ARF 2183-8
Summary Report

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

FRACTURE OF METALS

Contract No. DA-11-022-ORD-3108

Frankford Arsenal
Philadelphia 37, Pennsylvania

25 years of research

ARMOUR RESEARCH FOUNDATION

of

Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

ARF 2183-8

FRACTURE OF METALS

Summary Report

under

Contact No. DA-11-022-ORD-3108
ORD Project No. TB4-001, M219

August 1, 1960 to September 30, 1961

for

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

Attention: M. J. Leopold, Project Engineer
ORDBA-1320

September 20, 1961

FRACTURE OF METALS

ABSTRACT

The objective of this work has been to study the mechanism of brittle fracture produced in engineering metals under stress when wetted by certain low-melting liquid metals and to relate these phenomena to similar behavior in other environments.

The embrittlement by mercury of aluminum alloys in various states of anneal, cold work, and aging has been studied. Sub-yield point failure is confined to dispersion-hardened structures and is intensified by combinations of aging and small degrees of cold work. Large plastic strains imposed upon the aged state reduce the level of embrittlement. The case is made that a critical strain rather than a critical stress condition governs the occurrence of brittle fracture. A model for the various trends of embrittlement is built from considerations of slip plane population, coherency stress fields, and the interactions between these.

In another series of experiments it has been shown that the conditions for sub-yield point brittle fracture in quenched and tempered 300M steel as-hydrogen-charged or as-wetted with molten lithium are the same. This reinforces other evidence that the behavior of the two embrittlement processes are basically the same.

Some introductory work is reported which has as its objective to demonstrate that the embrittlement by stress-corrosion of aluminum alloys is basically similar to that produced by wetting with liquid mercury.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS

(continued)

FRACTURE OF METALS

I. INTRODUCTION

This report summarizes research performed during the period August 1, 1960 to September 30, 1961. The objective of this work has been to study the mechanism of brittle fracture produced in engineering metals under stress when wetted by certain low-melting liquid metals. There is now a substantial body of information describing the behavior of this phenomenon. It has been shown that this form of embrittlement is specific to certain combinations--that is, only certain liquid metals produce damage in any given engineering material. Embrittlement can be encountered in all degrees from mild diminution of total ductility to brittle fracture well below the engineering yield point. In cases of severe embrittlement, fracture can be immediate or, at lower stress levels, only after finite time of exposure to the liquid metal. The primary prerequisite to the process is the achievement of a true liquid-solid interface, i.e. effective wetting. The degree of embrittlement depends on temperature, strain rate of testing and upon certain structural conditions whose definition form part of the present accomplishment.

The major portion of the present report period was devoted to relating the degree of embrittlement to the strength and structure of aluminum alloys when wetted with mercury. A number of new behavior trends have been discovered which derive from the thermal-mechanical history of the alloy. These effects have been rationalized in terms of contemporary concepts of brittle fracture.

It has been pointed out on a number of previous occasions that there are similarities in behavior among embrittlement by liquid metals, hydrogen embrittlement, and stress-corrosion cracking. In particular these are the only three processes which can produce static fatigue or delayed failure. It seems appropriate, therefore, to attempt to demonstrate whether this similarity is broader than presently appreciated and therefrom to deduce whether all three forms of brittle fracture are fundamentally due to the same mecha

Delivered by Armour Research Foundation of Illinois Institute of Technology pursuant to Contract No. DA-11-022-ORD-3108. Government's use controlled by the provisions of Articles 26 and 27 of Title II (General Provisions).

nism. In the present work, the argument is made that all three forms of brittle fracture originate from reduction in the effective surface energy for fracture brought about by the special environment.

Toward this end, work will be reported comparing hydrogen embrittlement of a high strength steel with embrittlement by liquid lithium. In a second phase of work of the same nature, stress-corrosion cracking of the 2024 aluminum alloy is compared to embrittlement by mercury.

While all aspects of this subject are basically related, the various phases of work can be treated as individual topics. Each of these is written as a self-contained chapter of the report.

II. INFLUENCE OF THERMAL-MECHANICAL HISTORY ON THE EMBRITTLEMENT OF ALUMINUM ALLOYS BY MERCURY

In previous work(1) it was shown that the propensity of commerical aluminum alloys for embrittlement when wetted with mercury seems to be related primarily to the intrinsic strength in the normal unwetted condition. The data from a large number of commercial alloys in various states of anneal, cold work, and/or aging gave a generalized relationship. At low strength levels, the wetted fracture strength increases proportionately to the increase in tensile strength; but above 65,000 psi normal ultimate strength, the trend is abruptly reversed, and the wetted fracture stress decreases proportionately to the increase in tensile strength. This section of the report will demonstrate that the simple character of this relationship between normal tensile strength and wetted fracture strength is fortuitous. It will be shown that structure and thermal-mechanical history are clearly relevant factors and that their function can be interpreted in terms of contemporary concepts of brittle fracture.

For the purposes of this discussion, brittle fracture will signify a pattern of crack which runs in a plane transverse to the axis of the principal tensile stress in contradistinction to a ductile fracture wherein the fracture face describes a plane or ensemble of planes inclined at an angle of about 45° to the axis of principal tensile stress. When a liquid metal causes failure with zero or considerably reduced ductility, the fracture is always transverse and therefore, by the present definition, is brittle. Liquid metal embrittlement, of which mercury embrittlement of aluminum alloys is one example, can appear in any degree from somewhat reduced ductility to failure at stress levels of the order of 10% of the engineering yield strength. In previous publications(1-4) the case has been made that liquid metal embrittlement is a manifestation of the influence of reduced surface energy on the stress or strain to initiate brittle fracture. This theme will be continued in the present discussion with amplification.

A. Experimental Methods

The majority of the mechanical property data cited herein represent tensile testing of flat, sheet specimens machined to provide a 1 1/2 inch gauge length and a 3/8 inch width across the gauge length. Tests were performed on a Hounsfield Tensometer which plots a stress-strain diagram with an inexactly defined strain scale. The yield points cited are taken at the point of deviation from elastic behavior on the recorded charts. The yield stress so taken is very reproducible. By comparison with data for standard alloys in commercial states of heat treatment, the measurements made correspond closely to values for 0.2% offset yield.

To obtain reproducible results in tensile testing of aluminum alloys wetted with mercury, careful control must be maintained in the procedure for surface preparation and wetting. The surface in some commercial alloys as-received may give illusory results in testing. Table I illustrates the effect of removing surface metal prior to testing as-wetted with mercury. As a general procedure, it is advisable to remove one o[illegible] [illegible]o mils by etching with a sodium hydroxide solution. When, by heat treatm[illegible] a heavy oxide layer has formed, this is best removed by a fine abrasive paper followed by dissolution of a few units in caustic solution.

Wetting is most simply achieved by applying a drop of hydrofluoric acid to the gauge section of the specimen which is set unloaded in the testing machine. Into the drop of acid, add a drop of mercury. When the acid has removed the intervening oxide film, the mercury will spread out over the surface of the specimen. The presence of the acid itself on a tensile specimen has no influence on its resultant tensile properties. The time between wetting

TABLE 1

FRACTURE STRESS OF ALUMINUM 2024 ALLOY*
WETTED WITH MERCURY AT VARIOUS POSITIONS
FROM THE ORIGINAL SURFACE

Metal Removed, inches+	Wetted Fracture Stress, psi
0.0001	6,500
0.0003	11,100
0.0005	10,350
0.0114	16,900
0.029	16,900

*T3 as-received condition; initial thickness 0.128 in.; 2024 = 4.5% Cu, 1.5% Mg, 0.6% Mn, nominal composition.

+Reduced sections obtained by etching in NaOH solution.

and testing is not important except as de-wetting occurs. In mechanical testing it is advisable to load continuously to failure at a rate that completes the test in a few minutes. Slower rates of testing will become confused with delayed failure effects.

Residual stresses in a specimen will give spurious fracture stress results. Such a condition is not hard to recognize, for it leads to satellite cracks (in the wetted condition) which run in the plane of the sheet and cause it to exfoliate.

B. Stress or Strain Criterion for Brittle Fracture

Unalloyed aluminum and very dilute solid solution alloys of aluminum are not appreciably embrittled by wetting with mercury. Thus, for instance, 1100 alloy* normally shows an elongation of 25% before failure at a UTS of 15,400 psi. In the wetted condition this is 12.5%. On the other hand, the 2024 alloy in the T4 condition, with a normal UTS of 85,000 psi and 17% elongation at failure, breaks as-wetted well below the yield stress. That this is not simply the differences in stress levels achievable is demonstrated by testing 2024 alloy in the Alclad condition--which provides for a slightly alloyed aluminum skin. The results of tensile tests are shown in Table II to compare the conditions where the mercury wets only the unalloyed aluminum surface and where the clad has been removed by etching. These demonstrate that unalloyed aluminum whose yield stress has, by mechanical restraint been raised to the level of the 2024 alloy will not be embrittled by mercury.

As will be shown in subsequent sections, the stress at which aluminum alloys fail when wetted with mercury varies widely and seems more related to the thermal-mechanical history than the existing state of stress. For example, it will be seen that alloys with a yield strength of 45,000-50,000 psi can fail at stresses as high as 55,000 psi (above the yield point) and as low as 10,000 psi (well below the yield point).

Dorn[5] has shown that high-strength aluminum and magnesium alloys tested under biaxial stresses show a fracture stress envelope which defines a maximum shear stress criterion for fracture. There is no precedent for the stress law, if any, which ought to be followed for the case of brittle

* 99.0 + %Al.

TABLE II

TENSILE PROPERTIES OF ALCLAD* 2024 ALLOY RE-SOLUTION TREATED AND NATURALLY AGED

Sheet Thickness,** inches	Yield Stress, psi	Ultimate Tensile Strength, psi	Wetted Fracture Stress, psi
0.127	34,600	60,200	
0.127	35,000		60,000
0.057	36,600	61,400	
0.029	36,000	59,300	
0.090			32,300
0.080			24,600
0.065			32,600
0.030			31,400

*Surface skin of unalloyed aluminum is about 0.002 in. thick.

**Initial thickness = 0.127 in.
Reduced sections (clad removed) by etching in NaOH solution.

fracture at or below the engineering yield point. According to the dislocation model for crack nucleation, the critical dislocation pile-up is the product of the action of shear stresses on active slip planes. By this token one would expect a shear stress criterion for fracture. Deruyttere and Greenough[6] explored this point in the cleavage of zinc single crystals and came to the conclusion that neither normal nor shear stresses could be assigned pre-eminence.

The brittle fracture of thin-walled aluminum alloy (2024) tubing under conditions of wetting with mercury and biaxial loading has been studied. The tubular specimens had the dimensions 0.049 in. wall x 1.5 in. O. D. x 4-8 in. long. The tubular specimens were loaded in tension (circumferential) by pressurized water inside the tube actuated by a manual hydraulic jack independent of the compression system. The platens of the compression jig were grooved and gasketed to contain the pressurized water within the tubular specimens. A second and independent manual hydraulic jack actuated the compression ram whose force delivered to the specimen was calibrated with a proving ring in a series circuit with the specimen. With this system brittle fracture in the tension-compression quadrant of biaxial loading was studied for the case of the aluminum alloy wetted with mercury. Two states of heat treatment were studied--the freshly solution treated condition and the solution treated (920°F) and aged (RT for 170 hours) state. The results are summarized in Figures 1 and 2. The freshly solution-treated state appears to follow the normal stress criterion in contrast to Dorn's results.[5] Yet the strain at fracture also increased with higher compressive stresses, so one must wonder whether the stresses or strains were responsible for fracture. On the other hand, the well-defined trend for the aged state follows neither a normal nor a shear stress level.

All of these observations combine to negate the position that this form of brittle fracture is dictated by a critical state of stress. In default of this, we must turn logically to explore the possibility of a strain criterion for the initiation of brittle fracture. The behavior of aluminum alloys wetted with mercury as shown in subsequent sections will be rationalized in this light.

C. Results of Treatments

1. The Annealed or Overaged State

Both the 2024 and 5083* aluminum alloys have been studied in the overaged state produced by slow cooling in the furnace. This represents a structure containing a coarse dispersed phase, which contributes little to structure hardening, and a depleted matrix solid solution. These conditions are attested to by the low yield strengths of ~ 12,000 psi (2024 alloy) and ~20,000 psi (5083 alloy).

When wetted with mercury, both of these alloys fail above the yield point and after measurable elongation. Both of these alloys can be hardened appreciably by cold rolling. The influence of cold work on the yield strength and wetted fracture is shown in Figure 3. The wetted fracture behavior is characterized in this graph and in all succeeding ones by the ratio of the wetted fracture stress to the yield stress. A ratio greater than unity indicates that measurable plastic strain preceded fracture while a ratio of less than unity represents fracture in the elastic range. Of necessity, the yield point measurements were made on unwetted specimens although the yield point, if it precedes fracture, is unaffected by the presence of a liquid metal.

Even though the strength of these two alloys in their overaged or annealed state can be more than doubled by cold working, the ratio of wetted fracture to yield stresses only approaches unity but never goes below. The 5083 alloy is most remarkable in this respect.

2. The Solution-Treated State

Increased solid solution alloying in the 2024 alloy can be achieved by quenching from successively higher solution treatment temperatures and testing immediately thereafter. The results of such tests are shown in Figure 4. Similar to cold work, solid solution hardening also has the effect of lowering the ratio of wetted fracture to yield stresses toward unity. Also as in the case of cold work, solid solution alloying does not produce sub-yield failures.

---

* nominal composition, 4.5% Mg, 0.15% Cr, 0.6% Mn.

3. The Aged State

The 2024 aluminum alloy has a substantial capacity for age hardening, raising the yield strength from 25,000 psi in the solution-treated state to 43,000 psi in the commercially aged state. As shown in Figure 5, the precipitation condition produces sub-yield point failure by an amount proportionate to the time of aging. In the long time aged state, the wetted fracture stress is reduced to about 60% of the yield stress. The abrupt increase in embrittlement after 740 hours of aging is reproducible and similar to the trend of stress-corrosion cracking for the same alloy shown by Robertson.[7] Artificial aging in boiling water produces the same level of potential embrittlement. Only a few minutes of aging time at 100°C is sufficient to reach a minimum wetted fracture stress condition.

The 5083 aluminum alloy, which does not appreciably age harden, also is not appreciably more embrittled by previous aging heat treatments. Some limited data are given in Table III.

4. Combined Cold Work and Aging

One has two options in such a combination--cold work the solution-treated state and then age, or age and then cold work. Both alternatives have been studied in the present work, and both produce the same general trends as shown in Figures 6, 7, and 8. Prestrains of less than 10% were produced by stretching to assure uniformity of deformation through the section. Artificial aging is seen to act in the same way and to the same degrees as natural aging.

Particularly in the already aged state, very small amounts of cold work produce a dramatic increase in embrittlement in subsequent testing for wetted fracture strength. A fraction of one per cent strain is more damaging to the peak aged state than 95% reduction in the overaged state. Through combinations of aging and cold work the fracture stress can be reduced to less than 20% of the yield strength.

A second remarkable trend is to be noted. With large cold reductions there is an appreciable and progressive recovery of wetted fracture strength. This is also seen from tests on the 2024 alloy in the commercial

TABLE III

YIELD AND WETTED (Hg) FRACTURE BEHAVIOR OF 5083 ALUMINUM ALLOY

State of Heat Treatment	Yield Strength, psi	Wetted Fracture Stress, psi
solution treated	17,700	16,800
solution treated and aged at 100°C--2 hours	16,800	17,600
solution treated and aged at 100°C--168 hours	21,200	20,800
solution treated and aged at 100°C--336 hours	22,000	21,600

. . condition after cold rolling various amounts. The T4 condition represents an aged state with some cold work introduced, at least in straightening operations. The results shown in Figure 9 may be regarded as an extension of the upward trends in Figures 7 and 8.

Although aging of the 5083 alloy produces no appreciable change in degree of mercury embrittlement, the superposition of small amounts of cold work is effective in the same manner as with the 2024 alloy. The results of stretching to 5% elongation are shown in Figure 10.

D. Discussion

A comprehensive explanation of the various degrees of embrittlement encountered in aluminum alloys wetted with mercury must embrace several distinct behavior trends.

(a) The ductile failure of unalloyed aluminum even at high stress levels.

(b) The persistence of ductile failure in the solution-treated condition and in the overaged condition at all levels of cold work.

(c) The progression toward sub-yield brittle fracture with time of aging.

(d) The catastrophic increase in embrittlement with very small plastic strains applied to the age-hardened state.

(e) The appreciable recovery from maximum embrittlement with large plastic strains applied to the age-hardened state.

For the argument it is necessary to reconstruct the character of the model for brittle fracture as evolved by various approaches to the subject. The position is taken as developed in previous publications[3, 4] that wetted fracture begins at the liquid-solid interface by virtue of a reduction in the surface energy for fracture nucleation through absorption of atoms from the liquid. We add this modifying factor to the model for fracture nucleation at the head of a dislocation pile-up wherein a local tensile stress generates a critical strain energy sufficient to satisfy the energy requirements for the formation of fracture surfaces. Thus by lowering the energy requirements for fracture nucleation, the local stress requirements to initiate the process are correspondingly reduced.

The Stroh model for fracture nucleation emphasizes the existence of active slip as a necessary prerequisite to the fracture process. The creation of a localized critical stress is the result of blocking the propagation of slip--strain thereby being the intensifier of stress. At this point it is useful to adopt the philosophy of Stroh[8] that fracture nucleation is a statistical event. Any active slip plane has, in principle, the option of continued propagation or of discontinued propagation--i.e., pile-up and cracking. If some probability exists that any given active slip plane can meet a barrier of adequate strength, the probability of fracture of the specimen is proportional to the total number of slip bands activated. Thus, in terms of fracture, the engineering yield point is simply that stress at which the population of active slip planes abruptly increases from a very small to a very large number and the probability of fracture increases accordingly.

The minimum number of active slip planes necessary to satisfy statistical needs depends, in the first instance, on the average strength of barriers to slip. If the barrier strength is very high, it is conceivable that the fracture stress corresponds to the stress which initiates the first active slip plane. When the natural barrier strength of grain boundaries is low, yield and plastic flow may only be limited by the ability of intersecting and interlocking slip bands to synthesize enhanced barrier strength. In this respect, the face-centered cubic metals such as aluminum fall into the category of low barrier strengths as indicated by their small yield strength dependence on grain size.[9] Moreover, plastic strain does not appear very capable of synthesizing stronger barriers[9] as do body-centered cubic metals.[10]

While the critical tensile stress to cause fracture nucleation is primarily provided by the local stress field at the dislocation pile-up, the latter can be augmented or opposed by externally applied stresses from different principal directions and by internal stress fields of other origin. The equation of a critical stress magnitude can be the sum of a number of stresses of diverse origin of which the strain-induced component is only one but perhaps the major. There are numerous everyday examples of this. For example, the fracture stress of brittle materials in compression is invariably higher than in tension. Cracking resulting from inhomogeneous internal transformation is a common industrial hazard. The slip contribution to fracture can only be precluded with certainty in the balanced triaxial stress system which has not yet been synthesized in experiment. We must therefore keep in mind the interplay of stress origins, original and synthesized barriers to slip, and the surface energy requirements to produce fracture.

With this preamble, let us approach the subject of embrittlement and non-embrittlement of aluminum whose surface is wetted by liquid mercury. We shall adopt the position that mercury adsorbed onto aluminum reduces the surface energy to some level one-third to one-half of its normal value if the results of other work[3] can be taken as typical. This, in effect, has lowered a threshold so that some aluminum alloys in certain conditions are now brittle but some others remain ductile. The ability to introduce a depressed threshold of fracture therefore permits a study of the compositional, structural, and thermal-mechanical factors which influence the propensity to brittleness.

With only the weak barrier strength of grain boundaries, unalloyed aluminum cannot muster dislocation pile-ups of any significant intensity, and so the presence of mercury is insufficient to change its ductile nature. The essentially unalloyed aluminum on Alclad is restrained from yielding by the hard substrate of 2024 alloy to stress levels equivalent to the yield point of the latter. As far as fracture nucleation is concerned, this artificial condition does not change either the barrier strength or the strain hardening of the cladding. The whole process of yield and elongation is merely displaced to higher stress levels.

The overaged state in the 2024 and 5083 alloys is not basically different but more marginal. If a more surface-active agent than mercury were available, the 5083 alloy in particular would probably be very brittle rather than marginally ductile in the wetted state. The 2024 alloy, as overaged, represents a grossly depleted solid solution with a coarse, nonhardening dispersion of a compound phase. As with unalloyed aluminum, the natural barriers to slip are weak. However, the presence of the coarse compound dispersion makes for more effective interlocking of slip bands with the consequence that the wetted fracture stress approaches the yield point.

The wetted fracture behavior of the 5083 alloy and the 2024 alloy as freshly solution treated from various temperatures demonstrates that solid solution alloying significantly influences barrier strength probably through segregation to grain boundaries.

The occurrence of brittle fracture at stresses well below the engineering yield point requires the introduction of some new concept. This new concept must be based on structural conditions, for with the 2024 alloy (a) as-cold-rolled 90% from the overaged state, (b) as naturally aged (546 hours) and (c) as aged with 10% cold work, the yield strengths range only between 43,000 and 51,000 psi while the wetted fracture strengths are 55,000; 39,000; and 10,000 psi, respectively.

The new factor was postulated by Mehl and Jetter[11] when they argued that the most important contribution to hardening was not due to the differences in specific volume between matrix and precipitant but to the coherency strains in the matrix surrounding a metastable form of the precipitant. Since strains and stresses are concomitant and since the solid solution (fcc) is certainly more close-packed than the precipitant crystal, the coherency condition signifies a triaxial tension field in the matrix surrounding each particle.

Consider the action of dislocations in a slip plane traversing a field populated randomly by zones of high triaxial tensile stress. If one of these tensile stress zones exists near the head of a dislocation pile-up, the normal (transverse) stress field of the pile-up is augmented by the standing stress field. This is diagrammatically illustrated in Figure 11. The same triaxial tensile stress fields by opposing the externally applied shear stresses increase the apparent yield strength.[12] The internal stress system therefore performs a dual function in local reduction of shear stresses and local increase in transverse stresses.

The statistical occurrence of complete obstruction of one active slip plane oriented for maximum transverse tensile stress at the head of the dis location pile-up usually requires the initiation of a very large number of active slip planes, i.e., macroscopic yield. With the existence of local stress fields, the probability improves that any slip plane will meet the transverse stress requirements for crack nucleation. Thus it becomes possible that the far fewer slip bands initiated below the engineering yield point may be adequate to provide the microcrack that leads to failure. The probability of this event becomes dependent on the magnitude of the local coherency stresses and upon the mean distance of separation.

This is how, with the progression of aging, the wetted fracture stress falls below the normal yield point since with time the mean distance of separation decreases and the number of active slip planes required to satisfy the statistics of the critical stress field overlap becomes very small.

If the interpretation of the origin of sub-yield brittle fracture is correct, the maximum difference between the unwetted yield strength and the as-wetted fracture stress provides a direct measure of the magnitude of the coherency stresses. In the case of 2024 aluminum alloy, we shall take the state of natural aging for 750 hours. The difference between the unwetted yield stress and the wetted fracture stress is about 14,700 psi. Were it not for the existence of coherency stresses of this magnitude, the wetted fracture stress would be coincident with the yield stress or higher.

Sub-yield point brittle fracture can actually occur in the peak age-hardened condition without the influence of a surface-active agent. A case in point is the state of precipitation of the omega transition phase in titanium alloys. In this case the coherency stresses are very much higher than for the 2024 aluminum alloy.

The application of cold deformation to the fully aged state produces a remarkable reduction in the wetted fracture strength. Most of this decline occurs within the first few per cent deformation, and a minimum ratio of wetted fracture to yield stresses of about 0.15 occurs at about 10-15% deformation. With increasing degrees of prior deformation we are forced to account for a positive recovery of fracture strength.

To explain these effects we must introduce some new attributes to our model. The small degrees of prestrain send large numbers of slip bands through a field populated by the standing stress fields around particles of coherent precipitate. When the external stress is released, the dislocations at each pile-up will tend to migrate back along the slip plane in the direction of their origin. To a large measure, this will be prevented by the standing stress fields around the precipitate particles which they originally forced past. Since the dislocation assembly is held in its approximately piled-up state, the normal stress field at its head (in the reversed direction) is retained. By this process we have multiplied the number of standing stress fields and by overlap increased the intensity of some. This is illustrated diagrammatically in Figure 12. When new slip bands are activated on re-application of load in the presence of a surface-active agent, the probability that the first few newly active slip bands will produce a crack becomes large. This time the condition of critical local transverse stress is achieved by the summation of the stress at the head of the new pile-up and the contributions to standing stress fields by old and trapped dislocation pile-ups and by the coherent precipitate particles. This is illustrated in Figure 13.

The similar though less dramatic response of the aged 5083 alloy to small amounts of cold work (Figure 10) indicates that, even without coherency, precipitate particles can restrain the relaxation of slip bands and force them to interact with freshly activated slip.

It is necessary at this point to suggest the reasonable proposition that for any state of aggregation there is a minimum shear stress to activate the first slip band and that, while this stress is much lower than the engineering yield point, it is raised by progressive cold working just as the yield strength. In the fully aged state, the multiplication of standing stress fields by combination of precipitation and past deformation has lowered the fracture stress to about 10,000 psi. In this condition and at this stress level some slip bands can be initiated. With continued cold work before the application of a surface-active agent, the minimum stress for new slip is raised, and so at 10,000 psi of external loading no fresh slip can be started. Since wetted fracture cannot begin until some slip bands are started, the fracture stress must rise and by a degree proportionate to the prior cold work (see, for example, Figure 9).

E. Summary

New studies presented on the brittle fracture behavior of precipitation-hardened aluminum alloys require an explanation involving the interplay of dislocation dynamics and structure. An argument has been presented which makes use of certain postulates, some of which are generally accepted and some, though not new, are still considered speculative.

(a) Fracture cannot occur without the activation of slip.

(b) In single phase, recrystallized structures of soft metals the probability of crack nucleation by one active slip plane is so low that a multitude must be produced to satisfy statistical needs. Hence such materials in the presence of a surface-active substance will probably fracture at or above the engineering yield point.

(c) Some slip planes are activated at stresses below the engineering yield point, but a threshold stress exists below which none are activated.

(d) A standing triaxial tensile stress field exists in the matrix surrounding coherent precipitate particles.

(e) The tensile or transverse stresses at the head of a dislocation pile-up are additive to the standing stress fields for the purpose of microfracture.

(f) Cold deformation after aging serves both to multiply the number of standing stress fields through trapped dislocation pile-ups and to intensify the magnitude of existing stress fields.

III. COMPARISON OF EMBRITTLEMENT OF STEEL BY HYDROGEN AND BY LITHIUM

In previous work[1] it was shown that the grain size dependence of the fracture stress of mild steel charged with hydrogen, on the one hand and wetted with molten lithium, on the other, were nearly identical. Both trends were linear when fracture stress was plotted against the grain size function, $d^{-1/2}$. Moreover, the slopes were of nearly equal magnitude. The Stroh-Petch interpretation of the slope as a function of the surface energy associated with brittle fracture provides approximately the same magnitude for γ--about 550 ergs/cm^2. As Petch postulated for the case of hydrogen-charged iron, the origin of hydrogen embrittlement can simply be related to the reduced energy for crack nulceation brought about by adsorption of hydrogen to the surfaces of crack nuclei. Since there is an increasing body of evidence that hydrogen atoms segregate to dislocation assemblies, they are preferentially disposed to adsorb at a cleavage crack at the head of a dislocation pile-up. We have argued that the adsorption of lithium atoms at dislocation pile-ups occurring at the liquid-solid interface operates to reduce the fracture stress in the same manner.

In the light of the behavior of dispersion-hardened aluminum alloys described in section II of this report, we can predict a trend that as the dispersion becomes finer and more coherent with the matrix, the degree of embrittlement should increase. Translated into more practical terms, the ratio of wetted fracture stress to yield stress should decrease with increasing strength. It is this trend that has been chosen as a basis for comparison of lithium and hydrogen embrittlement.

For this exercise, a 300M steel* was chosen. Specimens were austenitized in argon to prevent decarburization, quenched and tempered to hardnesses over the full span of its capability. These specimens were then either charged with hydrogen or wetted with molten lithium. In either condition, they were tested in tension to failure at room temperature (hydrogen-charged) and at 200°C (lithium wetted). The difference in testing temperature makes no appreciable difference to the normal tensile properties of the steel.

Charging with hydrogen proved to be very unreproducible unless very special conditions of temperature control were exercised. The charging was done electrolytically using the specimen as the cathode and a platinum screen as the anode. The electrolyte was 4% H_2SO_4 in water with a trace amount of As_2O_3 added. A current density of 2 amps/in.^{2} was maintained for two hours. The bath was kept at -1°C for reproducibility of hydrogen absorption. Specimens were tensile tested to failure immediately upon removal from the bath.

---

* Nominal composition: 0.42% C, 0.75% Mn, 1.60% Si, 1.80% Ni, 0.80% Cr, 0.38% Mo, 0.05 min. V, 0.025% P max, 0.025% S max.

Wetting by lithium was no problem because molten lithium itself is capable of eliminating thin oxide films on steel. The only necessary pre caution was to prevent the specimen from heating above 200°C to prevent overly rapid oxidation of the lithium.

The results of tensile tests for both hydrogen-charged and lithium-wetted steels over a range of tempered strengths are shown for comparison in Figure 14. The trends are remarkably similar. Below a yield strength of 150,000 psi, brittle fracture occurs essentially at the yield point. Above that strength level there is a progressive drop in the fracture-yield ratio.

We now have several series of comparative experiments which illustrate the similarity between hydrogen and lithium as embrittling agents:

(a) linear dependence of fracture stress on the grain size function $d^{-1/2}$, and equivalence of slope of that function.
(b) static fatigue or delayed failure phenomenon.
(c) identical behavior of fracture stress plotted against mean free path of carbides (see page 65, ref. 1)
(d) trend toward sub-yield brittle fracture above a yield strength of about 150,000 psi in 300M steel.

IV. COMPARISON OF STRESS-CORROSION CRACKING AND MERCURY EMBRITTLEMENT OF HIGH-STRENGTH ALUMINUM ALLOYS

There are grounds for proposing that stress-corrosion cracking in aqueous and gaseous media represents another form of brittle fracture involving a reduction in surface energy for fracture produced by the environment.[13] To reinforce this hypothesis one may design experiments which permit only one rationalization. In the phenomenon of stress-corrosion cracking this approach seems almost impossible. Another tack is to build up a body of evidence to show that those factors, which militate for increased or decreased embrittlement by mercury, produce the same trend in a stress corrosion environment. Since most of our behavior trends for mercury embrittlement are in terms of tensile tests and those for stress-corrosion cracking are in terms of delayed failure, we shall assume for the present that the fracture stress/yield stress ratio is equivalent as an embrittlement index to loss in tensile strength after finite exposure to the stress-corrosion medium under a static load.

These parameters have been compared in two sets of circumstances. In one case it has been shown that three sets of thermal-mechanical history for the 2024 Al alloy can produce the same yield strength but quite different mercury-wetted fracture strengths. These ar... ...d in Table IV. These same materials have been subjected to static loading at 95% of their yield strength immersed in 5% NaCl solution with 0.3% H_2O_2. After the static load exposure, the specimens were loaded to fracture and the residual tensile strength taken as the measure of crack propagation due to stress-corrosion. The results are summarized in Table V. Unfortunately, this aqueous medium produces severe uniform corrosion as well, and the two cannot easily be distinguished. Moreover, even after 14 days of static load exposure in saline solution the loss in strength was too small to give a conclusive trend. Yet the indications, such as they are, favor the cold-rolled, overaged condition as most resistant both to stress-corrosion failure and mercury embrittlement.

A second set of experiments was made to parallel work published by Robertson some years ago.(14) In this paper it was shown that static loading (80% of the yield strength) while immersed in the saline solution quoted above resulted in a trend of loss of tensile strength which depended in a very specific manner on the aging time. Data for the aluminum 2024 alloy aged at 190°C are reproduced in Figure 15. The comparison with yield strength shows that the greatest loss of strength due to the saline environment coincides with peak age hardening.

For comparison, the same series of aging cycles at 190°C were performed on a commercial batch of 2024 alloy. Some of the specimens were then tested as-wetted with mercury. The comparison of embrittlement with age hardening is shown in Figure 16. Again it is seen that the maximum embrittlement occurs in the peak age-hardened condition. The actual kinetics of aging were somewhat different from Robertson's data, but this probably represents the normal variation within the chemical specification.

TABLE IV

THREE CONDITIONS OF ALUMINUM ALLOY 2024 GIVING EQUIVALENT YIELD STRENGTHS

Thermal-Mechanical Condition	Yield Strength, psi	Ratio, Wetted Fracture Stress / Yield Stress
overaged + 90% cold reduction	45,200	1.2
naturally aged	43,000	0.9
artificially aged at 100°C for 1/2 hour + 3/4% elongation	45,000	0.3

TABLE V

LOSS IN TENSILE STRENGTH OF ALUMINUM ALLOY 2024 AFTER STATIC LOADING AT 95% OF YIELD STRENGTH WHILE IMMERSED IN A SALINE SOLUTION

	Tensile Strength, psi			
Thermal-Mechanical Condition	initially	after 2 days	after 7 1/2 days	after 14 days
overaged + 90% cold reduction	56,300	64,000	64,000	64,600
naturally aged	70,000	66,800	61,300	60,600
artificially aged at 100°C for 1/2 hour + 3/4% elongation	70,000	68,000	52,500	62,700

These results are insufficient to make a strong case, but they provide some additional substantiation to the hypothesis that stress-corrosion cracking and mercury embrittlement are fundamentally similar. In further work it will be necessary to develop stress-corrosion cracking with less of the associated general corrosion to complicate interpretation.

V. PERSONNEL AND LOGBOOKS

The work reported was conducted by Mr. H. Nichols, assistant metallurgist, under the supervision of the author. Data submitted in this report are recorded in ARF Logbooks C-1091, C-9754, C-9773, C-10615, C-10879, and 11502.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

W. Rostoker
Metals and Ceramics Research

D. J. McPherson, Director
Metals and Ceramics Research

REFERENCES

1. W. Rostoker, J. W. McCaughey and H. Markus, Embrittlement by Liquid Metals, Reinhold (1960).
2. H. Nichols and W. Rostoker, Acta Metallurgica, 8 (1960), 848-850
3. H. Nichols and W. Rostoker, ibid., 8 (1960), 788-790
4. H. Nichols and W. Rostoker, ibid., 9 (1961), 504-509
5. J. E. Dorn, Fracturing of Metals, ASM (1948), 32-50
6. A. Deruyttere and G. B. Greenough, J. Inst. Metals, 84 (1955-56), 337-345
7. W. D. Robertson, Trans AIME, 166 (1946), 216-228
8. A. N. Stroh, Advances in Physics, 6 (1957), 418-465
9. N. J. Petch and R. W. Armstrong, Westinghouse Scientific Paper 10-01000-0-P1, Dec. 29, (1959)
10. A. H. Cottrell, Trans. AIME, 212 (1958), 192-203
11. R. F. Mehl and L. K. Jetter, Symposium on Age Hardening Metals ASM (1940).
12. N. F. Mott and F. R. N. Nabarro, Conference on Strength of Solids Physical Society, London (1948).
13. E. G. Coleman, D. Weinstein and W. Rostoker, Acta Metallurgica, 9 (1961), 491-496
14. W. D. Robertson, Trans AIME, 166 (1946), 216-228

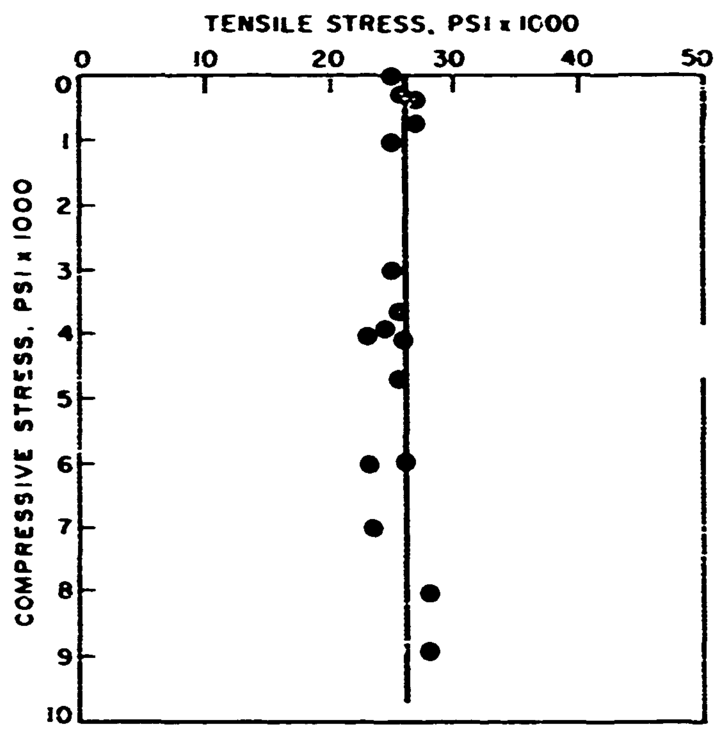

Figure 1 - Influence of biaxial stresses on the wetted fracture of aluminum 2024 alloy in the freshly solution-treated condition.

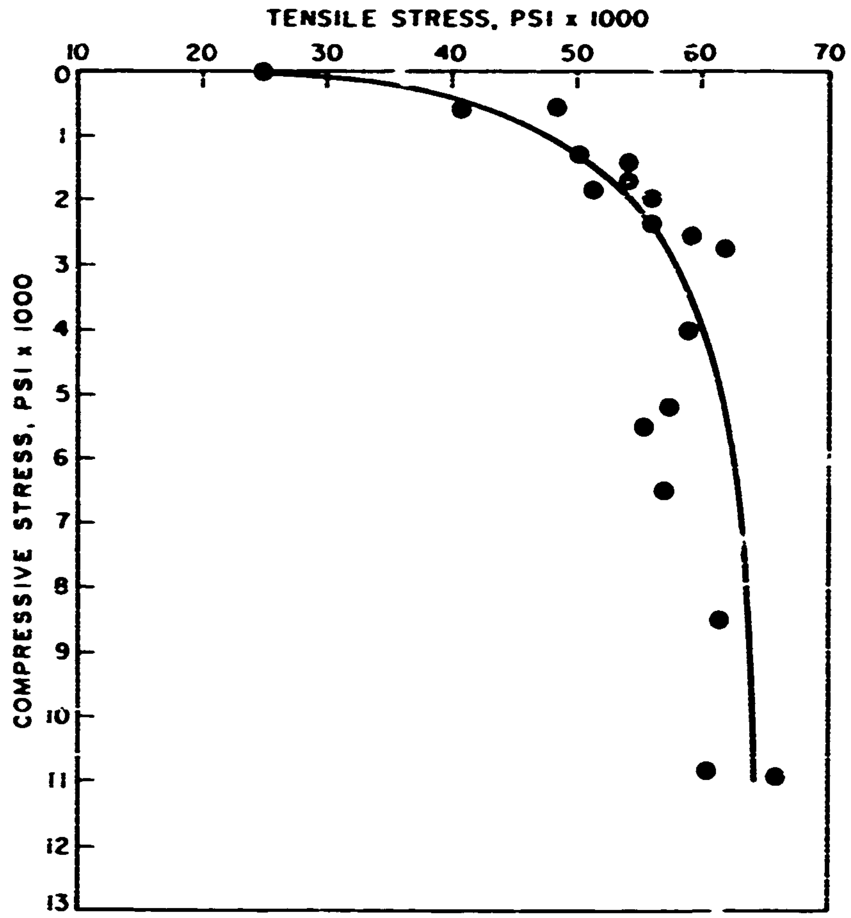

Figure 2 - Influence of biaxial stresses on the wetted fracture of aluminum 2024 alloy after re-solution treating at 920°F and aging at room temperature for 170 hours.

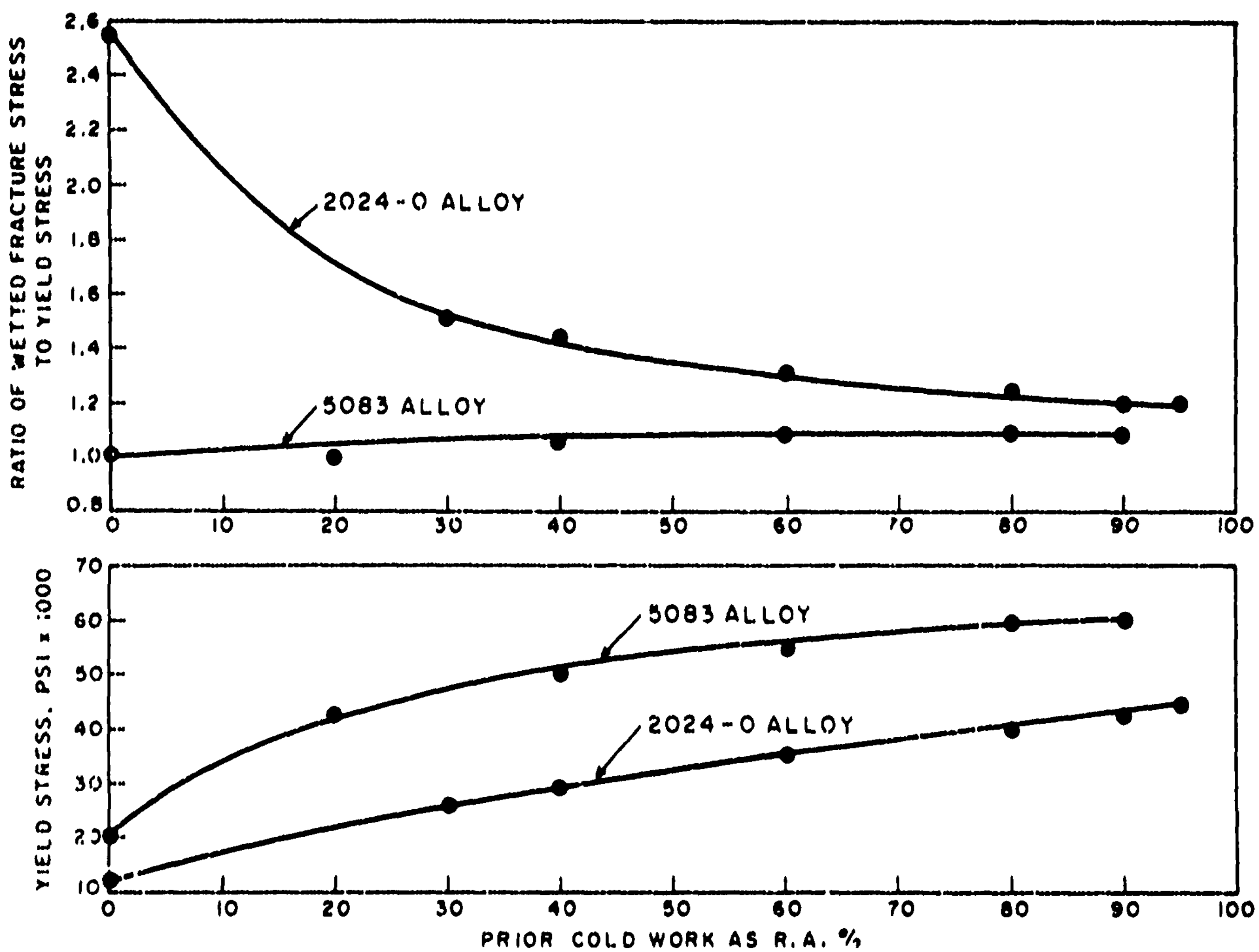

Figure 3 - Correlation Between Wetted (Hg) Fracture Strength and Yield Strength After Various Cold Reductions. Aluminum Alloy 5083 in the Solution-Treated Condition and Aluminum Alloy 2024 in the Annealed (Overaged) Condition.

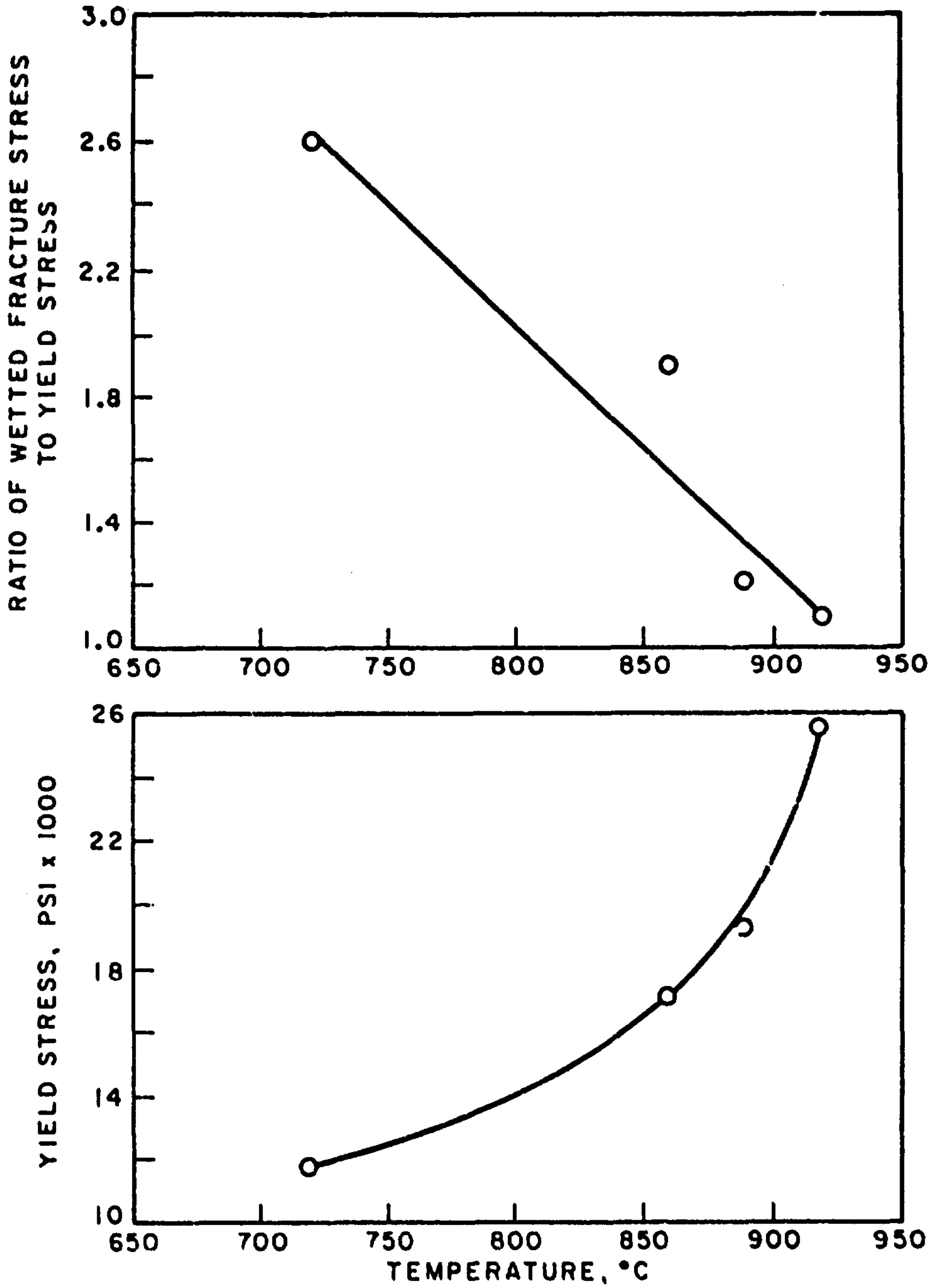

Figure 4 - Influence of Solution Treatment Temperature on the Wetted (Hg) Embrittlement of Aluminum 2024 Alloy in the Freshly Quenched Condition.

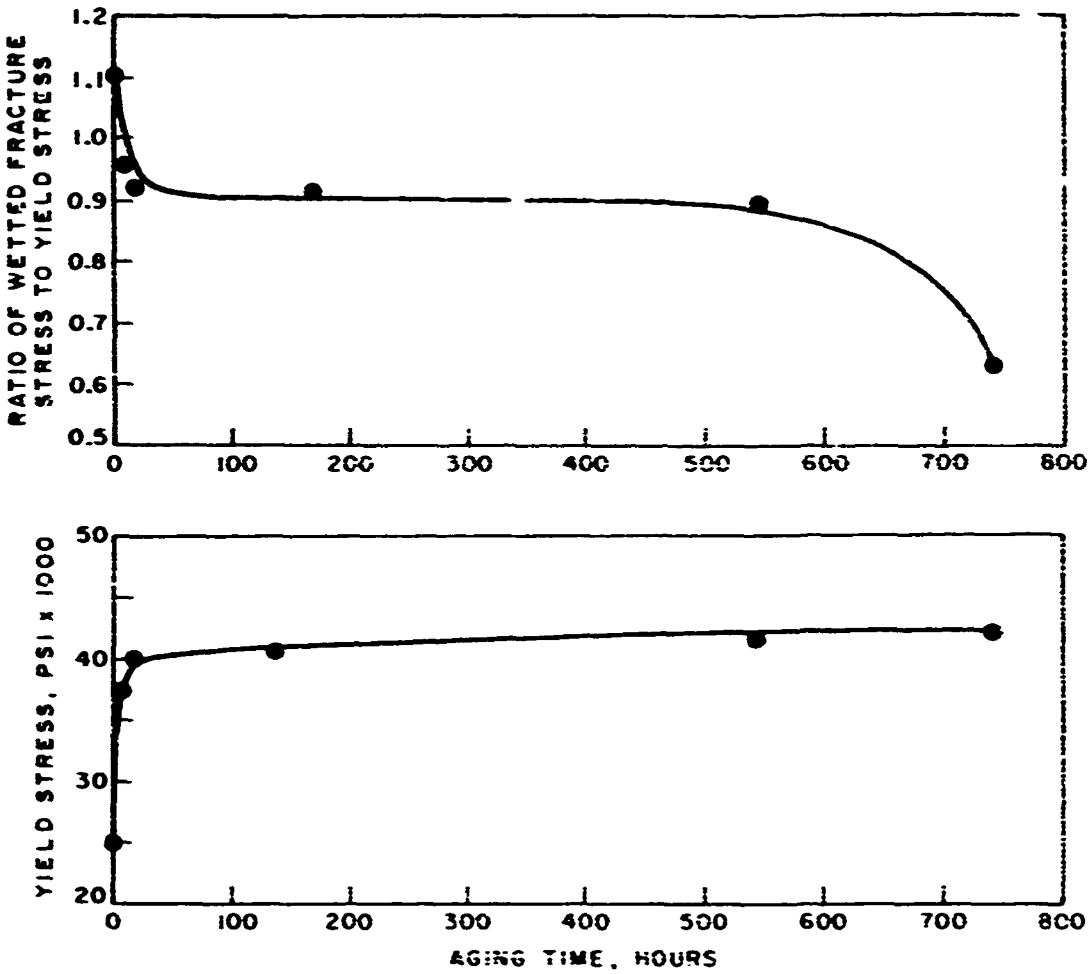

Figure 5 - Influence of Aging Time at Room Temperature on the Wetted (Hg) Fracture Stress in Aluminum 2024 Alloy Which Had Been Solution Treated at 920°F for 90 Min. and Quenched.

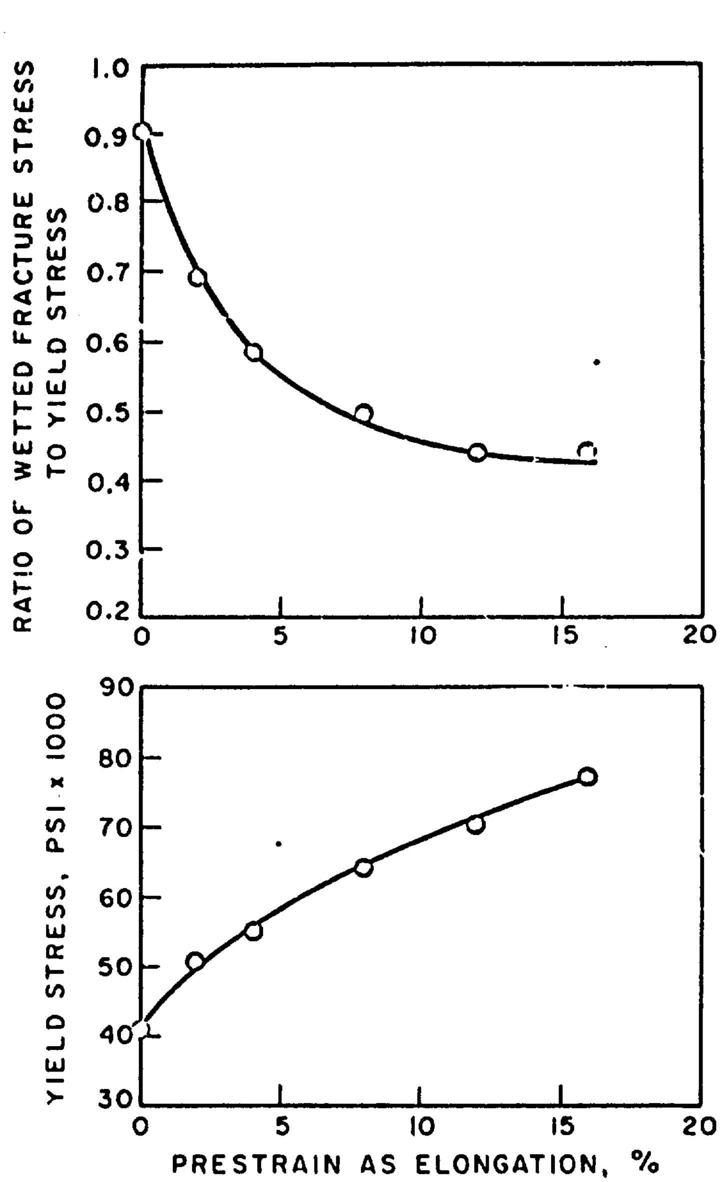

Figure 6 - Influence of Cold Work in the Solution Treated State Before Aging on the Wetted (Hg) Fracture Strength of Naturally Aged (120 hrs) Aluminum 2024 Alloy. Comparison with Normal Yield Stress When Not Wetted.

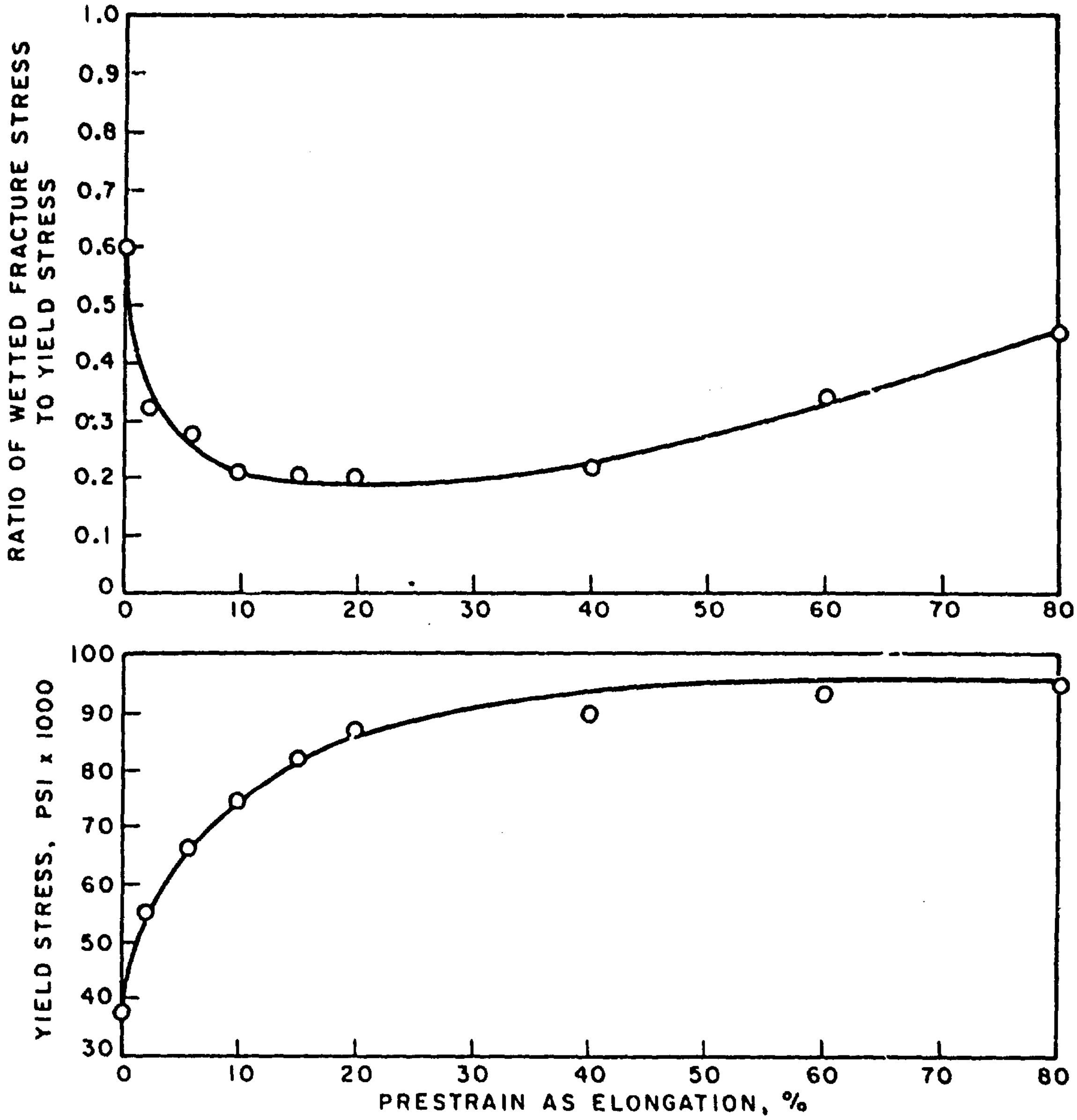

Figure 7 - Influence of Prior Plastic Strain on the Wetted (Hg) Fracture Stress of Aluminum 2024 Alloy which had been Solution Treated at 920°F for 90 minutes, Quenched, and Aged at 212°F for 30 minutes.

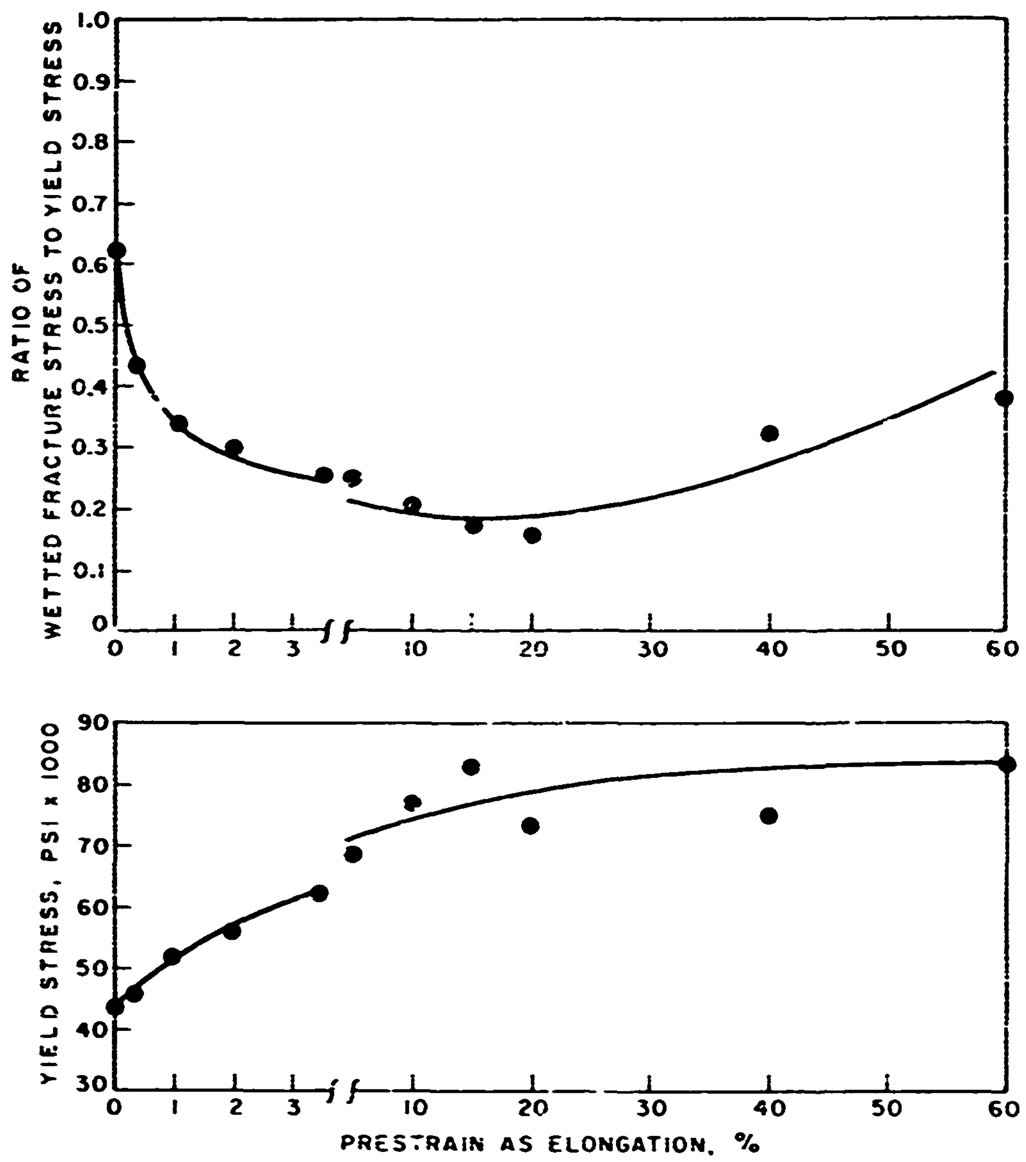

Figure 8 - Influence of Prior Plastic Strain on the Wetted (Hg) Fracture Stress of Aluminum Alloy 2024 which Had Been Solution Treated at 920°F for 90 Minutes, Quenched and Aged at Room Temperature for 720 Hours.

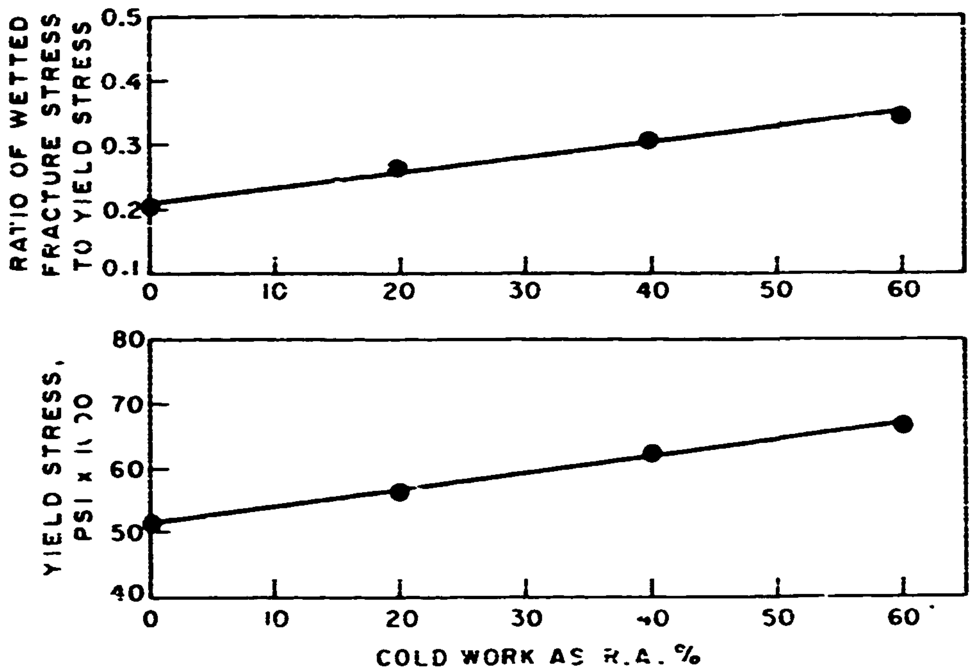

Figure 9 - Influence of Prior Cold Work on the Wetted (Hg) Fracture Stress of Aluminum Alloy 2024-T4. Comparison with Yield Stress in the Unwetted Condition.

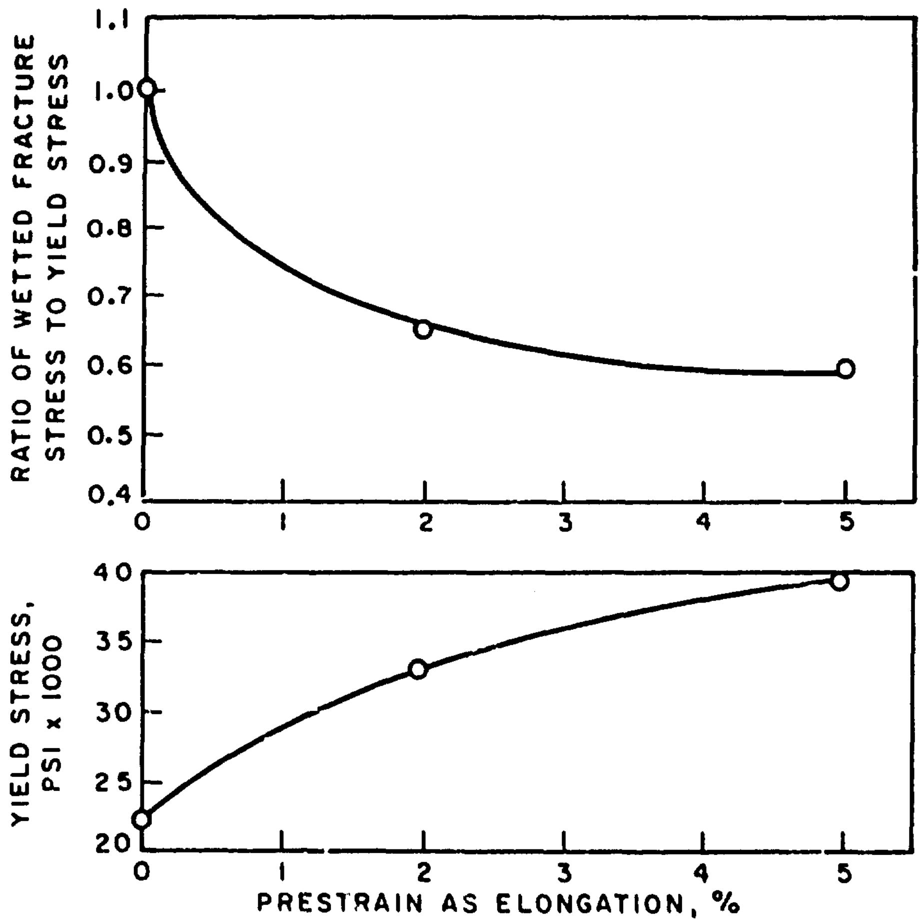

Figure 10 - Influence of Prior Plastic Strain on the Wetted (Hg) Fracture Stress of Aluminum 5083 Alloy which had been Solution Treated and Aged at 212°F for 336 Hrs.

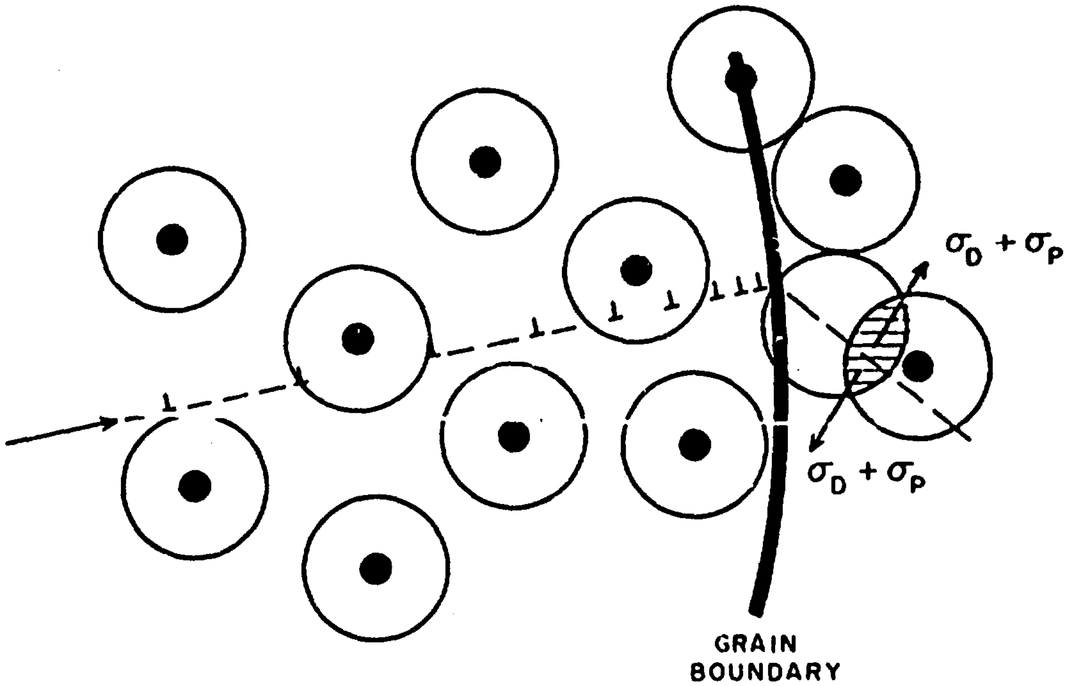

Figure 11 - Diagrammatic Illustration of the Intersection of the Tensile Component of the Stress Field at the Head of a Dislocation Pile-up (σ_D) and the Tensile Stress Field of a Coherent Particle (σ_P) in the Immediate Vicinity.

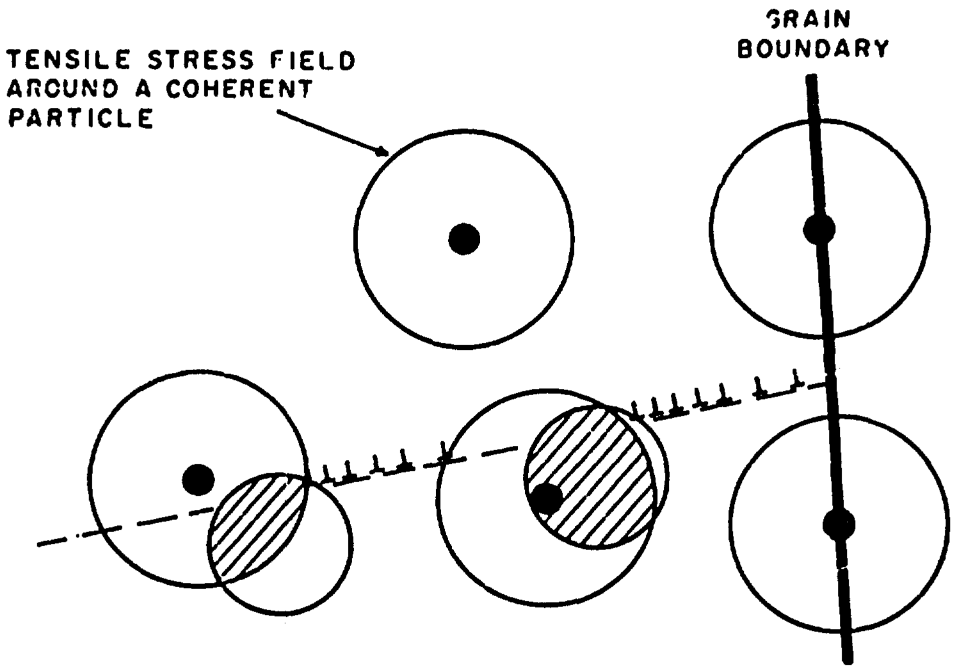

Figure 12 - Diagrammatic Illustration of the Expansion and Intensification of Internal Stress Fields Around Coherent Particles as a Result of Small Deformations.

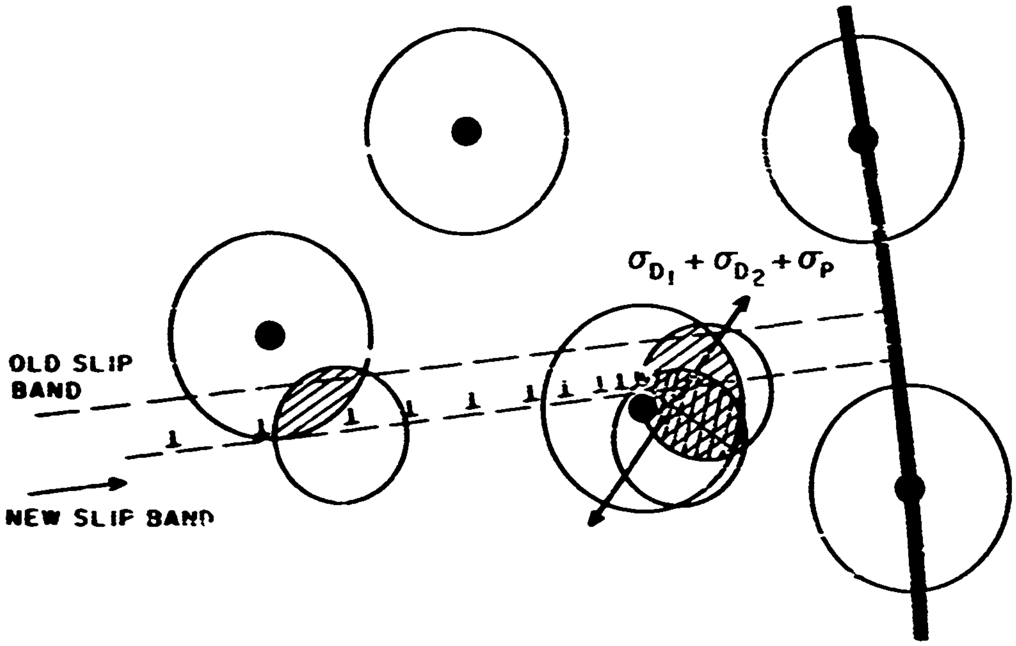

Figure 13 - Diagrammatic Illustration of the Superposition of the Stress Field (σ_{D_2}) About a Pile-up on a Newly Activated Slip Band on the Standing Stress Fields of a Coherent Particle (σ_P) and Locked Dislocation Pile-ups from Previous Small Strains (σ_{D_i}).

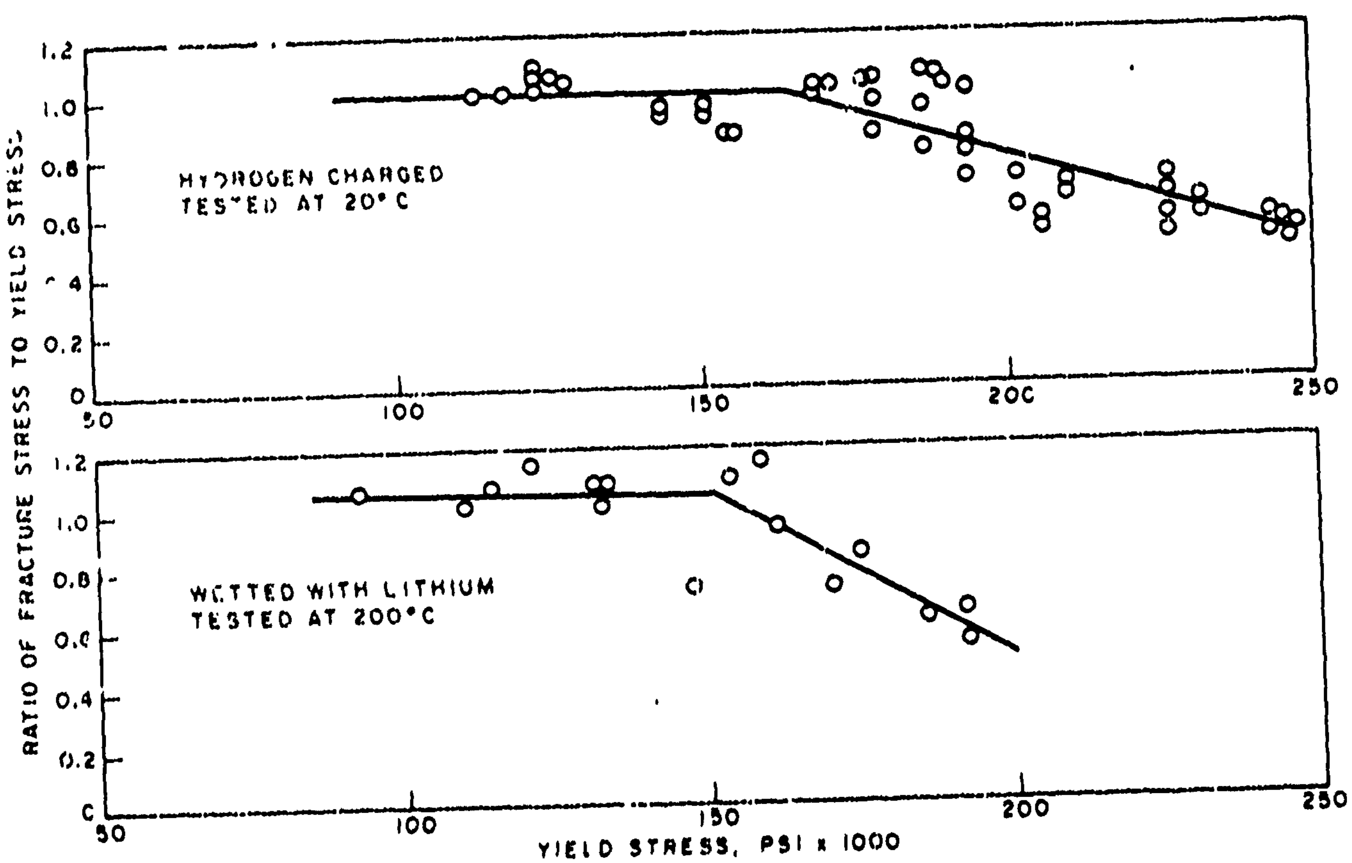

Figure 14 - Comparison of the Brittle Fracture of a 300M Steel at a Series of Quenched and Tempered Strength Levels As-Charged with Hydrogen and As-Wetted With Molten Lithium.

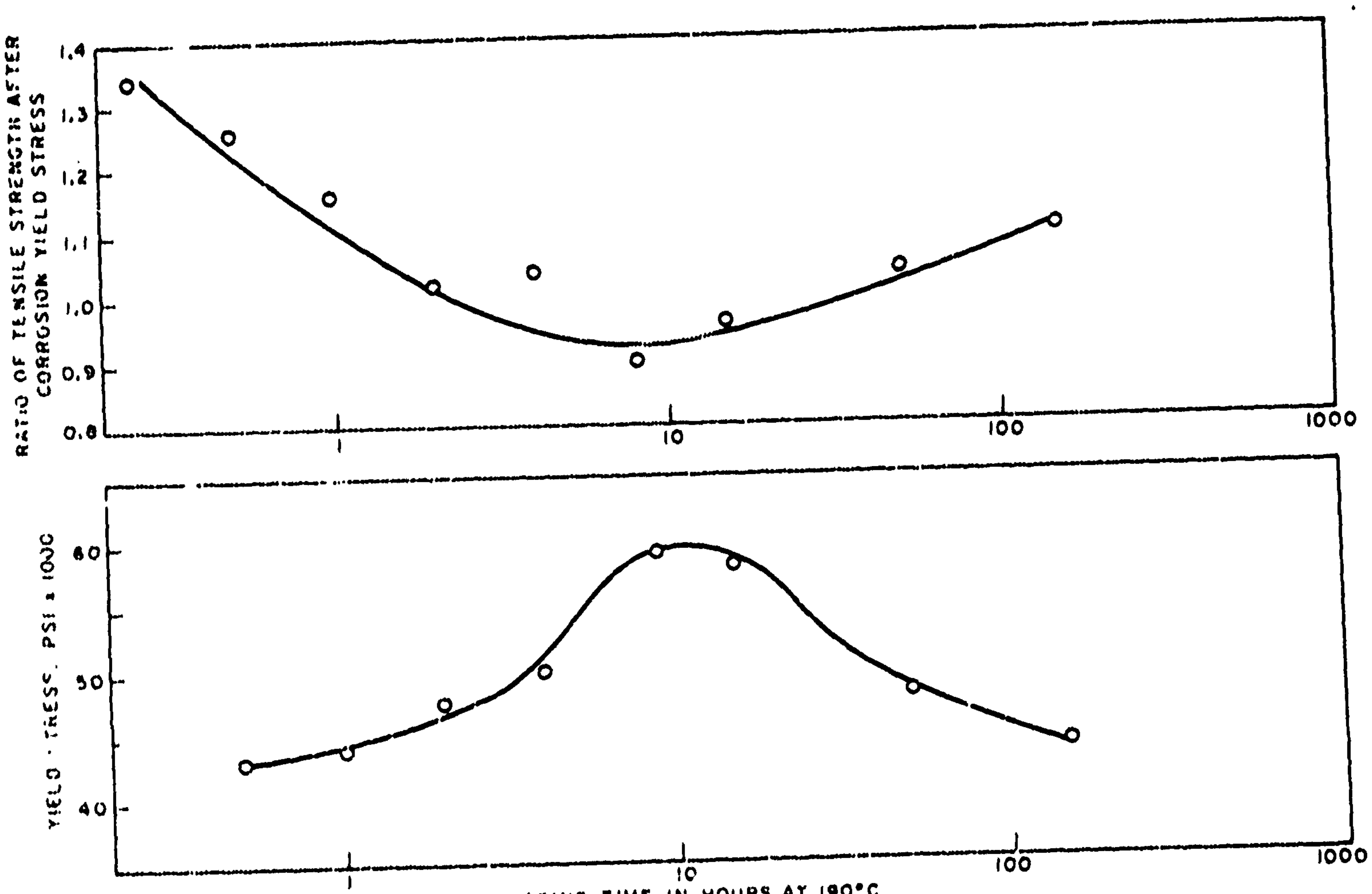

Figure 15 - Loss in Tensile Stress as a Result of Static Fatigue at 80% Yield Stress in a Saline Solution. (Robertson's Data).

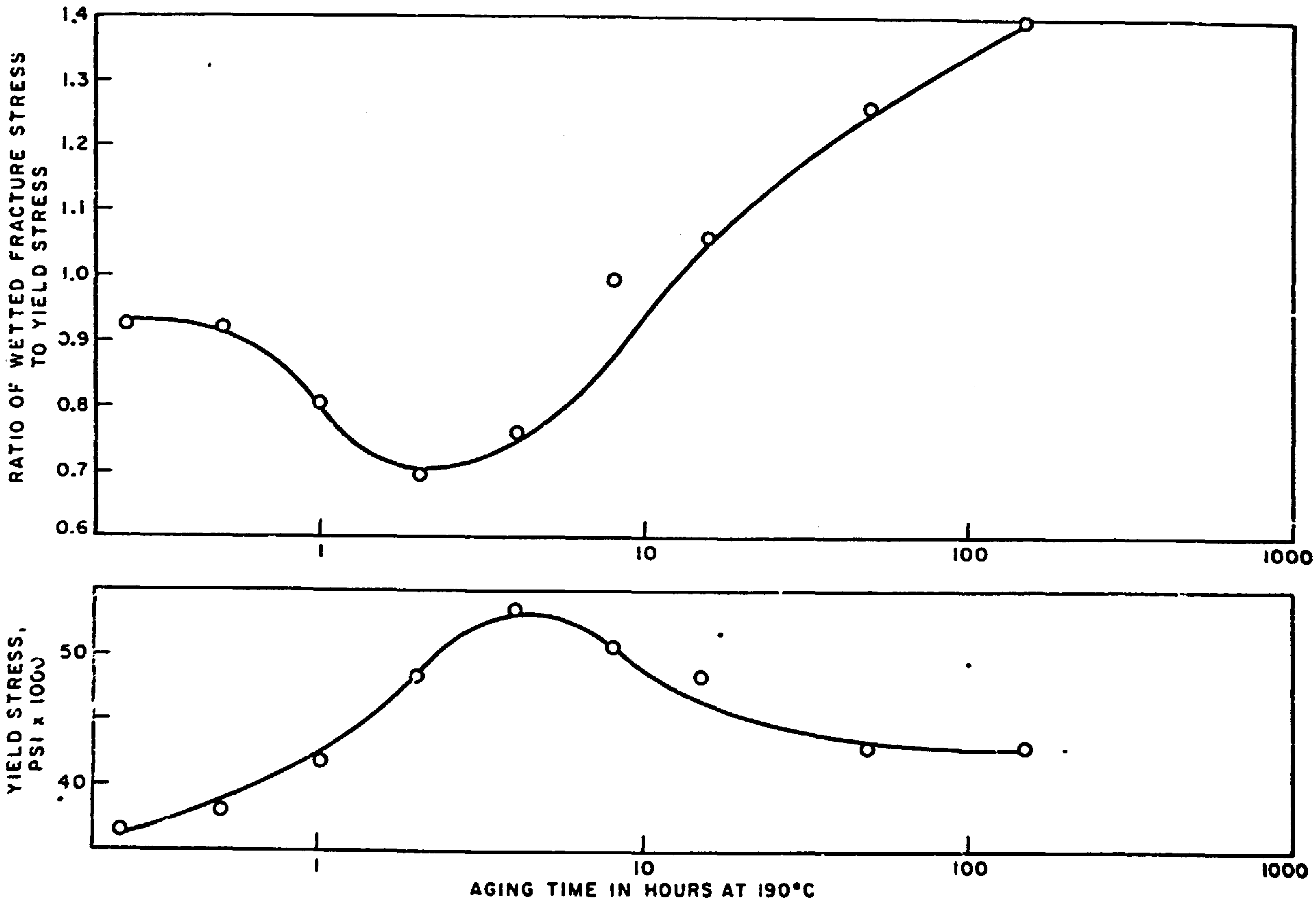

Figure 16 - Mercury Embrittlement of Al 2024 Alloy as a Function of Aging Time.