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A UNIFIED STRUCTURAL MECHANISM FOR INTERGRANULAR AND  
TRANSGRANULAR CORROSION CRACKING

by

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## ABSTRACT

A unified, structural mechanism is proposed to explain the phenomena of intergranular and transgranular stress corrosion cracking. The dependence of failure on composition and stress in copper alloys and in stainless steels is analyzed in terms of two general conditions: (1), a chemically reactive path and (2), a mechanism of concentrating stress across the reactive path.

Intergranular fracture in a chemical environment is considered in terms of the normal stress distribution at the head of a group of dislocations piled up against a grain boundary. It is shown that the available data are consistent with the proposed model with respect to (1), a grain size dependence (2), stacking fault energy, which defines the number of coherent twin boundaries per grain and thereby the stress concentration at the boundary and (3) the existence of an endurance stress, approximately equal to the macroscopic yield stress, below which the stress concentration at the boundary is insufficient to cause fracture.

The nucleating sites for transgranular fracture in single crystals, and in polycrystalline aggregates that fail transgranularly, are shown to be Cottrell-Lomer barriers. A detailed crystallographic mechanism of fracture is proposed which depends on (1), orientation with respect to applied stress and (2), the strength of the barrier, which is related to the stacking fault energy. Available data are consistent with the model in predicting the composition dependence of transgranular fracture and, in favorable cases, the plane of fracture. The same mechanism is capable of explaining the dependence on composition and plastic strain of the transition from intergranular to transgranular fracture, which is demonstrated with copper alloys.

A UNIFIED STRUCTURAL MECHANISM  
FOR  
INTERGRANULAR AND TRANSGRANULAR CORROSION CRACKING

W. D. Robertson\* and A. S. Tetelman\*

Introduction

As a result of recent investigations the gap between theoretical and apparent strength of materials has diminished considerably, and a detailed mechanism of strengthening processes is emerging. However, in operational terms, strength implies load carrying capacity at indefinite time (reliability) and, unfortunately, it is not always possible to take full advantage of the apparent strength. Weakening processes that are functions of time, temperature, and environment may limit operating conditions to a small fraction of apparent strength.

Among the most insidious and catastrophic of weakening processes are various manifestations of intergranular and transgranular corrosion cracking phenomena. Until the present time the complexity of these processes, and uncertainty concerning their relationship to the structure-dependent mechanical properties of materials, has delayed the emergence of useful generalizations that can be employed to predict the behavior of materials in a given chemical environment. This state of affairs is changing rapidly and it now appears that the problem can be stated in terms that provide a basis for predictions and for experimental verification.

Definition of the Problem

Discussion will be limited to: (a) homogeneous, face centered cubic solid solutions, and (b) chemical factors that can be condensed into an inclusive term, "specific reactivity", without detailed consideration of reaction kinetics.

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Within these limits, the three most significant phenomena requiring explanation are:

- (1) The dependence of intergranular cracking on the type and concentration of alloying components, for example, in copper solid solutions.
- (2) Composition dependence, and crystallographic characteristics of transgranular cracking, for example, in austenitic stainless steels.
- (3) The dependence of the transition from intergranular to transgranular cracking in a polycrystalline aggregate, on composition and plastic strain, for example, in copper alloys.

Reduced to the simplest terms, it appears that a large mass of empirical information concerning these phenomena may be unified and reduced to two necessary and sufficient conditions for stress corrosion cracking.

- (1) The existence of a structural path at which the intensity of chemical reactivity is high, relative to the surrounding matrix.
- (2) A mechanism for concentration of a normal stress across the path of chemical reactivity.

It will be shown that the connecting link between composition, strain and reactivity is the stacking fault energy, which defines the structural characteristics of the deformation process that is a prerequisite for failure by stress corrosion cracking.

#### Definition of Structure Dependent Reactivity

This term was defined and illustrated in a previous A.S.M. Seminar,<sup>(1)</sup> and further elaborated by Robertson and Bakish.<sup>(2)</sup> The essential ideas resulting from this work may be summarized in the following manner:

- (1) The term "structural sites" in a face centered cubic metal or alloy does not refer to crystal structure but to: (a), imperfections or discontinuities within individual crystals of a polycrystalline

aggregate, inherited from growth history or produced by subsequent deformation, and (b), to the grain boundary separating adjacent crystals.

- (2) Specific reactivity at structural sites denotes first, that chemical reaction between an alloy and a given environment is nucleated at sites that can be characterized by a structural specification (for example, the angular tilt defining a grain boundary) and, secondly, that the linear rate of penetration of reaction (cm/sec), parallel with a planar defect, or line defect, is large relative to the corresponding penetration through the adjacent lattice. This description of a chemical reaction removing one, or more, components of an alloy that is unstable with respect to its environment is identical with the concept of short circuit diffusion paths in the reverse process of adding a component to a metal or alloy by diffusion from the surface.

The trace of a grain boundary at the external surface of a pure metal, at equilibrium with its vapor phase, becomes a groove at which the dihedral angle  $\theta$  is defined by equilibrium between the energy of the free surface and the grain boundary energy. If the system is made unstable, for example by removing metal vapor with a vacuum pump, the dihedral angle is preserved while metal atoms are removed more or less at random from both the free surface and the surface of the groove, as indicated by the dotted line parallel to the surface in Figure 1. Similar behavior occurs when a polycrystalline pure metal is exposed to an aqueous oxidizing environment.

In an alloy that is unstable with respect to its environment, such as copper-gold in an oxidizing medium like ferric chloride, conditions are quite different. Chemical reaction is nucleated at a discontinuity, perhaps a grain boundary; but, only the more reactive component is oxidized and removed from the lattice, copper in this case being oxidized to a soluble cuprous ion accompanied by reduction of ferric ion. This reaction leaves a sponge of residual gold on the surface, which operates

FIGURE CAPTIONS

Figure 1. Equilibrium dihedral angle,  $\theta$ , at a grain boundary trace in a pure metal, which is preserved as the surface evaporates to the level of the dotted line in a dynamic vacuum.

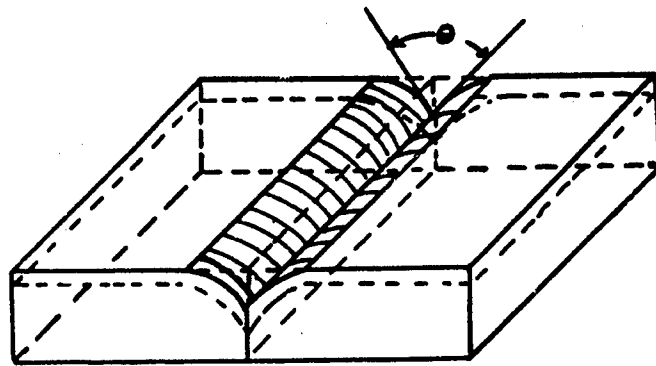
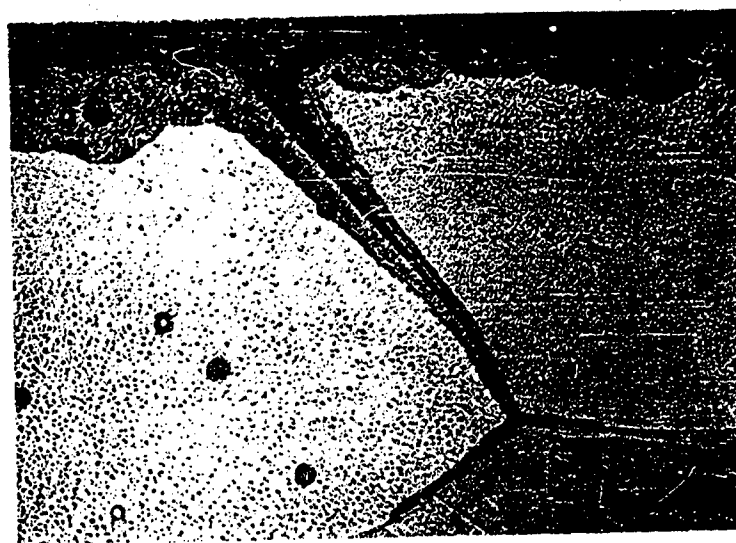
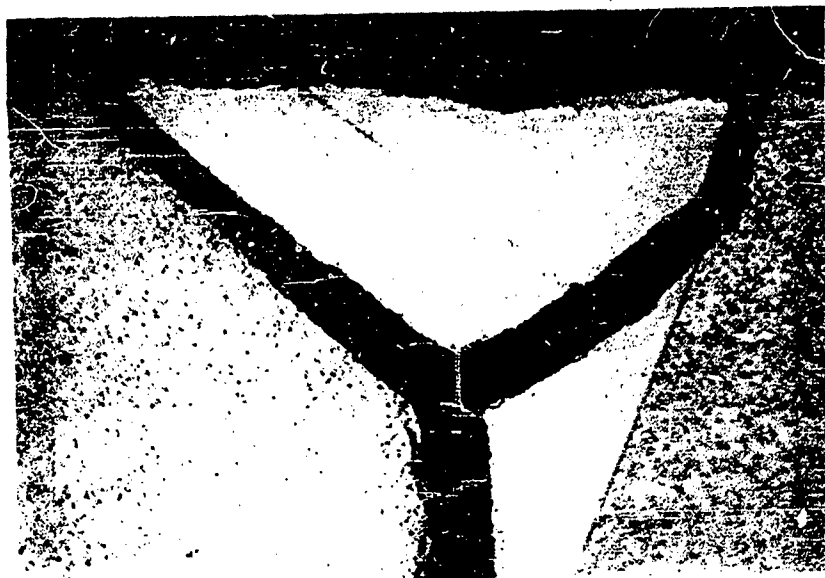


Figure 2. Illustrating relative rates of penetration of reaction parallel and perpendicular to a grain boundary; (a) Cu-Ni-Si alloy in ammonia (3) and (b) brass in mercury at 150°C. (4)





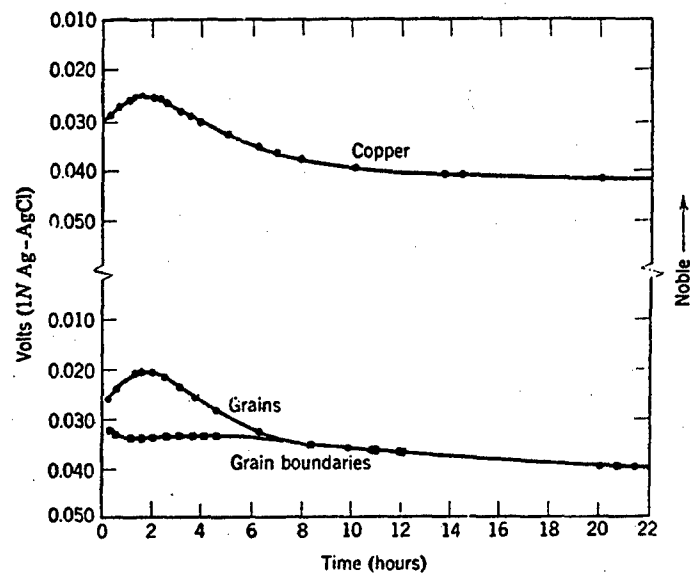
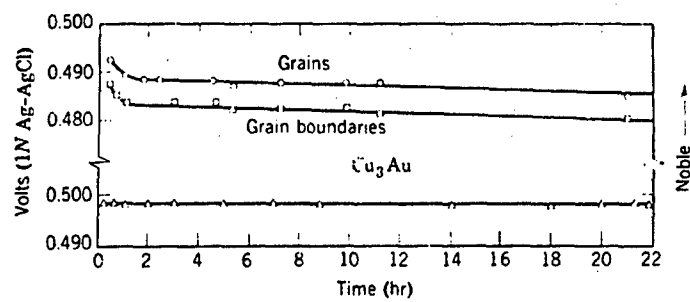
as a local cathode at the reacting site, accelerating subsequent reaction which proceeds rapidly down the boundary plane and, more slowly, normal to the boundary plane. Thus, the originally homogeneous alloy is made locally heterogeneous by selective removal of one component, and reaction proceeds continuously along the structural path.

The relative linear penetration rates, parallel and perpendicular to the reacting surface, are shown in Figure 2 for a grain boundary in a copper alloy exposed to ammonia<sup>(3)</sup>, and for brass in mercury<sup>(4)</sup> at 150°C. In both examples the trace of the original boundary is still evident at the center line of reaction product and, clearly, the relative rates parallel and perpendicular to the boundary plane differ by more than an order of magnitude.

The differences in chemical behavior at grain boundaries in a pure metal and in an alloy have been investigated by Bakish and Robertson<sup>(5)</sup>. Grains and grain boundaries were separated by masking one or the other with organic resin to about 0.5 mm of the boundary of each of two electrodes, and the change in galvanic potential between grains and grain boundaries was observed in pure copper and in Cu<sub>3</sub>Au, immersed in ferric chloride. As shown in Figure 3, the potential difference between grains and grain boundaries in copper increases to a maximum while the boundary groove is forming, and subsequently falls to zero when the equilibrium configuration is attained; in Cu<sub>3</sub>Au the potential difference remains constant, indicating that reaction at the boundary continues indefinitely, and subsequent microscopic observation confirms this conclusion.

Specific reactivity at structural sites has been illustrated by a grain boundary, but any structural discontinuity may function in the same manner. The magnitude of the discontinuity, such as the angle between adjacent grains, and/or the amount of strain energy concentrated at the site by dislocations piled up against the discontinuity (barrier), determines the degree of reactivity for a

Figure 3. Galvanic potentials of grains and grain boundaries in pure copper and in  $\text{Cu}_3\text{Au}$  illustrating that reaction at the boundary of a pure metal ceases when the equilibrium groove is attained, in contrast with the alloy in which the potential difference, and the reaction at the boundary, continue indefinitely. After Bakish and Robertson. (15)



particular system of alloy and environment. However, it is important to realize that high reactivity is not a sufficient condition for catastrophic failure. A certain amount of stress, directed across the reactive path, is also required.

### Stress Concentration

A group of  $n$  dislocations piled up against a barrier by an effective shear stress  $(\sigma_a - \sigma_o)$  constitutes a stress concentration  $n$  times the effective shear stress. In addition to the shear stress there is a field of normal stress in the vicinity of the barrier that has been investigated analytically by Stroh<sup>(6)</sup>, as a function of the angle  $\theta$  and distance  $r$  from the barrier. Stroh concludes that the maximum normal stress occurs across a plane at  $70^\circ$  to the slip plane, and diminishes with distance from the barrier as  $r^{-1/2}$ . In terms of the length  $L$  of an array of  $n$  dislocations under an effective shear stress  $(\sigma_a - \sigma_o)$ , the maximum normal stress is:

$$\sigma_{MAX} = (\sigma_a - \sigma_o) \left( \frac{L}{r} \right)^{1/2}$$

where  $\sigma_a$  is the applied shear stress and  $\sigma_o$  is the "frictional" stress associated with the forest of dislocations threading the slip plane, and the Peierls force required to move a dislocation through a perfect crystal. Since, under a shear stress, a blocked slip line resembles a freely slipping crack, Stroh has put this expression into the Griffith criterion for fracture, leading to the result that a crack will nucleate only when

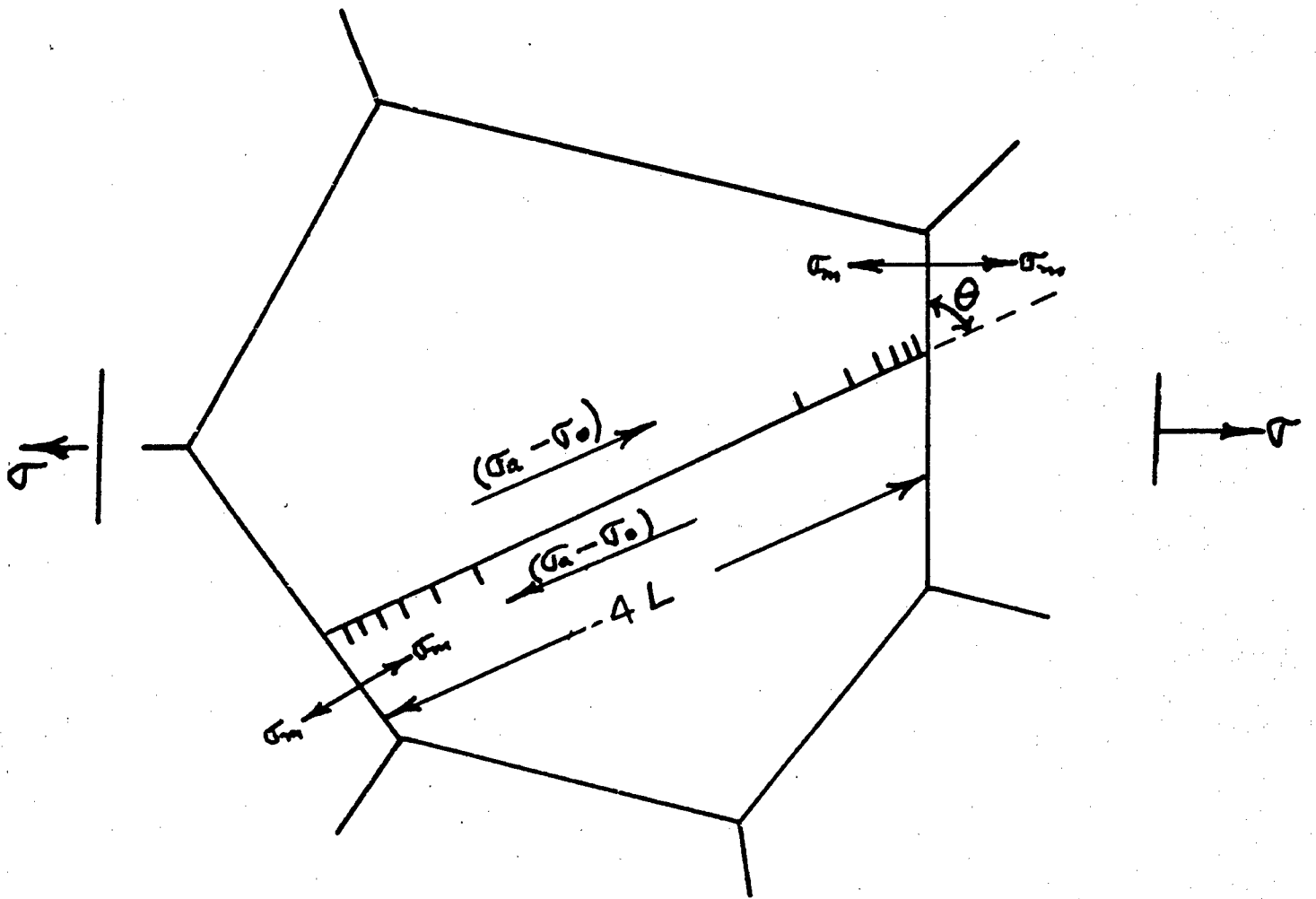
$$n (\sigma_a - \sigma_o) > 1.5 G$$

where  $G$  is the rigidity modulus.

Furthermore, by identifying the maximum stress with the fracture stress, and, following Eshelby et al<sup>(7)</sup>, one quarter of the grain diameter as the effective length  $L$  of the blocked slip line, Stroh<sup>(8)</sup> and Petch<sup>(9)</sup> have derived the relationship between the stress for transgranular cleavage and the grain size  $d$  as;

$$\sigma_c = \sigma_o + k d^{-1/2}$$

Figure 4. Maximum normal stress,  $\sigma_{\max}$ , at the head of a group of dislocations piled up at a grain boundary, oriented with respect to the slip plane so that the plane of maximum normal stress coincides with the boundary plane.



where  $\sigma_c$  is the stress for cleavage fracture, and  $k$  contains the surface energy associated with the formation of the cleavage surfaces. Both Petch<sup>(9)</sup> and Low<sup>(10)</sup> have found that this relationship describes the grain size dependence of trans-crystalline cleavage fractures in low carbon steels.

The essential results of Stroh's analysis<sup>(6)</sup>, for an isotropic medium, are schematically illustrated in Figure 4. For the purpose of describing intergran-luar fracture in face centered cubic alloys, the grain boundary plane has been oriented with respect to the slip plane so that it coincides with the plane of maximum normal stress.

A piled up group of dislocations concentrated at a barrier does not neces-sarily produce cleavage. Instead, the shear stress concentration associated with the piled up group may be large enough to produce slip in an adjoining grain, re-sulting in the inhomogeneous plastic deformation described as a Luder's band. When dislocations in an adjoining grain are pinned down by impurity atoms, or can-not move easily because of a large Peierls force, all of the concentrated stress at the tip of a group can be used to form a crack; complete cleavage results pro-vided the crack can propagate. Therefore, cleavage occurs most easily in alloys containing interstitial solutes which can pin the dislocations, and at low tem-peratures where the Peierls' force is largest.

Since face centered cubic alloys contain very small amounts of interstitial impurities, and since the Peierls' force is small in these structures because of the close packing of atoms, cleavage fracture is not observed (in the absence of a chemical environment). The stress associated with a piled up group can always be relaxed by plastic deformation rather than by cleavage. Since the stress necessary to nucleate a crack is proportional to the square root of the surface energy, which has been defined by Gilman<sup>(11)</sup> as the total energy consumed in pulling the two crack faces apart, the basic problem is one of determining how the presence



of a chemical environment lowers the amount of energy required to cause cracking, and/or raises the stress for yielding in the vicinity of the pile up so that stress concentrations are not relaxed by plastic deformation.

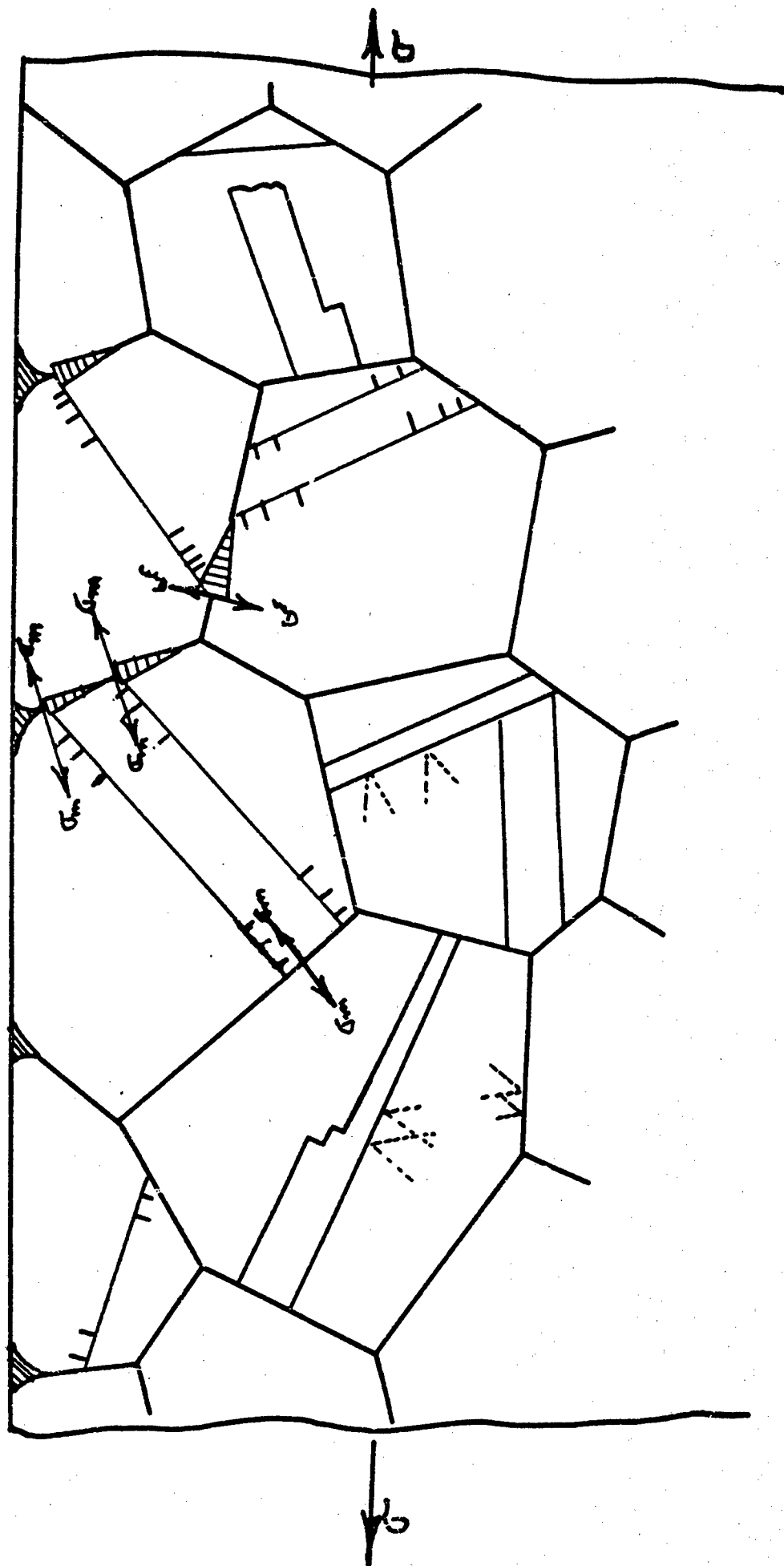
In the case of intergranular cracking, the fracture path is defined by the corroded grain boundary. It is not hard to imagine that the boundary can be weakened so that small stress concentrations at the boundary can provide the energy to cause fracture. In the case of transgranular cracking, the choice of a fracture path is not so obvious, and it is necessary to postulate a more esoteric mechanism to explain the experimental observations.

#### A Model for Intergranular Corrosion Cracking

The proposed model for intergranular cracking is schematically illustrated in Figure 5. It is assumed that a certain number of surface grains are oriented so that the resolved shear stress activates sources lying on planes at an angle to a boundary such that the component of normal stress causes fracture across the chemically reacting boundary plane. When the crack has opened, stress is relieved and dislocations run into the crack. Unlike cleavage at low temperatures where crack growth is limited only by the velocity of an elastic wave, the grain boundary crack in normally ductile alloys advances slowly, and probably never gets very far ahead of the diffusion limited corrosion process. Thus the growth of a macroscopic crack, ultimately extending along the length of one or more boundaries, may be visualized as a sequence of steps involving stress concentration, reaction down the boundary planes, fracture with local relaxation of stress, followed by continued reaction and fracture at a new site further from the free surface. Under a sufficiently large applied stress the individual steps in the process may, of course, be indistinguishable but, nevertheless, the growth rate is probably limited by the rate of the chemical reaction rather than by the mechanical process of cracking and, when the reactive environment is removed, the crack comes to rest. The major

Figure 5. A model for intergranular corrosion cracking involving stress concentration at reacting grain boundaries followed by fracture due to the component of normal stress operating across the boundary plane.

FREE SURFACE



supporting evidence for this model is:

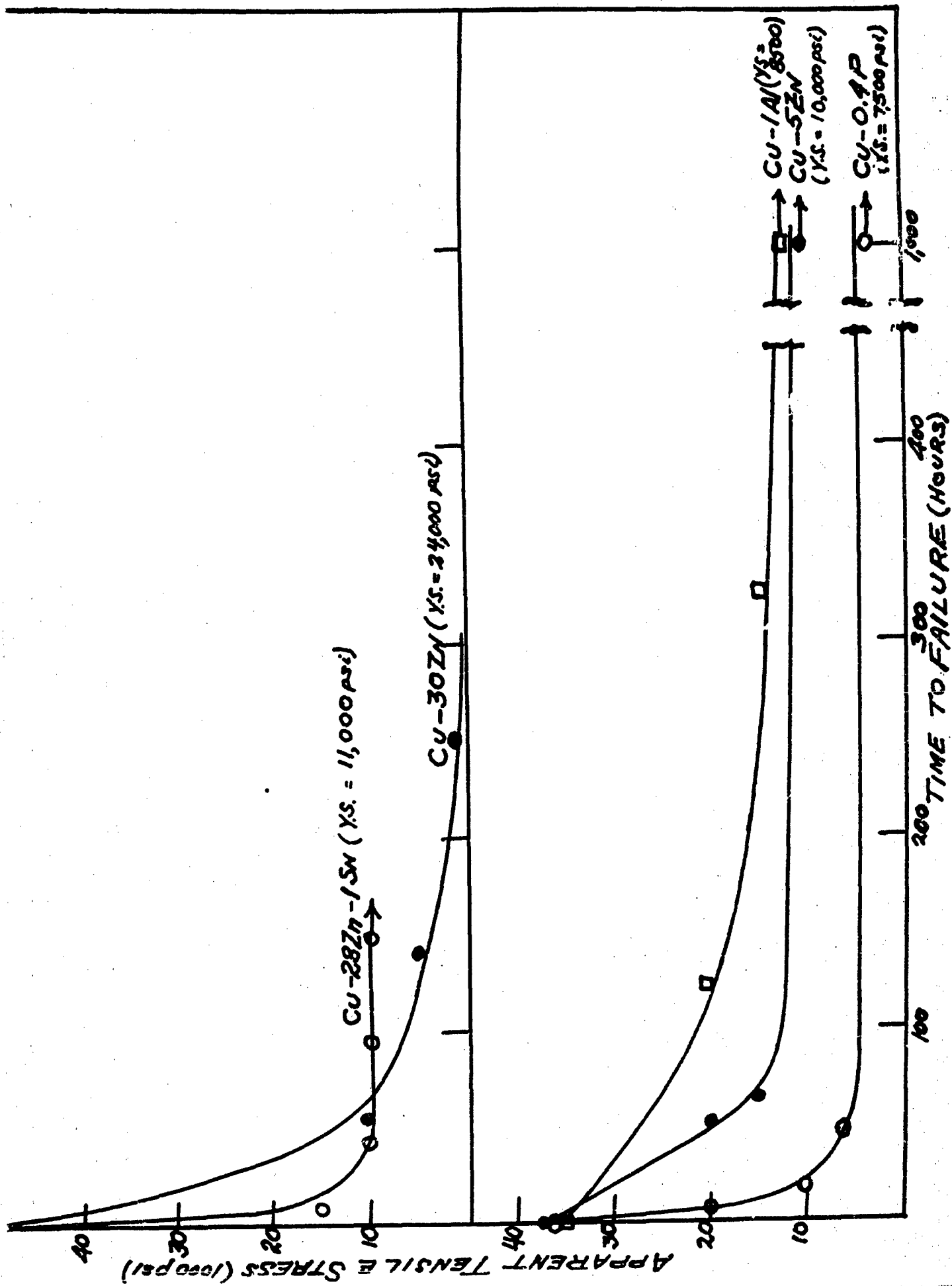
- 1) The required combination of angles between slip plane and boundaries, occurring close to the surface, is a relatively rare event in a three dimensional aggregate with the result that the number of boundaries that fracture may be expected to be small. This is, of course, in accord with the observations and is probably responsible for much of the scatter of experimental data.
- 2) The model requires some small plastic deformation of surface grains, in order to produce the necessary stress concentration, as a pre-requisite to intergranular failure. This condition implies a lower limit of applied stress below which cracking will not occur in a time short compared with intergranular corrosion in the absence of stress. This condition corresponds to a so called "endurance limit", which is shown in Figure 6 for a number of copper alloys.

Furthermore, the observed endurance stresses are approximately equal to the macroscopic yield stresses, which is consistent with the proposed model; the only exception is 70-30 brass, which is also exceptional in not exhibiting any well defined endurance stress. In evaluating these data, it must be recalled that the tests are conducted at constant tensile load, and that general corrosion processes are proceeding simultaneously at rates depending on composition; both of the latter qualifications lead to an increasing stress during the test instead of a constant stress.


- 3) Finally, if this model corresponds to reality, the process must be dependent on grain size, or some unit of length,  $L$ , defining the number of dislocations piled up at a boundary. This number, in turn, determines the magnitude of the stress concentration and hence the

Figure 6. Apparent tensile stress-time to fracture characteristics of copper alloys in ammonia indicative of an "endurance stress" for intergranular corrosion fracture.

Courtesy of Chase Brass and Copper Co., Research Laboratory.



macroscopic yield stress. Assuming the intergranular penetration of mercury to depend on the same structural processes involving barriers, one may use the data on the fracture stress of brass in mercury, which is shown in Figure 7, along with the data for similar specimens of brass in ammonia, in terms of the time to fracture at constant apparent stress, (replotted from the data of Edmunds).<sup>(12)</sup> Recently, data has become available for transgranular fracture of stainless steel<sup>(13)</sup> in  $MgCl_2$  as a function of grain size; this data has been included in Figure 7 for subsequent discussion concerning transgranular fracture. Clearly, a relationship does exist between grain size and intergranular fracture which is of a form consistent with a dislocation process of stress concentration.

However, when the problem is considered in terms of barriers in an annealed polycrystalline aggregate, an interesting issue arises. Grain size in face centered cubic alloys is normally measured without regard to annealing twins;<sup>(14)</sup> but, twin boundaries are effective barriers to the passage of dislocations,<sup>(15)</sup> as shown in Figure 8, and their presence will reduce the number of dislocations piled up at a grain boundary and hence the stress concentration. As a result, annealing twins can play an important part in the stress corrosion process, even though their own chemical reactivity is low when the material is in the annealed condition. Therefore, it may be anticipated that the susceptibility of two alloys of the same nominal grain size may be different (assuming equal chemical reactivity), depending on the number of twins per grain. Since a coherent twin boundary corresponds to one break in the correct stacking order of  planes, as indicated by an arrow in the sequence

A B C A B C B A C B A

↑

while a stacking fault corresponds to two breaks in the sequence it is not unreasonable

A B C A C A B C A B C

↑    ↑

- e 7. Fracture stress of 70/30 brass in mercury (12), time for failure of 70/30 brass in ammonia (12) and fracture stress of 18-8 stainless steel in  $\text{MgCl}_2$  (13) as a function of grain size.



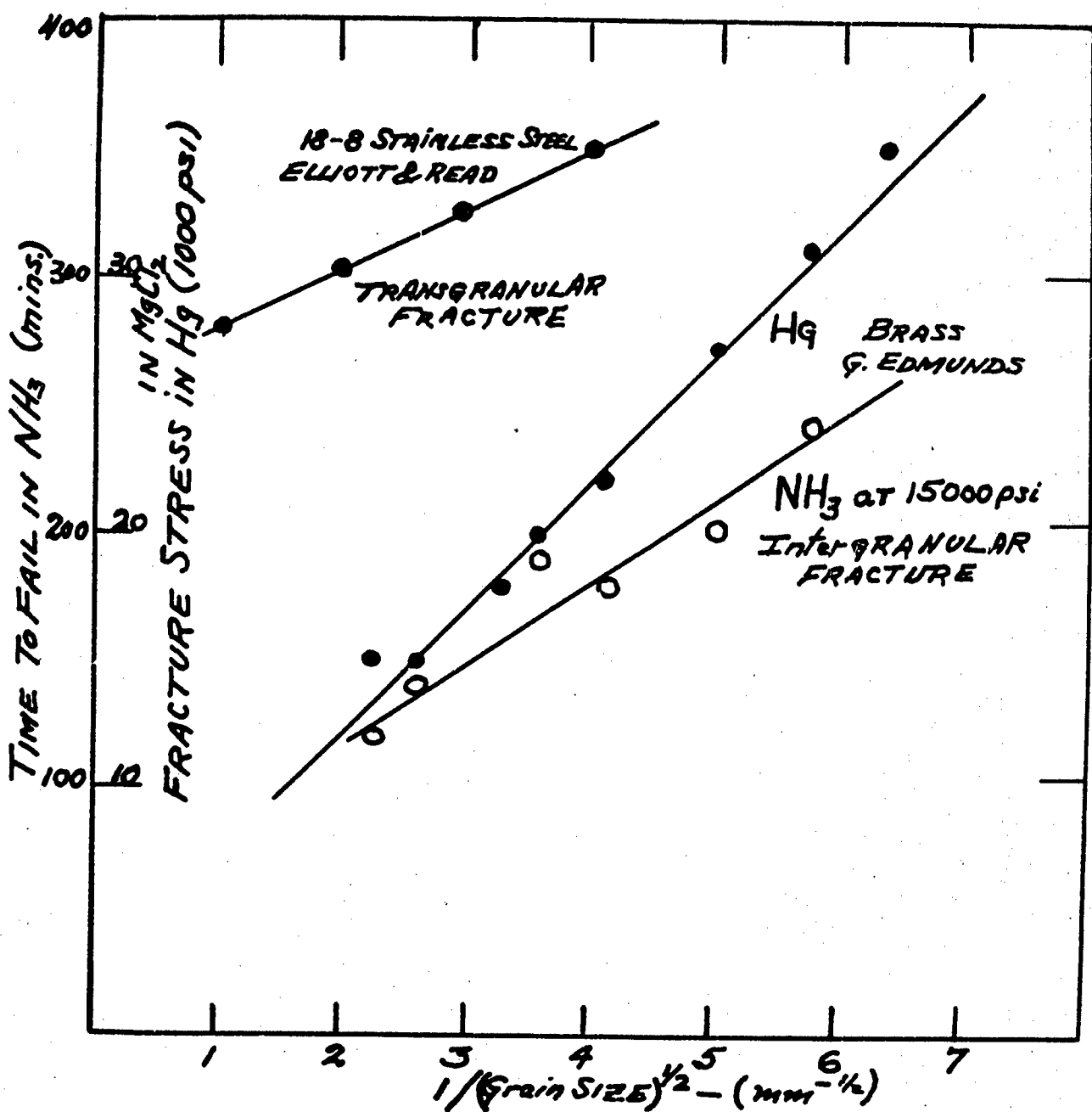
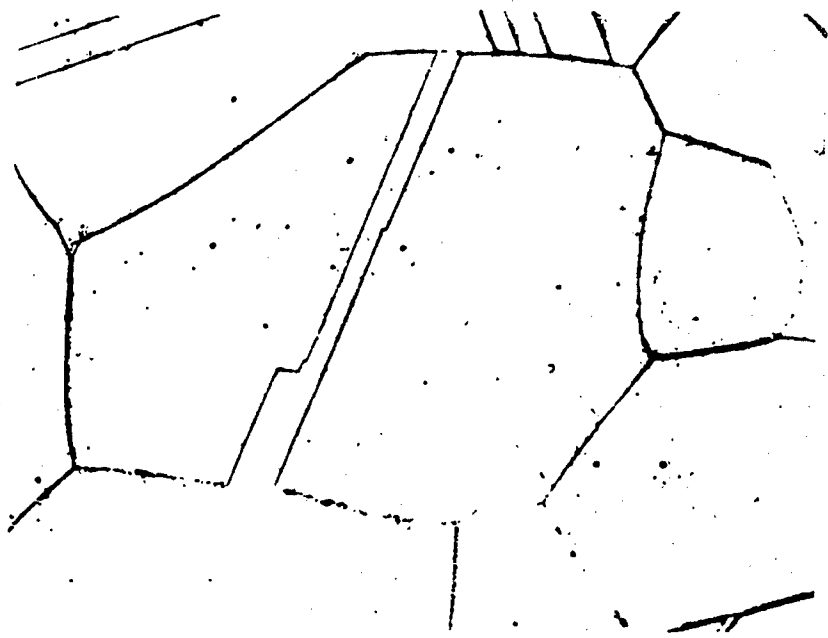


Figure 8. Arrays of dislocations piled against grain boundaries and coherent twin boundaries in an age hardening Cu-Ni-Si alloy. (15)



to suppose that a stacking fault has twice the energy of a coherent twin boundary. We then expect that the density of annealing twins should be greater in alloys of low stacking fault energy than in alloys of high stacking fault energy. Since the stacking fault energy is a sensitive function of composition,<sup>(16)</sup> comparison of different alloys must be made in terms of a grain size that has been corrected for the number of twin boundaries.

The number of annealing twins per grain in copper alloys is shown in Figure 9, obtained by counting the number of twin boundaries per grain after tensile strain and recrystallization; about 400 grains were counted in each alloy. It is evident that a substantial grain size correction is necessary when comparing the fracture characteristics of different alloys or, indeed, any property depending on barriers to dislocation motion.

Figure 10 shows a comparison of the fracture characteristics of two copper silicon alloys, of the same nominal grain size, fractured in an ammonia environment. First of all, it is noteworthy that the yield stress of the two alloys is quite different. While some of this difference results from an increased solution hardening with increasing silicon content, the smaller effective grain size in the 3% alloy is also important. Secondly, as in the case of the alloys presented in Figure 6, the endurance limit and the yield stress are almost identical for each of the two silicon alloys, indicating that some plastic deformation is a prerequisite for fracture. However, at a stress of say 30,000 psi, which is greater than the yield stress and hence sufficient to cause dislocation pile up in both alloys, the 0.5% silicon alloy is much more susceptible than the 3% silicon alloy. Although this difference might be attributed to differences in reactivity, it seems more reasonable to attribute it to the smaller distance between barriers produced by the higher twin density (Figure 9) in the 3% alloy. These results are consistent with those presented in Figure 7 where it is observed that for one alloy, at one stress level, the time for failure increases with decreasing grain size.

Figure 9. The number of annealing twins per grain in copper-silicon, copper-tin and copper-zinc alloys.

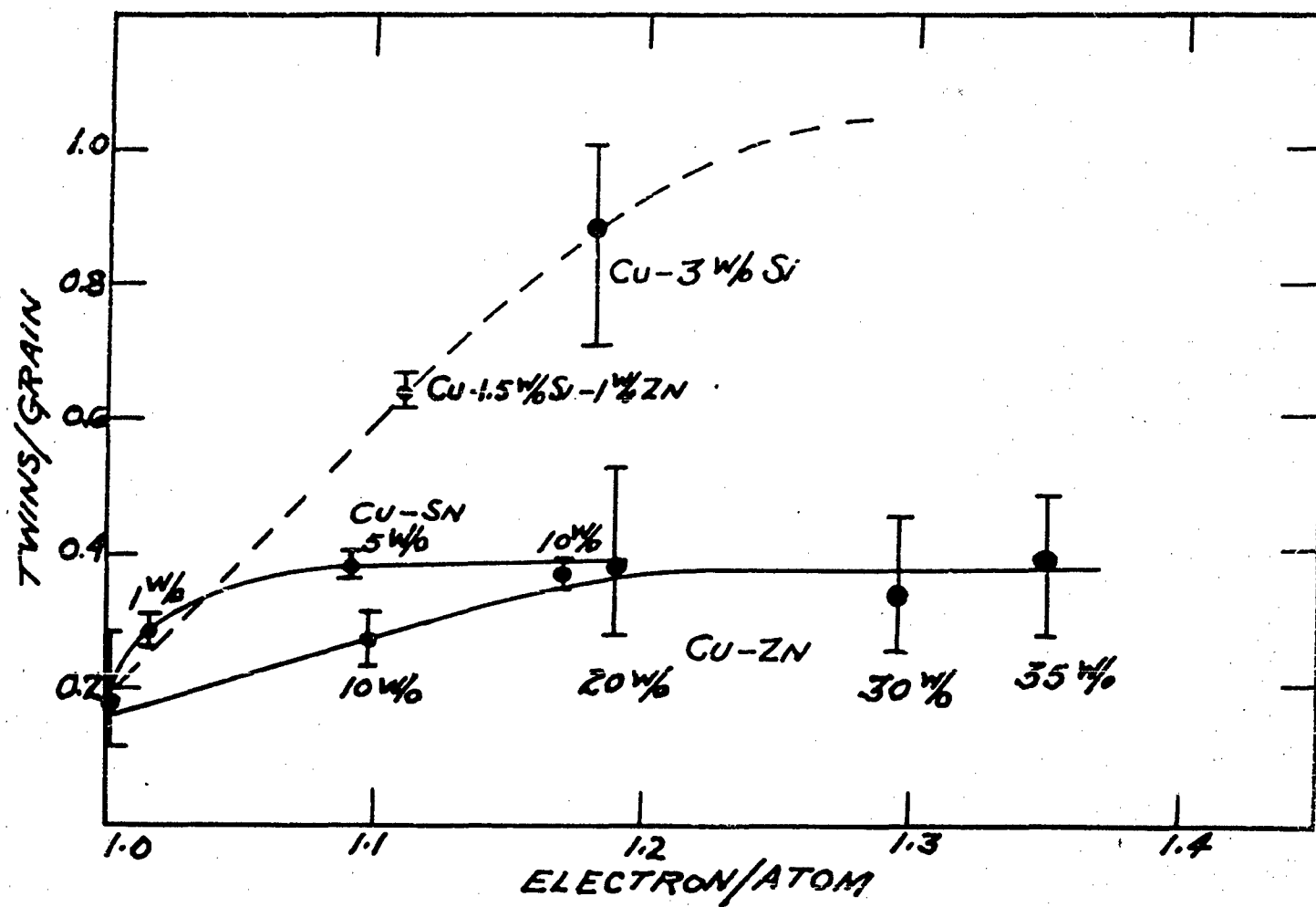
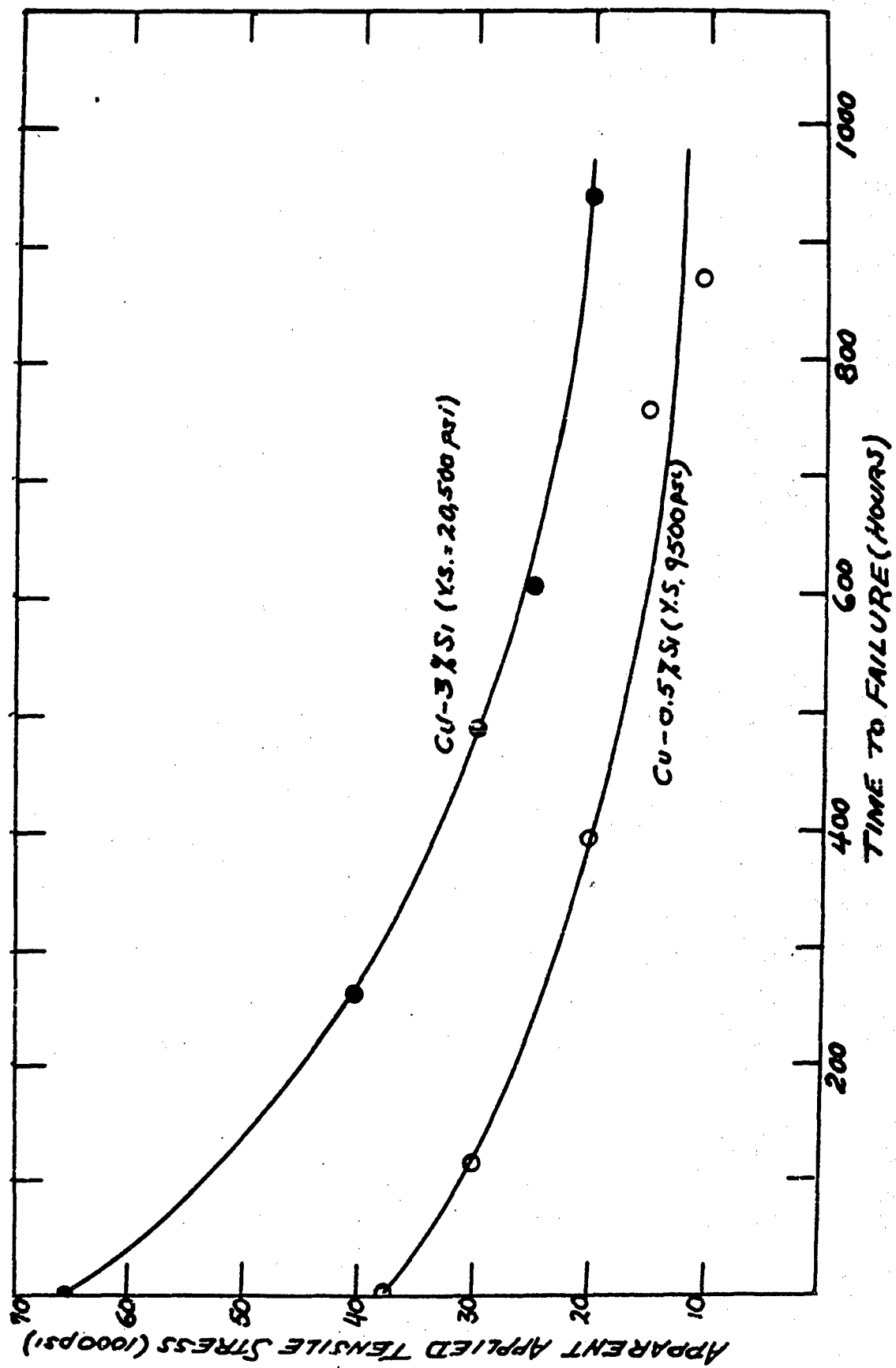


Figure 10. Stress-time to failure characteristics of two annealed copper-silicon alloys of the same nominal grain size but different members of twins per grain. Fracture data Courtesy of Chase Brass and Copper Co., Research Laboratory.





In summary, the proposed mechanism for intergranular corrosion cracking involves the two factors:

1. preferential and rapid chemical attack along the plane of the boundary which significantly reduces the fracture stress of the boundary plane and,
2. a concentration of normal stress across the boundary plane produced by dislocation pile ups.

In this mechanism, the concentration of alloying elements is directly important when the chemical reactivity is influenced by composition, and indirectly important because it affects the stress concentration by regulating the density of annealing twins and hence the number of dislocations that can pile up at a boundary. Similarly, stress is indirectly important in providing strain energy, which increases the chemical reactivity, and directly important in satisfying the Griffith criterion for fracture across an embrittled boundary plane. Since the Griffith criterion can only be satisfied if stress is concentrated in and near the boundary plane by piled up groups of dislocations, a minimum amount of plastic deformation is necessary and, accordingly, there is a lower limit, approximately equal to the macroscopic yield stress, below which fracture does not occur.

#### A Model for Transgranular Corrosion Cracking

##### 1) Nucleation of Stress Corrosion Fracture in Single Crystals

Only a relatively limited number of experiments have been performed with single crystals. Wassermann<sup>(17)</sup>, Edmunds<sup>(12)</sup>, and Denhard<sup>(18)</sup> have studied 70/30 brass crystals; Bakish and Robertson<sup>(19)</sup> investigated single crystals of  $\text{Cu}_3\text{Au}$ ; Reed and Paxton<sup>(20)</sup> have recently studied single crystals of austenitic stainless steels of three different compositions (18-9, 20-12, 20-20 Cr/Ni).

In all of these investigations the axis of the crystals and of the applied tensile stress were randomly oriented with respect to the principal crystallographic directions. Under these circumstances, the macroscopic path of fracture is generally observed to be normal to the tensile axis but, over short distances, there is some evidence for a crystallographically defined plane of fracture which is also observed occasionally in transgranular cracking of polycrystalline specimens. Denhard<sup>(18)</sup> obtained some evidence which was interpreted as fracture on  $\{111\}$  planes; Reed and Paxton<sup>(20)</sup> identified  $\{100\}$  as a fracture plane in Fe- 20% Cr- 20% Ni steel while fractures observed in Fe-20% Cr- 12% Ni and Fe-18% Cr - 9% Ni (Type 304 stainless steel) were not obviously associated with any specific plane. Bakish and Robertson<sup>(19)</sup> also concluded that the macroscopic plane of fracture in  $\text{Cu}_3\text{Au}$  was not clearly defined with respect to a definite crystallographic plane, though crack nucleation always occurred at external traces of slip clusters. In summary, the observations are certainly divergent, and no guiding principle has previously been proposed.

Following the general principles enunciated in the introduction, it is necessary to identify: (1), a chemically reactive path and (2), barriers at which sufficient stress can be concentrated to satisfy the Griffith criterion and nucleate a crack.

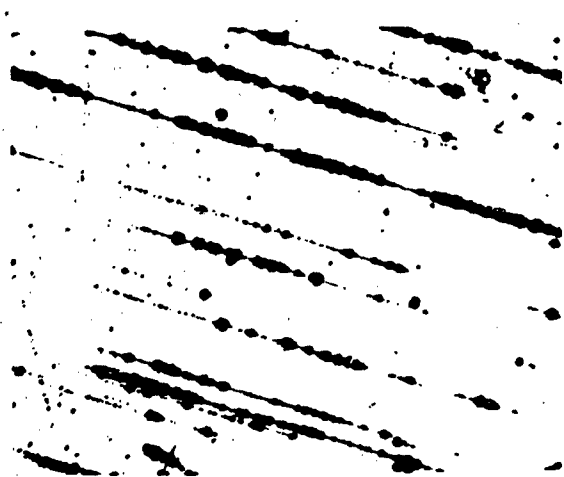
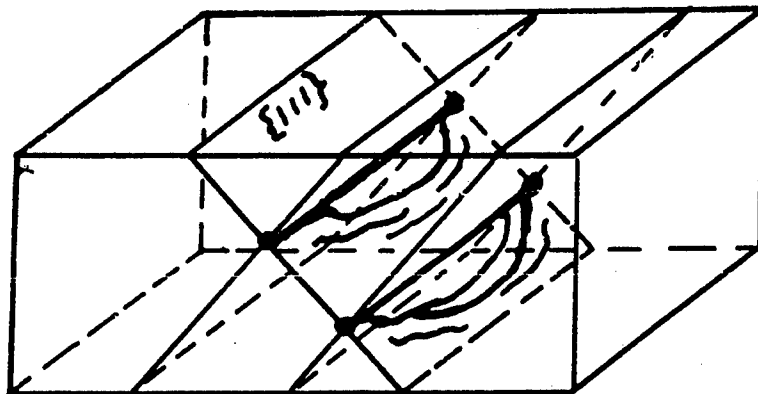
Reconsideration of the problem in these terms leads to the conclusion that the specific reactive path has in fact been observed in single crystals of  $\text{Cu}_3\text{Au}$  by Bakish and Robertson<sup>(21)</sup>. Disordered crystals, obtained by quenching after a homogenizing anneal of 300 hours at  $850^\circ\text{C}$ , were strained in tension about 5% and immersed in 2% ferric chloride for three months. The chemical reactivity of specific structural sites lying in surface traces of slip clusters is shown on the external face of a crystal in Figure 11b. These reactive sites do not represent individual dislocation pits but, more probably, aggregates of dislocations which are responsible for preferential reactivity in their vicinity. The reaction, beginning at the surface, propagates into the volume of the crystal along a  $\langle 110 \rangle$  direction, schematically

illustrated in Figure 11a. A polished but unetched section of the crystal, cut parallel with the slip plane, is shown in Figure 11c where two essentially continuous lines of attack are clearly evident, together with at least one line crossing at  $60^\circ$  which corresponds to a secondary  $\langle 110 \rangle$  direction, seen in the  $\{111\}$  plane of polish. The reaction has evidently moved rapidly along the line of discontinuity and spread normal to the line, producing a cylindrical volume of material from which copper has been selectively removed and which is sufficiently large in radius to have been intersected by the plane of polish ( $\pm 2^\circ$  to  $\{111\}$ ). That the lines along which reaction has occurred are, in fact,  $\langle 110 \rangle$  directions is shown in Figure 11d in which two additional sets of slip traces, produced by compressing the crystal after sectioning, are shown to form a  $60^\circ$  triangle with one of the lines of chemical reaction. It appears that the necessary reactive sites have been observed in a single crystal and it remains to define the mechanism of stress concentration at these specific crystallographic sites.

It is proposed that the sites of reaction, shown in Figure 11, are associated with the Cottrell-Lomer barrier<sup>(22)</sup>, and specifically with the  $\langle 110 \rangle$  sessile dislocation and the two stacking fault ribbons that lie at the intersection of two operating  $\{111\}$  planes. Independent evidence that barriers of this type can be created at small strains has recently been obtained by Meakin and Wilsdorf<sup>(23)</sup> for brass crystals strained in the easy glide region, slightly beyond the elastic limit. Thus, it is not too surprising that they are observed in the  $\text{Cu}_3\text{Au}$  crystals similarly strained in the easy glide range. Furthermore, Swann and Nutting<sup>(24)</sup> have obtained electron micrographs which show that chemical attack at stacking faults, produced in copper alloys by small strains, can readily occur provided that the right chemical environment has been chosen.

The crystal geometry is shown in Figure 12 where the two  $1/6 a [112]$  dislocations are represented by their stacking fault ribbons which bind them to the

Figure 11.  $\text{Cu}_3\text{Au}$  single crystal strained 5% and immersed for three months in 20%  $\text{FeCl}_3$ . (a) crystallographic planes represented by the micrographs; (b) chemically reactive sites lying in traces of slip clusters on the external surfaces; (c) a cross section parallel with the slip plane showing reaction along  $\langle 110 \rangle$  directions; (d) traces of slip lines introduced by deformation after sectioning crystal (21).



line of intersection and to the sessile  $1/6a [110]$  at the intersection of the two slip planes, in accordance with the following reactions.

Lomer <sup>(25)</sup> first pointed out that an edge dislocation, moving on a  $(111)$  plane in a face centered cubic crystal, with Burgers vector  $1/2a [10\bar{1}]$  will be attracted to an edge dislocation of vector  $1/2a [011]$  moving on a  $(1\bar{1}1)$  plane. At the line of intersection of the two slip planes, the dislocations can combine according to Frank's rule:

$$1/2a [10\bar{1}] + 1/2a [011] \rightarrow 1/2a [110] \quad (1)$$

and create a new edge dislocation whose vector  $1/2a [110]$  and line  $[1\bar{1}0]$  lie in the  $(001)$  plane. Since the  $(001)$  is normally not a slip plane for face centered cubic metals, the dislocation cannot move easily.

Cottrell <sup>(26)</sup> then showed that the dislocation may become sessile by dissociating into three partial dislocations:

$$1/2a [110] \rightarrow 1/6a [11\bar{2}] + 1/6a [\bar{1}12] + 1/6a [110] \quad (2)$$

Two of these partials are repelled away from the line of intersection. The dislocation of vector  $1/6a [11\bar{2}]$  moves into the  $(111)$  plane, while that of vector  $1/6a [\bar{1}12]$  moves into the  $(1\bar{1}1)$  plane. This movement creates stacking fault ribbons in the two slip planes, as shown in Figure 12a. Alternatively, if the original dislocations were dissociated into partials

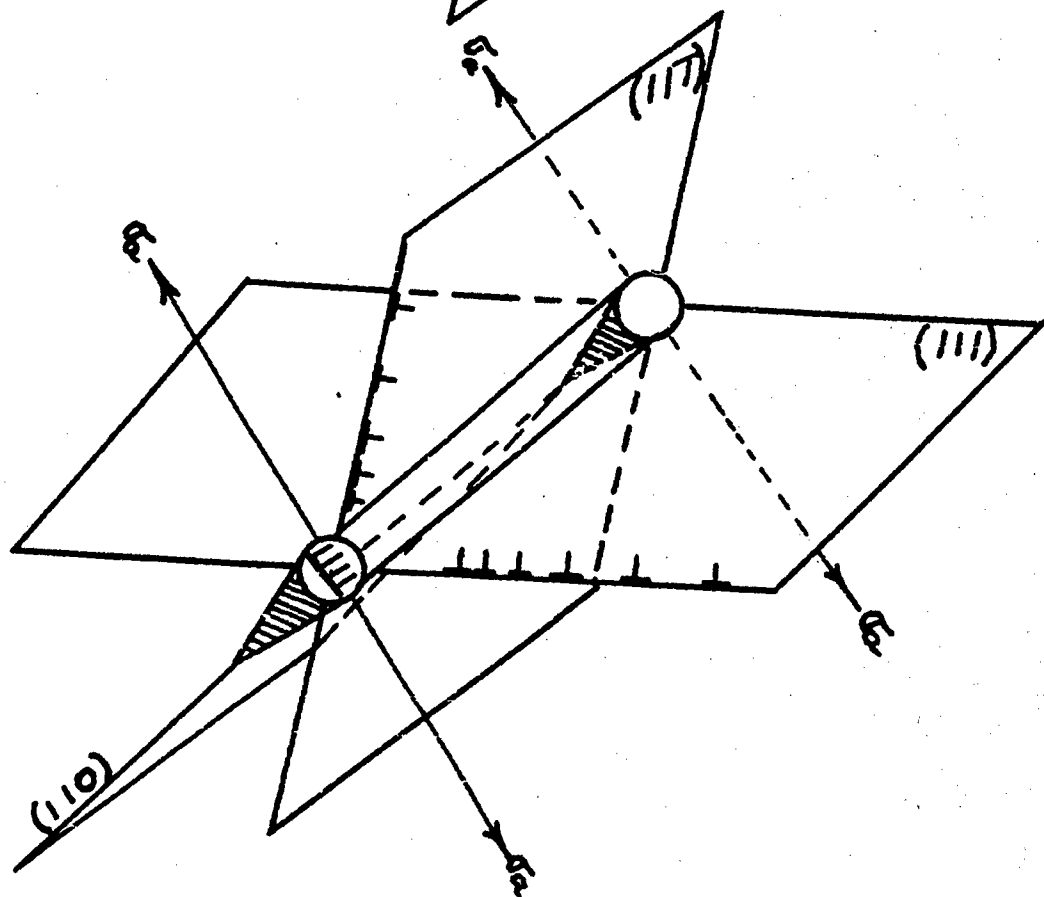
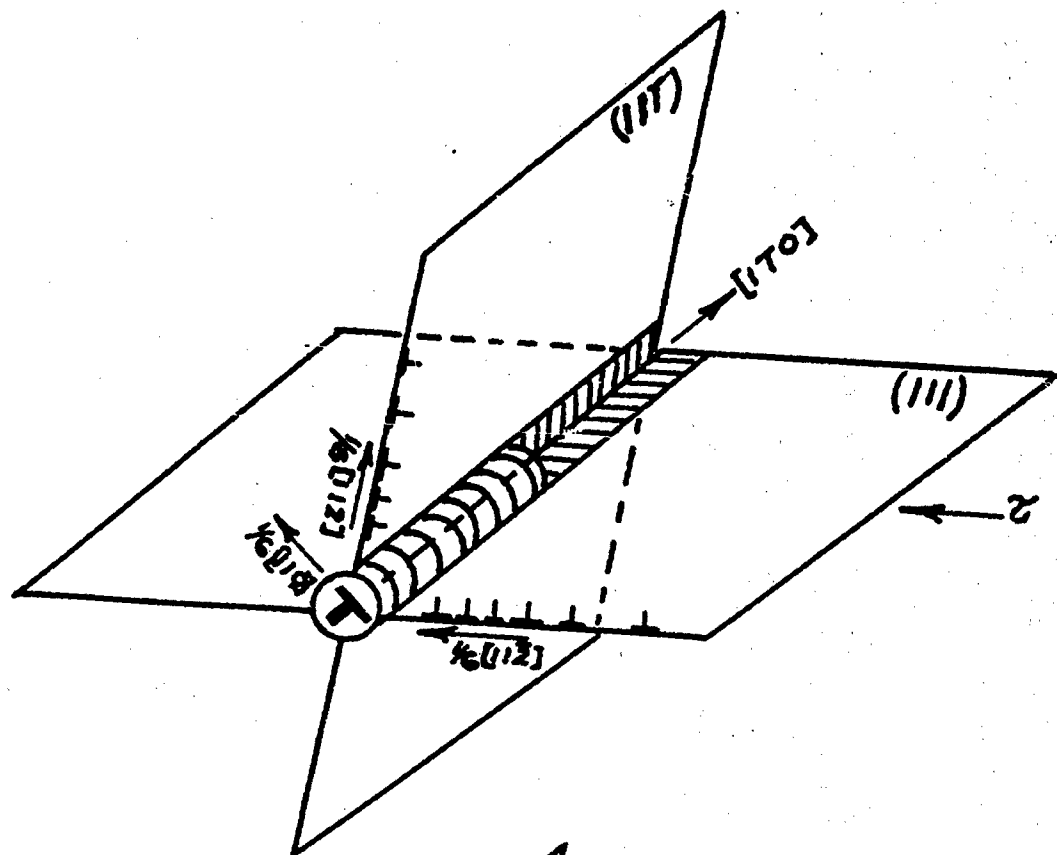
$$\begin{aligned} 1/2a [10\bar{1}] &\rightarrow 1/6a [11\bar{2}] + 1/6a [2\bar{1}\bar{1}] \\ 1/2a [011] &\rightarrow 1/6a [\bar{1}12] + 1/6a [\bar{1}21] \end{aligned} \quad (3)$$

the sessile dislocation may be formed by the direct combination of the second dislocation of each pair

$$1/6a [2\bar{1}\bar{1}] + 1/6a [\bar{1}21] \rightarrow 1/6a [110]$$

with the remaining partials joined to the line of the sessile dislocation by stacking fault ribbons, giving the same configuration as produced by equation 2 and shown in Figure 12. In analyzing all dislocation combinations that can produce the sessile,

Figure 12. Crystal geometry of the Cottrell-Lomer Barrier and its relation to the fracture plane. (a) showing the two partial dislocations,  $1/6a[112]$ , repelled from the  $1/6a[110]$  sessile dislocation to a distance determined by the stacking fault energy; the stacking fault ribbons have reacted with the environment to produce a cylindrical volume of disordered alloy. (b) edge dislocations have accumulated at the line of intersection to form a cavity dislocation nucleating a crack lying in the  $(110)$  plane.





Friedel<sup>(27)</sup> finds that the arrangement will be most stable when all dislocations involved are of  $\epsilon$  type. In a detailed calculation of the barrier strength of Cottrell-Lomer combinations of dislocations, Stroh<sup>(28)</sup> has shown that the stress on the sessile increases as dislocations, emitted from a source on the slip plane, pile up behind it. When the stress due to the pile up of  $n$  dislocations behind the barrier is sufficiently high, the barrier may give way by recombination (the reverse reaction of 2), or by dissociation (the reverse reaction of 4) and slip will again occur on the  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$  planes.

Both the recombination and the dissociation process depend on the width of the stacking fault ribbon joining the extended dislocations at the sessile, since a constriction in the ribbon is the first step in either process. The width of the ribbon depends sensitively on the stacking fault energy and accordingly, metals or alloys with low stacking fault energies will have widely extended dislocations. Therefore, more dislocations can be piled up behind a barrier in a metal such as copper or silver (low stacking fault energy) than against a barrier in aluminum or nickel (high stacking fault energy) before breakdown occurs.

Taking these and other factors into account, Stroh<sup>(28)</sup> has calculated the maximum number of dislocations that the barrier can withstand at room temperature, under a stress of  $1 \text{ kg/mm}^2$ , to be 500 in copper and 200 in aluminum. Although this number is quite large (and depends on the size of the dislocation core which is not precisely known), Stroh has emphasized that crack initiation will not occur (in the absence of a reactive environment) because the important quantity in spontaneous crack initiation is  $\frac{n\sigma}{G}$ . In copper, this quantity is 0.12 at room temperature, or an order of magnitude less than the value of  $\frac{n\sigma}{G} = 1.5$  required to initiate a crack.

There is another process which can occur and which may tend to keep the number of piled up dislocations well below 500. This process is the cross slip

of screw dislocations piled up behind the barriers, and the subsequent rearrangement of the edge components that are left behind to form deformation bands. Seeger<sup>(29)</sup> and his co-workers have developed a model for this process based on the principle that increasing deformation during the linear work hardening stage produces an increasing number of piled up groups, each containing about 25 dislocations. Cross slip, rather than barrier breakdown was postulated as the more favored process from considerations of the stress on the leading screw dislocation, which was assumed to be the same as that on the Cottrell-Lomer sessile just ahead of it. Since the repulsive forces that must be overcome to form the constriction are higher for the Cottrell-Lomer partials than for the leading screw, the screw may recombine and cross slip out of the piled up group.

In summary, barriers to dislocation movement exist in the crystal and are created by plastic deformation, even at small plastic strains. The strength of the barrier, and hence the number of dislocations that can pile up behind it, is primarily a function of the stacking fault energy which, itself, is a function of the type and composition of the metal or alloy involved.

At the site of the Cottrell-Lomer barrier in the crystal the strain energy of the piled up group of dislocations, and the stacking fault energy of the partial dislocations, provide a site for preferential chemical reactivity directed along the line of the barrier. Employing the concept of structural reactivity, as previously defined, a cylindrical volume of alloy may be expected to react with a suitable environment along  $\langle 110 \rangle$  directions, and to spread slowly normal to the line of the barrier, as shown schematically in Figure 12a, which corresponds in all respects to the structure observed in  $\text{Cu}_3\text{Au}$  and illustrated in Figure 11. As reaction proceeds and a component of the alloy crystal is removed from the lattice by chemical oxidation and diffusion to the free surface, the vacancies that remain condense to form a cavity or, at least, a disordered structure through which

dislocations cannot move freely to destroy the barrier by recombination or cross slip processes. The cavity also acts as a trap where edge dislocations, moving on either or both slip planes, can coalesce to form a cavity dislocation of Burgers vector  $\underline{nb}$  which is, in fact, the nucleus of a crack. Such a crack is shown schematically in Figure 12b, lying in the (110) plane bisecting the two operating slip planes from which the dislocations combined to form the Cottrell-Lomer barrier.

The initial growth of a crack produced by dislocation coalescence in a cavity has been treated by Cottrell<sup>(30)</sup>. Following his model for the most ideal case, we suppose that the two  $\{111\}$  planes which initiate the crack are oriented symmetrically at an angle of  $54^\circ 44'$  to the applied tensile stress (Figure 12b). The  $n$  dislocations originally piled up behind the sessile, run into the cavity and produce a cavity dislocation of Burgers vector  $\underline{nb}$  where  $\underline{b}$  is the Burgers vector of the individual dislocation. The crack of length  $c$  then extends normal to the applied stress, along the (110) plane. Similarly, if the stress  $\sigma$  shown in Figure 12b were rotated by  $90^\circ$ , the crack would extend along the (001) plane. Following Cottrell<sup>(30)</sup>, the energy of the crack  $W$  is given by:

$$W = \frac{Gm^2b^2}{4\pi(1-\nu)} \ln\left(\frac{4R}{c}\right) + 2\delta c - \frac{\pi(1-\nu)\sigma^2c^2}{8G} - \frac{\sigma mbc}{2} \quad (5)$$

where the first term is the energy of the stress field of the cavity dislocation,  $R$  being the effective radius of the field. The second term is the surface energy of the crack faces, and the third term is the elastic energy of the crack in the applied stress field. The fourth term, which is the most important term when crack growth is considered, is the work done by the applied stress in opening up the crack.

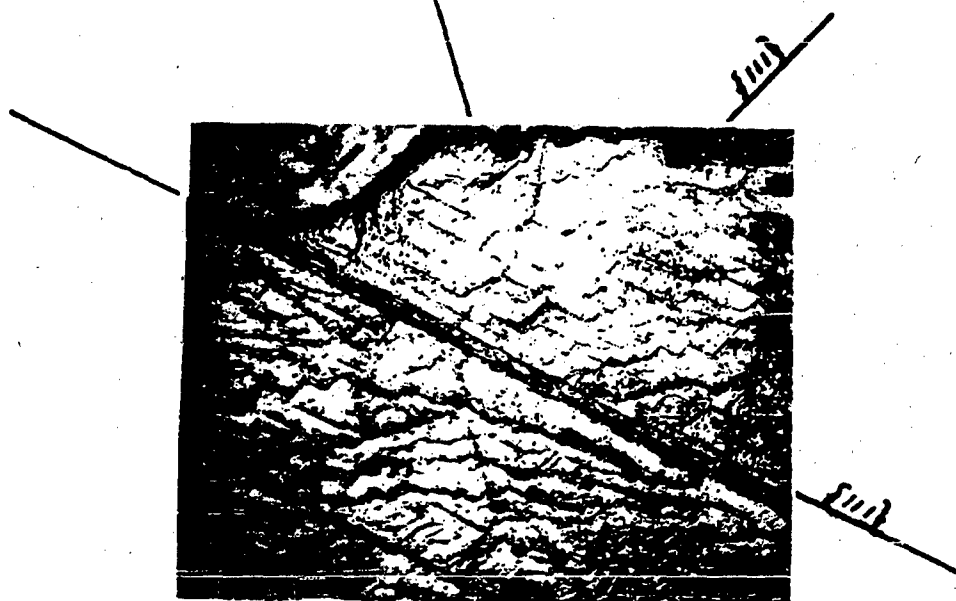
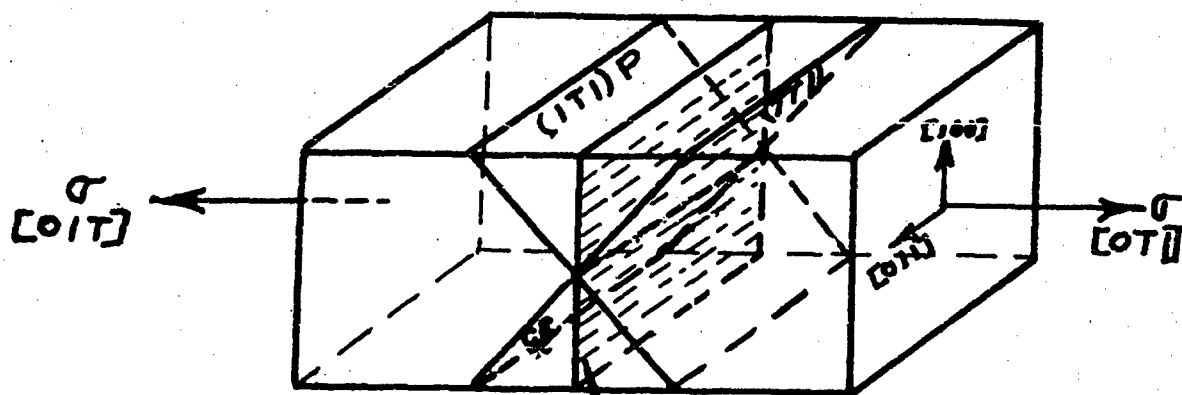
The equilibrium lengths of the crack are defined by the condition that  $\frac{\partial W}{\partial c} = 0$ . Taking the derivative, in the case when both dislocations and an applied stress are present, and solving for the crack lengths, shows that the crack will begin to spread when

$$\sigma mb = 2\delta \quad (6)$$

On a microscopic scale, the fracture process occurs on crystallographic planes, defined by the direction of the applied stress relative to crystal orientation, and relative to the planes that operate to produce Cottrell-Lomer barriers. Evidence for crystallographically defined cracks should be available, and it is. However, it appears from the preceding analysis of the problem that completely satisfactory evidence will be forthcoming only when investigations are conducted with crystals oriented with respect to the axis of tensile stress so that specific crystallographic processes can be directly evaluated. The mechanism outlined above predicts a  $\{110\}$  or  $\{100\}$  type fracture plane only when the crystal is oriented so that equal numbers of dislocations pile up on each of the two  $\{111\}$  planes. For a randomly oriented crystal, this situation may not exist, and the fracture plane would then be the one with the greatest normal stress across it, produced by the unsymmetrical dislocation arrangement at the Cottrell-Lomer lock. In the most extreme case, where dislocations are piled up on only one  $\{111\}$  plane, the fracture plane would be  $70^\circ$  from the  $\{111\}$  plane, in accordance with Stroh's<sup>(6)</sup> analysis described previously. Since another  $\{111\}$  plane is at  $70^\circ$  to the slip plane, cracking on a  $\{111\}$  type plane could occur, and observations to this effect have been reported by Denhard in crystals of alpha brass<sup>(18)</sup>.

One such experiment employing symmetrically oriented crystals has been performed by Bakish<sup>(31)</sup> with  $\text{Cu}_3\text{Au}$  single crystals which were strained in bending about a  $\langle 110 \rangle$  direction after immersion in ferric chloride for one month. The crystal geometry is shown in Figure 13a and the fracture surface produced by stress normal to a  $\{110\}$  plane is shown in Figure 13b. This surface exhibits all the characteristics associated with a completely brittle fracture, including cleavage steps. A Laue pattern taken normal to the fracture surface has the symmetry of a  $\langle 110 \rangle$  axis and shows reasonably sharp spots, indicative of very little plastic deformation. To the best of the authors' knowledge, this is the only case where

Figure 13. Fracture on a  $\{110\}$  plane in a  $\text{Cu}_3\text{Au}$  single crystal after immersion in 2%  $\text{FeCl}_3$  for one month followed by bending about a  $\langle 110 \rangle$  axis. Bakish (31).



completely brittle behavior has been observed in a normally ductile material, and thus the mechanism postulated in Figure 12 appears to have been verified by a direct experiment. Furthermore, the traces of macroscopic cracks on a  $\{110\}$  surface and a  $\{111\}$  surface of a  $\text{Cu}_3\text{Au}$  single crystal, shown in Figure 14, are at  $60^\circ$  and at  $35^\circ$  respectively to the slip traces, consistent with a  $\{110\}$  fracture plane.

The observations reported by Reed and Paxton<sup>(20)</sup>, indicating a  $\{100\}$  fracture plane in one stainless steel alloy (Fe-20Cr-20Ni) can be accounted for, in all essentials, in terms of the same crystallographic mechanism of stress concentration, since the stress system shown in Figures 12b and 13a can be rotated  $90^\circ$ , making it normal to a  $\{100\}$  plane. In the other two alloy crystals investigated by Reed and Paxton (Fe-20Cr-12Ni and commercial stainless steel type 304) random orientation of crystals produces an apparently random set of fracture planes, except in one crystal of type 304 stainless steel which is oriented near  $\langle 110 \rangle$  and in which the pole of the fracture plane is only about  $10^\circ$  from the  $\langle 110 \rangle$  axis.

## 2) Nucleation of Transgranular Cracking in Polycrystalline Aggregates

Transgranular cracking occurs in austenitic stainless steels when they are exposed to an environment containing chlorides. However, before any general mechanism of cracking phenomena in these alloys can be deduced from available information, it is necessary to consider some of the special characteristics of these alloys.

1. The existence of a chemically passive surface strongly influences the structure dependent reactivity. The elongated pits that are observed in association with slip lines <sup>(20)(32)</sup> may be caused by the destruction of the passive film at the surface where the slip trace emerges through the film. In the same connection, passivity is sensitively dependent on composition, which may lead to ambiguous conclusions when comparing different alloys with respect to their susceptibility to cracking.



Figure 14. Macroscopic cracks produced by ferric chloride on two surfaces of the same  $\text{Cu}_3\text{Au}$  crystal: (a)  $\{111\}$  surface and (b) a  $\{110\}$  surface. Bakish and Robertson. (19)

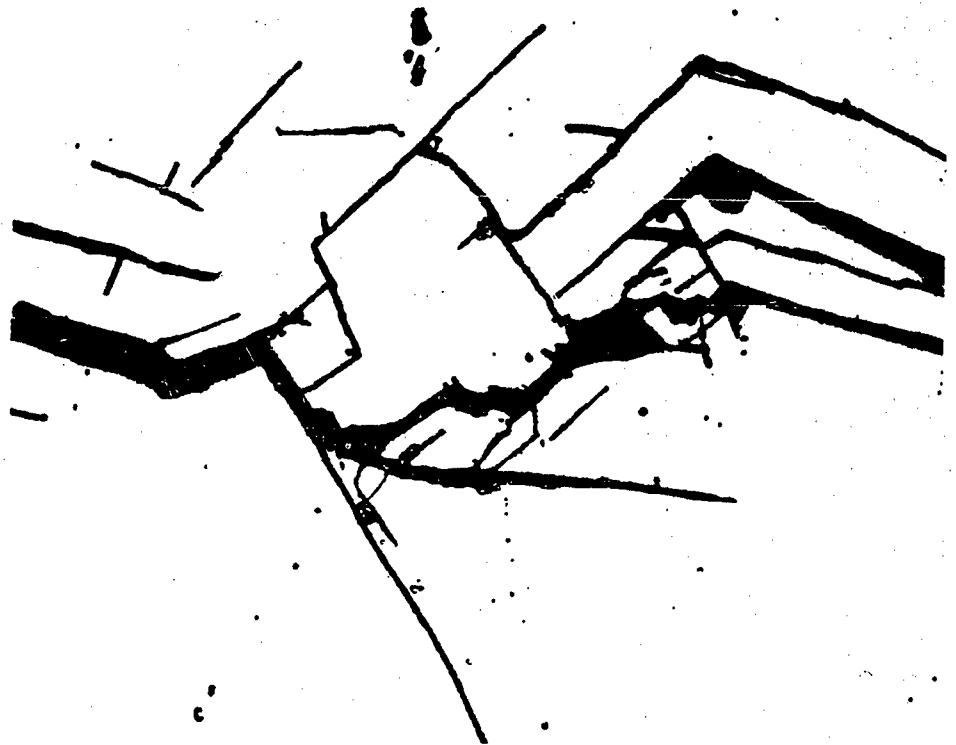




2. The iron-chromium - nickel alloys in the range of 16 to 20% Cr and 7 to 15% Ni are more or less unstable with regard to the body centered cubic phase. Transformation by a martensitic mechanism to a hexagonal close packed structure and<sup>(33)</sup> <sup>(34)</sup> or to the stable body centered cubic phase (martensite) may occur in the vicinity of room temperature on a  $\{111\}$  habit plane<sup>(34)</sup>, since both  $M_s$  and  $M_d$  are dependent on the concentration of nickel and nitrogen<sup>(35)</sup>. The presence of the hcp or bcc structure in the fcc matrix may influence reactivity and subsequent failure by stress corrosion cracking processes; also, the shear associated with the transformation may destroy locally the chemical passivity and, since the habit plane is  $\{111\}$ , it is difficult to differentiate strain produced by slip from that due to the transformation. However, alloys with a sufficient concentration of nickel (about 20%) fail by transgranular cracking in a temperature range well above  $M_d$  so the transformation in these alloys, at least, may be excluded as a necessary part of the mechanism and the results may be more easily interpreted.

Since intergranular cracking can be eliminated by heat treatment, or control of composition to prevent carbide precipitation at grain boundaries, transgranular cracking of a polycrystalline aggregate must be ascribed to processes operating within individual crystals that do not significantly affect the reactivity of grain boundaries, but can and do lead to fracture in chloride environments. Two examples of the crystallographic features of transgranular cracks in stainless steel are shown in Figure 15: Figure 15a, representing commercial stainless steel (Type 304), exhibits reaction at what appear to be surface traces of martensite on  $\{111\}$  planes and, in the center of the micrograph, cracks on some other plane. Figure 15b,

Figure 15. Corrosion cracking of austenitic stainless steels (a) type 304 and  
(b) high purity Fe-18% Cr-20% Ni alloy.  
Courtesy of H.R. Copson and Frances Lang, International Nickel Company.

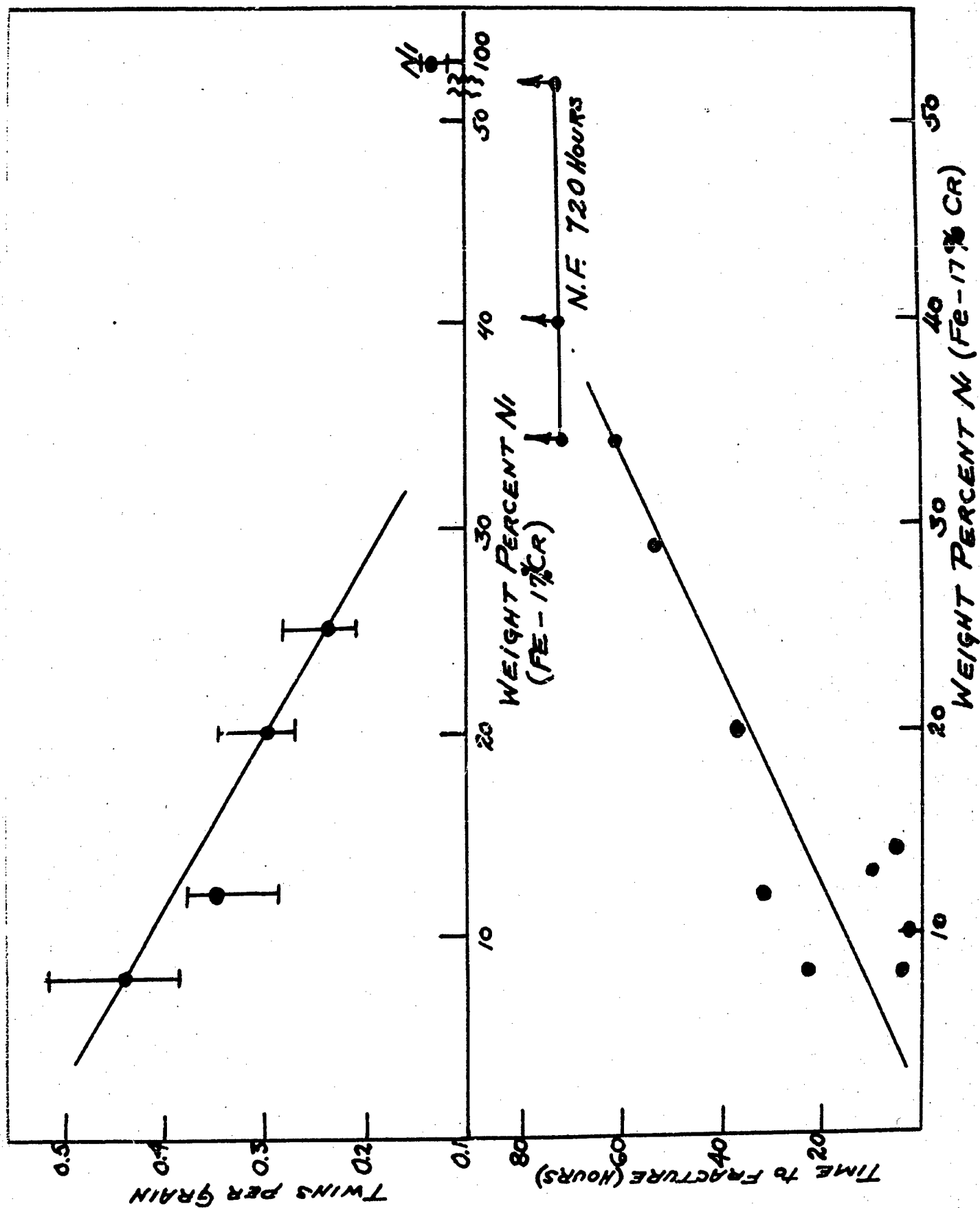


representing a high purity Fe-18%Cr-20%Ni alloy in which the fcc phase is completely stable, shows cracks that change direction at twin boundaries but which are not parallel to the twin boundary traces, indicating that while following some crystallographic pattern, the cracks are not associated with a  $\{111\}$  plane. It may also be noted that Denhard<sup>(18)</sup> observed cracks in Type 304 stainless steel which were parallel with the diagonals of the cubic etch pits. The observations were interpreted to mean that cracks follow a  $\{111\}$  plane but, of course, the same diagonal relationship would be observed if the cracks were parallel to a  $\{110\}$  plane.

That transgranular failure in iron-chromium-nickel stainless steels follows a trend with composition that is consistent with the stacking fault energy of the alloys is demonstrated in Figure 16. As the stacking fault energy increases with increasing nickel content (twins per grain decreasing) the number of dislocations n that can be piled up behind the Cottrell-Lomer barrier decreases, and the stress to form a crack increases according to equation (6). Therefore, susceptibility to transgranular cracking should decrease with increasing stacking fault energy, and Figure 16b shows that this prediction is borne out. In making this comparison it is assumed that chemical reactivity remains essentially constant over the range of nickel concentration, and it is the strength, and possibly also the number, of barriers that is changing with stacking fault energy. It should be pointed out that exactly the opposite composition behavior (susceptibility increasing with solute concentration) is exhibited in the transgranular cracking of copper alloys, in conformity with the fact (Figure 9) that the stacking fault energy decreases (twins per grain increasing) with the addition of zinc, silicon, and tin and most other alloying elements except nickel. In fact, nickel is one of the few alloying additions that significantly reduces the susceptibility to failure of both copper alloys and stainless steels.

Figure 16. Comparison of the dependence of stacking fault energy (twins per grain) and transgranular failure of approximately 17% Cr. stainless steels on nickel concentration.

Data for time to failure from H.R. Copson(36)



Finally, it should be emphasized that this model for transgranular cracking predicts that a minimum applied stress will be required for fracture, since dislocations have to be moved into the cavity in order to form a crack, and a tensile component of stress will be required in order to get the crack moving and keep it moving. In accordance with this prediction, endurance limits are observed for transgranular cracking.

Summarizing the preceding ideas regarding the nucleation of transgranular cracking, it can be said that (1) the evidence provided by optical and electron microscopy (2), the dependence of cracking susceptibility on relative stacking fault energies and (3), the identification of both  $\{110\}$  and  $\{100\}$  planes as fracture planes are all in accord with the proposed model; namely, that crack initiation is produced by coalescence of dislocations at chemically reactive Cottrell-Lomer barriers.

### 3) Transgranular Crack Growth and Ultimate Failure

The problem of final crack growth and fracture is a complicated one in normally brittle materials; it is even more complicated in the case of ductile materials which become brittle upon exposure to a reactive environment. In the latter case, account must be taken of the fact that failure occurs in time under static loading, and the fact that the reacting environment must be present at all times or ductility will be restored.

The preceding sections have shown that when  $\frac{\sigma_m b}{2} \geq \gamma$ , the crack formed by dislocation coalescence will begin to spread, where  $\gamma$  is the energy consumed in pulling the two faces of the crystal apart. Since the exposed faces of a growing crack react with the environment, the energy of the spontaneous chemical reaction,  $\gamma_r$ , is available for the propagation of a crack, thereby diminishing the energy required from  $\gamma$  to  $(\gamma - \gamma_r)$ . With respect to the rate of this process, interatomic bonds



near the crack tip go through all stages of stretching until they finally break and it seems unlikely, therefore, that the rate can be limited by the rate of the actual chemical reaction at the leading edge of the crack. However, in order to get to the reaction site, molecules of reactant must diffuse along the surfaces separating sides of the crack, and products may be required to diffuse out of the crack; neither diffusion process is exceptionally fast and probably both of them limit the rate of crack growth.

Another factor that limits crack growth is the loss of energy due to plastic deformation at the crack tip. Gilman<sup>(11)</sup> has considered this problem in the case of cleavage in normally brittle materials, and his analysis shows that if the surface energy  $\gamma$  of the crack faces is small, the stress necessary to propagate a crack will also be small. (See equation 6). Since the propagation stress will be small, the stresses at the crack tip will be kept low and little plastic flow will occur. Therefore, the energy expended in plastic deformation,  $\gamma_p$ , depends directly on the energy consumed in making the crack faces.  $\gamma_p$  also depends on the yield stress of the material and, according to Gilman,<sup>(11)</sup>

$$\gamma_p = K \gamma \ln \left( \frac{1}{T_y} \right)$$

where K is a constant and  $T_y$  is the yield stress. In a reactive environment

$\gamma$  may be replaced by  $(\gamma - \gamma_n)$  and  $\gamma_p$  is correspondingly reduced to

$$\gamma_p = (\gamma - \gamma_n) K \ln \left( \frac{1}{T_y} \right)$$

If, on the other hand, the environment is removed,  $\gamma_p$  will increase and eventually the crack will stop. Furthermore, chemical reactions on the surface will hinder dislocation motion by disordering the lattice, and thus prevent surface sources from operating. This effect will raise the yield stress  $T_y$  and accordingly lower  $\gamma_p$ .

It should be pointed out that as the crack advances, surface roughness will occur if the crack wanders off the plane on which it initiated. The 'large crack' observed in Figure 14 does not follow one plane, but spreads across the crystal

moving essentially perpendicular to the applied stress. The reason for the absence of a well defined cleavage plane, and the observation that most cracks run perpendicular to the applied stress, lies in the fact that there is no preferred cleavage plane for face centered cubic crystals when they are fractured in a reactive environment. Following Gilman's<sup>(11)</sup> analysis that the cleavage plane is the plane that requires the least force for crack propagation along it, this plane should be the one of lowest surface energy. However, any small differences in  $\sigma$  that exist between one plane or another will be insignificant since it is  $(\sigma - \sigma_c)$  that is important. Therefore, the fracture plane will be the one that is normal to the stress axis, since less stress will be required when all of the stress is resolved normal to the fracture plane. If the plane normal to the stress axis is a  $\{110\}$  or a  $\{100\}$ , we might expect complete cleavage since these are the planes on which the crack can form most easily. In all other cases, the dislocation arrangement at the Cottrell-Lomer lock will probably be unsymmetrical, resulting in crack nucleation on a plane that is not normal to the applied stress, and the crack will eventually curve around to align itself normal to the stress axis. Under these circumstances, complete cleavage is not expected nor is it observed. Since a crack growing normal to the applied stress axis will probably not follow a crystallographic plane, (except in the most symmetric case- Figure 13) it will develop a stepped pattern, which will expend more energy in proportion to the additional area of the steps, and eventually come to rest.

Furthermore, when a crack propagates in a polycrystalline alloy, a certain amount of energy will be consumed as the crack moves through a grain boundary, and susceptibility should decrease with decreasing grain size. We attribute the grain size dependence of susceptibility (shown in Figure 7 for stainless steel in magnesium chloride) to the propagation stage rather than to the nucleation stage, since it is the Cottrell-Lomer barrier, and not the grain boundary, that serves as the nucleation site for transgranular failure.

Finally, since cracks propagate through regions containing slip bands, where the dislocation density is highest, we would expect that these bands serve as final resting places for the cracks. Figure 14 does show that microcracks, which follow along  $\{110\}$  planes and have not aligned themselves perpendicular to the applied stress, do end up in slip bands, while Figure 13 shows that the traces of  $\{111\}$  slip planes roughen the cleavage surface.

As a crack advances through a slip band, it will pass close by piled up groups containing too few dislocations for crack nucleation. Under these conditions, the stress at the crack tip could be sufficient to trigger this piled up group, either by acting on its source to produce more dislocations, or by increasing the normal stress  $\sigma$  in equation (6). This behavior would account for the "side stepping" of cracks at slip bands observed by Edlemau<sup>(37)</sup>.

Our model predicts that failure eventually occurs by the linking up of cracks that have nucleated on planes consistent with the dislocation arrangement at the barriers and the applied stress, but have propagated perpendicularly to the applied stress. In alloys which have been pre-strained small amounts before exposure, the number of cracks will be small, especially in single crystals strained in the easy glide range, because only a few barriers will have formed and not all of these will have sufficiently large groups piled up behind them for crack initiation. However, the distance these cracks can travel will be large since the slip line density, and thus the dislocation density, ahead of them will be small. As a result, less energy will be consumed by tearing. In heavily cold worked alloys, both the number of barriers and the size of the groups behind them should be large, so that many cracks should form, but more slowly, since the rate of chemical attack at each reaction site will be less than when there are few reactive sites. Observations to this effect have been reported by Hines and Hour<sup>(38)</sup>. However, these cracks will not be able to grow very far because they must pass through regions of high dislocation density.

Figure 17. Variation of time to fracture with amount of previous cold working for specimens of an 18-8 Ti steel tested in boiling 42%  $MgCl_2$  solution. After J.G. Hines(39)

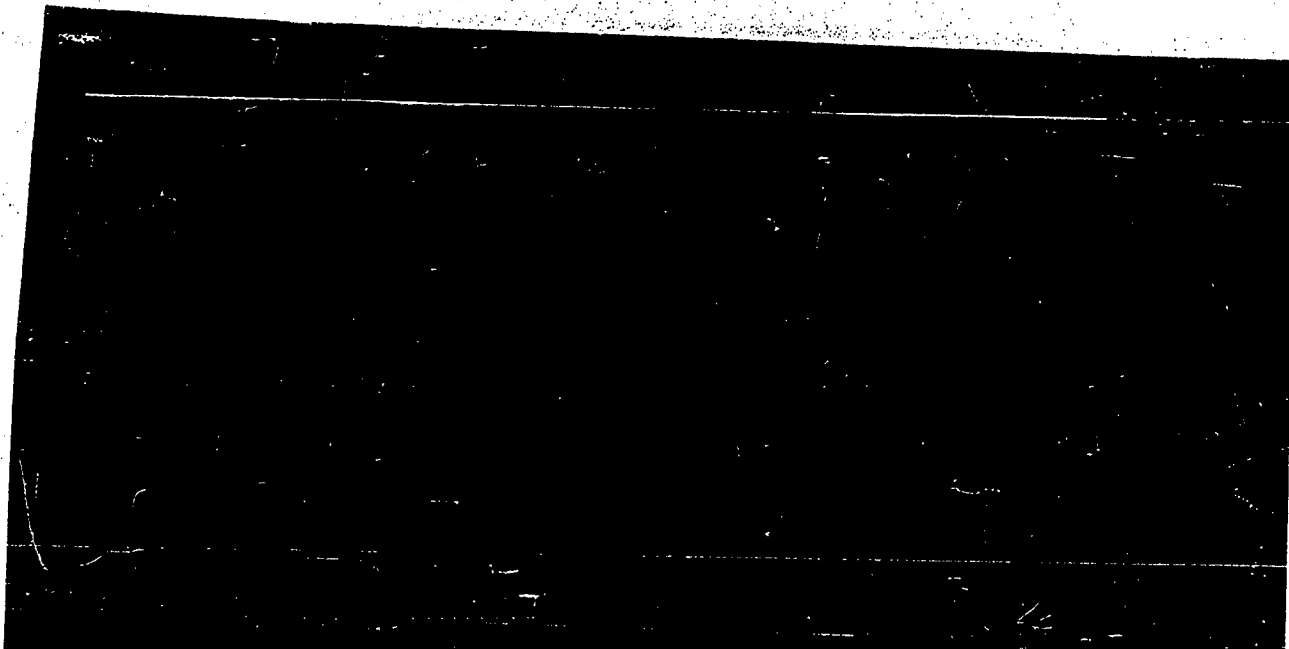
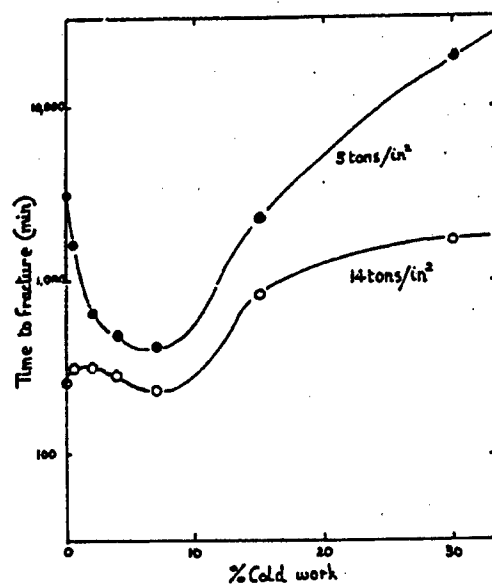


Figure 17. Variation of time to fracture with amount of previous cold working for specimens of an 18-8 Ti steel tested in boiling 42%  $MgCl_2$  solution. After J.G. Hines(39)



At some intermediate degree of pre-strain, conditions should be such that the alloy will be most susceptible, and we should expect a maximum in a curve of susceptibility vs. amount of prior cold work. These predictions are borne out in a curve presented by J.G. Hines<sup>(39)</sup> at the AIME symposium on stress corrosion cracking, for 18-8 stainless steel exposed to magnesium chloride after varying amounts of prior cold work. His curve, presented in Figure 17, shows an interesting feature in that pre-strain is more important in producing maximum susceptibility (minimum time to fail) for this alloy tested at a stress of 5000 psi. than at 14,000 psi. This fact can also be explained by our model since it is  $\sigma = \frac{2\gamma}{m\bar{\epsilon}}$  that determines initial crack growth. At low stresses  $\bar{\epsilon}$  must be large and more prior cold work is required, but at higher stresses the value of  $\bar{\epsilon}$  is not so critical since this relationship will be satisfied for the  $\bar{\epsilon}$  obtained by only small amounts of prior strain. Thus, the variation of susceptibility with prior strain should diminish with increasing stress.

#### The Transition from Intergranular to Transgranular Fracture

Except for stainless steels in magnesium chloride, the mode of fracture in a polycrystalline aggregate may be either intergranular or transgranular, and both modes are frequently found in the same specimen. For the purpose of a mechanistic analysis of the transition from one mode to another only data that distinguish between the two modes are useful. Unfortunately, such data do not appear to be available and, therefore, a limited investigation was undertaken for the immediate purpose of evaluating the application of the preceding ideas.

To study the transition from one mode to another, and its dependence on composition (because of stacking fault energy change with composition) and plastic deformation, it is necessary to establish a criterion that discriminates between inter and transgranular cracking. A possible criterion is the fraction of grains containing transgranular cracks, per unit area of exposed surface. Complete intergranular failure will then be represented by zero and complete transgranular failure by unity.

A qualitative evaluation of the transition in copper-zinc alloys was made by straining four annealed alloys in tension to the onset of necking (37% strain in 2 inches) and subsequently exposing the alloys to ammonia vapor under an applied tensile stress of 25% of the stress required to produce 37% strain in each alloy. The results are represented in Figure 18 by microstructures superimposed on a schematic diagram illustrating the composition dependence of the transition from intergranular to transgranular cracking, at constant plastic strain.

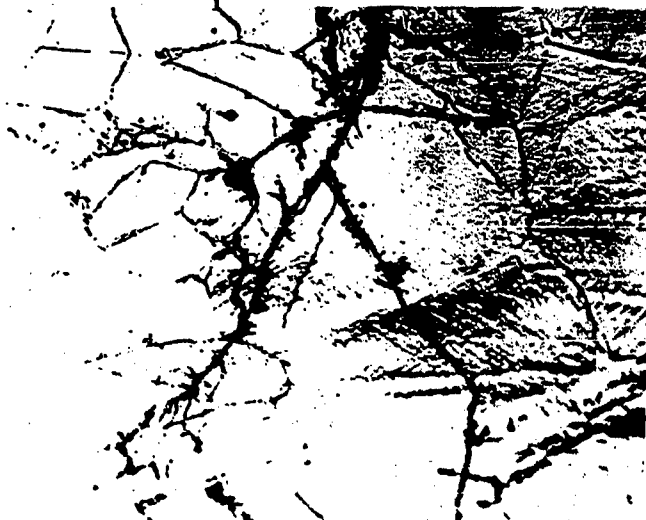
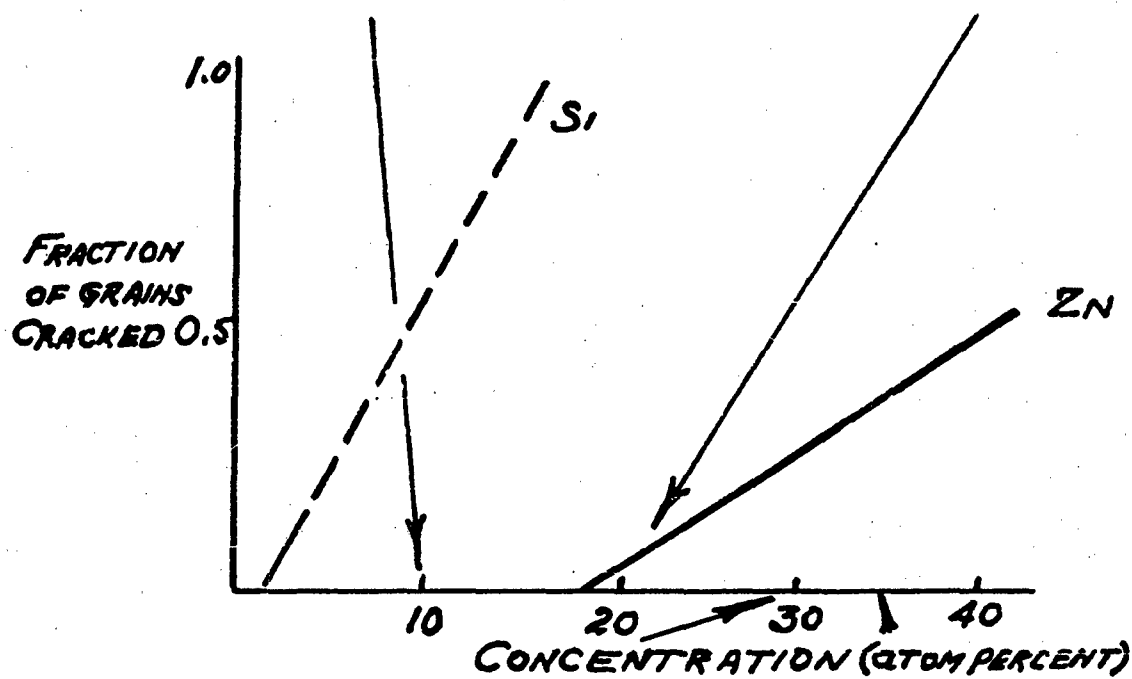
The transition in copper-zinc alloys occurs at something less than 20% zinc for a prior plastic strain of 37%. The transition, for a given alloy type, is dependent on plastic strain and of course, moves to higher or lower compositions in accord with smaller or larger strains, respectively.

These observations, of a change in fracture mode from intergranular to transgranular that depends on prior deformation and stacking fault energy, are consistent with the models presented above. Intergranular fracture is favored at small strains because few structural sites of reactivity exist, and most of the corrosion occurs at the boundary; it is also favored in alloys of high stacking fault energy because more dislocations can be piled up at the boundary when the annealing twin density is low. Transgranular fracture will be favored at higher strains and in alloys of low stacking fault energy because more barriers exist which can serve as reactive sites, and more dislocations can be piled up behind any one of them.

Similar experiments have not yet been performed with copper-silicon alloys, but there is sufficient experimental evidence to predict the result indicated by the dashed line in Figure 18. In accord with the evidence, the data in Figure 9 indicate that small silicon contents raise the twin density by a large amount.



Figure 18. Transition from inter- to transgranular failure in copper-zinc alloys strained 3% in tension prior to exposure to ammonia at 25% of the stress required to produce the plastic strain. The dotted line represents a prediction for copper-silicon alloys. Stress-cracking experiment performed by E.G. Grenier, Chase Brass and Copper Research Laboratories.



This analysis also explains the observation<sup>(40)</sup> that annealed copper zinc alloys, which normally fail intergranularly, fail transgranularly provided 1% silicon, tin, or aluminum have been added to them. These additions simply reduce the stacking fault energy to the point where the small strain associated with a constant load test or with a constant deformation test (a bent beam) is sufficient to produce transgranular cracking. The mixed transgranular and intergranular failures are, of course, only intermediate cases between these extremes defined by composition and strain.

#### Discussion of Alternative Mechanisms

In the preceding treatment of the problem of stress corrosion cracking an attempt has been made to assemble the most significant features of the phenomena in a framework of a few essential principles; namely, (1) reactivity at specific sites that can be characterized in structural terms, (2) stress concentration at these sites and (3) stacking fault energy which defines the mode of deformation and the magnitude of the stress that can be concentrated at barriers in a crystal or in a polycrystalline aggregate.

Forty<sup>(41)</sup> originally proposed a model which depends on reactive sites along slip lines and where crack formation occurs by the coalescence of dislocations at these sites. However, this model does not account for a susceptibility dependence on prior deformation, or a change in fracture mode from intergranular to transgranular that depends on composition and prior strain. Furthermore, it does not predict the dependence of susceptibility on stacking fault energy; a dependence which the preceding discussion has shown to be very important.

Various connections between stacking faults and stress cracking have been previously suggested by Paxton et. al.,<sup>(42)</sup> Bassett and Edeleanu<sup>(43)</sup> and Swann and Nutting<sup>(24)</sup>. Paxton suggests that the connection is obtained through the fact

that the stress required to force one dislocation through another depends on the width of the faulted ribbon joining two partials and therefore the local stresses are unrelieved by plastic deformation while the corrosion crack continues to grow as a result of this stress at sites that are otherwise unspecified. Both Bassett and Edeleanu, and Swann and Nutting, suggest that the composition dependence of stress cracking in copper alloys is controlled by the segregation of solute atoms at the stacking fault, following Suzuki's<sup>(44)</sup> model for solid solution hardening. The principal evidence for this suggestion is that the faulted structure observed by Swann and Nutting in copper-silicon and copper-germanium alloys is unreactive in an electropolishing solution of nitric acid and methyl alcohol, whereas stacking faults in copper-zinc and copper-aluminum alloys are attacked in this solution. Swann and Nutting attributed the differences in reactivity to differences in segregation tendencies in each of the alloys.

One obvious difficulty with the latter interpretation is that none of these alloys stress crack in the nitric acid-methyl alcohol environment, whereas all four of them fail more or less rapidly and completely in ammonia, for example see Figures 6 and 10, by intergranular cracking in the annealed condition and by transgranular cracking after plastic deformation. Thus, while solute segregation to stacking faults may be a sufficient condition for failure, there is no definite evidence that it is a necessary one. The situation is analagous to the case of solute segregation at grain boundaries which has been proposed<sup>(45)</sup> to explain intergranular reactivity.

Alternatively, it seems that the fault is important primarily through its control of the structural mechanism of deformation, which defines the limit of the concentration of stress (and strain energy). With respect to intergranular corrosion cracking, it seems that this must be so since the twins and faults exist only within the crystal. In transgranular cracking, the existence of barriers has

been demonstrated and their characteristics, particularly with respect to stress concentration, are certainly controlled by the stacking fault energy; the reactivity of the crystal in the vicinity of these faults would seem to be associated with both the strain energy concentrated at the site and also with the structure of the fault which, being a hcp stacking sequence, is unstable (reactive) with respect to the fcc matrix.

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