations where the latter meet the surface[15]. From considerations of the model illustrated in the inset to Fig. 9, it was concluded[15] that in the presence of adsorbed polar molecules, such as the fatty acids, the operation of half-loop sources should be hindered, and that the yield stress of lithium fluoride should therefore be increased (not decreased as suggested by Rebinder and Likhtman[40]). This restraining effect has been termed "adsorption-locking", and an estimate of the magnitude of such locking can be made by use of the relationship $\Delta\tau = 2H/b^2 \cdot \ell$: where, Fig. 9, $\Delta\tau$ is the increase in stress required to move the screw component A-B of a half loop because of its adsorbed polar molecule; b is the Burgers vector of the dislocation; ℓ is the length A-B; and H is the heat of adsorption of the fatty acid molecule on lithium fluoride[15]. Assuming $b = 2.85 \times 10^{-8}$ cm, $\ell = 10\mu$ and $H \simeq 14 \times 10^{-3}$ ergs (~ 20 K cal/mole), $\Delta\tau$ is estimated to be of order 35-40 g/mm^2.

Experimental confirmation of the existence of adsorption-locking is shown in Fig. 9; the increases in yield stress observed averaged about 16 g/mm^2. However, such increases were then followed by a decrease in the rate of work hardening. Metallographic observations revealed that the latter effect was caused by differences in dislocation distribution between specimens having locked and unlocked surface sources.

In other studies it was found that solutions of fatty acids in water can serve as dislocation-revealing etchants for lithium fluoride, and that the C_{14} - C_{18} acids are particularly useful for they are capable of revealing the points of emergence of screw dislocations cross-gliding under the action of residual stresses in the crystal[18], Fig. 10. Now according to the

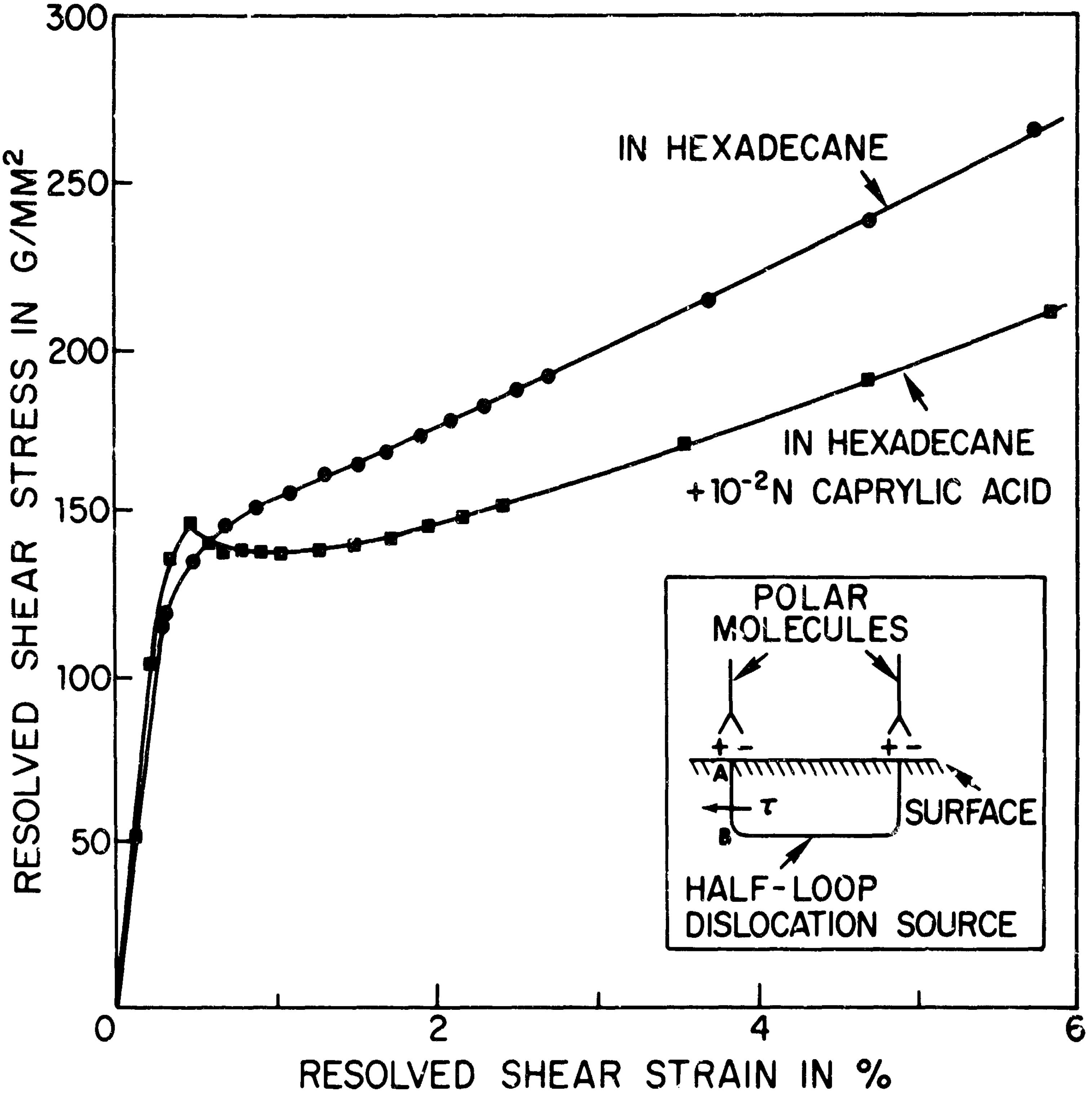

Fig. 9- Effect of adsorbed caprylic acid molecules on the yield and flow behavior of an as-cleaved lithium fluoride crystal. Inset illustrates adsorption-locking concept. (Westwood[15].)

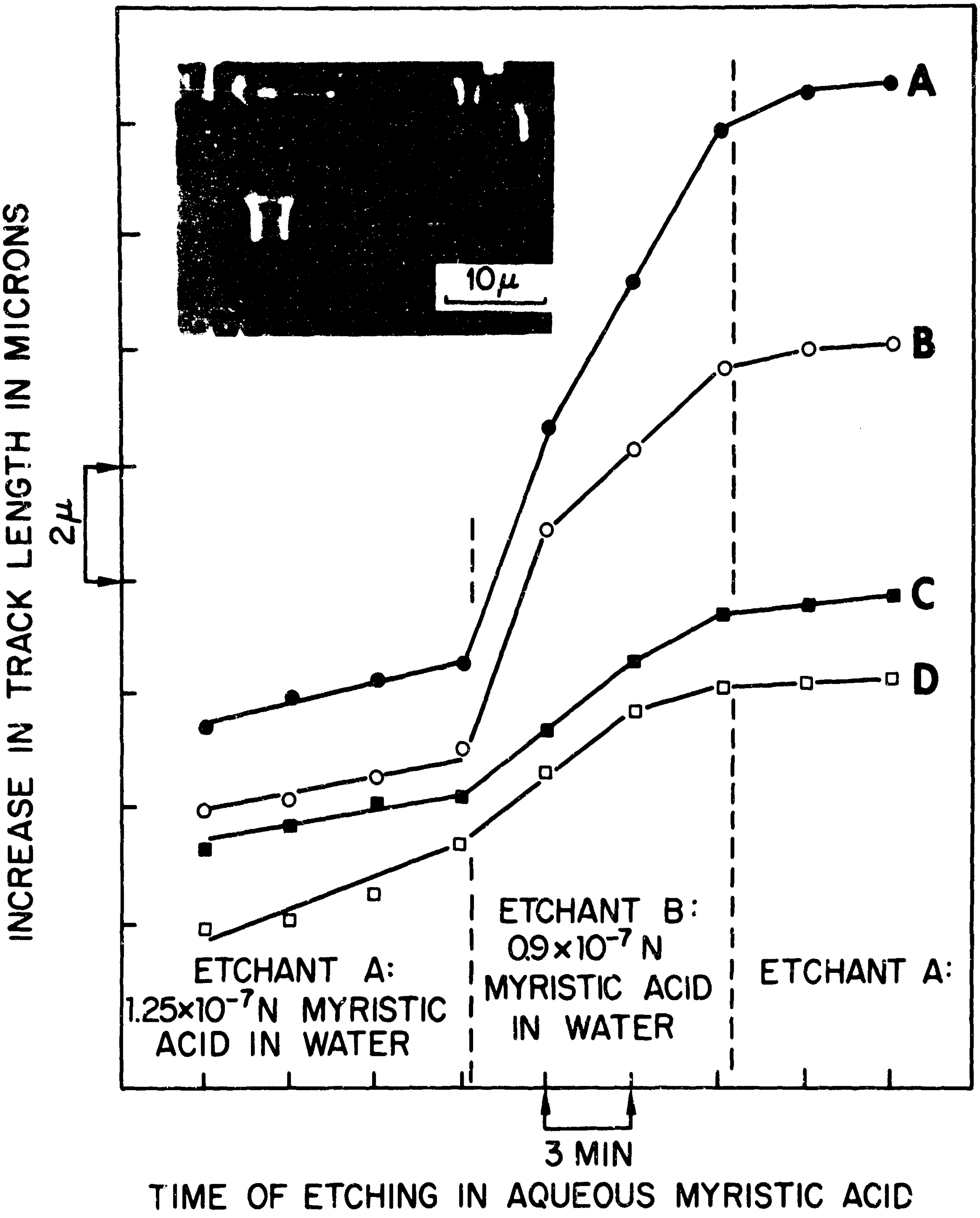

Fig. 10- Effect of concentration of myristic acid on the rate of cross-gliding (tracking) of screw dislocations at the surface of a lithium fluoride crystal. The inset provides an example of the dislocation tracks studied. (Westwood[15].)

adsorption-locking hypothesis[15], a dislocation is pinned when a polar molecule adsorbs on its emerging end, but is free to move when the molecule desorbs. Thus the rate of cross-gliding, or "tracking", should be inversely proportional to the fraction of time for which the dislocation is locked by an adsorbed polar molecule. This fraction can be controlled by the concentration of polar molecules present in the environment - the higher the concentration, the greater the fraction of time a polar molecule will be adsorbed at the dislocation, and vice versa. Figure 10 presents data from observations on four individual dislocations, and demonstrates that tracking rates were greater in the more dilute solution, as predicted. These data provide an interesting example of the environmental control of an individual lattice defect.

Recently, some possible examples of adsorption-locking effects in metal systems have been observed. During a study of the embrittlement of copper foils by molten bismuth involving electron transmission microscopy, Vook[42] noted that as dislocations were nucleated and moved away from a crack tip, liquid bismuth was pulled along with them. When the surface tension forces of the liquid bismuth finally overcame the apparent attraction of the dislocation, the bismuth film snapped back into the liquid reservoir, and the now free dislocation moved away at a much greater velocity. In other studies on liquid metal embrittlement, Tint[43] has observed that hardening occurs in the micro-strain region when brass is coated with mercury. Such an effort could result from the pinning of surface sources of dislocations by adsorbed mercury, although other explanations also may be suggested, e.g., a "hardening" of the surface layers to dislocation movement as a result of preferential removal of zinc by mercury.

The alternate possibility that liquid metal embrittlement involves inhibition of plastic relaxation in the solid by the liquid metal, for example at a crack tip, so that an otherwise ductile solid is induced to behave in a brittle manner, has been suggested by Meakin[16] and Gilman[44], and also considered independently by Westwood and Kamdar[45]. In the crack-tip example cited, the model assumes that crack-blunting dislocations are generated primarily at the surface in the vicinity of the crack tip, rather than in the bulk ahead of the crack tip, and that the presence of an "active" liquid metal can severely restrict the generation or operation of such surface-sources. On this hypothesis, however, one would expect that those liquid metals which are most strongly adsorbed on the solid metal would produce maximum source-locking, or inhibition, and hence maximum embrittlement. Thus, for example, those systems in which solid metal A and liquid metal B exhibit relatively low solid solubility, perhaps because of size factor considerations, but an otherwise high mutual affinity, as evidenced by a marked tendency to form intermetallic compounds, should constitute embrittlement couples. In practice this is not so - systems which exhibit intermetallic compound formation rarely exhibit embrittlement phenomena[23]. Indeed, some of the most severe examples of embrittlement occur in systems where even the two liquid phases are immiscible, e.g. cadmium-gallium[8].

Another way in which an adsorbed species might affect strength is by causing some change in the core structure of dislocations at the surface and thereby affecting their mobility. Such a possibility has been considered by

Holt[17] in connection with the photomechanical, electromechanical and anomalous creep-indentation effects observed in semiconductor materials, Figs. 6 and 7. Holt's suggestion is based on the hypothesis that dislocations in covalently bonded crystals contain broken or "dangling" bonds, which can lower their energy either by acting as electron acceptors, or by becoming involved in rearrangements which produce dragging points and reduce dislocation mobility. These are mutually exclusive alternatives; any change in the fraction of dangling bonds which are occupied by electrons changes the number of dragging points, the mobility of dislocations, and hence hardness. Now it is known that the adsorption of water induces a negative surface charge in germanium[14], and therefore changes the density and distribution of electrons in the surface states. Thus it does not seem unreasonable to suppose that such a phenomenon might in turn increase the ratio of occupied dangling-bonds to rearranged-bonds, increasing dislocation mobility, and hence reducing hardness, as demonstrated in Fig. 6. On the other hand, anomalous indentation creep effects also have been observed in ionic crystals such as lithium fluoride and magnesium oxide[30]. It would appear, therefore, that the mechanism proposed by Holt cannot be the general mechanism for these phenomena.

4. ADSORPTION AND STRESS-CORROSION CRACKING

At the present time, there does not appear to be any evidence which suggests, unambiguously, that stress-corrosion cracking involves an adsorption mechanism of the type thought to be involved in liquid metal or complex-ion embrittlement, namely, an adsorption-induced reduction in cohesion at regions of stress concentration. However this possibility was investigated recently[46-48] when, bearing in mind the complex-ion embrittlement of silver chloride, it was recalled that complex-ions play a significant role in the stress-corrosion cracking of α-brass in ammonia environments[49-50]. It was found that preconcentrating an aqueous ammonia environment with $Cu(NH_3)_5^{2+}$ ions reduced the time to failure of polycrystalline brass specimens at a given stress by two to three orders of magnitude, Fig. 11[48] (note the similar effect of preconcentration in complex-ion embrittlement phenomena; compare the curves for 6N sodium chloride in Fig. 3). However, subsequent experiments, such as weight loss determinations, revealed that embrittlement in the α-brass-ammonia system is not adsorption but dissolution controlled, and that more than one embrittlement mechanism is operative, the specific mechanism depending on the concentration of Cu^{2+}, OH^- and NH_4^+ ions present[47]. For example, in environments containing > 3 g/l Cu^{2+} ions, embrittlement is caused by the repeated formation and rupturing of a brittle surface layer or "tarnish"[51,52]. For environments containing < 2 g/l of Cu^{2+} ions, the embrittlement mechanism is less certain, but is believed to involve dezincification of the brass by reaction with the copper complexes. This may occur preferentially at piled-up groups of dislocations in the vicinity of grain boundaries, as indicated in the electron microscope observations of Tromans and Nutting[53].

However, the presence in solution of certain strongly adsorbing species may be relevant to stress-corrosion cracking in other systems by virtue of their significant effect on dissolution behavior. For example, in the mechanism proposed by Swann, Pickering and Embury[54,55] for the transcrystalline stress-

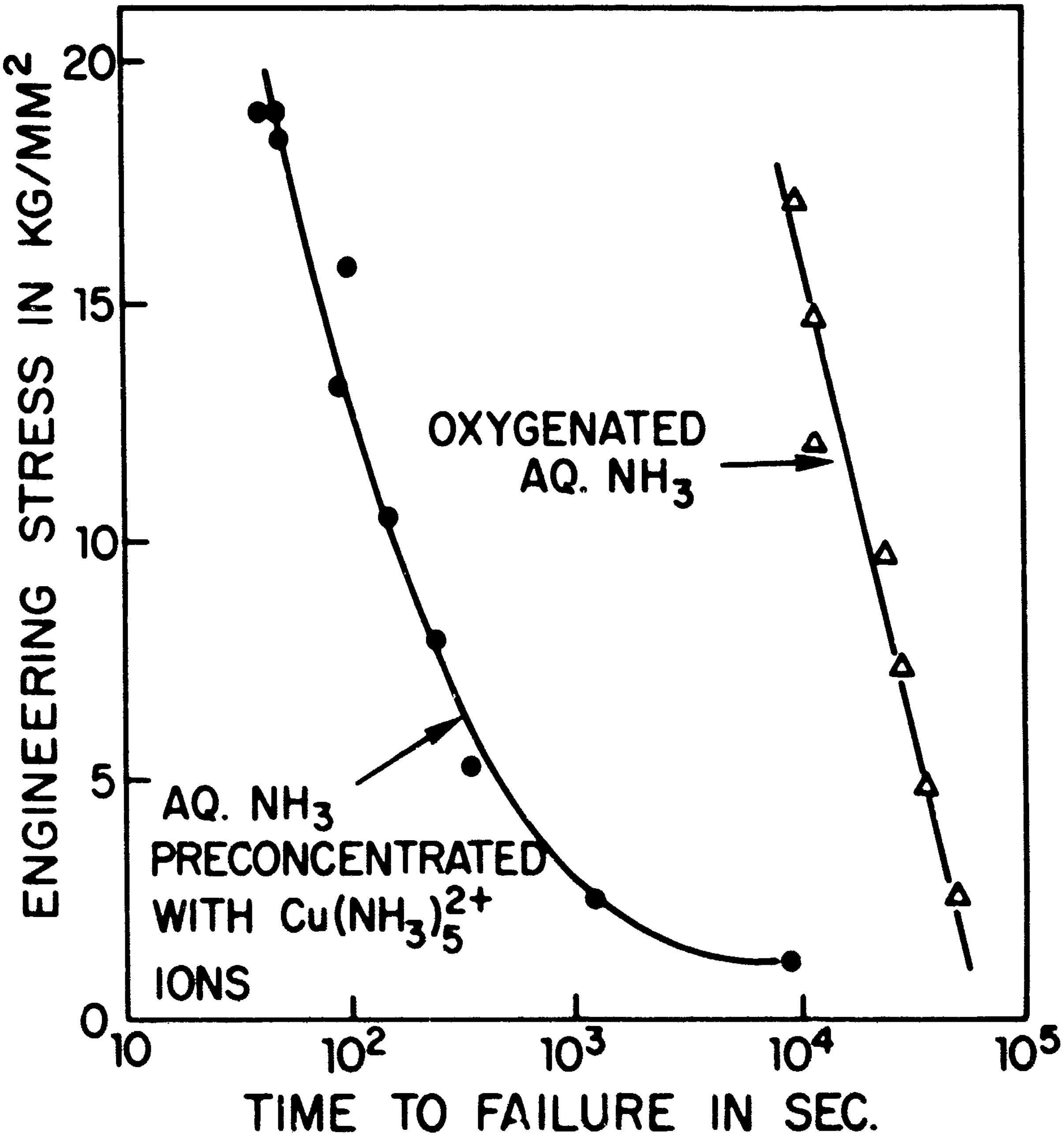

Fig. 11- Stress corrosion data for α-brass stressed in oxygenated aqueous ammonia (~ 15N), and in the same solution when preconcentrated with 6 g/l of copper as $Cu(NH_3)_5^{2+}$. (Pugh and Westwood[46].)

corrosion cracking of alloys of low stacking fault energy, or which exhibit short range order, it is postulated that the role of stress is to produce coarse slip lines which rupture pre-existing surface films, exposing temporarily "clean" slip steps (as proposed earlier by Champion[56] and Logan[57]). Tunnel corrosion then occurs at these steps, the tunnels occasionally, but not necessarily being nucleated at the points of emergence of dislocations or stacking faults, and sometimes tending to follow close-packed directions. Cracking then occurs by the ductile rupture of a slot weakened by many tubular corrosion pits, as illustrated in Fig. 12. Examples of such tunnels have been noted in copper - 25% gold exposed to 10% aqueous ferric chloride, magnesium - 7% aluminum exposed to sodium chloride-potassium chromate solutions, type 301 stainless steel exposed 42% magnesium chloride at 140°C[55], and aluminum exposed to aqueous sodium chloride[58]. Now similar tunnels have been found in lithium fluoride following immersion in a slightly corrosive environment (water) containing a strongly adsorbing step-poison, e.g. fatty acid molecules[19], Fig. 1, or ferric fluoride complexes[20]. In the absence of such poisons, tunneling did not occur. It is possible that tunnel corrosion in metals also is associated with the presence of strongly adsorbing step-poisons. For example, it is known that the chloride ion is strongly adsorbed on stainless steel[59]. Alternately, the adsorbing species might be a complex-ion, for example a metal-halide complex. Such complexes would be produced as a result of the initial general dissolution of the material in the corrosive environment. The metal ion in the complex need not necessarily be one of the major alloying constituents of the material, for concentrations of

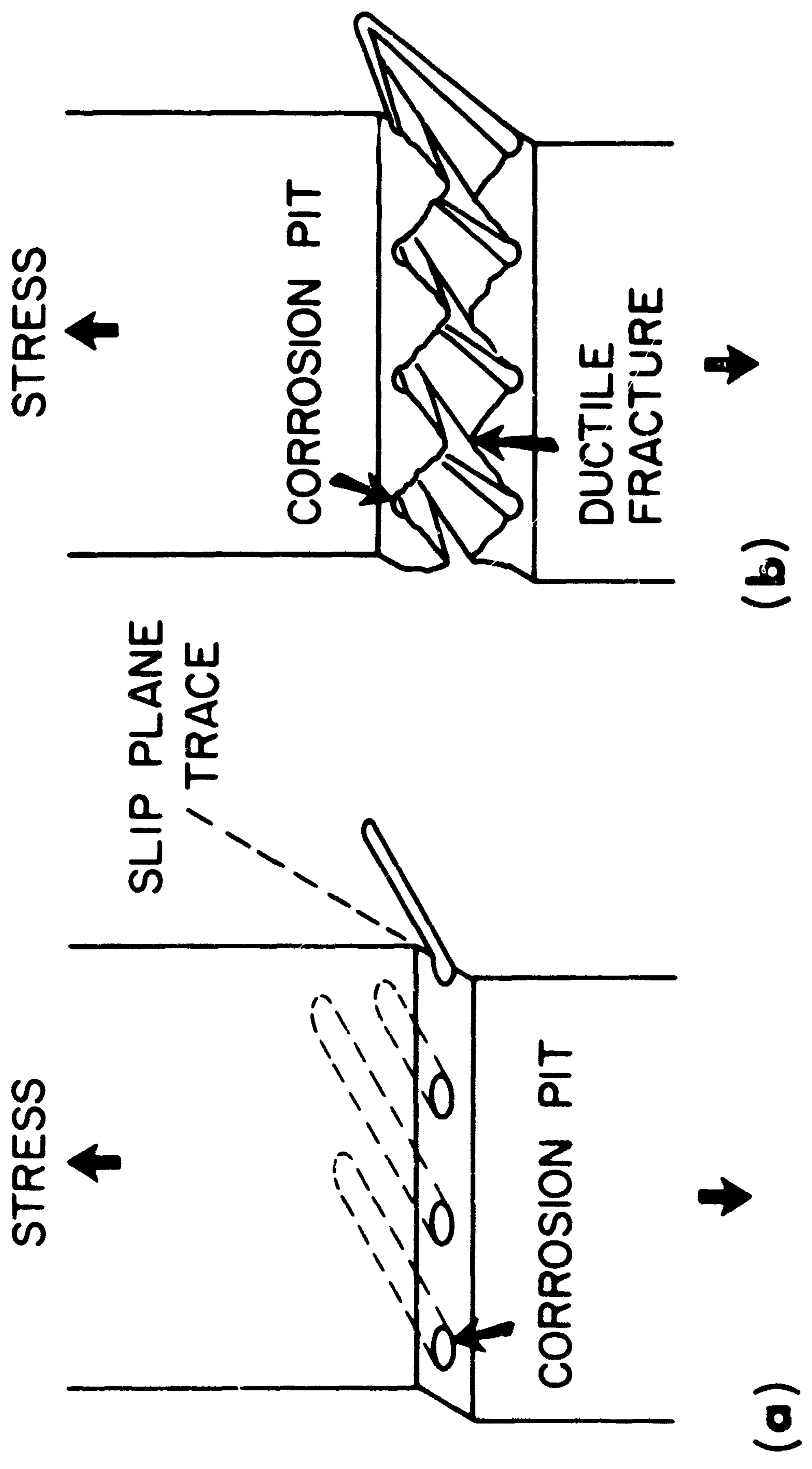

Fig. 12- Mechanism for transcrystalline stress-corrosion cracking proposed by Swann, Pickering and Embury[54,55]. (a) Pits are initiated at areas where surface films are ruptured by slip, and under suitable environmental conditions, grow into corrosion tunnels. (b) Fracture occurs by ductile rupture of slot weakened by many tubular pits.

only 10^{-6}N of a sufficiently active step-poison can significantly affect the dissolution behavior of a solid[19,20]. It follows that minor alloying additions could significantly affect stress corrosion behavior - as has been observed with the stainless steels[*] [60]. If complex-ions can indeed act in this manner to produce stress-corrosion cracking in certain materials, then there are several ways in which this deleterious effect could be reduced, for example, by the addition of inhibitor ions to the environment, these being "designed" to screen or cause breakdown of the troublesome complex species (as in the inhibition of complex-ion embrittlement, Fig. 4); or by varying the chemical composition of the solid, either (i) eliminating the relevant complexing element (ii) adding an "excess" of this complexing element - which would have the effect of eliminating or considerably reducing the rate of tunnel corrosion[19], or (iii) adding another element designed to counter the effect of the troublesome ion or its complexes in solution (the "built-in inhibitor" approach).

5. OTHER PHENOMENA OF INTEREST

The problems associated with obtaining a more fundamental understanding of the liquid metal embrittlement of metals have led to a search for similar, but hopefully less complicated phenomena in solids for which cohesion is better understood, e.g., certain covalent and ionic solids. In

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[*] For example, the addition of 1-2% molybdenum significantly increases the susceptibility of a 20%Ni-20%Cr stainless steel to stress-corrosion cracking in boiling 42% magnesium chloride solutions. The addition of 1-2% copper, on the other hand, markedly reduces susceptibility[60].

this context some experiments on the fracture behavior of germanium crystals coated with liquid metals were recently undertaken[61]. It was envisioned that if liquid metal embrittlement did occur, some correlation between the electronic properties of the liquid metal phase and the degree of embrittlement might be observed. Experiments involving liquid metals from Groups II through V were performed, and significant embrittlement effects were observed. Figure 13, for example, illustrates the effects of liquid gallium coatings on the bend strength of germanium monocrystals over the temperature range 0-600°C. For temperatures between 100° and 350°C, the fracture stress in bending was reduced from about 120 kg/mm^2 in air, to about 10 kg/mm^2 in gallium. However, it was found that this remarkable effect was not a genuine example of adsorption-induced liquid metal embrittlement, but was in fact caused by a combination of selective dissolution[62] and the intrinsic notch brittleness of germanium, for cracks were observed to have initiated at crystallographic notches (left inset of Fig. 13) etched into the surface by the liquid metal. This observation has obvious implications for the ultrahigh strength materials of the future. Such materials, while intrinsically notch brittle, are likely to be too hard to be notched mechanically under ordinary working conditions, but may be notched by chemical means - with potentially disastrous results.

At temperatures above 400°C, germanium crystals exhibited "true" liquid metal embrittlement, sometimes fracturing below the upper yield stress following measurable plastic strain (Fig. 13, right inset). The variation in susceptibility to embrittlement with Group of the liquid metal, and with the

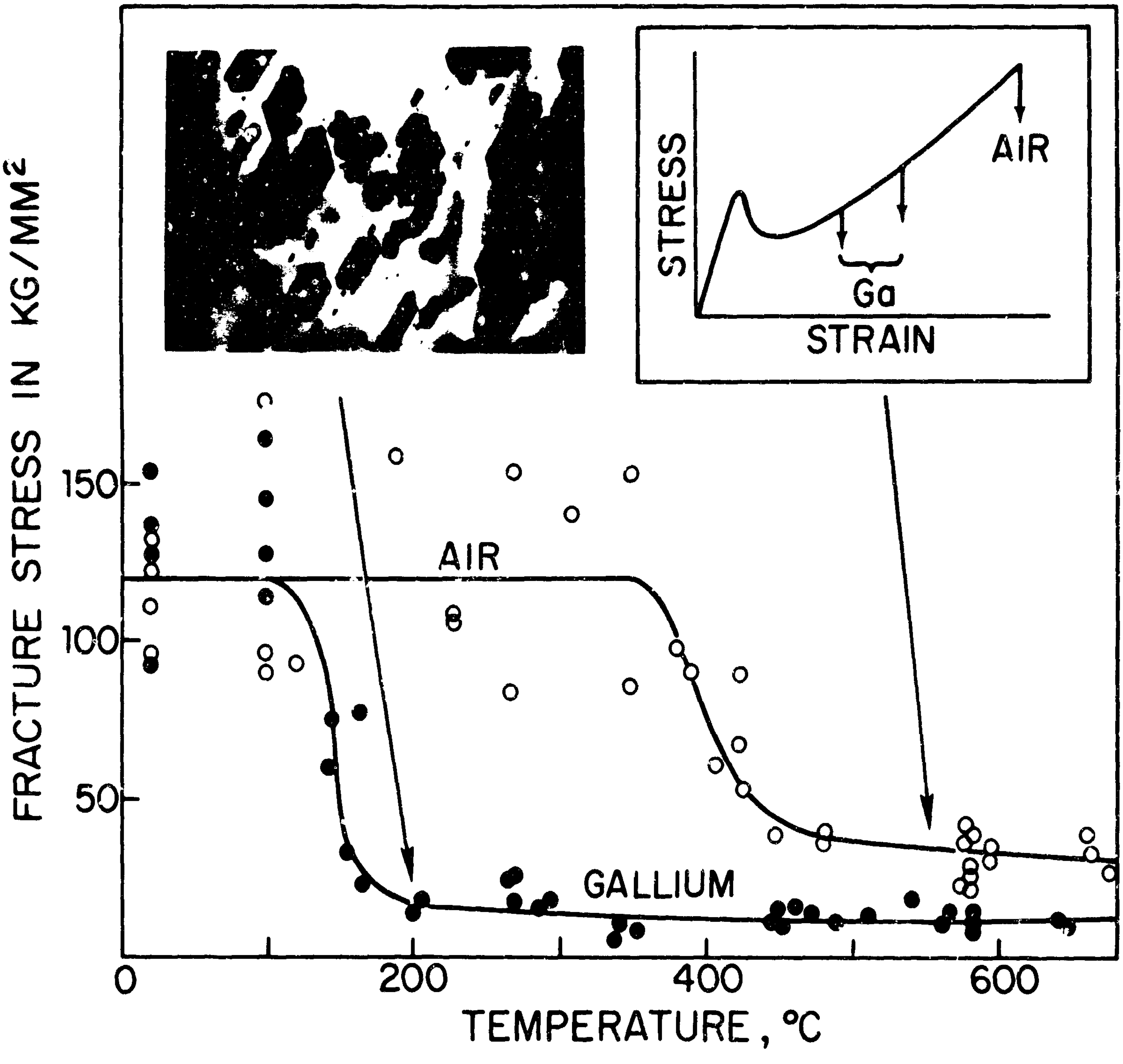

Fig. 13- Embrittlement of germanium by liquid gallium. Below about 350°C, embrittlement is associated with the notch-etching effect illustrated in left inset. Above about 450°C, true liquid metal embrittlement effects predominate, right inset. (Pugh, Westwood and Hitch[61].)

solubility of germanium in the liquid metal were then investigated. It was found that the degree of embrittlement was not related to the solubility of germanium in the environment, nor did extensive solubility prevent embrittlement. Group IV liquid metals were least embrittling, but Groups II, III and V liquid metals all induced approximately the same degree of embrittlement, and there was no correlation between degree of embrittlement and electron affinity of the liquid metal. Several other possible correlations have been examined, but to date none has been found significant.

In conclusion, this brief survey has been concerned with only one of several important aspects of environment-sensitive mechanical behavior. Nevertheless, it has served to demonstrate that environments can play a significant, and sometimes dominant role in determining the strength of crystalline materials. It has been shown, for example, that adsorbed water can reduce the fatigue life of steel by an order of magnitude, or the hardness of germanium by 40%, and that mildly corrosive liquids containing step-poisons can introduce notches into notch-sensitive materials. It is also known that, in general, susceptibility to embrittlement by liquid metals and to stress-corrosion cracking increases with strength[1,23]. It is clear that the chemical variable,environment,is a factor which should not be overlooked in any considerations of the strength and reliability of structural materials.

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