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ADSORPTION-INDUCED BRITTLE FRACTURE IN LIQUID METAL ENVIRONMENTS

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A.R.C. Westwood, C. M. Preece and M. H. Kamdar

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U. S. Army Ballistic Research Laboratory
Aberdeen Proving Ground, Md. 21005
Contract No. DA-18-001-AMC-1109(X)

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Research Institute for Advanced Studies
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ABSTRACT

Solid metals can be caused to behave in a brittle manner by exposure to a variety of physical or chemical environments. Perhaps the most dramatic examples of such effects, however, result from exposure to surface active liquid metals. Specimens prestressed above some critical value fail virtually instantly on being wetted by an appropriate liquid metal, and "brittle" crack propagation rates of order 100 cm per sec. have been recorded in otherwise ductile metals under such environmental conditions.

Such effects are presently considered to result from adsorption-induced reductions in the cohesive strength of atomic bonds at regions of stress concentration in the solid metal, e.g. at the tips of cracks or in the vicinity of piled up groups of dislocations. This paper describes the results of a number of recent investigations on this type of liquid-metal embrittlement, and discusses the prerequisites and possible mechanisms for its occurrence. Also discussed are the effects of such variables as chemical composition of the solid and liquid metal phases, temperature, prestrain, rate of loading, etc., on severity of embrittlement, and such topics as the possible correlation between severity of embrittlement and electronegativity, the use of "inert carrier" liquid metals, possible means of inhibiting liquid-metal embrittlement, and criteria for brittle failure.

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1. INTRODUCTION

When an oxide-free solid metal is coated with a liquid metal and then immediately deformed in tension, its yield and flow behavior are not significantly affected. Its fracture behavior, however, can be markedly different from that observed in air. In many instances a reduction in fracture stress or strain results, fig. 1, the magnitude of which is dependent on various chemical and mechanical parameters of the solid metal-liquid metal system. Under certain experimental conditions, embrittlement can be quite dramatic; specimens stressed above some critical value appear to fail "instantly" on wetting with an appropriate liquid metal. It is also possible to cleave such otherwise ductile metals as cadmium in certain liquid metal environments, and "brittle" crack propagation rates of order 50-500 cm per sec. have been reported for aluminum alloys in mercury. Such effects belong to the class of environment-sensitive fracture phenomena known as liquid-metal embrittlement (L-ME).

Embrittlement can also occur in the absence of stress, by corrosion, or by diffusion controlled intergranular penetration processes. This paper, however, will not be primarily concerned with such effects, and will concentrate instead on those examples of L-ME which are presently considered to result from chemisorption-induced reductions in the strength of atomic bonds at regions of stress concentration in the solid metal (Westwood 1963, Stoloff and Johnston 1963, Kamdar and Westwood 1963). It appears that such examples of L-ME may be considered as a special case of brittle fracture and, as such, present a particularly appropriate topic for discussion in these volumes.

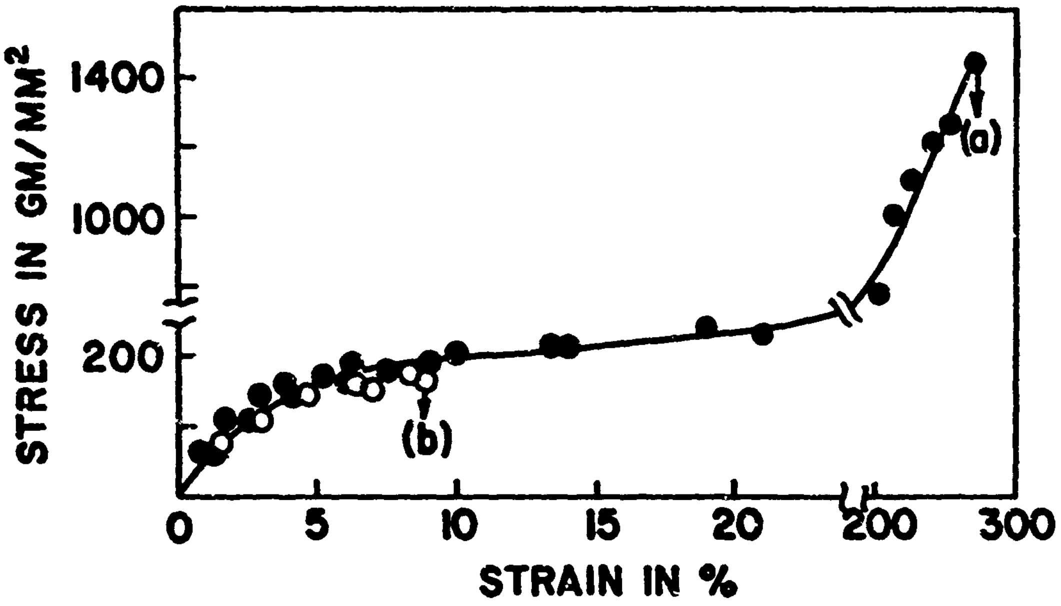

Fig. 1 - Stress-strain curves for (a) unamalgamated and (b) amalgamated Zn monocrystals at room temperature. $\chi_0 = 48^\circ$. (After Likhtman and Shchukin 1958.)

Other reviews of L-ME may be found in Rostoker et al. (1960), Kraai et al. (1960), and Likhtman et al. (1962).

II. OCCURRENCE AND MECHANISM OF L-ME

One of the most intriguing aspects of L-ME is its apparent specificity. It is often stated that only certain liquid metals embrittle certain solid metals. For example, liquid gallium (Ga_L) embrittles solid aluminum (Al_S) but not solid magnesium (Mg_S); Hg_L embrittles Zn_S, but not Cd_S. However, the fundamental factors which determine whether or not a given liquid metal will embrittle a particular solid metal, and then the severity of embrittlement that will be induced, are not yet understood. Several workers have proposed that L-ME is associated with a reduction in the surface free energy of the solid metal by the adsorbing liquid metal species (Likhtman et al. 1958, Rostoker et al. 1960, Nichols and Rostoker 1961, Likhtman et al. 1962). Since surface free energy is defined as the work necessary to create unit area of surface by a process of division (Shuttleworth 1950), such a proposition is undoubtedly correct, but this approach is not particularly informative. It does not provide any insight into the mechanism of embrittlement on an atomic or electronic scale, nor does it account for the apparent specificity of the observed phenomena. In view of the limitations of this approach, therefore, it has been suggested that it might prove more worthwhile to consider that embrittlement is associated with a localized reduction in the strength of atomic bonds at the surface of the solid metal by certain chemisorbed species (Westwood 1963, Stoloff and Johnston 1963, Westwood and Kamdar 1963), and then to seek an understanding of the manner in which such an effect could occur. With this possibility in mind, consider the crack shown in fig. 2. Crack propagation will occur by repeated breaking of bonds of the type $A\text{-}A_0$, $A\text{-}A_1$, etc. Such bonds might be expected to have potential energy-separation distance curves of the form $U(a)$ indicated in fig. 3, a_o being the equilibrium distance between atoms across the fracture plane. The resulting stress, σ, between atoms A and A_0 as they are separated, varies as (dU/da) from $\sigma = 0$ at $a = a_o$, to a maximum value of $\sigma = \sigma_m$ at the point of inflection U_1 of the curve $U(a)$. It follows that a tensile stress of magnitude σ_m acting at the crack tip would cause the bond $A\text{-}A_0$ to break. Assuming that the actual $\sigma(a)$ curve can be approximated by one-half of a sine curve, and that its half wavelength, λ, represents the effective range of the interatomic forces, it can be shown that (Gilman 1960a)

$$\sigma_m = (E\lambda/\pi a_o). \qquad [1]$$

If the work done in breaking $A\text{-}A_0$ bonds is then equated to the surface free energy of the thereby created fracture surfaces, γ, it can also be shown that (Gilman 1960a)

$$\sigma_m = (E\gamma/a_o)^{1/2}. \qquad [2]$$

Next assume that the role of the liquid metal atom B at the crack tip is to reduce the strength of the bond $A\text{-}A_0$. The chemisorption reaction presumably involved in such a process may occur spontaneously, or only after the atoms A and A_0 have been strained to some critical separation distance, a_c. In any event, as a result of the electronic rearrangement involved in this process the

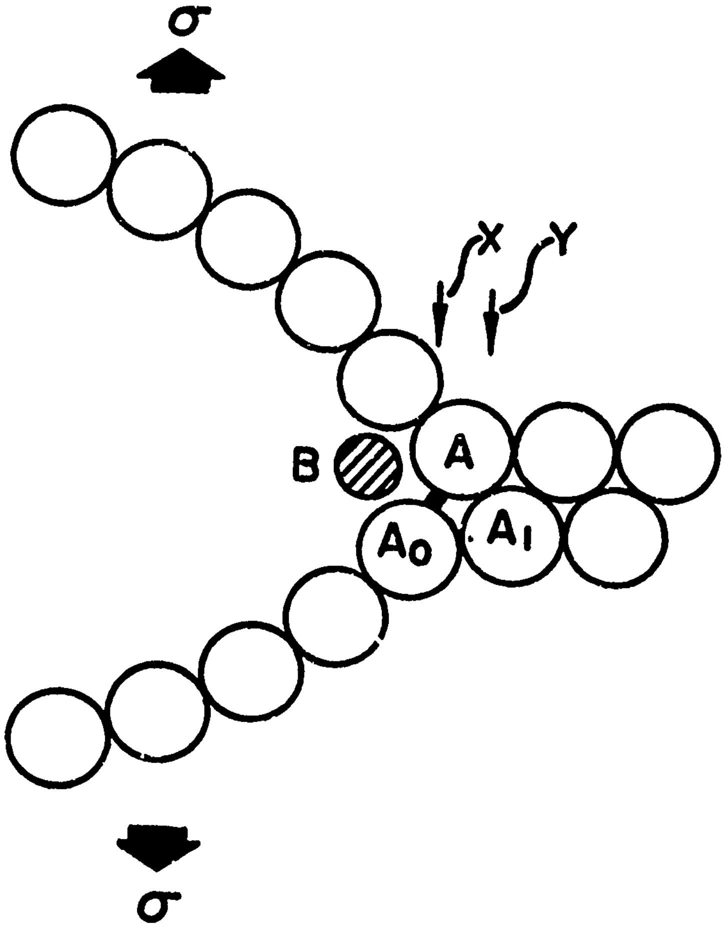

Fig. 2 - Illustrating displacement of atoms at the tip of a crack. The bond A-A_0 constitutes the crack tip and B is a liquid metal atom (Westwood and Kamdar 1963).

bond A-A_0 becomes inherently weaker, and thus its potential energy-separation curve may now be considered to be of form and displacement similar to $U(a)_B$, fig. 3. As the applied stress is increased, the stress acting on the bond A-A_0 eventually exceeds its now reduced breaking stress, $\sigma_{m(B)}$, the bond breaks, the crack propagates to Y, fig. 2, and the atom B becomes stably chemisorbed on the freshly created surface. This procedure is then repeated until the specimen fails.

On this hypothesis, crack initiation at the surface also will be facilitated by the adsorption of liquid metal B atoms. Moreover, if chemisorption is strain-activated, it will occur preferentially at sites of stress concentration, such as in the vicinity of piled-up groups of dislocations at high angle grain boundaries.

Focussing attention on what is actually occurring at, for example, a crack tip, rather than adopting the "before and after" thermodynamic approach, is considered to be a step in the right direction. Theoretical studies of the interactions between single adsorbed atoms and metal surfaces (Bennett and Falicov 1966, Grimley 1967, Gadzuk 1967a,b,c) and experimental investigations of the nature of the bonding (i.e. ionic, covalent, etc.,) between adsorbed alkali metals and such refractory metals as W_S (Utsugi and Gomer 1962, Schmidt and Gomer 1966) are now being undertaken. Unfortunately, however, these studies are not yet sufficiently advanced for any predictions of specific embrittlement behavior to be based on them. For the time being, therefore, we are forced to rely on the following empirical rules to indicate potential embrittlement systems (Rostoker et al. 1960, Kraai et al. 1960): (1) If the two metals involved form stable,

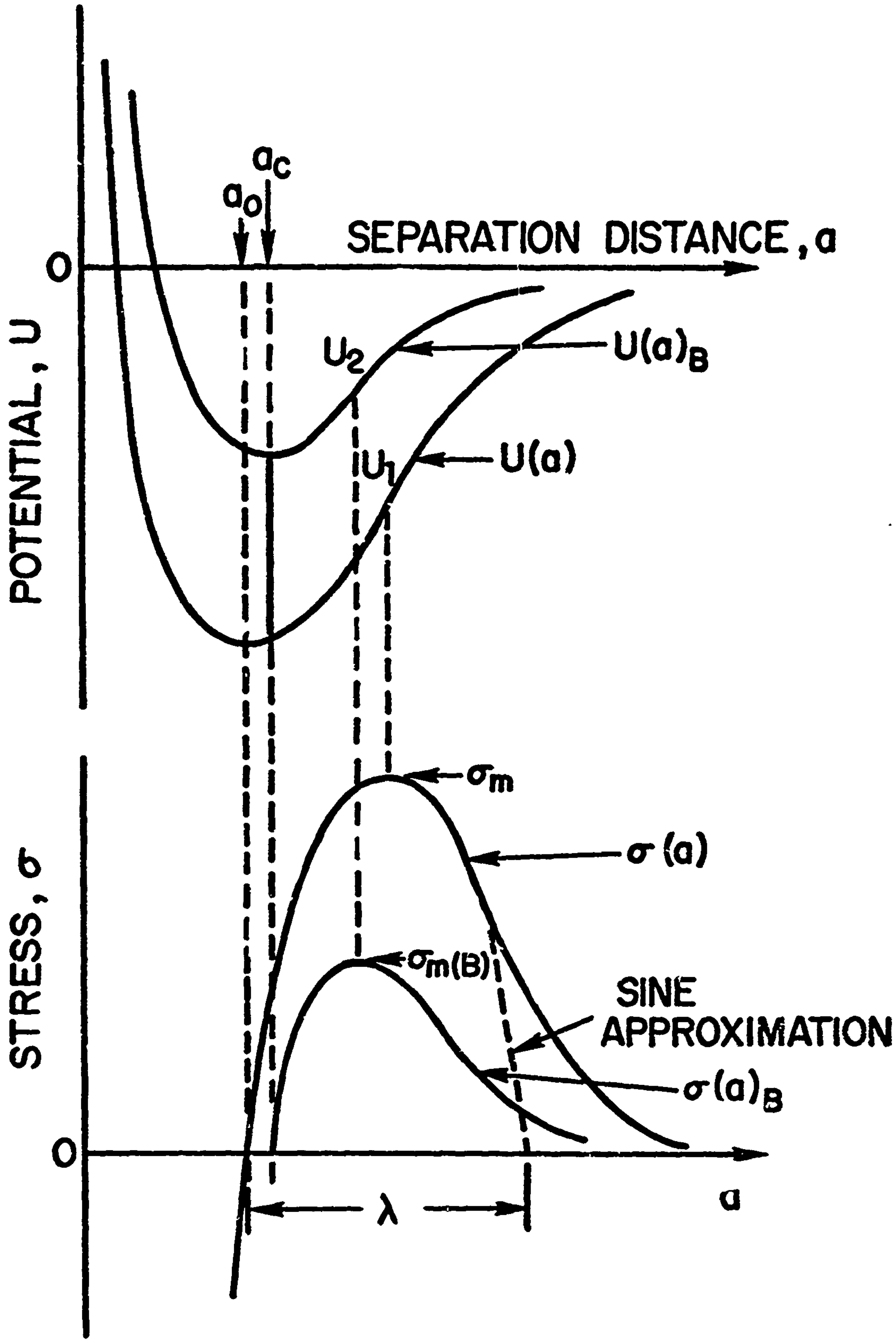

Fig. 3 - Schematic potential energy, $U(a)$ and $U(a)_B$, and resulting stress, $\sigma(a)$ and $\sigma(a)_B$, versus separation distance curves for bonds of type $A\text{-}A_0$ (fig. 2) in the absence and presence of chemisorbed atom B. For spontaneous chemisorption of B, $a_c = a_o$. For strain-activated chemisorption, $a_c > a_o$ (Westwood and Kamdar 1963).

high melting point intermetallic compounds in the solid state, then it is unlikely that they will constitute an embrittlement couple. This is in accord with the "reduction-in-bond strength" model for embrittlement in that the adsorption of liquid metal atoms which are 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. (2) Embrittlement rarely occurs in systems in which the two metals exhibit significant mutual solubility. It is not known, however, whether limited mutual solubility represents a genuine chemical prerequisite. It could be simply related to the difficulty of propagating a brittle crack in a "solvent" environment because dissolution processes would tend to blunt the crack tip. It is sometimes stated that a certain minimum amount of solubility of the liquid metal in the solid metal is required in order to facilitate "wetting" (Pertsov and Rebinder 1958, Likhtman et al. 1962, Shchukin and Yuschenko 1966). On the other hand, embrittlement occasionally occurs in systems in which the two component elements are so mutually incompatible in the equilibrium state that they form immiscible liquids on melting (e.g., Cd_S-Ga_L, Fe_S-Cd_L). It is possible that stress, i.e., lattice strain, plays a role in inducing chemisorption in such systems (Westwood and Kamdar 1963).

In addition to the models involving reductions in surface free energy or cohesive strength, a third possibility, that embrittlement may involve a high speed, stress-assisted dissolution process (Westwood 1963), has recently been discussed by Robertson (1966). Nevertheless, there appear to be a number of problems with such an hypothesis. While it is conceivable that stress could aid the dissolution of a solid metal into a "solvent" liquid metal environment, it is difficult to see how it could affect dissolution into a "non-solvent" liquid metal, since stress is unlikely to affect the solvating ability of the liquid environment. However, as just mentioned, embrittlement is occasionally observed in systems for which the solubility of the solid metal in the liquid metal is barely detectable. For example, the solubility of Fe_S in Cd_L is only 2×10^{-4} w/o at 400°C, but Cd_L severely embrittles Fe_S. Moreover, embrittlement is not observed when significant solubility occurs -- empirical rule (2) above. There is also the problem of explaining the relative temperature insensitivity of the type of L-ME under consideration in this paper. Robertson's model involves (i) dissolution of solid metal atoms from the crack tip, (ii) transport of these atoms by diffusion through the liquid metal phase, and (iii) precipitation of them some distance from the tip on a crack face. Such a process would certainly be expected to be thermally activitated. Moreover, on this model, the liquid metal phase serves only as a transporting medium, and is not used up in the embrittlement process. Thus, in theory, a small quantity of liquid metal could cause the failure of a large component. In practice this is not so, for the liquid metal is expendable in the embrittlement process (Rostoker et al. 1960).

In view of such problems, the examples of L-ME to be described will be assumed to be a consequence of a chemisorption process rather than a dissolution process, and on the basis of this assumption, a possible rationalization of some of the factors involved in L-ME has recently been proposed by Westwood et al. (1967). This involves considerations of (i) the short range nature of the interactions between adsorbed species and metallic surfaces, and (ii) a criterion for the ductile or brittle behavior of a solid introduced by several workers in the past, including Gilman (1960a), and discussed in detail by Kelly et al. (1967). The argument presented by the latter is essentially as follows: An equilibrium crack in a solid subjected to an increasing force F, fig. 4, will either propagate catastrophically by cleavage*, or grow slowly by shear depending on whether the tensile fracture stress, σ, for the bond A-A_0, or the shear stress, τ, to cause dislocation motion (flow) on the most favorably oriented slip plane S-P, is achieved first. As a rough approximation, if the ratio of σ/τ is ≤ 5, then failure will be predominantly by cleavage; if σ/τ is > 5, failure will be predominantly by shear.

Consider now the effect of a surface-active liquid metal atom B at the crack tip A-A_0 in fig. 4. As a consequence of the chemisorption of this atom, it is suggested that some variation in the strength of the bond between the atoms A and A_0 will result, and hence that the magnitude of σ will be changed. On the other hand, because of free electron screening in a metal (Brattain 1959), the effects of such a chemisorbed liquid-metal atom will not be felt at depths greater than a few atom diameters from the crack tip, S. Thus the chemisorbed atom will be unlikely to influence the strength of bonds across the slip plane S-P for a distance from S sufficient to significantly affect the ease of dislocation motion in the vicinity of the crack tip. It follows that the magnitude of τ should not be affected by the presence of atom B.

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*It is suggested here that the term "cleavage" may be used in connection with brittle crack propagation by either transcrystalline or intercrystalline paths. In the latter case, the bond A-A_0 under discussion would be oriented across a grain boundary, but the arguments presented are equally applicable. In practice, failure in liquid metal environments frequently occursin an intercrystalline manner -- presumably because less energy is required than for transcrystalline cleavage in most ductile metals. For anisotropic metals such as Zn_S, however, failure of polycrystalline specimens occurs predominantly by cleavage on basal planes.

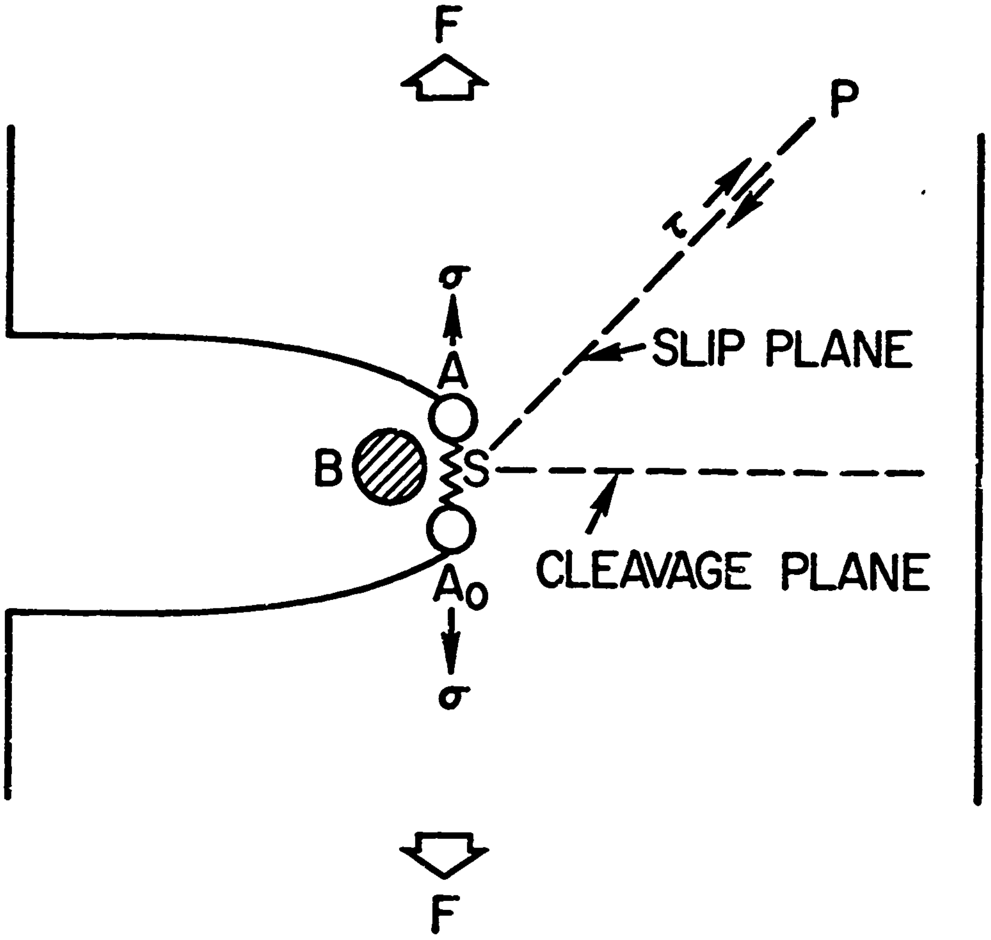

Fig. 4 - Schematic illustration of an "equilibrium" crack in a solid, subjected to an increasing force F. The bond A-A_0 constitutes the crack tip. B is a surface active liquid metal atom (Westwood, Kamdar and Preece 1967).

If the adsorption of liquid-metal atom B leads to a reduction in σ while τ is unaffected, then the ratio σ/τ will be decreased. This effect will be manifested as an increased tendency to cleavage, i.e., as some degree of liquid-metal embrittlement*, the severity of which will be related to the magnitude of the reduction of σ. Alternatively, the ratio σ/τ could be increased by adsorbing some liquid-metal species which interacts at the bond $A\text{-}A_0$, fig. 4, to produce an increase in σ. An element known to form high melting point (strongly bonded) intermetallic compounds with the solid metal element might be expected to act in this way. Another way of reducing the ratio σ/τ is by increasing τ. This can be readily achieved by alloying, irradiation, cold work, or decreasing the temperature; all of which factors are known to increase the susceptibility of solid metals to L-ME.

From the foregoing, it may be suggested that in connection with L-ME phenomena, it is a convenient first approximation to think of σ as the environment-sensitive parameter, and τ as the metallurgical structure-sensitive parameter. These parameters are not always independent - alloying can affect both σ and τ, but where appropriate, this simple approach will be adopted in the present paper.

So far, only pure liquid metals have been mentioned, but substantial variations in the severity of embrittlement can be induced by changing the chemical composition of the liquid metal environment by the addition of minor quantities of other elements in solution (Rostoker et al. 1960, Kraai et al. 1960,

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*Providing there is an adequate supply of liquid metal atoms, and their diffusion rate is sufficient to allow them to keep up with the propagating crack tip.

Rosenberg and Cadoff 1963, Summ et al. 1965, Westwood 1966). It is not yet clear whether such effects are caused by changes in "wetting" (Klein Wassink 1967), or rates of surface diffusion of the liquid metal (Summ et al. 1966), or whether they can be related to some fundamental interaction parameter between the solute element and the solid metal. The results of studies in progress at RIAS appear to support the latter possibility. Certainly one would anticipate that if embrittlement does involve chemisorption, then the severity of embrittlement should be related to some electronic parameter of the solid metal-liquid metal system. Such a possibility is under active consideration (Shchukin and Yuschenko 1966, Kamdar and Westwood 1966a), but as far as the authors are aware, no such correlation has yet been confirmed. A possible correlation with electronegativity will be discussed in Section V-B.

The severity of embrittlement observed is also dependent upon the metallurgical-structure dependent factors which determine τ, so that, in addition to the chemical prerequisites mentioned earlier, there are also mechanical prerequisites. For a ductile, unprecracked metal specimen these are (i) an applied tensile stress, (ii) some measure of plastic deformation, and (iii) the existence in the specimen of some stable obstacle to dislocation motion, capable of serving as a stress concentrator; this obstacle can be either preexisting (e.g. a grain boundary) or be created during deformation (e.g., a kink band). There should also be, of course, a sufficient supply of the active liquid to ensure adsorption <u>at</u> this obstacle, and subsequently <u>at</u> the propagating crack tip. If the specimen contains a pre-existing crack, then prerequisites (ii) and

(iii) are no longer necessary. If the solid is notch brittle, it may not be necessary for the liquid metal to keep up with the propagating crack once it is greater than critical size.

Some of the important factors in L-ME will now be considered in more detail utilizing examples drawn primarily from studies at RIAS on several simple embrittlement couples. A number of examples also will be taken from the extensive, but unfortunately not always reliable, literature on L-ME. Section III, which follows, is concerned with the mechanical prerequisites for L-ME, and includes an account of some studies in which L-ME was utilized as a means of evaluating the validity of several fracture criteria. Section IV presents a discussion of the physical and metallurgical factors in L-ME, and Section V is concerned with the results of some of the rather limited amount of work that has been done on the chemical factors involved in this phenomenon. Such a division into sections is convenient for literary purposes, but it will be appreciated that, in fact, it is artificial. In reality, the various mechanical, physical and chemical factors operate simultaneously, and sometimes are interrelated.

III. MECHANICAL FACTORS

A. The Stress-Concentrator Requirement

The necessity for some stable obstacle to dislocation motion to be present in order for L-ME to be observed in a ductile, unprecracked metal has been demonstrated by a number of workers, e.g. for α-brass in Hg_L by Edmunds (1944), Nichols and Rostoker (1961), and Rosenberg and Cadoff (1963), and for Cu_S in Bi_L

by Morgan (1954). On the other hand, Likhtman and Shchukin (1958), and Shchukin et al. (1959) have reported that Zn monocrystals, oriented for single slip, can be significantly embrittled by Hg_L or Ga_L. According to Likhtman and Shchukin (1958), the room temperature stress and strain at fracture of 1mm dia. crystals of orientation $\chi_o = 48^{o*}$ were respectively reduced from ~ 1400 gm/mm^2 and 260% in air, to ~ 200 gm/mm^2 and 10% in Hg_L, fig. 1. This result is unexpected because the existence or nature of any stable obstacle to dislocation motion in monocrystals of pure Zn oriented for single slip is not evident, either from this work or that of Garber and Gindin (1960). Kamdar and Westwood (1966b) have recently investigated this apparent anomaly using considerably larger Zn monocrystals, 6mm square in section. These were handled with extreme care to prevent accidental bending or the introduction of surface damage. Moreover, since it is known that deformation in Zn_S occurs in a markedly inhomogeneous fashion in the vicinity of the grips, usually with the formation of kink bands (Morton, Treon and Baldwin 1954), the crystals were coated with Hg_L over the center portion of their length only, and not within a region approximately 1.5 cm long in the vicinity of the grips ("partially-coated" specimens). Thus, for specimens of orientation $15^o < \chi_o < 70^o$, the embrittling liquid metal was confined to that portion of the crystal for which slip might be expected to occur predominantly on the basal plane.

Some of the results obtained in this work are presented in fig. 5(b). The difference between this data and that of Shchukin et al. (1959) (fig. 5(a)) is readily apparent. In direct contrast to the previous work, it was found that

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[*] χ_o is the angle between the (0001) basal plane and the tensile axis of the specimen before testing, and χ_F is this angle at fracture.

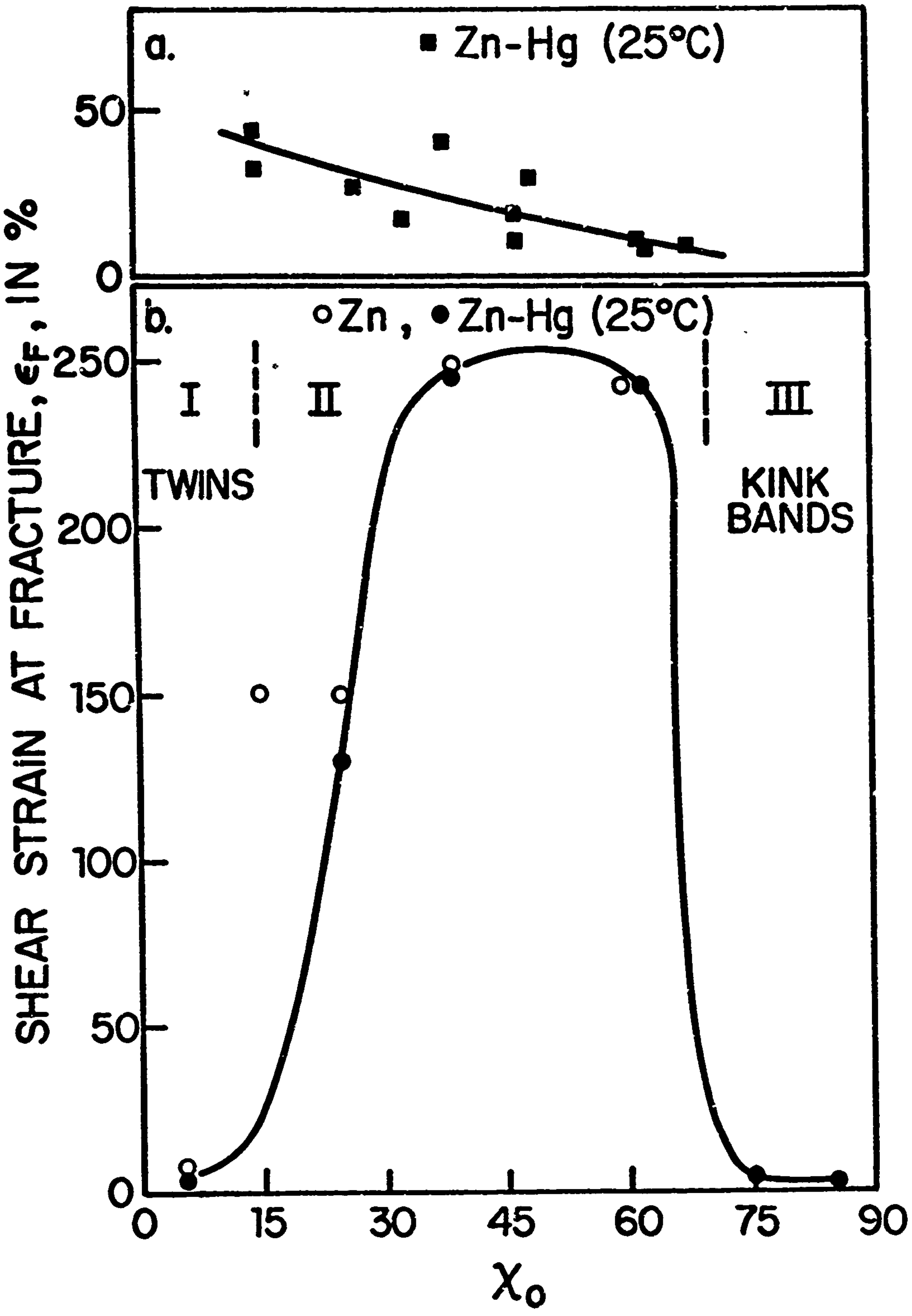

Fig. 5 - Orientation dependence of shear strain at fracture for (a) amalgamated 1mm dia. Zn monocrystals (after Shchukin et al. 1959) (b) uncoated or partially amalgamated 6mm square Zn monocrystals (Kamdar and Westwood 1966b).

crystals of orientation $15^{\circ} < \chi_o < 70^{\circ}$, for which deformation occurs predominantly by single slip in the basal plane, are not significantly embrittled by Hg_L. However, crystals of orientation $\chi_o > 75^{\circ}$ were embrittled; values of the resolved shear stress and strain at fracture being respectively some 5 and 25 times lower than those for similar but uncoated specimens. For these specimens it was noted that fracture always occurred at a kink band formed during deformation in the amalgamated gauge section. Likewise, crystals of $15^{\circ} < \chi < 70^{\circ}$ which were amalgamated overall, failed by cleavage nucleated at a kink boundary located in the vicinity of the grips. Crystals having $\chi_o < 5^{\circ}$, on the other hand, deform predominantly by twinning, and both amalgamated and unamalgamated crystals failed after only a few percent strain by secondary cleavage on the (0001) planes of a twin.

It is apparent from these studies that the experiments performed by earlier workers with Zn_S had utilized either accidentally deformed crystals, or specimens amalgamated in the vicinity of the grips where deformation is not homogeneous and kink bands provide the necessary obstacle for crack initiation.

B. Criteria for Crack Initiation

Several criteria have been proposed for crack initiation in solids which slip and cleave on the same plane, and also contain a suitable obstacle to slip. Such criteria, of course, apply to brittle failure in general. However, by optimizing the conditions for brittle behavior, deformation in active liquid metal environments has proved to be a very convenient method of examining both their qualitative and quantitative validity. The various criteria are summarized below, and are then compared with experimental data obtained from studies on the Zn_S - Hg_L system.

The first criterion is that due to Likhtman and Shchukin (1958), namely

$$\sigma_{NF}\tau_F L = k^2 G\gamma \qquad [3]$$

where σ_{NF} and τ_F are the normal stress and the shear stress at fracture, respectively, k is a dimensionless coefficient of order unity, G is the shear modulus, and γ is the fracture surface energy. In several published applications of this criterion to fracture in Zn_S (Shchukin et al. 1959, Likhtman et al. 1962, Bruyukhanova et al. 1965), L is equated to the crystal diameter. However, in the original derivation of Eq. [3], L is the maximum dimension of the slip plane along a slip direction. If λ_o (the angle between the slip direction and the tensile axis) = χ_o, then $L = D_o/\sin\chi_o$, where D_o is the crystal diameter or side dimension and is assumed constant for a given set of experiments. If only a limited amount of deformation occurs in the material before fracture, so that χ_F can be taken as equal to χ_o, then Eq. [3] becomes

$$\sigma_{NF}\tau_F = (k^2 G\gamma/D_o)\sin\chi_o = K_1^{\,2}\sin\chi_o. \qquad [4]$$

Thus the product of the normal stress and shear stress at fracture is not constant, as is often stated in the Russian literature, but instead is orientation dependent.

Gilman (1958) has proposed that the condition for cleavage fracture in the basal plane of Zn_S is given by

$$n = 4\gamma[E(1-\nu)/G]^{1/2}/\sigma_{NF}b \qquad [5]$$

where n is the number of edge dislocations held up at some stable obstacle and b is their Burgers vector, γ is the surface energy of the (0001) plane in Zn, E is Young's modulus and ν is Poisson's ratio.

Now the shear stress required to hold n blocked edge dislocations in a slip plane of length L is given by (Eshelby, Frank and Nabarro 1951)

$$\tau = Gbn/\pi(1-\nu)L \qquad [6]$$

and if such a pile-up nucleates a crack, τ can be regarded as τ_F. When Eqs. [5] and [6] are combined, the following criterion for fracture is obtained*:

$$\sigma_{NF}\tau_F L = 4\gamma[EG/(1-\nu)]^{1/2}/\pi. \qquad [7]$$

Putting $L = D_o/\sin X_o$ as before, Eq. [7] can be written

$$\sigma_{NF}\tau_F = K_2^2 \sin X_o \qquad [8]$$

where $K_2^2 = 4\gamma[EG/(1-\nu)]^{1/2}/\pi D_o$. Equation [7] is of the same form as Eq. [3] derived by Likhtman and Shchukin (1958), and similarly Eq. [8] may be compared with Eq. [4].

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*In an earlier derivation of this criterion (Kamdar and Westwood 1966b), Eq. [6] was taken as $\tau = 3Gnb/2\pi L$, which is valid if $\nu = 0.33$. This led to the following version of Eq. [7]: $\sigma_{NF}\tau_F L_F = 6\gamma[EG\ (1-\nu)]^{1/2}/\pi$. However, ν for zinc is actually 0.26 (Gilman 1958), and as a result, the values of the fracture surface energy of Zn_S in Hg_L previously published by Kamdar and Westwood are in error by about -9%. Equation [7] represents a generalized version of the Kamdar-Westwood criterion.

Stroh's (1958) analysis of this problem is based upon the consideration that large local tensile stresses exist at the end of any dislocation tilt boundary which terminates within a crystal. It is postulated that fracture is initiated when a complete tilt boundary is converted into a pair of terminating tilt boundaries by basal slip. Assuming that the original tilt boundary lay perpendicular to the slip planes, and that the length of the longer of the created pair is W, then $W_{Max} \simeq D_o/\cos \chi_o = L \tan \chi_o$. Stroh's criterion for fracture by this mechanism is then

$$\sigma_{NF}\tau_F = K_3^{\,2} \cos \chi_o \qquad [9]$$

where $K_3 = (4G\gamma/\pi D_o)^{1/2}$. Alternatively, Eq. [9] may be written

$$\sigma_{NF}\tau_F L = (4G\gamma/\pi)\cot \chi_o . \qquad [10]$$

Bullough (1964) has criticized the Stroh model on the grounds that it seems unlikely that such a maximum length sub-boundary would exist in every crystal. Instead, he has proposed an alternative criterion based on the Bullough (1956)-Gilman (1958)-Rozhanskii (1959) model for the formation of cracks in the slip plane, as follows:

$$P_F = 4\gamma[(1-\cos \chi_o)/\sin^2 \chi_o]/nb \qquad [11]$$

where P_F is the tensile fracture stress.

From Eq. [11], he derives

$$\begin{aligned} \sigma_{NF} &= K_4[(1-\cos \chi_o)/\sin \chi_o] = K_4/\tan(\chi_o/2) \\ \tau_F &= K_4[(1-\cos \chi_o)\cos \chi_o/\sin^2 \chi_o] = K_4[\cos \chi_o/(1+\cos \chi_o)] \end{aligned} \qquad [12]$$

where $K_4 = 4\gamma/nb$.

Smith and Barnby (1967) have recently proposed a shear stress criterion for crack initiation in a plane containing a pile-up of edge dislocations. They suggest

$$\tau_F = [G\pi\gamma/2L(1-\nu)]^{1/2}. \qquad [13]$$

Again putting $L = D_o/\sin \chi_o$, Eq.[13] may be written

$$\tau_F = K_5[\sin \chi_o]^{1/2} \qquad [14]$$

where

$$K_5 = [G\pi\gamma/2D_o(1-\nu)]^{1/2}.$$

The variations of the theoretically derived values of τ_F and σ_{NF} with crystal orientation can also be simply derived for the criteria of Likhtman-Shuckin, Kamdar-Westwood and Stroh. For the small deformations expected to occur in a brittle or embrittled material, it can be assumed that $\chi_F \simeq \chi_o$, and thus

$$\tau_F = P_F \sin \chi_o \cos \chi_o,$$

and

$$\sigma_{NF} = P_F \sin^2 \chi_o,$$

so that

$$\sigma_{NF}/\tau_{NF} = \tan \chi_o. \qquad [15]$$

Combining Eq.[15] with Eqs.[4], [8] and [9], and assuming D_o constant throughout, one obtains

(i) For the Likhtman-Shchukin and Kamdar-Westwood criteria:

$$\begin{aligned} \tau_F &= (K_1 \text{ or } K_2)(\cos \chi_o)^{1/2} \\ \sigma_{NF} &= (K_1 \text{ or } K_2)(\sin^2 \chi_o / \cos \chi_o)^{1/2}. \end{aligned} \qquad [16]$$

(ii) For the Stroh criterion:

$$\begin{aligned} \tau_F &= K_3(\cos^2 \chi_o / \sin \chi_o)^{1/2} \\ \sigma_{NF} &= K_3(\sin \chi_o)^{1/2} \end{aligned} \qquad [17]$$

Eqs.[12], [14], [16] and [17] may be used to examine the validity of the proposed fracture criteria, provided that the comparative experiments are performed on specimens of constant D_o, and that fracture occurs after only a small amount of deformation such that the approximation $\chi_F = \chi_o$ is valid. When specimens of constant D_o are not available, however, then the Likhtman-Shchukin and Kamdar-Westwood criteria can be examined by means of Eqs.[3] and [7], where L is taken as L_F, the length of the fractured slip plane as determined after failure. If these criteria are valid, then the product $(\sigma_{NF}\tau_F L_F)$ should be constant. For the Stroh criterion to be valid, the product $(\sigma_{NF}\tau_F L_F \tan \chi_o)$ must be constant; for the Smith-Barnby criterion to be valid, the term $[\tau_F/(\sin \chi_o)^{1/2}]$ must be constant.

1. Crack Initiation in Pure Zinc: Studies of the behavior of asymmetric bicrystals of Zn in Hg_L at room temperature have provided a convenient means of evaluating the above criteria (Kamdar and Westwood 1966b). The boundary in such crystals (see insert in fig. 6) provides a strong barrier to the emergence of edge dislocations from one of the component crystals (Gilman 1958), and failure occurs after only 0.5-4% strain. Tensile experiments were performed with two types of asymmetric Zn bicrystals: Type I was grown by electron beam welding two monocrystals together (D_o constant). Type II was grown by seeding (D_o not constant). Both types were 5mm x 10mm in section and 7-9 cm in length, and were amalgamated over the center part of the gauge section only. In testing, cleavage cracks were initiated at the grain boundary, and these propagated completely through the crystals of orientation such as B in fig. 6.

Experimental data points presented in figs. 6 and 7 are from crystals of Type I. The solid curves drawn in fig. 6 correspond to Eq.[16], assuming $\chi_F = \chi_o$ and putting $K_1 = K_2 = 178$ gm/mm^2. It can be seen that the theoretical values of τ_F and σ_{NF} calculated from Eq.[16] are in good agreement with experimentally determined values, with the exception of those from crystals of $\chi_o = 25^\circ$ for which a relatively large amount of plastic deformation occurred before failure (~ 4% compared with ~ 0.5% for crystals of $\chi_o = 60^\circ$.

Now if L in Eq.[3] is equated to the specimen diameter (width) D_o, and this is assumed constant, and if $\lambda_o = \chi_o$, then

$$\sigma_{NF} = K(\tan \chi_o)^{1/2}$$
$$\tau_F = K(\cot \chi_o)^{1/2}. \qquad [18]$$

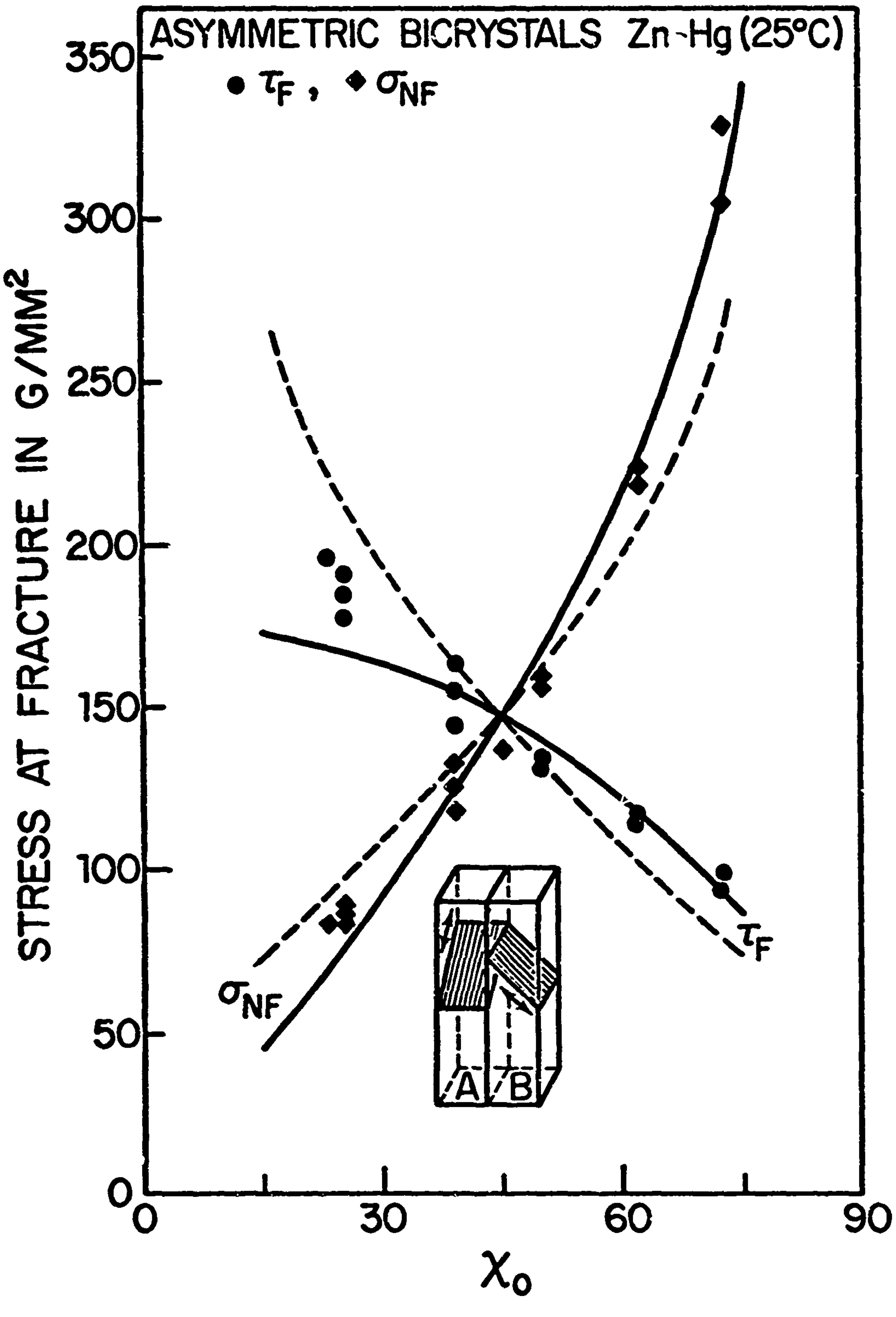

Fig. 6 - Orientation dependence of the normal stress, σ_{NF}, and shear stress, τ_F, at fracture for Type 1 asymmetric Zn bicrystals in the partially amalgamated condition. For comparison, the theoretically constructed curves correspond to Eqs.[16] (solid lines - Likhtman-Shchukin or Kamdar-Westwood criteria) or Eqs.[18] (dashed lines) when $K_1 = K_2 = 178$ gm/mm² and K = 148 gm/mm² (Kamdar and Westwood 1966b).

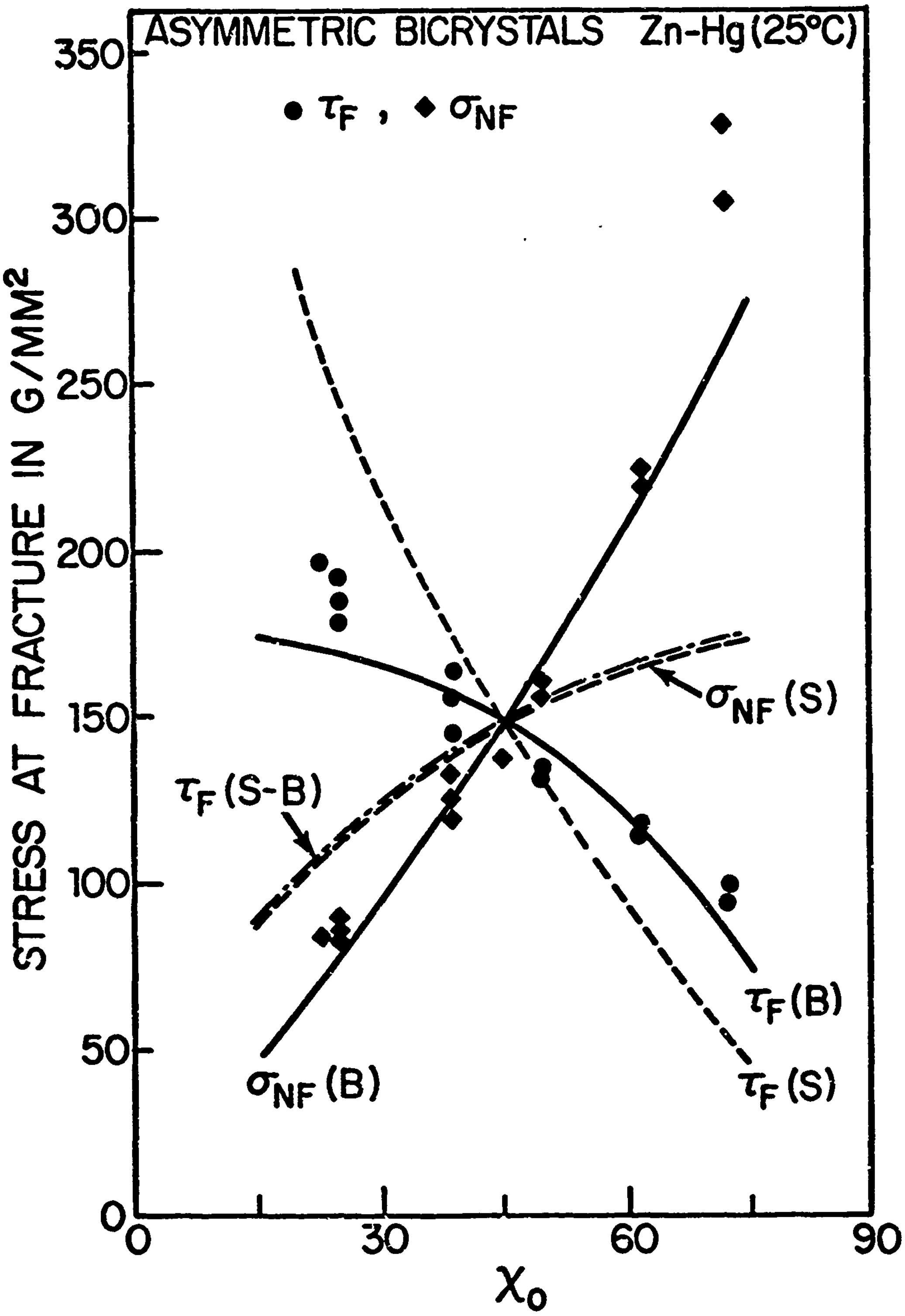

Fig. 7 - Same data as fig. 6. The solid lines, B, correspond to Eqs. [12] (Bullough's (1964) analysis); the dashed lines, S, to Eqs. [17] (Stroh's (1958) analysis), and the other line, S-B, to Eq. [14] (Smith-Barnby's (1967) analysis) when $K_3 = K_5 = 178$ gm/mm² and $K_4 = 359$ gm/mm².

The dashed curves in fig. 6 correspond to Eqs.[18], putting $K = 148$ gm/mm^2. It can be seen that if L is equated to D_o, the analysis does not fit the data quite as well as when L is taken as the slip plane length.

Figure 7 presents the data again in order to compare it with the Stroh (S) (1958), Bullough (B) (1964) and Smith-Barnby (S-B) (1967) theoretical estimates of τ_F or σ_{NF}, obtained by means of Eqs.[17], [12] and [14], and with $K_3 = K_5 = 178$ gm/mm^2 and $K_4 = 358$ gm/mm^2. Bullough's estimates are in fair agreement with the experimentally determined values except for crystals having $\chi_o > \sim 70^o$. However, neither Stroh's analysis nor that of Smith and Barnby are in accord with the data.

For bicrystals of Type II, grown by seeding, D_o was not constant from specimen to specimen, so that it is not possible to analyze the test data in the manner just presented. Accordingly, it was examined in terms of the product $(\sigma_{NF}\tau_F L_F)$, Eqs.[3], [7] and [10], for specimens of various orientations. The data are shown in fig. 8. It can be seen that the strain at fracture for these specimens remained essentially constant at 0.5%, regardless of orientation, fig. 8(a). Moreover, in accord with the fracture criteria of Likhtman-Shchukin and Kamdar-Westwood, Eqs.[3] and [7], the product of $(\sigma_{NF}\tau_F L_F)$ was constant over the range of orientations for which slip might be expected to occur predominantly on the basal plane, and failure by a Bullough-Gilman-Rozhanskii type mechanism. Since the product of $(\sigma_{NF}\tau_F L_F)$ was independent of orientation, it is apparent that the Stroh criterion, Eq.[10] is not valid for these experiments. Taking $(\sigma_{NF}\tau_F L_F) = 30{,}250 \pm 2{,}000$ gm^2/mm^3 from fig. 8, $E = 2.54 \times 10^{11}$ dynes/cm^2, $G = 3.84 \times 10^{11}$ dynes/cm^2 (Huntington 1958), and $\nu = 0.26$ (Gilman 1958), the cleavage fracture surface energy for the basal plane of Zn_S in the presence of Hg_L was calculated from Eq.[7] to be 53 ± 3 ergs/cm^2.

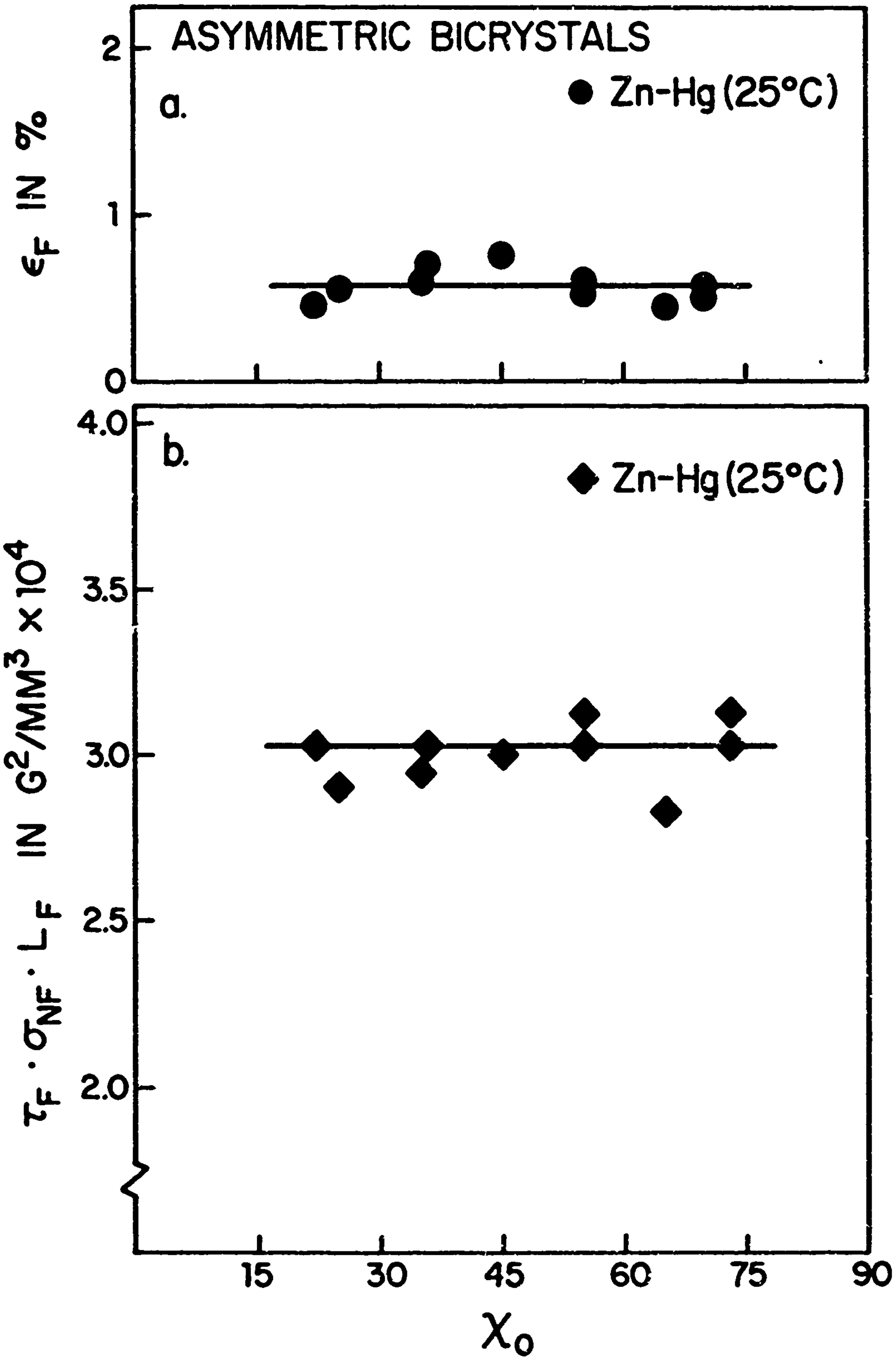

Fig. 8 - Orientation dependence of (a) the strain to fracture, and (b) the product of the shear stress, τ_F, normal stress, σ_{NF}, and slip plane length, L_F, at fracture for Type II asymmetric Zn bicrystals in the partially amalgamated condition (Kamdar and Westwood 1966b).

2. Crack Initiation in Zn Alloys: In the derivation of Eq.[7] it was assumed that τ_F truly represented the stress acting on the piled up group of dislocations which nucleated the crack. In fact, however, the effective stress acting on the dislocations in the pile up at fracture is somewhat less than τ_F, namely $(\tau_F - \tau_o)$ (Petch 1956, Stroh 1957), and this term should replace τ_F in Eq.[7]. There then arises the problem of deciding what value of stress to assign to τ_o. On this point the work of Ku and Johnston (1964) on crack initiation in MgO bicrystals is relevant. These workers found that their fracture data was capable of rational interpretation if τ_o was equated to the dislocation multiplication stress, τ_C, but not if τ_o was equated to the much smaller stress at which dislocations first became mobile. They suggested that the plastically induced stress concentrations which lead to crack initiation arise only after a slip band is formed. Thus the critical threshold event is dislocation multiplication, not mereby dislocation motion.

Now for pure Zn_S, $\tau_C \ll \tau_F$, so that it may be neglected without serious error. However, for alloyed crystals, τ_C is a significant fraction of τ_F. For example, for Zn-0.2 a/o Cu crystals, the ratio $\tau_C/\tau_F = 0.7$, and in this case, τ_C must be taken into account if meaningful values of γ are to be derived. Accordingly, in their studies of the embrittlement behavior of asymmetric bicrystals of dilute Zn_S alloys in Hg_L, Kamdar and Westwood (1967a) have equated τ_o to τ_C, the critical resolved shear stress (c.r.s.s.) for monocrystals of the appropriate alloy. The value of τ_C was taken as that stress at which the first deviation from linearity occurred in the tensile stress-strain curve. The modified form of Eq.[7] is then

$$\sigma_{NF}(\tau_F - \tau_C)L_F = [4\gamma[EG/(1-\nu)]^{1/2}/\pi \qquad [19]$$

and this equation has been used to analyze the fracture data from Zn-0.5 a/o Cu and Zn-0.2 a/o Cu crystals ($20^\circ < \chi_o < 80^\circ$). Using the values for E, G, and ν quoted above, the value of γ obtained for both alloys was 62 ± 9 ergs/cm^2, that is, about 20% greater than the value obtained for pure Zn_S bicrystals tested in Hg_L (~ 53 ergs/cm^2). Whether this is a significant increase is not yet clear. The important conclusion to be drawn, however, is that although the solute element additions raised the c.r.s.s. some 4-6 times and, as a consequence raised the fracture stress(since flow is a prerequisite for fracture), the cleavage fracture energy remained approximately constant. In other words, the fracture process for these dilute alloys remained effectively controlled by the energy required to break Zn-Zn bonds across the basal plane.

Geometric considerations dictate that the value of L, the slip plane length, should vary considerably with orientation χ_o. For example, for a 6mm square crystal, L varies from about 6 to 18 mm as χ_o varies from 80° to 20°. According to Eq.[19], the product $[\sigma_{NF}(\tau_F - \tau_C)]$ should be inversely proportional to L, and an average value for γ should be obtained from the slope $[4\gamma[EG/(1 - \nu)]^{1/2}/\pi$ of the line fitted to the data. The required relationship is shown in fig. 9, and the value of γ derived from the slope of the line is 61 ergs/cm^2.

C. Crack Propagation in L-ME

It is not easy to devise experiments capable of evaluating directly the hypothesis that L-ME results from a localized, chemisorption-induced reduction

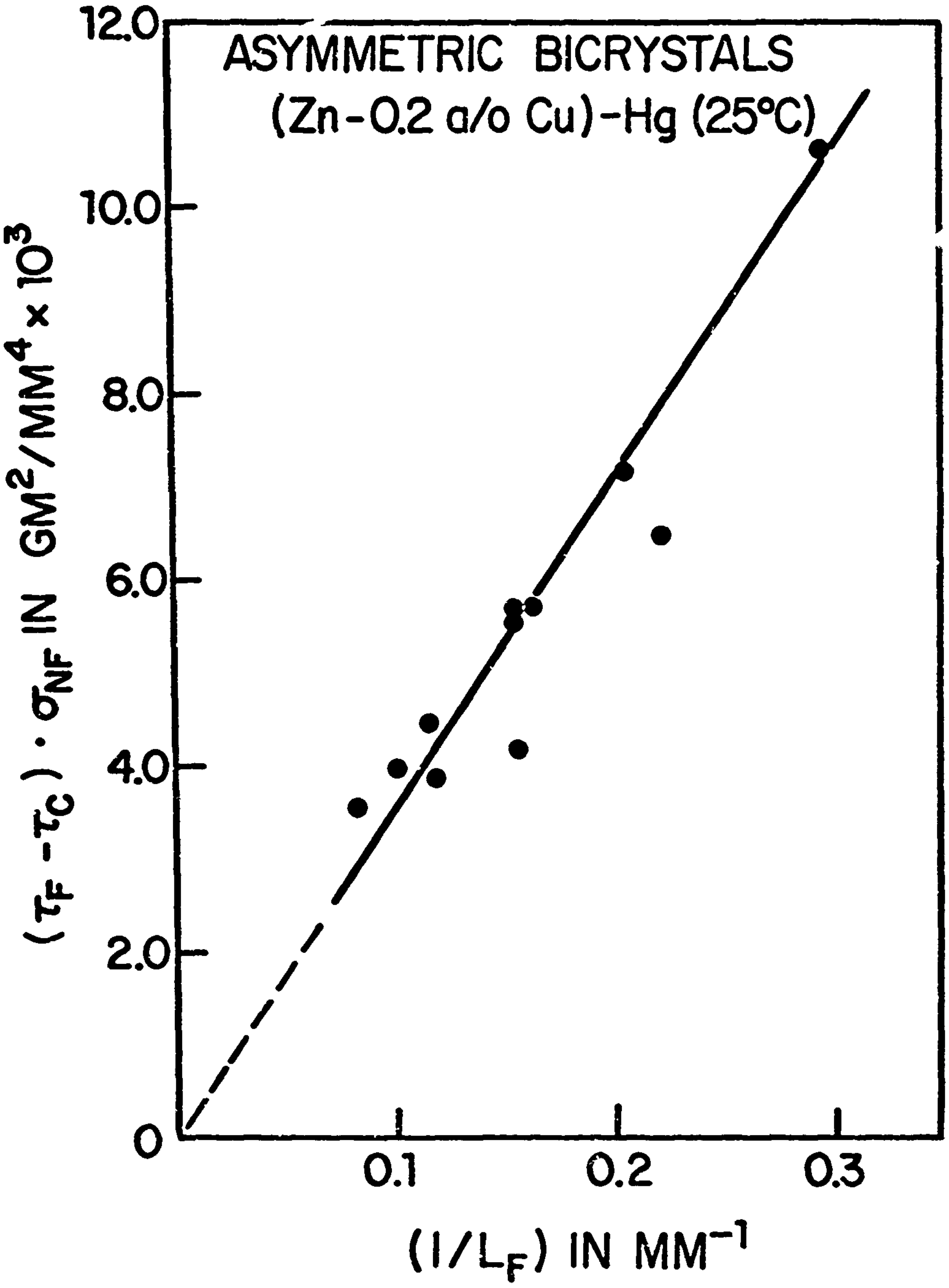

Fig. 9 - Illustrating linear relationship between the product $(\tau_F - \tau_C)\sigma_{NF}$ and $(1/L_F)$, for alloyed Zn asymmetric bircystals (Type II). τ_C is the critical resolved shear stress of the component alloy monocrystals (Kamdar and Westwood 1967a).

in bond strength and not, perhaps, from some effect which inhibits dislocation motion in the vicinity of the crack tip, fig. 4, raising τ and thereby accomplishing an equivalent reduction in the ratio σ/τ. Ideally, the experimental technique should be capable of detecting any adsorption-induced variation in electron distribution in the surface bonds, leading to weakening, without applying a stress; but since any such effect would be confined to the immediate surface layer of atoms, it would not be readily observed in studies involving some variation in the physical properties of the specimen as a whole. Nevertheless, recent studies of variations in electrical conductance, ferromagnetic moment and ferromagnetic anisotropy of W, Fe and Ni with chemisorption of oxygen, carbon monoxide and nitrogen have been interpreted to indicate that these species weaken the binding of the metal surface atoms (Geuss 1964). It is possible, therefore, that these or similar techniques could be advantageously applied to the problem of liquid-metal embrittlement in certain systems.

An alternative approach is to determine the true fracture surface energy for the cleavage plane of a particular solid metal, γ, which is directly related to σ ($\sigma = \sigma_m$ in Eq. [2]), and then to show that γ is reduced in the presence of an active liquid metal. With this in mind, consider the propagation of a semi-elliptical crack of length c in a thin plate under the action of a tensile stress σ_a acting perpendicular to the length of the crack (Inglis 1913, Griffith 1920-1). The maximum tensile stress acting at the crack tip, σ_c, is

$$\sigma_c = 2\sigma_a(c/R)^{1/2} \qquad [20]$$

where R is the radius of curvature at the tip. The minimum radius of curvature having physical significance is given by $R = a_o$ (Orowan 1949). For such an 'atomically sharp' crack to propagate, σ_c must exceed σ_m (Eq.[2] and fig. 3), and the applied stress necessary to achieve this, $\sigma_a = \sigma_p$, from Eqs.[2] and [20] is

$$\sigma_p = (E\gamma/4c)^{1/2}. \qquad [21]$$

In practice, most cracks are not atomically sharp, but are blunted by plastic relaxation in the vicinity of the crack tip. Thus the radius of curvature at the tip becomes increased from $R = a_o$ to some larger value, $R = R_1$. Nevertheless, to propagate a plastically blunted crack it is still necessary that the stress acting on the bond A-A_0 at the tip exceed σ_m. Now, if $R_1/a_o = \rho$, then from Eqs.[20] and [21] it can be shown that

$$\sigma_p(\text{blunted crack}) = (E\rho\gamma/4c)^{1/2}. \qquad [22]$$

In other words, the energy ϕ_p involved in propagating a blunted crack is simply $(\rho\gamma)$, where ρ is a dimensionless, variable ratio (R_1/a_o) dependent upon the amount of plastic relaxation at the crack tip, and therefore upon temperature, propagation rate, yield stress, metallurgical composition and structure, etc.

Note that this analysis* suggests that the crack propagation energy, ϕ_p, is related directly to the surface free energy, γ, and should not be thought of as the <u>sum</u> of the surface free energy <u>plus</u> a plastic relaxation energy term, p. It will be appreciated that if ϕ_p is equated to $(\gamma + p)$, and $p \gg \gamma$ - as is

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*Also presented by Gilman (1960a) and Stoloff and Johnston (1963).

ordinarily the case for ductile metals - it is difficult to see how the magnitude of ϕ_P could be significantly affected by the testing environment.

Consider next the situation depicted in fig. 2. It will be noted that to propagate the crack from X to Y under a reduced stress, because of the presence of embrittling liquid-metal atom B, it is only necessary that the strength of the bond A-A_0 be affected. In other words, the embrittling action of B is independent of the radius of the crack tip. This possibility leads to the suggestion that it might be useful to define a coefficient of embrittlement, η, relating the energy adsorbed in breaking bonds at the crack tip in the presence and absence of an embrittling phase. A convenient definition is

$$\eta = \left(\phi_{P_{A(B)}} / \phi_{P_A}\right)_{\rho = 1} \qquad [23]$$

The total energy involved in the propagation of a crack in a metal, ϕ_P, can then be written as:

$$\phi_P = (\eta\rho\gamma) \qquad [24]$$

where η and ρ are simple and independent ratios, η being an environmental variable, and ρ a plastic relaxation variable.

1. <u>Crack Propagation in the Zn_S-Hg_L System:</u> To examine the validity of this approach, Westwood and Kamdar (1963) determined values of ϕ_P for Zn_S from liquid nitrogen temperature to 60°C, and for the Zn_S-Hg_L embrittlement couple from the melting point of Hg, -39°C, to 60°C utilizing the double cantilever cleavage technique. A diagram of the type of specimens used in included in fig. 10. Following Gilman (1960b), the cleavage fracture energy, ϕ_P, was computed from the relationship

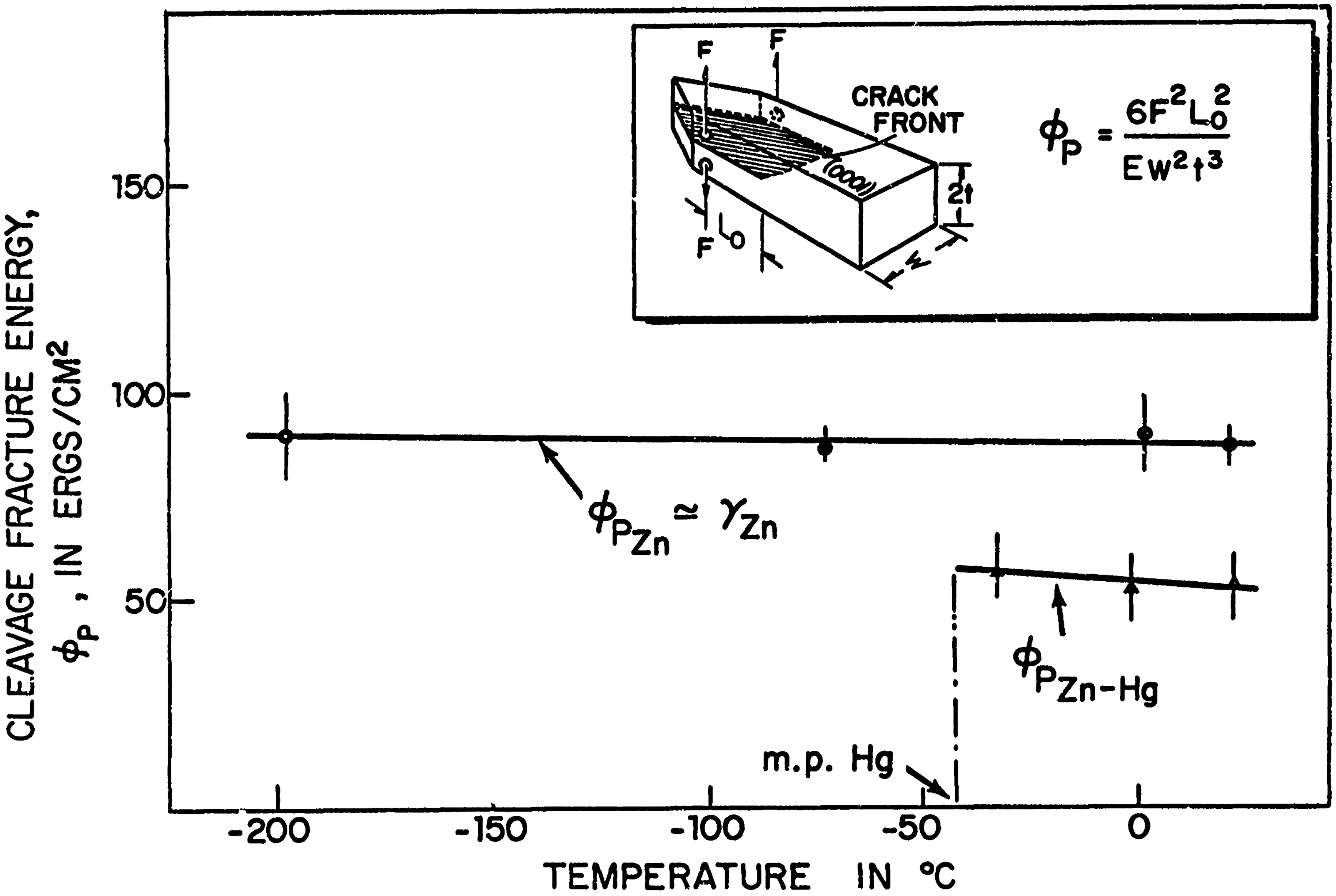

Fig. 10 - Effects of temperature and Hg_L environment on the cleavage crack propagation energy, ϕ_P, for the (0001) planes of Zn. The inset shows the formula and type of specimens used to determine ϕ_P (Westwood and Kamdar 1963).

$$\phi_P = (6F^2 L_o^2 / Ew^2 t^3) \qquad [25]$$

where F is the load to propagate a pre-existing crack of length L_o (introduced at -196°C), and w and t are the specimen dimensions designated in the figure. The results are presented in fig. 10. It can be seen that the value of ϕ_P for zinc, 90 ± 10 ergs/cm^2, is essentially independent of temperature. This value is therefore regarded as the true fracture surface energy for cleavage on the basal plane of Zn_S, i.e., γ_{Zn}. When Hg_L was present at the crack tip, however, ϕ_P was reduced to 53 ± 8 ergs/cm^2. This value is identical with that for the energy to initiate a crack in Zn_S in the presence of Hg_L(53 ± 3 ergs/cm^2, Section III-B-1), as is to be expected since both crack initiation and propagation occur in the basal plane and involve the breaking of Zn-Zn bonds across this plane. The coefficient of embrittlement for the Zn_S-Hg_L couple, η, where $\eta = \left(\phi_{P_{Zn-Hg}} / \phi_{P_{Zn}}\right)_{\rho=1}$, is 0.61 ± 0.12.

Similar experiments were also performed using Ga_L as the embrittling liquid metal for Zn_S. In this case, $\phi_{P_{Zn-Ga}}$ was 42 ± 13 ergs/cm^2 and $\eta = 0.48 \pm 0.17$, indicating that Ga_L is more embrittling for Zn_S than is Hg_L. Several tests were made in which Hg_L presaturated with Zn was used as the embrittling environment. Again, ϕ_P was ~ 53 ergs/cm^2, thus providing support for the view that L-ME does not involve a simple dissolution effect (Rostoker et al. 1960).

It may be concluded from this work that the values of ϕ_P observed in the presence of Hg_L or Ga_L, which are less than γ for the basal plane of Zn_S, provide support for the reduction-in-bond-strength model for L-ME.

IV. METALLURGICAL AND PHYSICAL FACTORS

If adsorption-induced L-ME can be regarded as a special case of brittle fracture, it follows that those metallurgical parameters which tend to induce brittle behavior in a metal also will increase susceptibility to this type of embrittlement. This aspect of L-ME has been discussed recently by Stoloff et al. (1966) and the relevant factors suggested by these workers are (i) a coarse grain size, (ii) a high yield stress caused by solid solution or dispersion hardening, (iii) an inability to deform on a sufficient number of slip systems to satisfy the Von Mises criterion for ductility in a polycrystalline solid, and (iv) a reduced tendency for cross slip caused by lowering the stacking fault energy (SFE) via alloying, reducing the temperature, increasing the strain rate, or by the presence of long range order.

A. Effects of Alloying

The effect of reducing the SFE of Cu_S by alloying with Al, Zn, Si or Ge on the susceptibility of this metal to embrittlement by Hg_L is shown in fig. 11(a) (Stoloff et al. 1966). For alloys of low stacking fault energy, the ratio of the fracture stress in Hg_L to the flow stress in air, $\sigma_{F(Hg)}/\sigma_{f(Air)}$, is about one, reflecting the observation that fracture occurred at or just above the flow stress. As the stacking fault energy increases, $\sigma_{F(Hg)}/\sigma_{f(Air)}$ increases approximately linearly to the limit of experimentally determined stacking fault energies (by transmission microscopy, Swann 1963). Rosenberg and Cadoff (1963) also have studied the embrittlement of Cu alloys in Hg_L, but have attributed the increasing embrittlement of these alloys with solute content to the increase in flow stress. Stoloff et al. (1966) comment, however, that the fact that

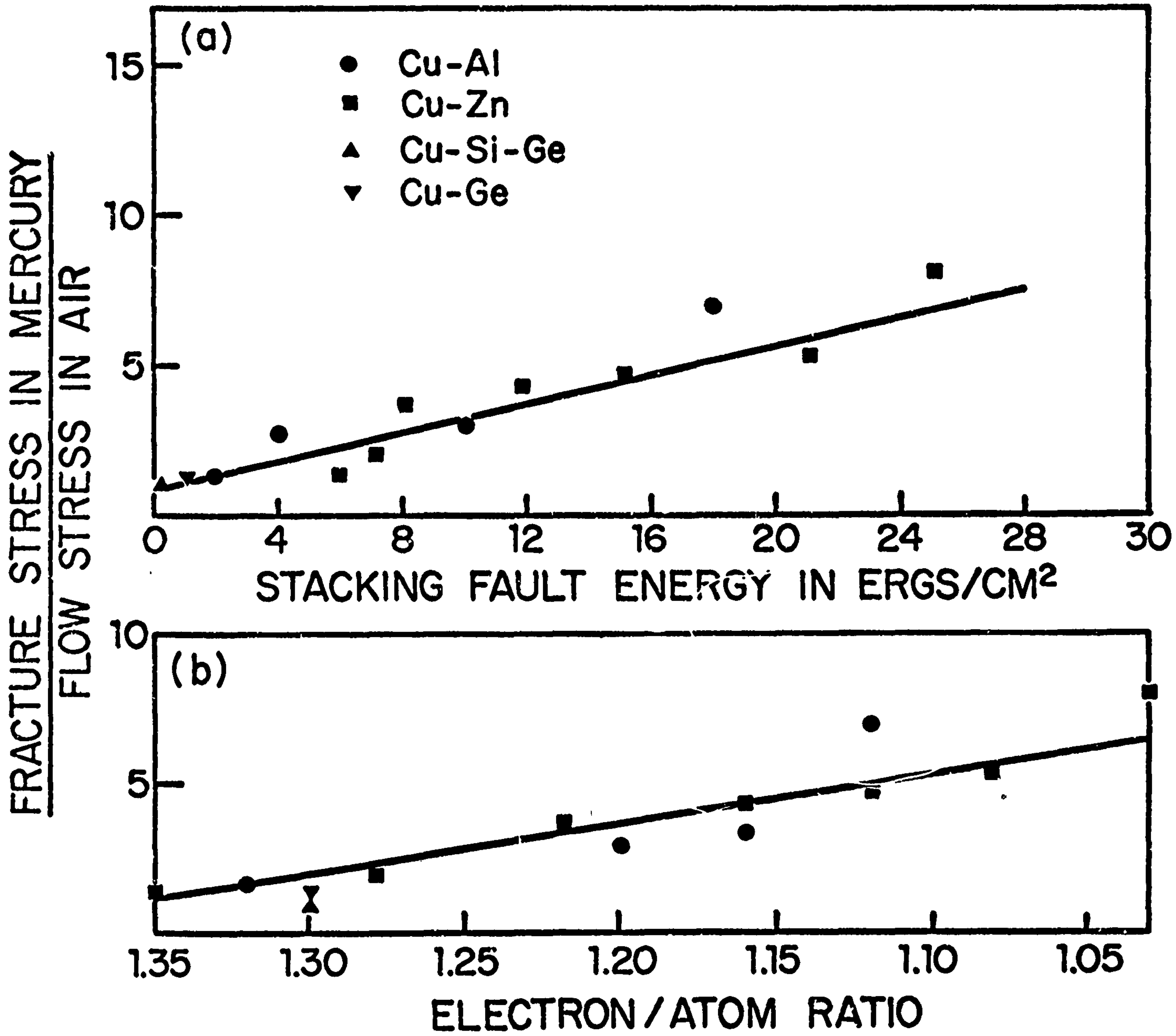

Fig. 11 - Embrittlement of Cu base alloys as a function of (a) stacking fault energy (after Stoloff et al. 1966), and (b) electron/atom ratio.

$\sigma_{F(Hg)}/\sigma_{f(Air)}$ is reduced as $c_{f(Air)}$ increases may be related to the observation that the magnitude of $\sigma_{f(Air)}$ for polycrystalline materials is itself a function of SFE, probably through the influence of this factor on the grain boundary contribution to the flow stress (Armstrong et al. 1962).

In view of the observed relationship between SFE and susceptibility to embrittlement in these alloys, it might at first be thought that alloying additions control embrittlement simply via the metallurgical parameter, τ, and that, as Rosenberg and Cadoff (1963) and Stoloff et al. (1966) have suggested, the chemical nature of solute species has no pronounced effect. However, it is known that the electron/atom ratio determines the SFE of Cu-Zn, -Al, -Si or -Ge alloys (Smallman and Westmacott 1957, Howie and Swann 1961, Foley et al. 1963), and also affects their elastic constants. For example, the observed decreases in $[(c_{11} - c_{12})/2]$ with additions of solutes of valency higher than that of Cu are related to the electron/atom ratio of the alloys (Neighbours and Smith 1954). It is apparent, then, that alloying can also affect the bond strength of an alloy, so that in some instances at least, it may be this factor which actually controls susceptibility to embrittlement. With this possibility in mind, it is of interest to note that the data of Stoloff et al. (1966), shown plotted against SFE in fig. 11(a), exhibits an equally good relationship with electron/atom ratio, fig. 11(b). It may be concluded, therefore, that the chemical nature of the solute species does play a role in the embrittlement of certain copper alloys because it determines the electron/atom ratio of these materials and hence (i) their SFE and the factor τ, and (ii) their elastic properties and hence the parameter σ.

When slip character does not change significantly with alloy composition, or for very dilute alloys, it appears that the flow stress determines the severity of embrittlement. For example, commercially pure Al_S extends some 25% in air, and this strain at fracture is reduced to about 12% when the specimen is amalgamated. However, an Al 2024 alloy specimen (4.5% Cu, 1.5% Mg, 0.6% Mn) in the solution treated and naturally aged condition, and normally exhibiting some 17% elongation, breaks below its flow stress when amalgamated (Nichols and Rostoker 1962).

Even more dramatic are the effects of alloying polycrystalline Zn on its susceptibility to embrittlement by Hg_L (Kamdar and Westwood 1967a), fig. 12. Additions of only ~ 0.2 a/o of Cu, Ag or Au, present in solution, reduce the fracture stress of 1mm grain size material from about 1.4 Kg/mm^2 to 0.4 Kg/mm^2. The latter value is about 20% of the engineering flow stress for these alloys. It can be seen that the fracture stress for the alloyed crystals is not sensitive to a temperature variation of ~ $60^\circ C$, whereas that for pure Zn_S is reduced approximately 20% by decreasing the testing temperature from $25^\circ C$ to $-33^\circ C$. Since it is known that the stress to propagate a crack in Zn_S in the presence of Hg_L is not affected by temperature in this range, fig. 10, it follows that it must be the crack initiation process which is temperature sensitive for pure Zn_S in Hg_L.

It does not seem likely that increases in the susceptibility of Zn_S to Hg_L could be explained in terms of a decrease in SFE or bond strength on alloying because of the low concentrations of solute element present, but it is known that such additions serve to raise the critical resolved shear stress of monocrystals by a factor of about 6 (see Section III-B-2). Thus it is not unreasonable

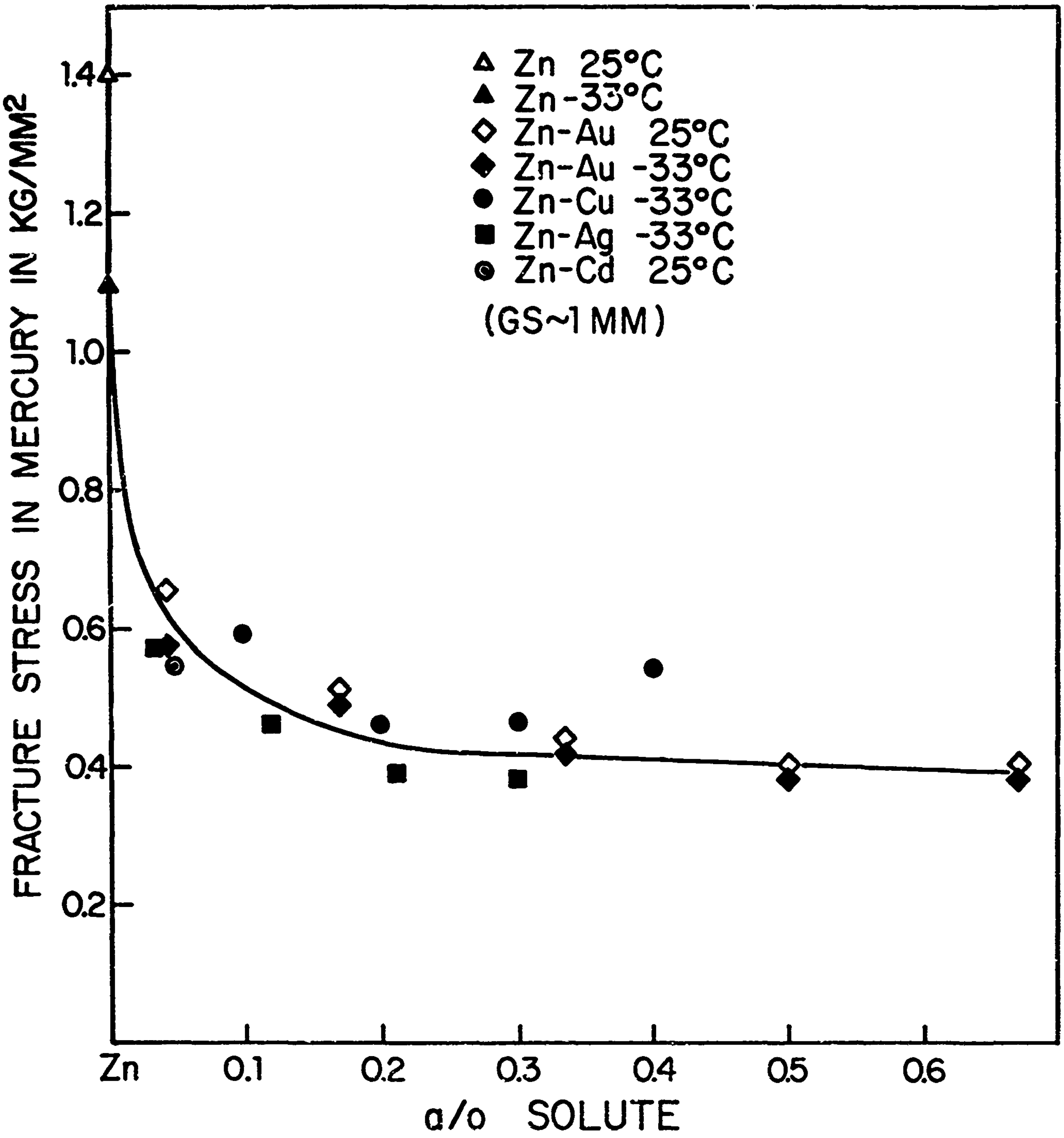

Fig. 12 - Illustrating effects of small solute element additions on susceptibility of polycrystalline Zn to embrittlement by Hg_L (Kamdar and Westwood 1967a).

to suppose that the addition of say 0.2 a/o Cu effectively locks dislocation sources at grain boundaries without creating alternate sources in the form of precipitate particles. As a result, dislocation generation is delayed, eventually occurring in a more catastrophic and inhomogeneous manner than in pure Zn_S, facilitating the production of stress concentrations at boundaries. Such stress concentrations could be relaxed either by crack formation at the boundary, plastic deformation in the neighboring grain (not likely to happen in many instances because the applied stress is far below the macroscopic flow stress), or dislocation leakage from the pile-up by climb. The latter effect may be responsible for the temperature sensitive nature of the fracture initiation stress in pure Zn_S - for it is known that dislocation climb can occur in this material at room temperature (Drouard, Washburn and Parker 1953). At -33°C, however, climb out of pile ups is significantly reduced, as demonstrated by Mader (1963), and presumably this phenomenon is also reduced by alloying.

It can be seen from fig. 12 that a fracture stress of about 0.4 Kg/mm^2 is achieved by the addition of some 0.2 a/o of solute to Zn_S, and that this value is not reduced further by greater additions. This suggests that 0.4 Kg/mm^2 may be the minimum stress for crack initiation in Zn_S of this grain size. In this case it may be possible to apply Eq.[19] and compute a crack initiation energy for these alloys. Assuming that fracture initiates by cleavage (though propagation may sometimes be partially intercrystalline) and on a basal plane making some angle between 30^o and 60^o to the tensile axis, and taking τ_C to be 80-100 g/mm^2 (the c.r.s.s. for Zn - (0.2-0.4 a/o) Cu alloys), γ is found to be between 45 and 65 $ergs/mm^2$. Considering the assumptions, this value is in remarkable agreement with that of $\gamma = 62$ ergs/cm^2 derived from the alloyed bicrystal studies discussed in Section III-B-2.

The significant effects of small alloying additions to Zn_S on its susceptibility to L-ME may be the exception rather than the rule, however, and probably result from the large effect of such additions on the c.r.s.s. of individual grains and possibly on slip distribution. On this point, Rostoker et al. (1960) cite a number of examples to show that small alloying additions (~ 1%) of various elements to 70-30 brass have no significant effect on its susceptibility to embrittlement by Hg_L. On the other hand, this result may be a consequence of the fact that 70-30 brass is already close to the susceptibility maximum for Cu alloys in Hg_L, so that further additions could have only a minor influence.

It is generally observed that high-strength alloys are more severely embrittled than low strength alloys based on the same metal. Rostoker et al. (1960) have demonstrated this for both steels and a wide variety of Al alloys. For the latter materials, a comparison was made between the fracture stress in air and that in $(Hg\text{-}3\%\ Zn)_L$, and these data are shown replotted in fig. 13. Below about 65 kpsi, the fracture strength in $(Hg\text{-}3\%\ Zn)_L$ and in air are not significantly different. Above this critical stress, however, the Hg_L environment causes increasingly severe embrittlement. That is, the greater the intrinsic strength of the alloy, the weaker it becomes when exposed to $(Hg\text{-}3\%\ Zn)_L$. The data also indicate, however, that this environment has a significant effect on the ductility of even the weakest alloys, and for materials of strength greater than 65 kpsi failure occurs below the flow stress.

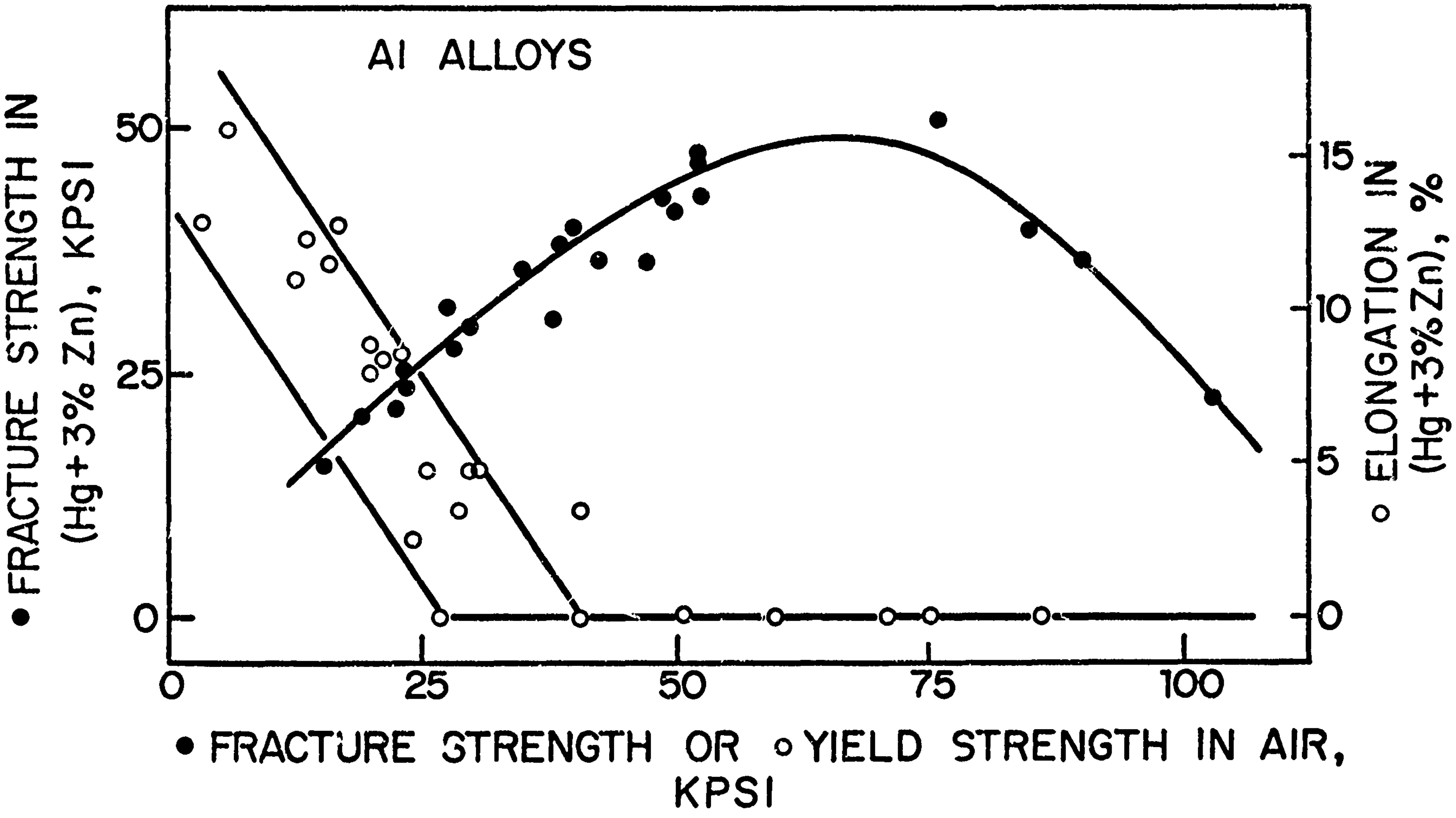

Fig. 13 - Correlation for Al alloys between ● fracture strength in air and in (Hg + 3% Zn) amalgam, and ○ yield strength in air and elongation at failure in (Hg + 3% Zn) amalgam. (After Rostoker et al. 1960.)

Although it is a general observation that alloying increases susceptibility to L-ME, the possibility of alloying a metal, say Al_S, so as to inhibit embrittlement in a specific environment, say Hg_L, is intriguing. It is conceivable that this could be accomplished by choosing an alloying element which forms strongly bonded, high melting point intermetallic compounds with the liquid metal element. For the Al_S-Hg_L system such an element could be Mg; but not Zn. This and similar possibilities are currently being investigated by the authors.

B. Effects of Temperature

The observation that susceptibility to L-ME sometimes increases with decreasing temperature, fig. 14, is often quoted in support of the view that L-ME does not involve any thermally activated or dissolution dependent process. In fact, however, very little quantitative work of sufficient precision has been done to establish the true role of temperature in determining the severity of embrittlement. The two extreme effects of temperature are readily envisaged .... at low temperatures the liquid metal solidifies and no embrittlement results; at high temperatures the solid metal becomes excessively ductile (τ decreases) and cannot initiate or sustain a sharp crack, and, again, L-ME is not observed. According to Petch (1959), the brittle to ductile transition temperature, T_C, should be proportional to log of the grain diameter, d. Data from studies by Nichols and Rostoker (1960) on 70-30 brass in Hg_L, fig. 15, are in accord with this relationship, fig. 16.

At temperatures between the upper and lower extremes, however, it does appear that the severity of embrittlement is relatively insensitive to temperature, except in situations where the rate of diffusion of the liquid metal atoms

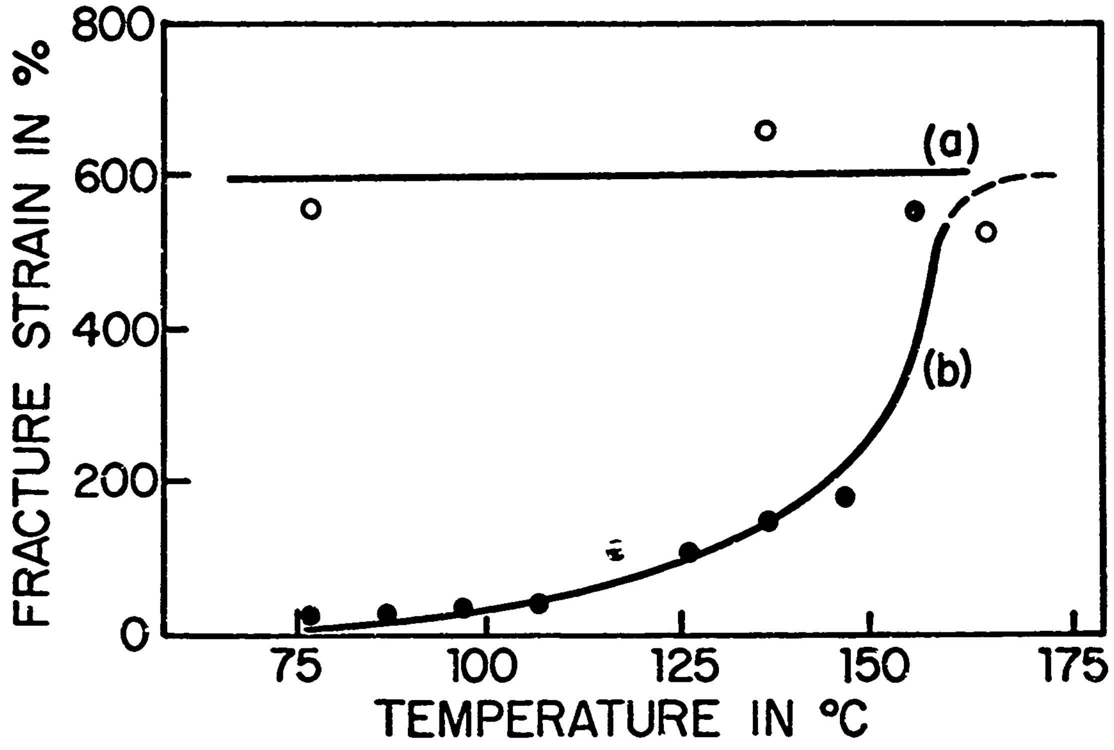

Fig. 14 - Dependence of strain at fracture on temperature for (a) unamalgamated, and (b) amalgamated Zn monocrystals of ~ 1mm diameter. (After Rozhanskii et al. 1957.)

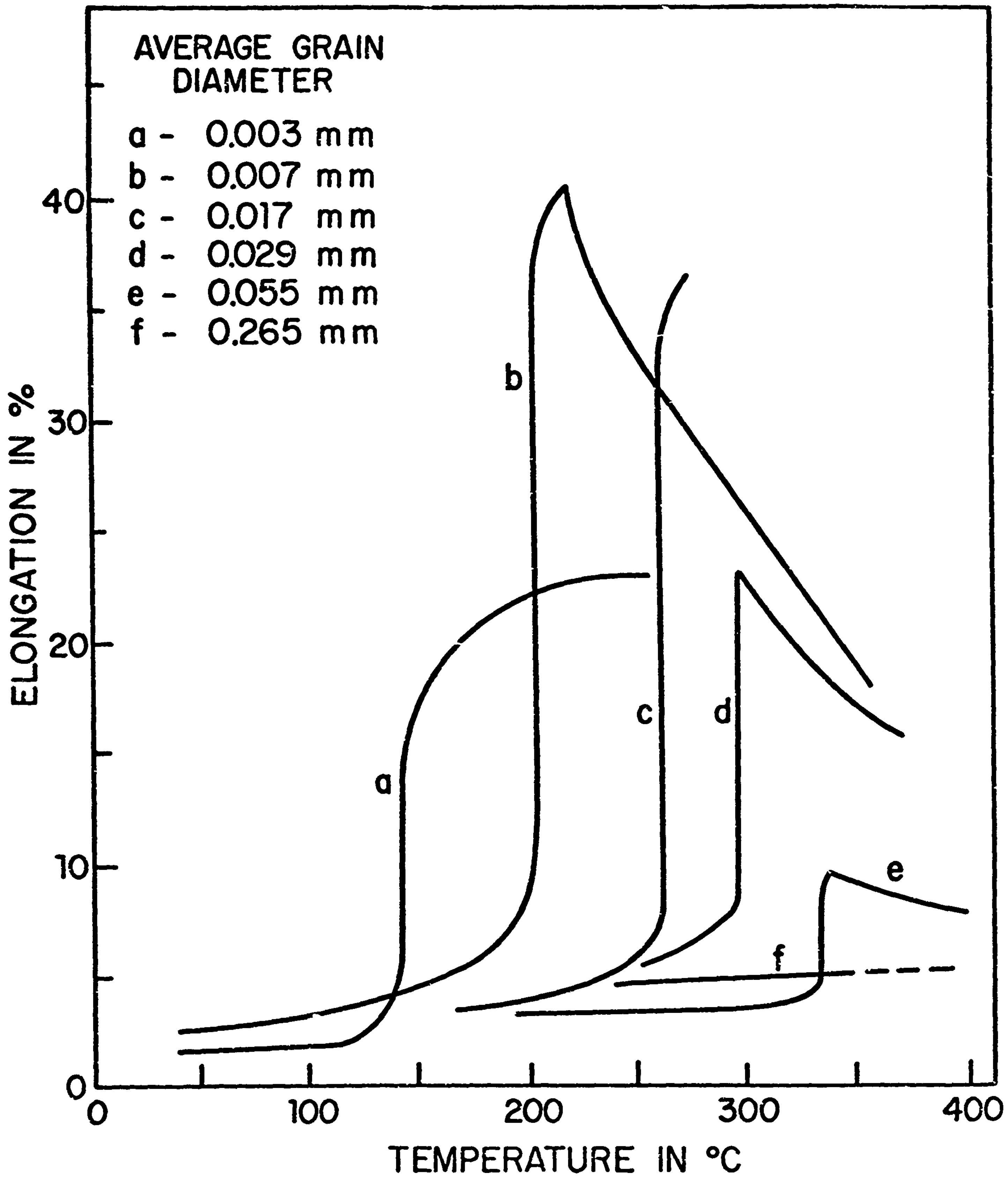

Fig. 15 - Variation in brittle to ductile transition temperature, T_C, for 70-30 brass specimens of various grain diameters, a-f, tested in Hg_T (After Nichols and Rostoker 1960.)

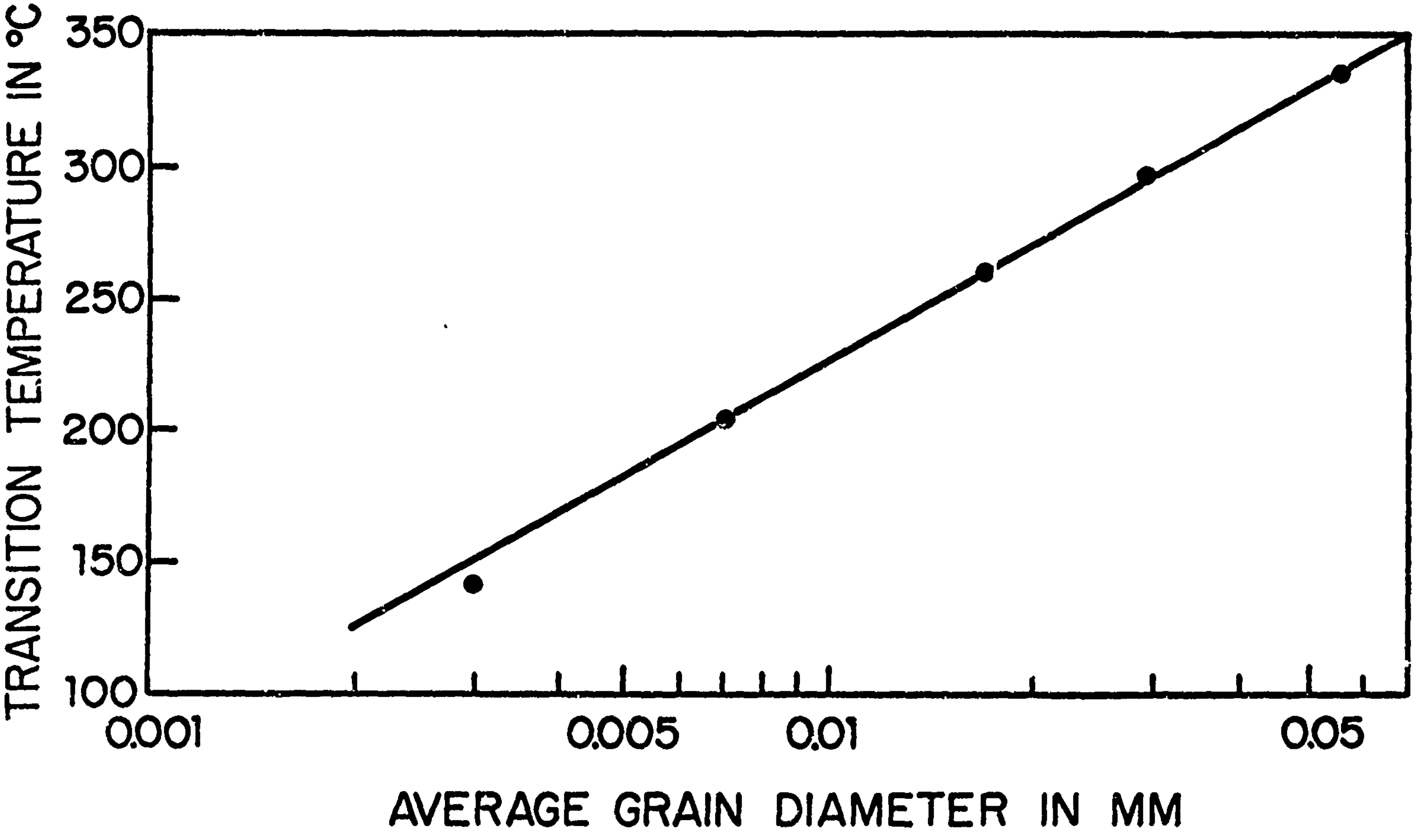

Fig. 16 - Correlation between brittle to ductile transition temperature for amalgamated 70-30 brass specimens and log of the grain diameter (after Nichols and Rostoker 1960).

to the crack tip is a controlling factor. When the liquid metal is already at the crack tip before the material is stressed, then the magnitude of Φ_P is not markedly affected by variations in temperature of, say, 60 degrees C, fig. 10. Studies of the rate of crack propagation through polycrystalline sheet, on the other hand, have revealed various effects (Rhines et al. 1962). For Al 2024-T4 plate wetted with Hg_L, fig. 17, the rate of crack propagation increases with temperature. The variation is small, however, and leads to apparent activation energy of only about 0.05 eV. Rhines et al. (1962) comment that it seems doubtful that this value could be associated with any chemical reaction process, but it may be associated with a change in viscosity of the Hg_L with temperature. An alternate possibility is that this value represents the activation energy for second monolayer diffusion of Hg atoms to the crack tip (see below). For polycrystalline 70-30 brass, the cracking rate at first increases and then decreases, fig. 17. Rhines et al. (1962) suggest that the decrease at temperatures above 50°C in brass is associated with the formation of intermetallic compounds with components of the brass which "choke off" the mercury flow to the crack tip. However, the solubility of Cu_S in Hg_L is very small at 50°C, and Zn_S, which is soluble to about 10 a/o in Hg_L at 50°C, does not form compounds with Hg which are stable at this temperature. An alternative possibility is that the reduced rate of crack propagation is associated with an increased rate of "sideways" intergranular penetration. Studies with bi-crystals could clarify the actual cause of this effect.

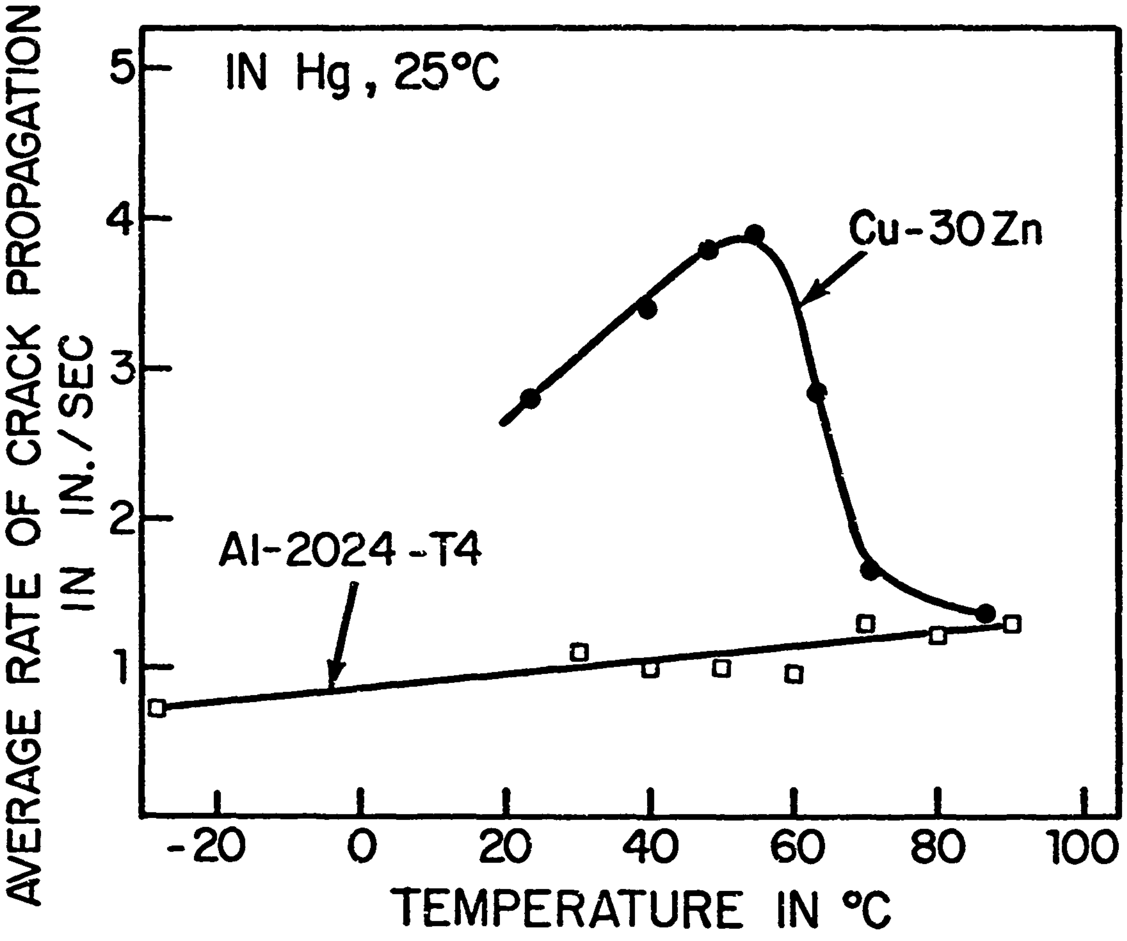

Fig. 17 - Variation of crack propagation rate with temperature for amalgamated polycrystalline brass or aluminum alloy specimens (after Rhines et al. 1962).

One of the major points of concern in understanding the nature of L-ME has been to explain the high rates of cracking sometimes observed in otherwise ductile metals in view of the requirement that the liquid metal be continuously present at the propagating crack tip. There is evidence that the fluid mechanics of the system controls the rate at which the bulk liquid metal travels to the vicinity of the crack tip (Rhines et al. 1962). However, there is some discussion of how close the bulk liquid metal can get to the tip before transport by some other process, such as mono- or bi- layer diffusion, is required. Rostoker et al. (1960) suggest that a driving force of 10^5 atmospheres would be required for "bulk" liquid metal to be present at an atomically sharp crack. Robertson (1966), however, has pointed out that capillarity effects could provide "negative" pressures of order 10^4 - 10^5 atmospheres which would pull the liquid metal into very small cracks, aiding transport to the tip.

If it is assumed that the liquid metal atoms proceed from the bulk liquid phase to the crack tip by monolayer diffusion, say of Hg_L on Zn_S, then the observed crack propagation rates may be difficult to explain because this can be rather a slow process. On the other hand, since it is known that liquid metal atoms are expendable in the embrittlement process- presumably because they become stably adsorbed on the freshly created fracture surfaces - it can be argued that transport to a propagating crack tip probably occurs by a second monolayer process, e.g., by Hg atoms over Hg atoms, and not Hg atoms over Zn atoms (Westwood and Kamdar 1963). While the actual value of the activation energy, Q, for the second monolayer diffusion of Hg on Hg has not, to the authors' knowledge, been determined, Q for Cs on Cs is $\sim$ 0.1 eV, and $D_o \sim 10^{-2}$ cm^2/sec at about 30°C (Smithells 1955). These values suggest that second monolayer diffusion should be capable of maintaining a sufficient supply of liquid metal atoms at the crack tip to explain observed rates of crack propagation.

Robertson (1966) has also considered the problem of high rates of crack propagation on the basis of a dissolution model for L-ME. He estimates that the diffusion of solid metal atoms away from a crack tip via the liquid metal phase can occur sufficiently rapidly to produce crack propagation rates of 10-4000 cm per sec.

C. Static Fatigue and Strain Rate Effects.

When a ductile solid metal is subjected to a tensile stress σ_a in an inert environment, the relationship usually observed between time to failure, t_F, and σ_a is

$$t_F = t_o \exp(U_o - \Gamma\sigma_a/kT)$$

(Zhurkov 1966), where t_o is a constant of order 10^{-13} sec, U_o is a term related to the binding energy of the solid and is approximately the heat of sublimation, Γ is a structure dependent coefficient, and k is Boltzmann's constant. Such a relationship is displayed by the data of Bruyukhanova et al. (1962) for Zn_S in fig. 18, curves (a) and (c). For amalgamated Zn crystals, however, once a critical tensile stress is exceeded, a very abrupt decrease in lifetime occurs over a small range of stress, curves (b) and (d). For example, amalgamated Zn polycrystals fractured instantaneously at a stress of 1000 g/mm^2; under a stress of 960 g/mm^2 they remained unbroken after more than 10^6 sec. The magnitude of this critical stress was not significantly affected by temperature over the range

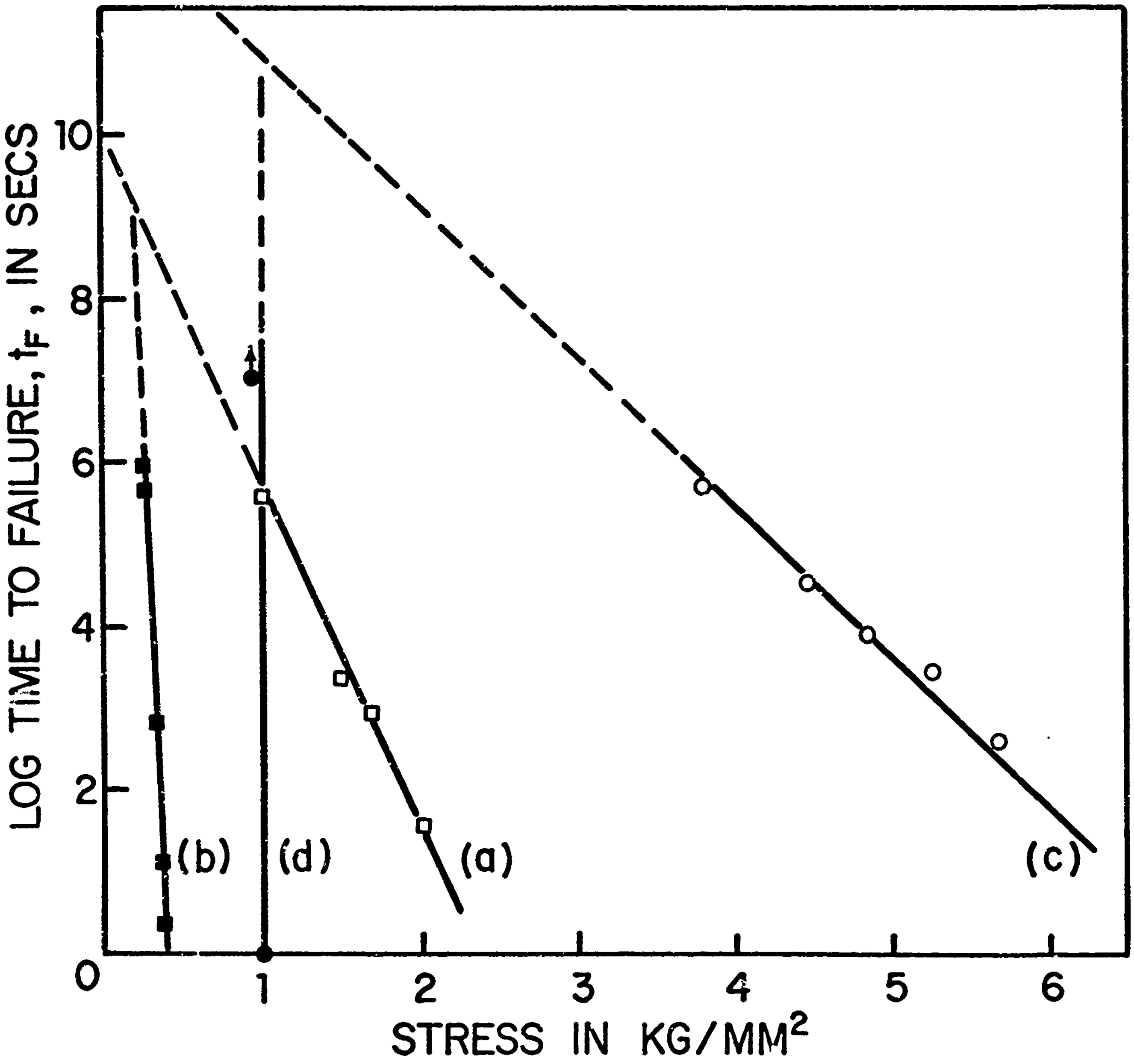

Fig. 18 - Variation of time to failure with applied stress for Zn_S at room temperature. Curves (a) and (b) for unamalgamated and amalgamated monocrystals ($\chi_0 = 50^o$, ~ 1mm dia.), respectively; curves (c) and (d) for unamalgamated and amalgamated polycrystals, respectively, (After Bryukhanova et al. 1962).

20°-100°C. Similar results were obtained for Cd_S specimens in Ga_L and, by Preece and Westwood (1967), for Cd_S specimens in Hg-In solutions. The latter observations will be discussed in Section V-E. Bruyukhanova et al. (1962) have concluded from their work that in the presence of a pure, embrittling liquid metal, the fracture process is not thermally activated. The catastrophic nature of the failure process further suggests that fracture under such testing conditions is controlled by the crack initiation process. This view would seem to be in accord with the suggestion of Stroh (1957), later verified by Smith and Barnby (1967), that provided the effective fracture surface energy for crack propagation, ϕ_P, is equal to (or less than) the true surface energy at all stages, then in an applied tensile stress field the crack initiation process controls the fracture behavior of the solid.

It is interesting to note that the critical stress for rapid failure in static fatigue tests is approximately equal to the dynamic fracture stress for both Zn_S in Hg_L (Bruyukhanova et al. 1962) and Cd_S in $(Hg\text{-}In)_L$ (Preece and Westwood 1967).

A number of Russian workers have reported that the strain at fracture, ϵ_F, of 1mm dia. Zn monocrystals coated with Hg_L, Ga_L or Sn_L is markedly dependent on strain rate, $\dot{\epsilon}$ (e.g., Labzin and Likhtman 1959, Shchukin et al. 1963). In the region of $\dot{\epsilon}$ = 10-15% per min, all three liquid metals reduced ϵ_F from that in air; but at very low strain rates (10^{-1}-10^{-3}% per min) the ductility of wetted crystals was markedly increased, fig. 19 (lower curve). These results, however, were not confirmed by the more recent investigation of Kamdar and Westwood (1966b), in which carefully prepared and handled 6mm square Zn monocrystals were coated with Ga_L

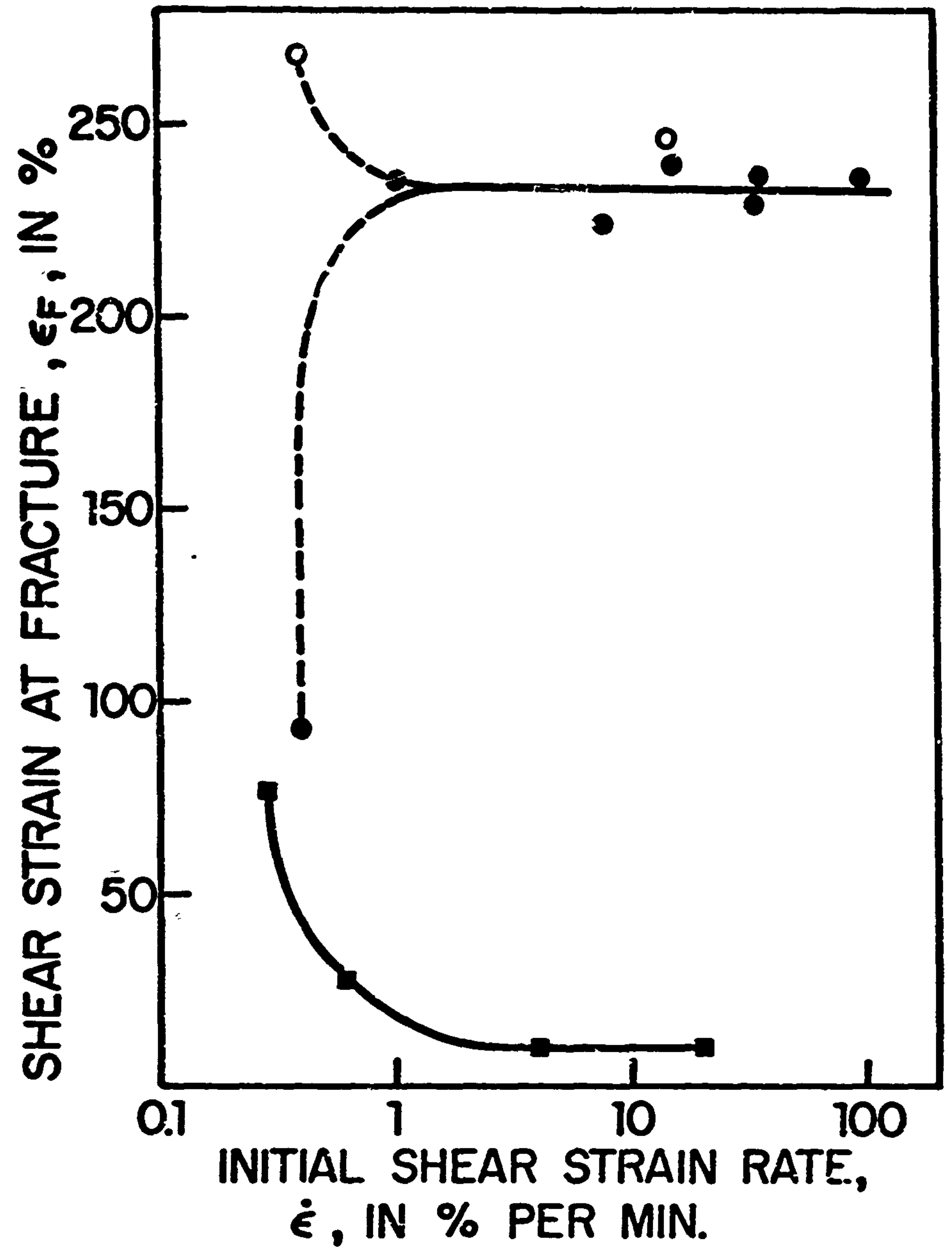

Fig. 19 - Strain rate dependence of the shear strain at fracture for (i) lower curve, 1mm dia. Zn monocrystals coated with Ga_L (After Shchukin et al. 1963). Note "plasticizing" effect at low strain rates. (ii) upper curves, 6mm square Zn monocrystals partially coated with Ga_L (o) or uncoated (o) (Kamdar and Westwood 1966b).

or Hg_L in the center of the gauge length only. They found that for shear strain rates of 1-100% per min., neither Ga_L coatings nor Hg_L coatings produced any significant embrittlement of crystals deforming principally by single slip, fig. 19, upper curves. Moreover, whereas Shchukin et al. (1963) reported a "plasticizing" effect for Ga_L coated specimens tested at $\dot{\epsilon} < 1\%$ per min, the converse effect was found in the more recent work. Specimens tested at $\dot{\epsilon} < 1\%$ per min deformed in a markedly inhomogeneous manner, with well developed kink bands forming in the gauge section. In the presence of Hg_L or Ga_L, cleavage fractures initiated at such kink bands at relatively low stresses and strains. For uncoated crystals deformed at low strain rates on the other hand, the strains at fracture increased, though fracture stresses were not significantly affected. Since the experiments performed with uncoated crystals at initial shear strain rates of ~ 0.4% per min required more than 12 h for completion, it is likely that the increased strains at fracture observed can be explained in terms of simultaneous deformation and recovery in Zn_S at room temperature (Deruyterre and Greenough 1956).

The discrepancies between the earlier observations and those of Kamdar and Westwood (1966b) probably result from problems in handling the 1mm dia. crystals used by the earlier workers. At "high" strain rates, accidentally introduced damage causes inhomogeneous deformation behavior and kink band formation in such crystals. Cracks then nucleate at these kink bands at relatively low strains. At "low" strain rates, however, time is available for some of this damage to anneal out, and this results in an apparent plasticization effect. Even so, the "enhanced" value of ϵ_F

observed for "pre-damaged" specimens at low strain rates (~ 75%), lower curve of fig. 19, is less than the "reduced" value obtained at similar strain rates for undamaged crystals (~ 90%), upper curve of fig. 19.

The effect of strain rate on the deformation behavior of polycrystalline materials in the presence of liquid metals does not appear to have been extensively examined. In general, because increasing the strain rate raises τ (fig. 4) and introduces an increasing tendency toward brittleness, it can be expected that increased strain rates will produce a greater susceptibility to L-ME. Figure 20 illustrates such an effect of increasing $\dot{\epsilon}$ on the embrittlement behavior of Al 2024-T4 in In_L at 160°-$170^\circ C$ (Rostoker et al. 1960). The latter workers have also investigated the strain rate sensitive behavior of this alloy in $(Hg + 3\% \ Zn)_L$ solutions over the temperature range 50°-$300^\circ C$ for values of $\dot{\epsilon}$ from 0.18% per min to 30% per min. They noted that the greater $\dot{\epsilon}$, the higher the ductile-to-brittle transition temperature. Unfortunately, interpretation of the results of studies utilizing Al alloys such as Al 2024 is difficult because of the complicating effects of simultaneous changes in structure due to aging and strain aging effects. More readily interpretable work on pure metals would be of value.

D. Effects of Prestrain

For ductile pure metals, or non-strain aging alloys, the fracture stress usually increases approximately linearly with prestrain, while strain at fracture is decreased (Rosenberg and Cadoff 1963, Pargeter and Ives 1967). However, for fine grained material, or strain aging alloys, the effects of prestraining are not always those expected. For example, note the peculiar variation in fracture

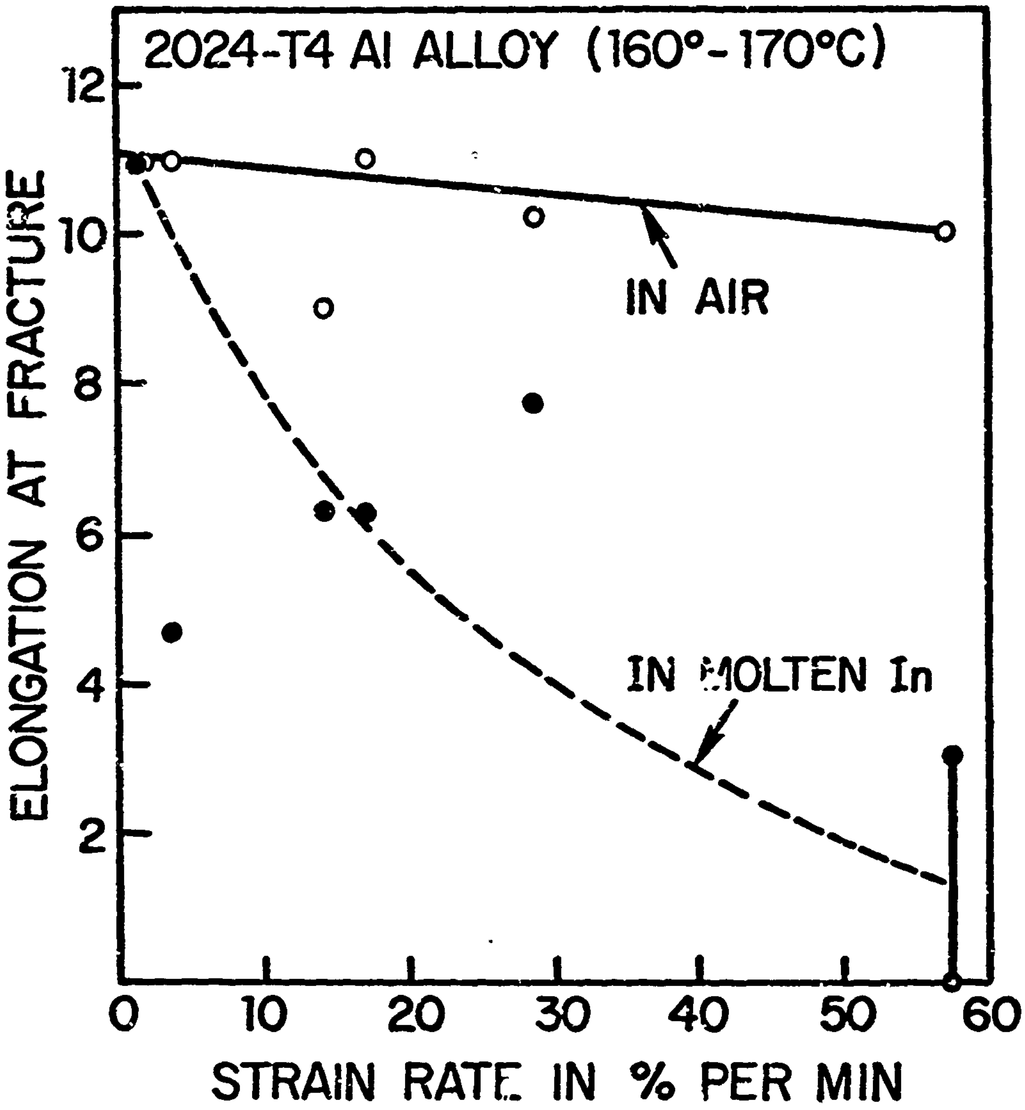

Fig. 20 - Effect of strain rate on susceptibility of polycrystalline Al alloy to embrittlement by In_L. (After Rostoker et al. 1960.)

stress of amalgamated, fine grained 70-30 brass with prestrain in fig. 21. Figure 22 presents some data obtained with a strain-aging alumium alloy, Al 5083 containing 4.5% Mg, 0.7% Mn; Rostoker (1963). It is apparent that the data for the prestrained and amalgamated aluminum alloy specimens do not conform to a Petch-type relationship - unless the fracture energy is actually negative! Figure 23 illustrates the effect of prestrain on the fracture stress of Al 2024 alloy specimens in the aged and amalgamated condition (Nichols and Rostoker 1963). Again an unexpected variation is observed. Nichols and Rostoker (1962) have attempted an explanation of such phenomena in terms of strain aging effects and coherency strains, etc., but, as they remark, the explanation cannot be simple. They conclude that for Al alloys (i) fracture in single phase and non-precipitation hardened structures cannot be initiated without measurable prior yielding, even after large degrees of cold work, (ii) fracture below the flow stress is peculiar to the precipitation hardened state, and the severity of embrittlement is greater when precipitates are coherent with the matrix, (iii) small degrees of cold work superimposed on the aged condition produce the severest embrittlement; large degrees of prior plastic strain cause some reduction in susceptibility.

Recent studies with Cu-4% Al alloys in Hg_L indicate that conclusion (i) also holds for this material (Pargeter and Ives 1967). However, work by Westwood (1964) and Kamdar and Westwood (1967a) indicates that conclusion (ii) is not valid for Zn_S. Polycrystalline pure Zn specimens in Hg_L can fracture at stresses substantially below those at which any marked deviation from linearity in the stress-strain curve occurs.

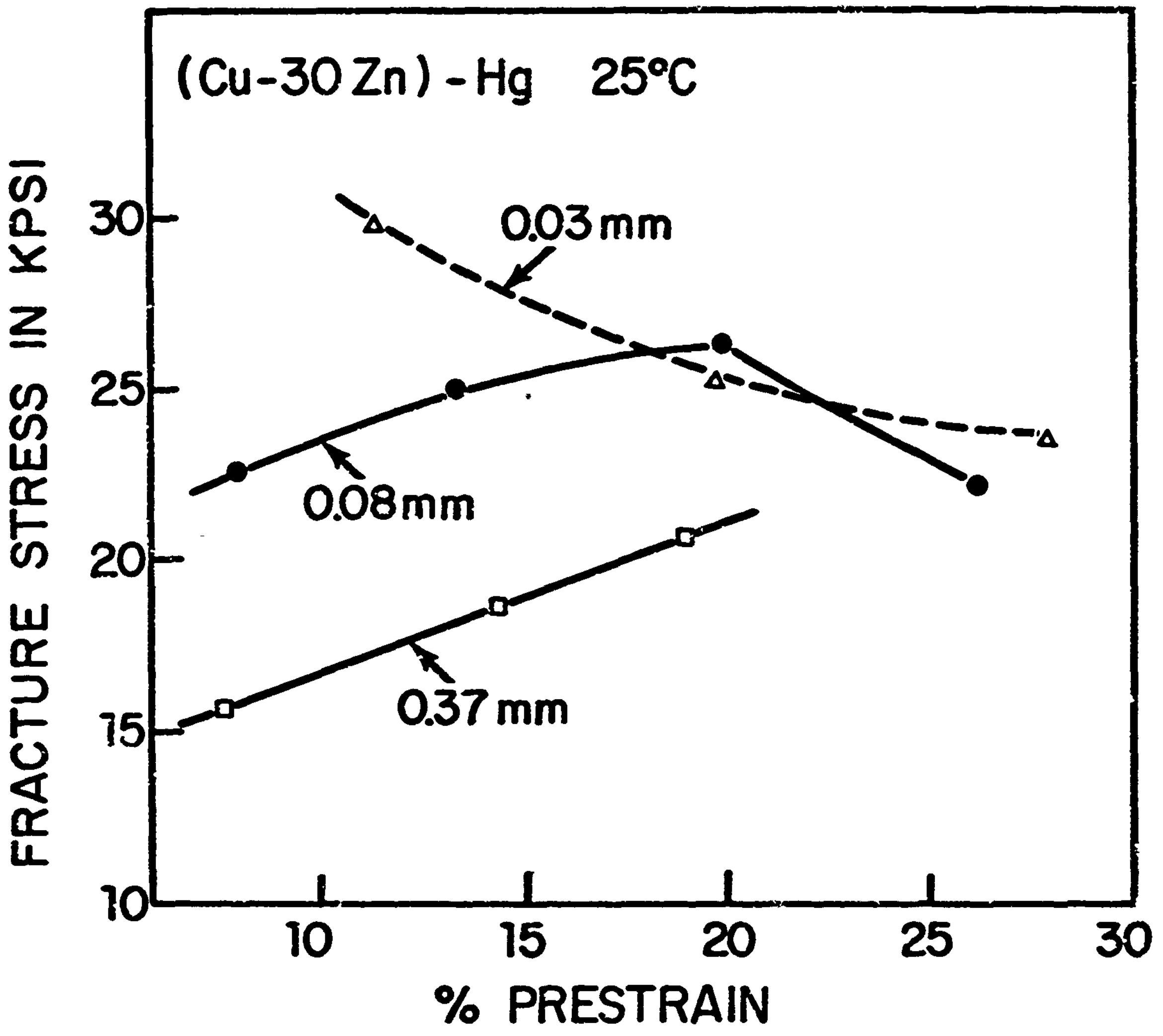

Fig. 21 - Variation with grain size of effects of prestrain in air on fracture stress of 70-30 brass in Hg_L at 25°C. (After Rosenberg and Cadoff 1963.)

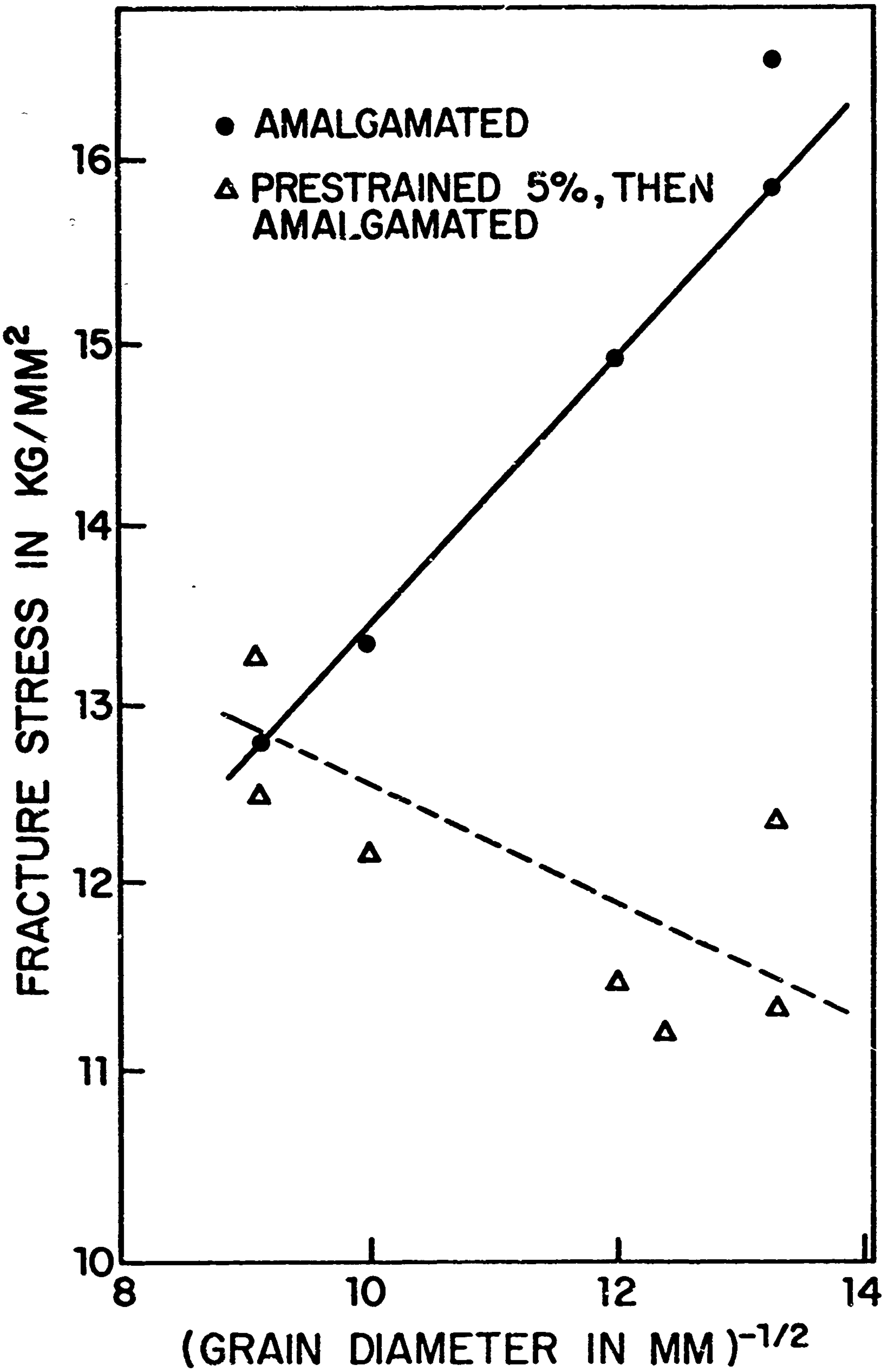

Fig. 22 - Effects of grain size and prestrain on fracture stress of amalgamated Al 5083 alloy specimens. Note that the data from prestrained specimens do not conform to a Petch relationship (after Rostoker 1963).

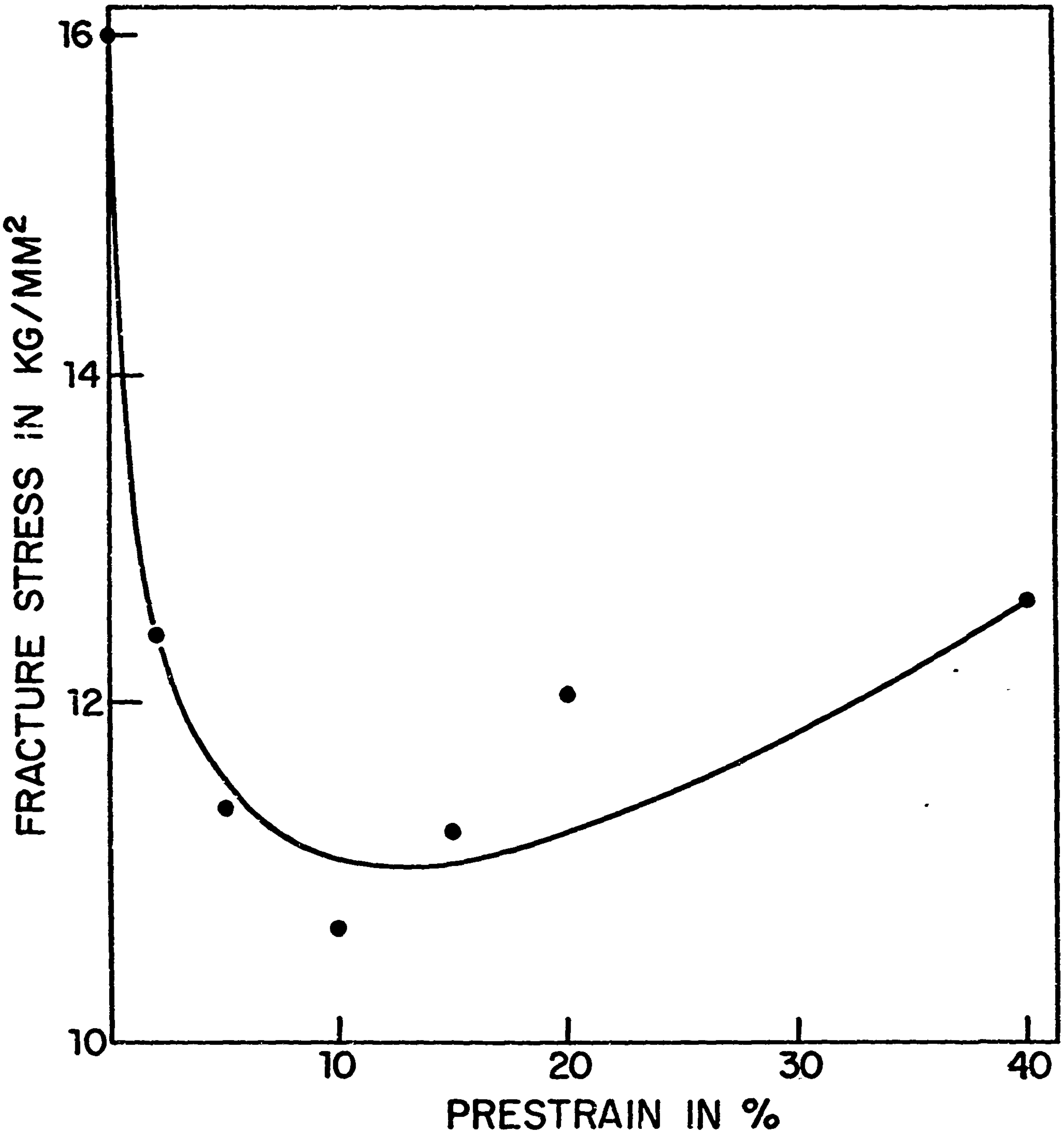

Fig. 23 - Influence of prestrain on fracture stress of amalgamated polycrystalline Al 2024 alloy specimens in aged condition (100°C for 30 min.). (After Nichols and Rostoker 1963.)

V. CHEMICAL ASPECTS

Although many of the physical-metallurgical factors in L-ME have been investigated, very few studies have been made of the chemical aspects of this phenomenon. Yet this is the most important area for study, because the latter parameters decide whether or not embrittlement will occur in a given system. Moreover, a better understanding of the chemical factors determining the selectivity of the process may lead to controlled enhancement or inhibition of embrittlement in a given system (Westwood 1965). Nevertheless, it is only during the past year or so that any systematic studies have been undertaken in this area.

In most work on effects of the chemical composition of the liquid metal phase on degree of embrittlement induced in a given solid metal, it has been customary to utilize an active liquid metal as the environment, and then attempt to modify its action on the solid metal by the addition of solute elements (Rostoker et al. 1960, Kraai et al. 1960, Rosenberg and Cadoff 1963, Westwood 1966). Thus Rostoker et al. (1960) report that additions of up to 0.8 a/o Sn to Hg_L slightly reduce the embrittlement of Al 2024-T3 by this liquid metal; additions of up to 7.0 a/o Cd increase embrittlement slightly, and additions of some 3 a/o Zn or Ga markedly increase embrittlement, i.e., reduce the fracture stress. Other examples of such behavior have been reported for Cu alloy-Hg_L couples (Rosenberg and Cadoff 1963) and for the Cu_S-Bi_L couple (Kraai et al. 1960). In the former systems, additions of Zn, Cd or In to the Hg_L have been reported to reduce the degree of embrittlement, while additions of Au have no observable effect. For the pure Cu_S-Bi_L couple at 345°C, minor additions of either Pb, Tl, Cd or Zn to the molten Bi reduce the embrittlement of Cu_S somewhat, but the addition of as little as 0.4 a/o of Sb produces a considerable effect, raising the fracture stress of Cu_S in Bi_L some 60%. No explanations have been offered for such effects.

A. The Concept of "Inert Carriers"

One of the most useful approaches to be adopted recently, however, is that of "inert carriers" (Kamdar and Westwood 1967b). Among other advantages, this technique allows the possibility of evaluating the effects of several potentially embrittling elements at one temperature. The need for such a technique is evident when it is appreciated that direct investigation of the embrittlement behavior of many potentially interesting solid metal-liquid metal couples is not feasible. This is because, at temperatures just above the melting temperature of the liquid metal, the solid metal is either too ductile to maintain the stress concentrations necessary to initiate and propagate a brittle crack, or is excessively soluble in the liquid metal, resulting in crack blunting. The solution to this problem is to dissolve the potentially active element in an "inert-carrier" liquid metal of lower melting point. In this way, the active element can be present effectively in the liquid state, though actually at some temperature far below its melting point.

To determine the utility of this approach, a study was made of the fracture behavior of Cd_S in Hg_L and several $(Hg\text{-}In)_L$ solutions. Cd and In exhibit only limited mutual solubility at 25°C, and do not form stable intermetallic compounds (Heumann and Predel 1959). Thus, according to the empirical rules discussed by Rostoker et al. (1960) and Kraai et al. (1960), In_L is a potentially embrittling species for Cd_S. Hg_L, on the other hand, does not embrittle Cd_S (Shchukin et al. 1959), but is capable of dissolving up to 70 a/o of In in homogeneous solution at 25°C (Eggert 1962). It can be used, therefore, as the inert, low-melting point carrier metal for the system (Cd_S-In_L).

The data of fig. 24 indicate that Hg_L or $(Hg\text{-}5\ a/o\ In)_L$ solutions do not embrittle Cd_S; failure in these environments occurs by necking and ductile shear after more than 45% elongation. However, in $(Hg\text{-}8\ a/o\ In)_L$ solutions, intercrystalline failure occurs after only 15-20% elongation, and the severity of embrittlement then increases markedly with In content of the Hg_L. In solutions containing more than 40 a/o In, intercrystalline fracture occurs at stresses as low as 55% of the macroscopic flow stress. These results demonstrate, therefore, that a solid metal can be embrittled, in a controlled manner, by exposing it to an "inert", low-melting point liquid metal containing an appropriate concentration of some "active" metallic element in solution. This conclusion was not entirely unexpected, of course, since in other embrittlement phenomena, e.g. stress-corrosion cracking or complex-ion embrittlement (Westwood et al. 1967), it is customary for the active species to be dissolved in some relatively inert medium, such as water, which serves principally as a carrier.

B. A Possible Correlation between L-ME and Electronegativity

If it is assumed that L-ME is caused by a chemisorption-induced reduction in bond strength, then there should be a correlation between severity of embrittlement and some parameter of the system which indicates the nature and

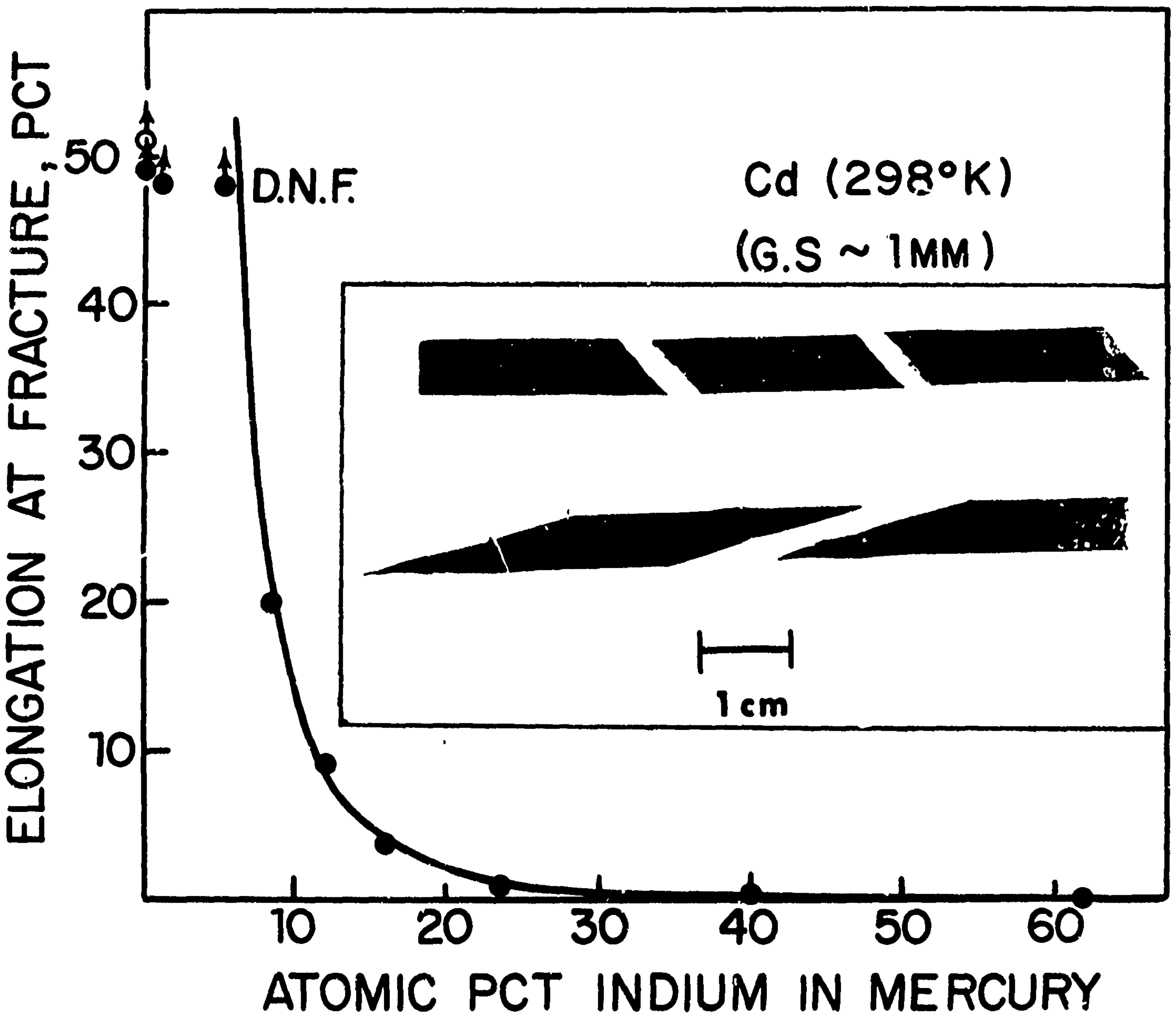

Fig. 24 - Variation in ductility of polycrystalline Cd specimens with In content of (Hg-In)$_L$ testing environment. Inset demonstrates cleavage of Cd monocrystals at 25°C following coating with (Hg-60 a/o In)$_L$ solution. (Kamdar and Westwood 1967b).

strength of the interactions between the components of the embrittlement couple. Current studies at RIAS utilising the "inert carrier" technique indicate that L-ME is not nearly as "specific" a phenomenon as has been generally supposed. Many elements, when available effectively in the liquid state at some appropriate temperature for the particular solid metal, cause some degree of embrittlement. Moreover, there are indications that the severity of embrittlement observed may be related (inversely, qualitatively) to the difference in electronegativity (X) between the solid metal element and the most active element in the liquid metal environment.

In fig. 25 the stress-strain curve shown is an "averaged" curve from a number of high purity Al (99.999 + %) specimens, of gauge dimensions 6mm x 0.5mm, tested under cyclohexane to prevent confusing oxidation effects. The results from tests conducted in Hg_L or various Hg_L solutions (also under cyclohexane) are likewise averaged. It can be seen that, for equivalent solute element concentrations (~ 3 a/o), the severity of embrittlement is related to the difference in Pauling-electronegativity between Al_S (1.5) and the active species in the Hg_L, namely Ga (1.6), Zn (1.6), Cd (1.7), Tl (1.8), Sn (1.8) or Hg (1.9). Similar results have also been obtained for brass in Hg solutions. In this instance, additions of elements to the Hg environment of X different from that of Hg and Cu (~ 1.9) decreased the severity of embrittlement. In other studies it has been shown that Ag_S (1.9) is severely embrittled by Hg_L (1.9), but that additions of up to 70 a/o In (1.7) to the Hg_L gradually restore ductility, fig. 26 (Preece and Westwood 1967). Note that this is exactly the opposite effect to that observed for Cd_S in these solutions, fig. 24.

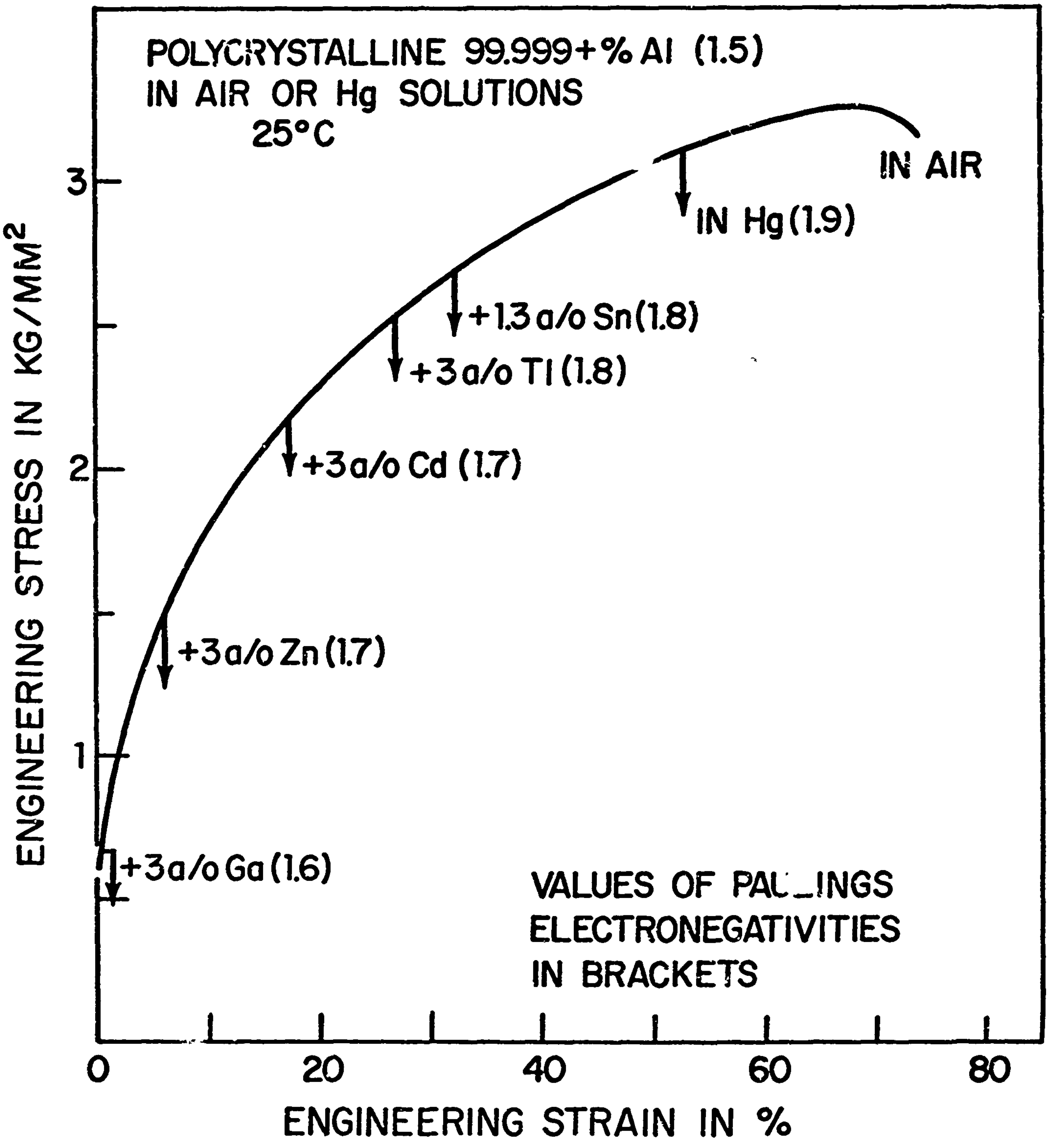

Fig. 25 - Embrittlement of polycrystalline pure Al by various Hg solutions. Note apparent correlation between Pauling electronegativity of solute element and severity of embrittlement (Westwood, Kamdar and Preece 1967).

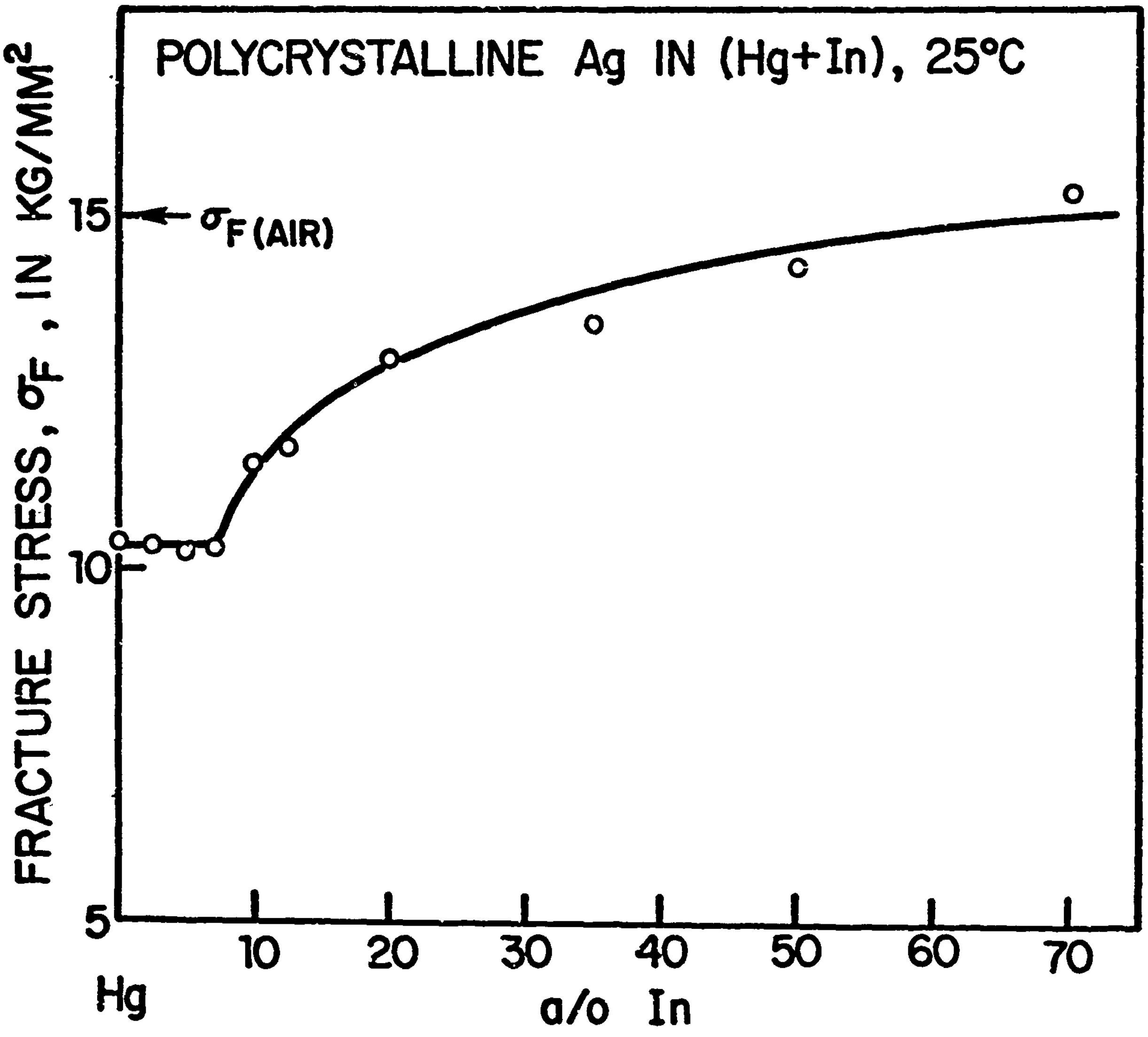

Fig. 26 - Effect of In concentration in Hg_L testing environment on fracture strength of polycrystalline Ag_S (Preece and Westwood 1967).

A similar correlation may also be noted in the embrittlement of solid metals by pure liquid metals. For example, Bi_S (1.9) is embrittled by Hg_L (1.9) but not by Ga_L (1.6) (Westwood and Goldheim 1966); Cu_S (1.9) is embrittled by both Hg_L (1.9) and Bi_L (1.9), but not Ga_L (1.6); Zn_S (1.6) is more severely embrittled by Ga_L (1.6) than Hg_L (1.9) (Westwood and Kamdar 1963); Fe_S (1.8) is equally embrittled by Hg_L (1.9) or In_L (1.7)(Stoloff et al. 1966).

Of course, since electronegativity difference, ΔX, is a measure of the tendency for two elements to form ionically-bonded compounds, the existence of such a correlation could be regarded simply as a semi-quantitative restatement of the empirical rule that embrittlement does not occur in systems which exhibit stable, intermetallic compounds. However, possible exceptions to the correlation also have been noted, for example, the embrittlement of Al_S (1.6) by Na_L (0.9), and of Fe_S (1.8) by Li_L (1.0), and the absence of embrittlement of Cd_S (1.7) by $(Hg + 40\ a/o\ Tl\ (1.8))_L$ at 25°C (Kamdar and Westwood 1967b). Questions could also be raised regarding the use of Pauling's values for atomic electronegativity rather than, say, those of Gordy and Thomas (1956). Indeed, there has been much discussion of the whole concept of electronegativity during the past ten years (Pritchard and Skinner 1955, Hinze and Jaffee 1962, Huheey 1965, Klopman 1965, Peters 1966), and this more recent work has involved detailed considerations of the electronic interactions between specific orbitals of the participating atoms, and has also taken into account such factors as the state of hybridization and the self energy of the molecular orbital of the bond formed, etc. Certainly it would be preferable for any prospective correlation with electronegativity to be made with recently derived values of X rather than the less easily interpreted values of Pauling (1960). It is interesting to note, however, that the values of X derived by recent workers are, for a wide range of elements in the "atomic" state, related to those of Pauling by a simple numerical formula, fig. 27.

The present situation, then, is that the apparent correlation between severity of L-ME and electronegativity difference should be regarded as interesting, but not established, and its fundamental significance remains to be discovered.

C. Inhibition of L-ME by Additions to the Liquid Phase

A possible means of inhibiting embrittlement may be suggested by considering the implications of the "rule" that embrittlement tends not to occur in systems in which the component metals form stable intermetallic compounds. For example, embrittlement of a solid metal A by a liquid metal B might be inhibited by adding a sufficient concentration 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. Inhibition could then 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-A_0 bonds at a crack tip such as that in fig. 2, reducing the ability of the crack to propagate under the applied stress.

Several possible examples of such behavior have been reported, e.g. (i) the addition of 0.4 a/o Sb to Bi_L significantly reduces the embrittlement of Cu_S in this environment (Kraai et al. 1960), (Cu and Sb form compounds such as Cu_2Sb, m.p. ~ 590°C), (ii) additions of In to Hg_L inhibit the embrittlement of Ag_S by Hg_L, fig. 26 (Preece and Westwood 1967) (In forms several compounds with Ag), and (iii) the addition of 0.4 a/o Ba to Hg_L increases the fracture stress of polycrystalline Zn_S some 65% in this environment (Westwood 1966) (Zn and Ba form $Zn_{13}Ba$, m.p. ~ 950°C).

D. Effects of Exposure to the Liquid Metal Environment Prior to Stressing

As remarked earlier, penetration of the solid metal by solid state diffusion of liquid metal atoms is not fundamental to the occurrence of adsorption-induced L-ME. However, if the specimen is left in contact with the liquid metal environment for a sufficient length of time, variations in subsequent mechanical behavior can result from intergranular or sub-boundary penetration processes. The occurrence of such variations, and the magnitude of the effects observed are dependent upon such factors as the particular solid metal-liquid metal couple, time, temperature, grain size, state of stress and amount of liquid metal available. No general rules for predicting the occurrence of such effects appear to have been developed as yet. However, observations on a few systems will serve to demonstrate the types of phenomena that may result.

(i) Al_S-(Hg-3% Zn)$_L$ and $Brass_S$-Hg_L. Ichinose (1966) has studied the effects of prior exposure of polycrystalline brass and pure Al to (Hg-3% Zn) amalgams at room temperature, fig. 28. His analysis of the behavior of these

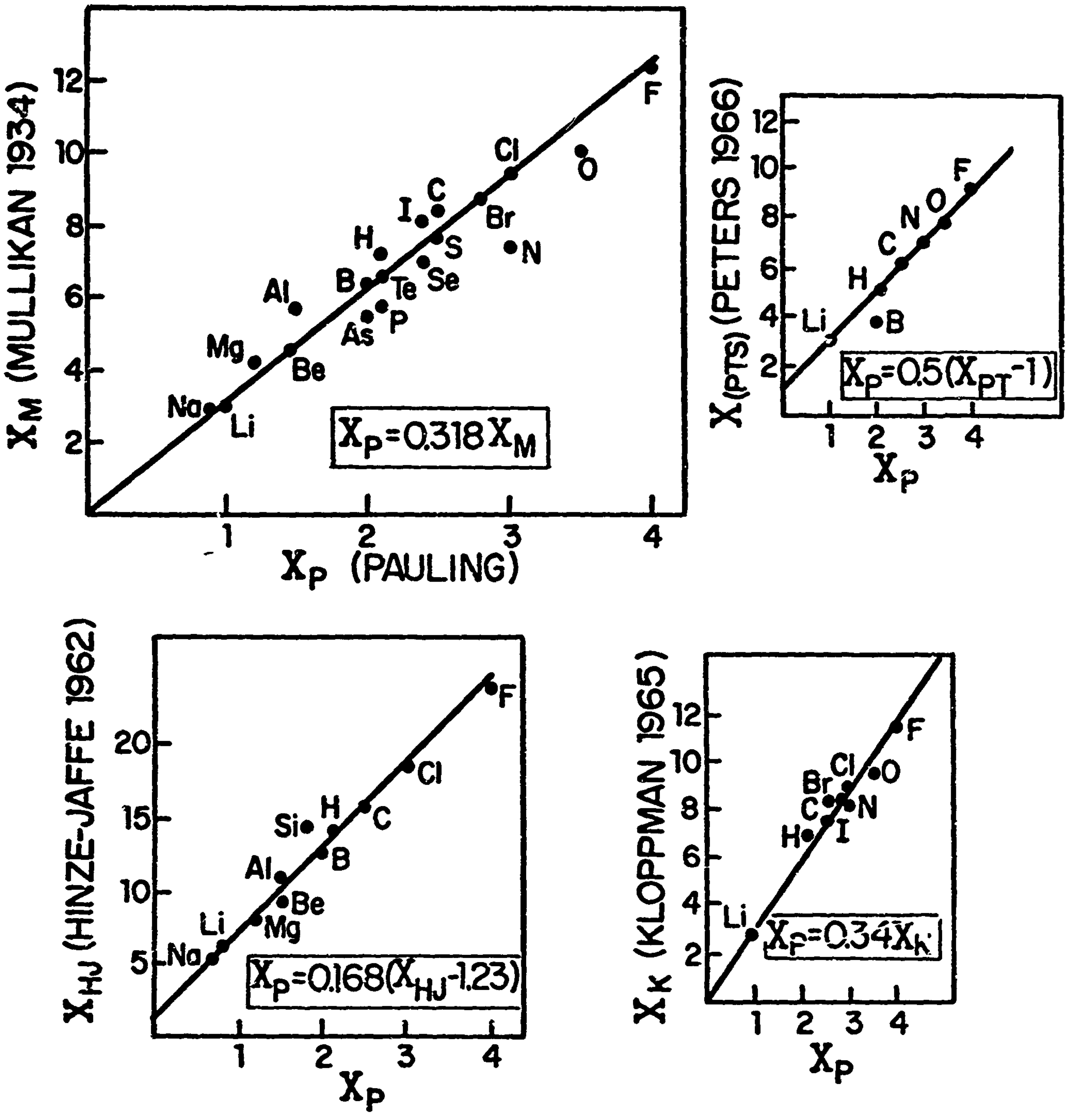

Fig. 27 - Relationships between values of electronegativity proposed by authors cited and those of Pauling (X_P).

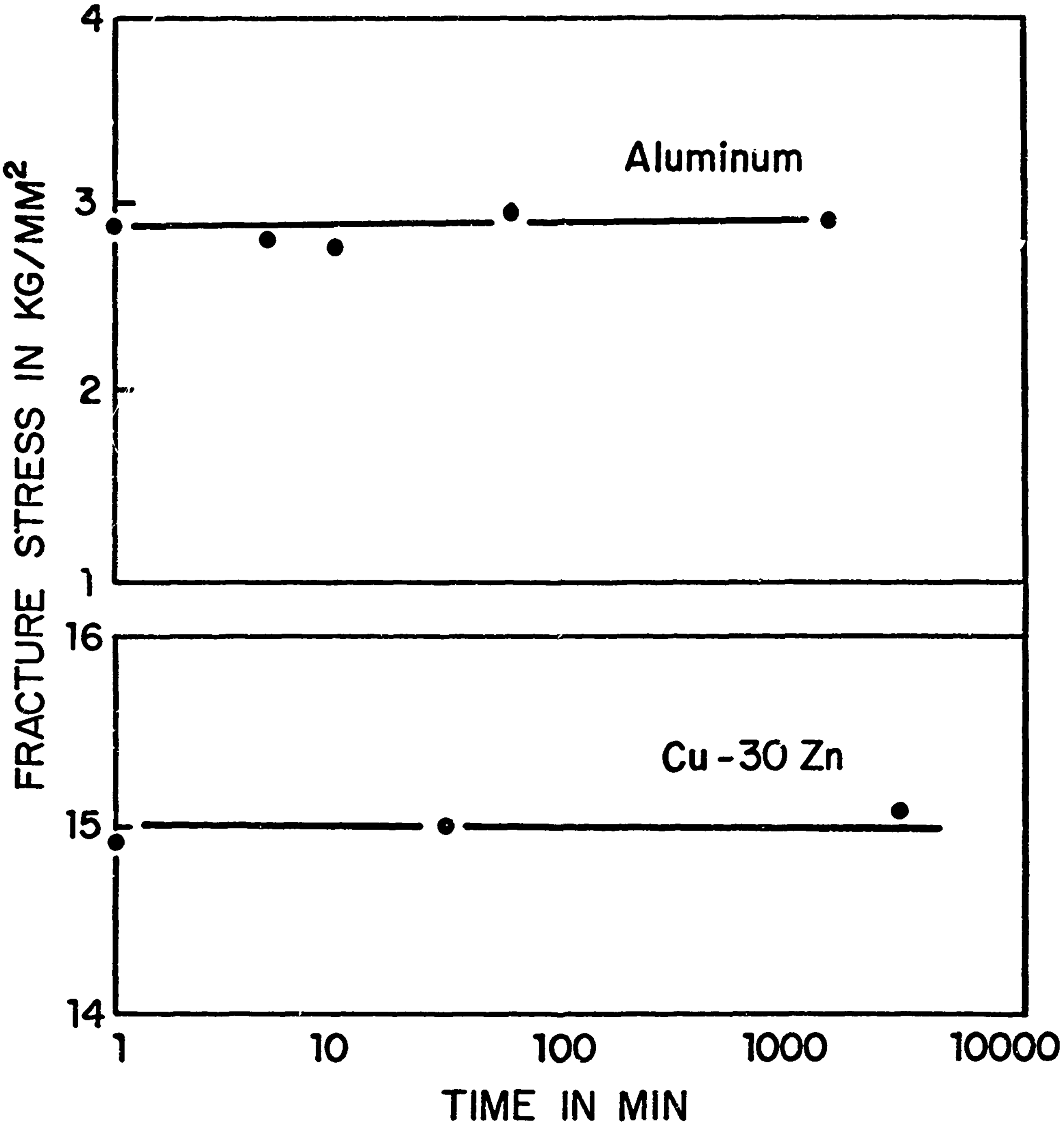

Fig. 28 - Fracture stress of polycrystalline Al or 70-30 brass as function of time of exposure to Hg_L prior to testing in this environment (After Ichinose 1966).

systems, based on measurements of the magnitude of decreases in strength with pre-exposure at temperatures between 150° and 250°C and known diffusion constants at 20°C, suggests that times of exposure of order 875 days and 4500 days, respectively, would be required to produce a 5% reduction in the fracture stress of the brass_S or Al_S specimens used by him.

(ii) Zn_S-Hg_L; Zn_S-Ga_L. Flegontova et al. (1964) have shown that a variety of effects can be produced at room temperature in these systems depending on the ratio, C_o, of the mass of liquid metal available to the mass of the zinc sample. Specimens of Zn_S of about 98.7% purity and 50μ grain diameter were used, and the variations in fracture stress with time of pre-exposure and C_o obtained are shown in fig. 29. Though it may not be readily apparent from this figure, the fracture strength of 9.6 Kg/mm^2 recorded immediately on wetting the Zn_S with Hg_L decreased to about 8.4 Kg/mm^2 after 20-35 min. [For Zn_S in contact with Ga_L, the fracture stress decreased from 4.8 Kg/mm^2 to about 1 Kg/mm^2 in this initial period.] For small values of C_o, say ≤ 0.002, all of the Hg_L diffused into the Zn_S in about 80 h, producing an alloyed surface layer and consequent strengthening - note curves a, b, and c cross over the line indicating the strength of Zn_S in air. For much greater values of C_o, e.g. $C_o \sim 0.01$, there was always an adequate supply of liquid Hg to embrittle the crystal despite surface alloying effects. Accordingly, the fracture strength was not particularly sensitive to time of prior exposure (curve f).

According to Flegontova et al. (1964), the extra reduction in strength occurring after short exposure times is associated with intergranular (or subboundary) penetration, and they suggest that this process results in an

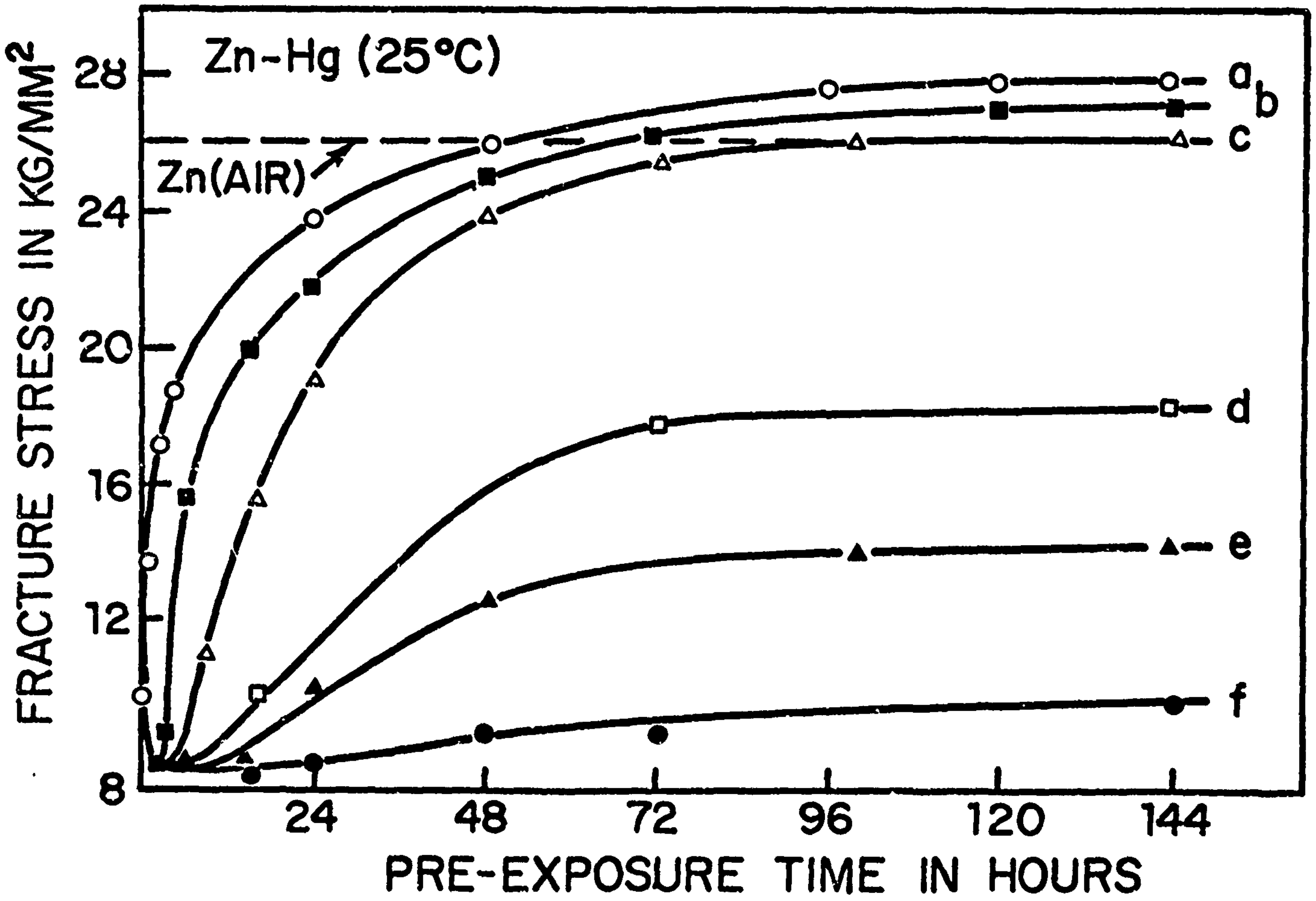

Fig. 29 - Fracture strength of polycrystalline Zn as function of (i) time of exposure to Hg_L environment prior to testing in this environment (ii) ratio, C_o, of mass of Hg_L on the surface to mass of the specimen. Values of C_o are: a - 3×10^{-4}; b - 7×10^{-4}; c - 2×10^{-3}; d - 3×10^{-3}; e - 7×10^{-3}; f - 1×10^{-2}. (After Flegontova et al. 1964.)

"adsorption drop" in strength of the boundary. On the other hand, it can be seen from fig. 29 that, for small values of C_o, as time of pre-exposure increases and the Hg atoms diffuse into the Zn_S, the strength actually increases to values greater than that for pure Zn_S. Moreover, one would suspect that once in the solid, the Hg atoms segregated at the grain boundary would produce boundary hardening due to solid solution strengthening and source locking rather than any adsorption-induced reduction in strength. It is suggested, therefore, that a more likely explanation of the initial drop in strength is that the diffusion of Hg into grain boundaries (or sub-boundaries) at the surface hardens (not weakens) these boundaries, facilitating crack initiation at the surface.

(iii) $\underline{(\text{Cu-2\% Be})_S\text{-}(\text{Hg-2\% Na})_L}$. Several workers have studied the delayed failure of Cu-2% Be alloys in Hg_L and Hg amalgams and have also considered the effects of prior exposure to the liquid metal environment (Rinnevatore et al. 1964, 1966; Nichols and Rostoker 1965). Rinnevatore et al. (1964) have shown that the ratio of fracture stress in the Hg_L environment to flow stress in air, $\sigma_{F(Hg)}/\sigma_{f(Air)}$, decreases with time of exposure and with increasing prestrain, fig. 30. The magnitude of the decrease was found to be a function of prior heat treatment of this age-hardening alloy, maximum decreases in $\sigma_{F(Hg)}/\sigma_{f(Air)}$ being observed for specimens aged to peak hardness (~ 1 h at 370°C). It was noted that specimens exposed to the amalgam for a sufficient length of time to produce observable grain boundary penetration (GBP), but then removed from the environment and "dried" before testing, were not

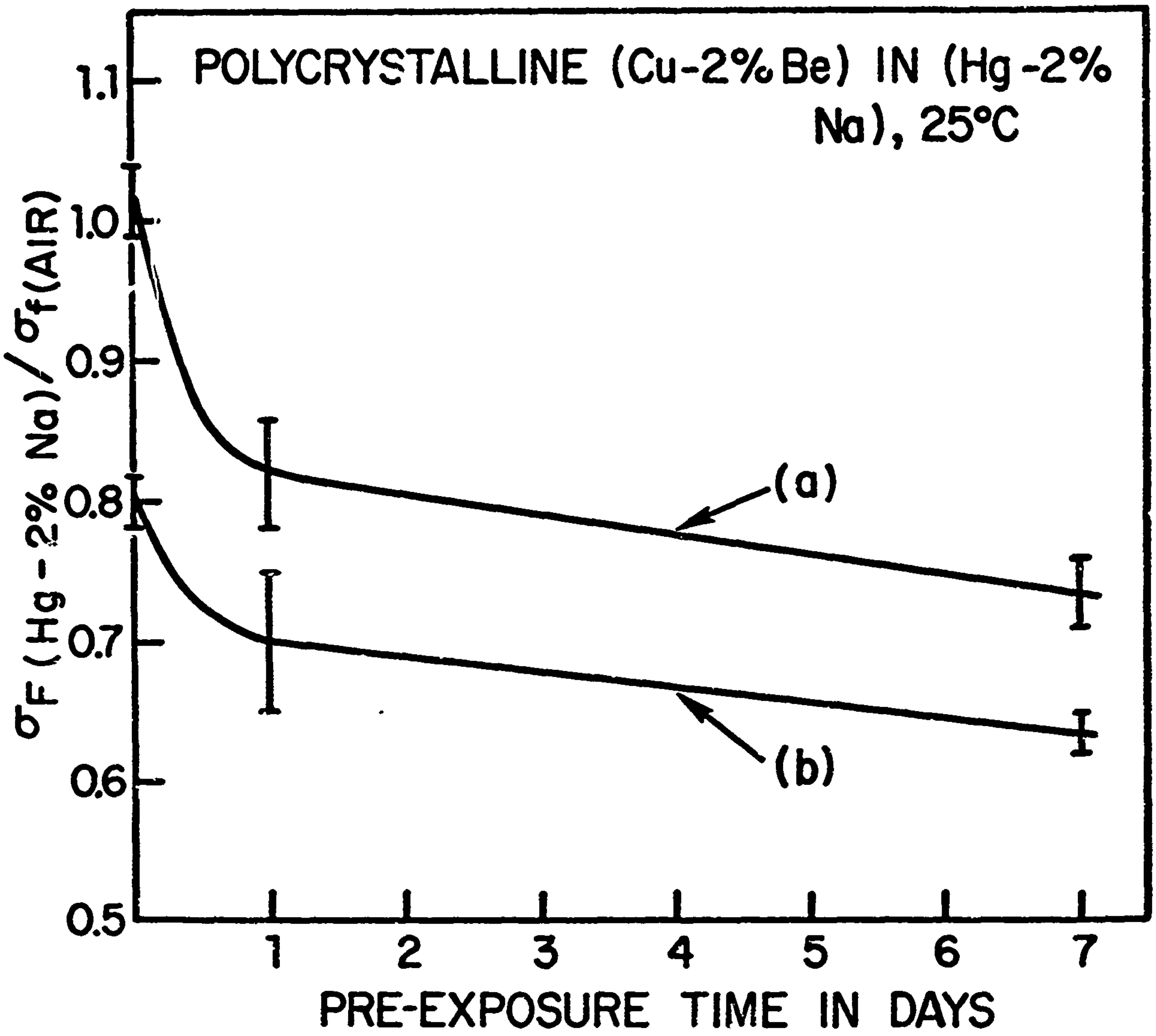

Fig. 30 - Effect of time of exposure to (Hg-2% Na) amalgam on the embrittlement of Cu-2% Be alloy aged 1 h at 370°C. (a) unprestrained specimens. (b) prestrained 6% prior to amalgamation. (After Rinnevatore et al. 1964.)

embrittled. Thus both GBP and a sufficient supply of liquid metal are required to produce embrittlement. Rinnevatore et al. (1964) suggest that the regions of GBP are sites for preferred crack initiation in the wetted condition, but comment that in the unwetted condition these regions have no significant effect. These observations may also be interpreted as follows: In the presence of a sufficient supply of the embrittling liquid metal, failure is crack initiation controlled, and GBP facilitates this process. In the absence of a sufficient supply of embrittling liquid metal, failure is propagation controlled, and this process is not significantly affected by grain boundary hardening effects right at the surface.

E. Effects of Liquid Metal Solutions on Static Fatigue Behavior

It was mentioned in Section IV-C that failure in pure, active liquid metal environments was initiation controlled. It might be anticipated, however, that failure in liquid metal solutions containing only low concentrations of some active species would instead be controlled by the rate of arrival of these species at the propagating crack tip, and therefore be propagation controlled. Current experiments by Preece and Westwood (1967) with polycrystalline Cd_S tested in $(Hg\text{-}In)_L$ solutions indicate that this is not so. The data presented in fig. 31 reveal that only for the nonembrittling Hg-(0-5 a/o)In solutions (see fig. 24) is failure propagation-controlled. It appears that as soon as sufficient In is present in the Hg_L to cause detectable embrittlement, then failure becomes initiation-controlled.

In fig. 32 the critical stress for crack initiation, σ_I, is plotted against log of the concentration of In (C_{In}) in the environment. The absence of embrittlement when $C_{In} < \sim 5$ a/o, Area I, may be related to the anomalous

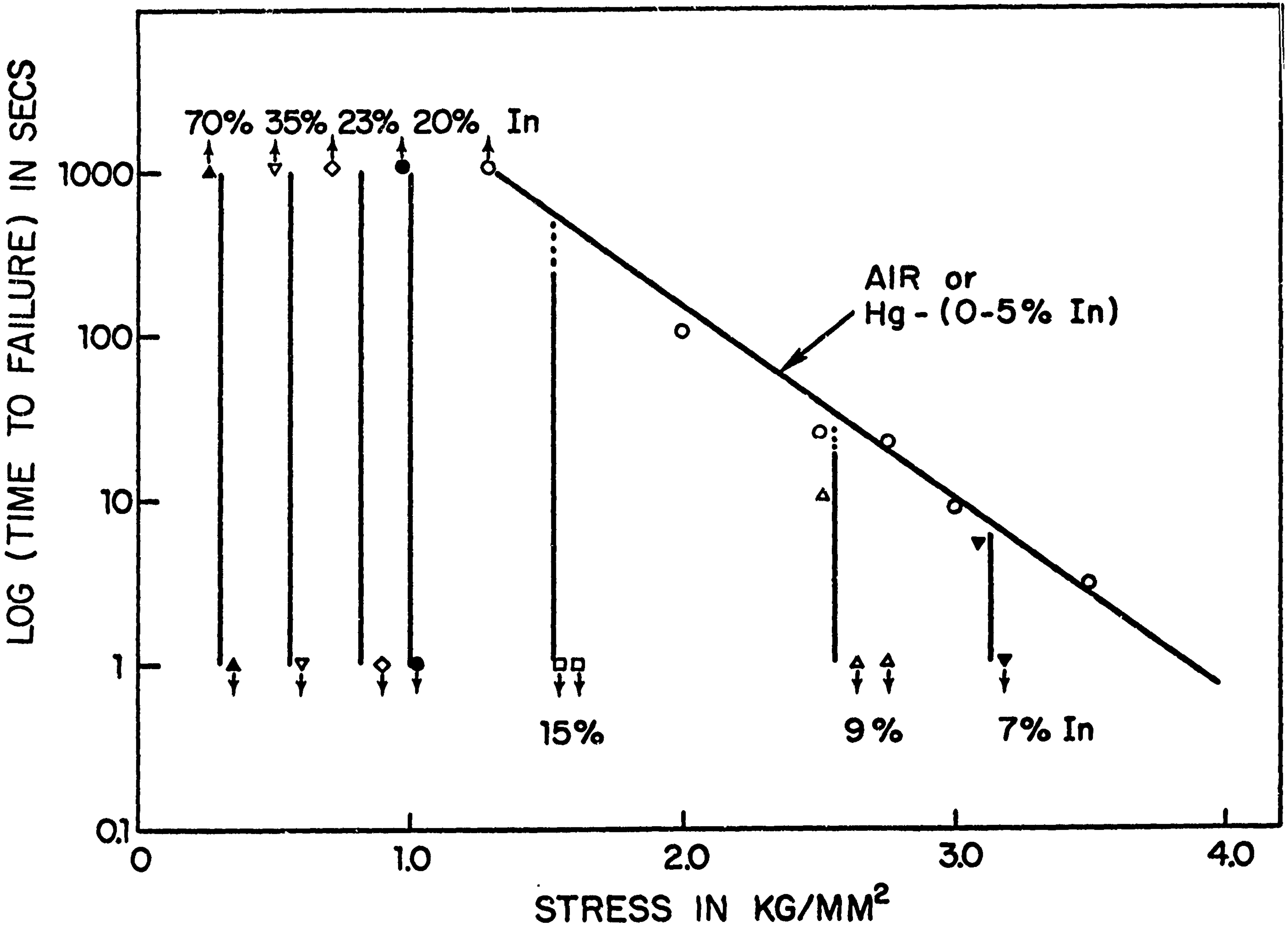

Fig. 31 - Variation in time to failure with stress for polycrystalline Cd specimens (~ 1mm grain dia.) tested in various (Hg-In) solutions (0-70 a/o In) at 25°C (Preece and Westwood 1967).

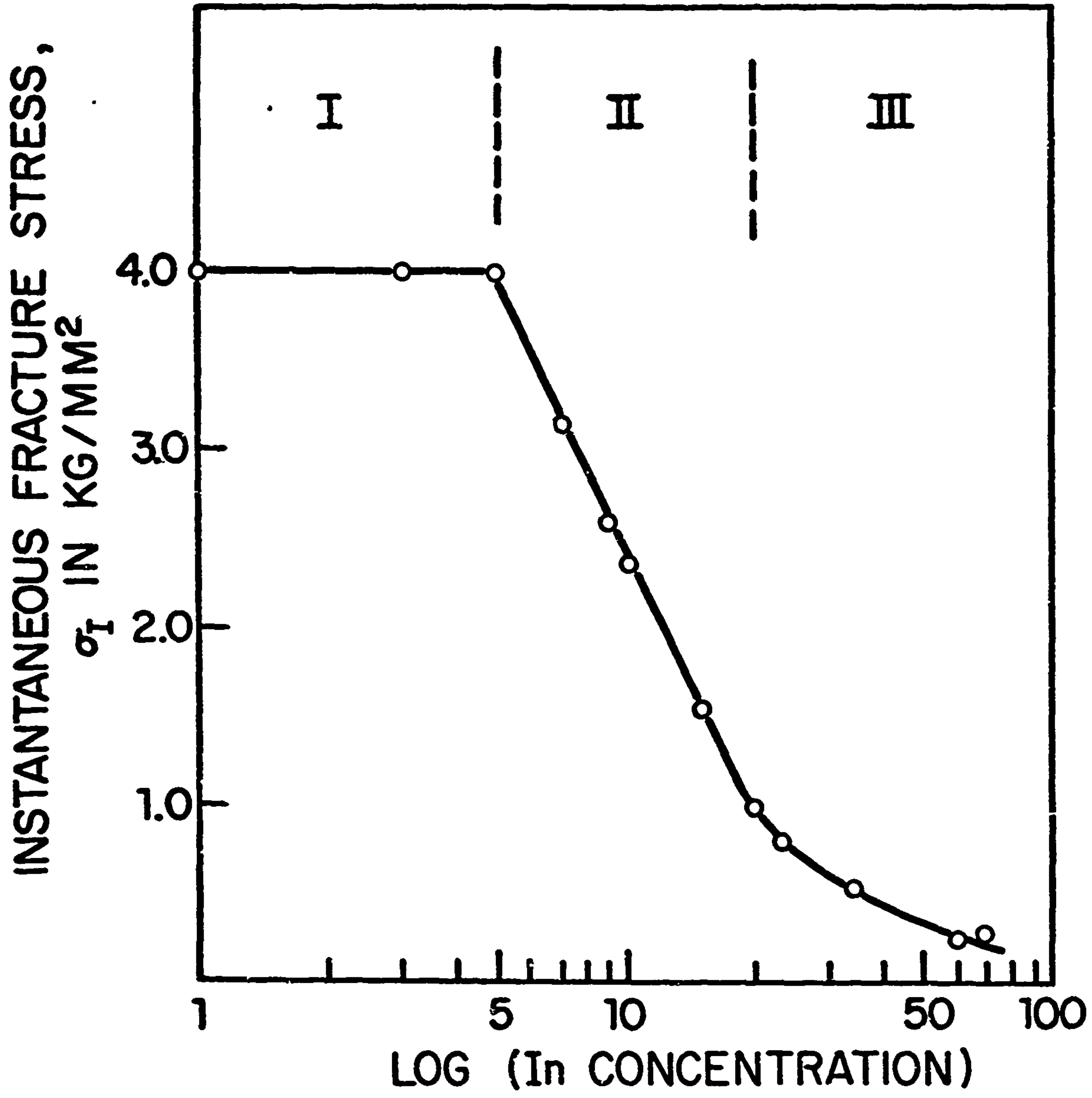

Fig. 32 - Variation of critical stress for instantaneous fracture, from Fig. 31, with In concentration of the $(Hg\text{-}In)_L$ environment. Note linear relationship for In concentrations of 6-20 a/o (Preece and Westwood 1967).

behavior of dilute Hg-In solutions noted previously by other workers, e.g., in thermopower studies (Cusak et al. 1964, Bradley 1966), and also recently in the inhibition of embrittlement by Hg_L of Ag_S, fig. 26. Mott (1966) has suggested that a strong interaction occurs between the Hg and In atoms in these solutions, and it is possible that such an interaction could lead to a "solvation sheath" of Hg atoms around the In atoms, thereby reducing the activity of the In atoms. For concentrations between 5 and 20 a/o, however (Area II, fig. 32), σ_I is inversely proportional to log C_{In}, but the significance of this relationship is not yet established. When C_{In} is > 20 a/o, Area III, σ_I decreases slowly to a limiting value of ~ 0.3 Kg/mm^2, this being approximately the macroscopic flow stress of the specimen.

It is of interest to note that a similar, but inverse, relationship is obtained when the dynamic fracture stress data for Ag_S specimens in Hg-In solutions, fig. 26, are plotted against log (a/o In). After the region of anomalous behavior in dilute solutions, 0-5 a/o In, fracture stress increases linearly with log (a/o In). [It will be recalled that Bruyukhanova et al. (1962) noted that for the Zn_S-Hg_L system the dynamic fracture stress and critical stress for failure in static fatigue were approximately equal.] This observation suggests that the inhibiting action of In does not result from a mere dilution of the embrittling Hg_L environment, but perhaps from specific strengthening of surface Ag-Ag bonds by adsorbed In atoms.

VI. SUGGESTIONS FOR FURTHER WORK

Much work remains to be done before any good understanding of the fundamentals of L-ME can be expected. Although some progress has been made, the overall situation has not changed significantly from that in 1962, when one of us commented that there was a great need for "experimentation utilizing (i) specimens of simple composition and structure, (ii) environments of known and closely controlled purity, and (iii) direct experimental techniques capable of providing interpretable data" (Westwood 1963).

Further work is required in each of the three, inter-related aspects of L-ME, namely, surface-physics, chemistry, and metallurgy.

(i) Surface-physics of L-ME. Assuming that the type of L-ME discussed in this paper does involve chemisorption, and the evidence for this appears convincing at the moment, then theoretical studies are required of the manner in which the electrons in surface bonds are redistributed during chemisorption such that significant reductions in cohesive strength result. It is possible that, during the next few years, developments in the theory of adsorption and results obtained from low energy electron diffraction and field ion microscopy studies, etc., may provide much useful information on the interactions causing such bond strength reductions. In addition, as mentioned in Section III-C, recent studies of the variations in electrical conductance, ferromagnetic moment and ferromagnetic anisotropy of W_S, Fe_S and Ni_S during chemisorption of gases have indicated that certain of these species weaken the bonding of metal surface atoms (Geuss 1964). It is possible that such techniques could be advantageously used for comparative studies of known embrittlement and non-embrittlement systems.

Reliable measurements of the fracture surface energies of solid metals of known band structure, exposed both to active and inactive liquid metal environments, would be of particular use in conjunction with the above theoretical and experimental studies of the chemisorption process.

The search for some parameter of the solid metal-liquid metal system which will correlate with severity of L-ME should be continued. It may be that this objective represents too naive a view of the complexity of the L-ME phenomenon. However, this possibility has yet to be investigated by scientists equipped with both an interest in L-ME, and a sufficient knowledge of the fundamentals of surface physics and the band structure approach to chemisorption.

(ii) Chemical factors in L-ME. The chemical aspects of L-ME represent an area of study in which almost everything remains to be done. Very few studies have been made of the variation in embrittlement behavior of a pure solid metal with chemical composition of its liquid metal environment. Moreover, most previous work has involved the effects of minor additions to already very active environments, with the result that, in most instances, only small variations were observed. Wider application of the "inert carrier" technique could be particularly useful in this regard. However, solvent-solute interactions in the liquid can introduce new variables into the problem, as already evidenced by the anomalous behavior of Hg-(0-5 a/o) In solutions. It is therefore necessary for investigators to become familiar with the nature of liquid metals and alloys, i.e., with the structure and type of atomic interactions in the liquid, as well as with diffusion characteristics and kinetics.

One disadvantage of the "inert carrier" technique is that there are not many truly inert liquid metals, and even when a suitable inert liquid metal is available for a particular solid metal, its solvating ability may be quite limited for a number of potentially interesting embrittling elements. Nevertheless, those systems to which the technique can be applied should be examined thoroughly if any understanding of the behavior of practical systems is to be achieved.

The significance of the variation in severity of embrittlement with log of the concentration of the most active species in a liquid metal solution, and the reasons why failure is crack-initiation controlled even when only low concentrations of the active species are present in the solution, have yet to be determined. Both of these problems require considerable investigation.

The variations in embrittlement behavior with composition of the solid metal in a given liquid metal environment also require further study. If possible, this work should be oriented to focus attention on changes in such properties of the solid as the electron/atom ratio, and the strength and type of bonding, etc., rather than on changes in the yield stress or slip mode. The possibility of alloying to produce built-in inhibition of embrittlement for a given environment appears intriguing, and certainly should be considered further.

(iii) Metallurgical and physical parameters in L-ME. Although there is now a considerable literature on the metallurgical and physical factors involved in L-ME, most of this work has been performed on commercial alloys, e.g. the age-hardening aluminum alloys. Unfortunately, because of the complex deformation behavior intrinsic to such materials, the effects of the liquid metal environment, per se, are not always readily extricated from the data - or easily interpreted once obtained. Studies on simple embrittlement couples are still required. These should be quantitative whenever possible, preferably involving direct determination of changes in the fracture surface energy. Studies of cleavage crack propagation in suitable monocrystals, crack initiation in asymmetric bicrystals, and the propagation of intercrystalline cracks in suitably oriented bicrystals as a function of temperature, composition of both solid and liquid components, amount of prestrain, rate of loading, etc., would be most useful.

Such work should aid considerably our understanding of the phenomenon of brittle fracture in liquid metal environments, and hopefully prevent the occurrence of this form of catastrophic failure in future systems in which liquid metals are used as coolants.

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13. ABSTRACT

Solid metals can be caused to behave in a brittle manner by exposure to a variety of physical or chemical environments. Perhaps the most dramatic examples of such effects, however, result from exposure to surface active liquid metals. Specimens pre-stressed above some critical value fail virtually instantly on being wetted by an appropriate liquid metal, and "brittle" crack propagation rates of order 100 cm per sec. have been recorded in otherwise ductile metals under such environmental conditions.

Such effects are presently considered to result from adsorption-induced reductions in the cohesive strength of atomic bonds at regions of stress concentration in the solid metal, e.g. at the tips of cracks or in the vicinity of piled up groups of dislocations. This paper describes the results of a number of recent investigations on this type of liquid-metal embrittlement, and discusses the prerequisites and possible mechanisms for its occurrence. Also discussed are the effects of such variables as chemical composition of the solid and liquid metal phases, temperature, prestrain, rate of loading, etc., on severity of embrittlement, and such topics as the possible correlation between severity of embrittlement and electronegativity, the use of "inert carrier" liquid metals, possible means of inhibiting liquid-metal embrittlement, and criteria for brittle failure.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Liquid metal embrittlement						
Brittle fracture						
Atomic bond strength						
Adsorption						
Surface energy						
Dissolution processes						
Diffusion						
Stress concentrations						
Electronegativity						
Crack initiation						
Crack propagation						
Static fatigue						
Inhibition of liquid metal embrittlement						
Liquid metal solutions						

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