NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
FRACTURE OF METALS

ARF-B183-12
(Summary Report)

November 13, 1961 to November 13, 1962
ABSTRACT

Results show that the mercury embrittlement of an Al-4 1/2 Mg alloy is related to the strain-aging behavior of this alloy and that strain aging produces embrittlement effects which are similar to precipitation hardening.

The temperature dependence of stress-corrosion cracking is shown in two cases to be small compared to that expected for corrosion processes and more closely comparable to that encountered in liquid-metal embrittlement. There is also shown to be a close similarity between liquid metal and stress corrosion cracking in their strong dependence on small degrees of plastic prestrain.

Evidence is presented in terms of kinetics and appearance of intergranular penetration without external application of stress to suggest that large stresses exist between grains of an age-hardened polycrystalline aluminum alloy.
TABLE OF CONTENTS

I. INTRODUCTION .................................................. 1

II. THERMAL-MECHANICAL HISTORY AND MERCURY EMBRITTLEMENT OF AN AI-Mg ALLOY ........... 2

III. ANALYSIS OF STRESS-CORROSION CRACKING ........................................... 11
   A. An Appraisal of Stress-Corrosion Cracking Theories ........................................ 11
   B. An Initial Comparison of Liquid Metal Embrittlement With Stress-Corrosion Cracking . 17

IV. TEMPERATURE DEPENDENCE OF CRACKING IN AN AI 2024 ALLOY .................................... 20
   A. Stress-Corrosion Cracking ........................................................................ 20
   B. Temperature Dependence of Intergranular Penetration in the Al 2024 Alloy by a NaCl Na₂CrO₄ HCl Solution ......................................................... 24
   C. Temperature Dependence of Delayed Failure of the Al 2024 Alloy Wetted with Mercury 27
   D. Penetration of Mercury into Unstressed Al 2024 ............................................. 29

V. TEMPERATURE DEPENDENCE OF CRACKING IN 70/30 BRASS .......................................... 33
   A. Stress-Corrosion Cracking ........................................................................ 33
   B. Temperature Dependence of Mercury Cracking of 70/30 Brass ......................... 35

VI. INFLUENCE OF PLASTIC PRESTRAIN ON CRACKING OF AI 2024 ALLOY IN THE AGED CONDITION ................................. 37

VII. SUMMARY .............................................................. 37

VIII. LOGBOOKS AND PERSONNEL ................................................................. 41

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF B181-12
(Summary Report)
**LIST OF ILLUSTRATIONS**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INFLUENCE OF GRAIN SIZE ON THE YIELD STRESS AND WETTED FRACTURE STRESS (Hg) OF Al 5083 ALLOY.</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>INFLUENCE OF GRAIN SIZE ON THE WETTED FRACTURE STRESS (Hg) OF Al 5083 ALLOY WITH PLASTIC PRESTRAIN.</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>INFLUENCE OF TEMPERATURE AND PLASTIC PRESTRAIN ON FRACTURE OF Al 5083 ALLOY WETTED WITH MERCURY.</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>INFLUENCE OF HCl ADDITIONS TO NaCl Na₂CrO₄ SOLUTION ON THE TIME TO FAILURE OF AGED Al 2024 ALLOY STRESSED TO 68,000 PSI.</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>INFLUENCE OF PRIOR IMMERSION IN STRESS CORROSION SOLUTION ON TIME TO FAILURE OF Al 2024 ALLOY AT VARIOUS STATES OF AGING AND LOADED TO 90% OF THE YIELD STRESS.</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>INFLUENCE OF TEMPERATURE ON THE TIME TO FAILURE OF Al 2024 ALLOY AT A STRESS OF 90% OF THE YIELD POINT.</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>ILLUSTRATION OF INTERGRANULAR PENETRATION OF Al 2024 ALLOY IN THE AGED STATE AL A RESULT OF IMMERSION IN THE NaCl Na₂CrO₄-HCl SOLUTION</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>INTERGRANULAR PENETRATION OF Al 2024 ALLOY IN THREE HEAT-TREATED STATES.</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>INFLUENCE OF TEMPERATURE ON THE TIME TO FAILURE OF Al 2024 ALLOY WETTED WITH MERCURY</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>MERCURY PENETRATION INTO Al 2024 (AGED 100°C-30 MIN.)</td>
<td>32</td>
</tr>
<tr>
<td>11</td>
<td>MERCURY PENETRATION INTO Al 2024 (ANNEALED, &quot;O&quot; CONDITION)</td>
<td>34</td>
</tr>
<tr>
<td>12</td>
<td>INFLUENCE OF TEMPERATURE ON THE TIME TO FAILURE OF 70/30 BRASS (COLD WORKED 23%) IN AMMONIA UNDER A STRESS OF 52,000 PSI.</td>
<td>36</td>
</tr>
</tbody>
</table>

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY
**LIST OF ILLUSTRATIONS (Cont'd)**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>FRACTURE STRESS OF 70/30 BRASS (WITH 23% PRIOR COLD WORK BY STRETCHING) WHEN WETTED WITH MERCURY.</td>
<td>36</td>
</tr>
<tr>
<td>14</td>
<td>INFLUENCE OF PRIOR PLASTIC PRESTRAIN ON THE DELAYED FAILURE CURVES OF AL 2024 (AGED 100\°C 30 MINUTES) WETTED WITH MERCURY.</td>
<td>38</td>
</tr>
<tr>
<td>15</td>
<td>DELAYED FAILURE BY STRESS-CORROSION OF AL 2024 ALLOY (AGED 100\°C 90 MINUTES) AS A FUNCTION OF PRIOR COLD WORK. STRESSED AT 90% OF YIELD STRESS.</td>
<td>39</td>
</tr>
</tbody>
</table>
INTRODUCTION

This is a summary report for the period November 13, 1961 to November 13, 1962, describing the results of a continuing program of research on a special form of brittle fracture produced by wetting structural metals with low melting point liquid metals. There is now a substantial body of evidence that under specific conditions wetting by a suitable liquid metal can produce brittle fracture in normally ductile higher melting metals. The significance of this phenomenon has been interpreted in terms of the ability of the liquid metal to lower the critical normal stress at obstructed slip bands at the surface so that fracture occurs without appreciable plastic strain and at stresses much below those normally encountered. The liquid metal not only reduces the stress and plastic strain associated with fracture initiation but also, by following the crack, reduces the energy to propagate the crack.

The present year's work has been divided into two phases. The first phase has been a continuation of prior work on the influence of thermal-mechanical history on the embrittlement of aluminum alloys by liquid mercury. An Al-Mg alloy which possesses strain-aging characteristics has been under study to compare the influence of strain-aging characteristics with precipitation-hardening.

The second and major phase of the program has been an attempt to demonstrate similarities between embrittlement by liquid metals and by certain aqueous or gaseous media. The latter is more commonly known as stress-corrosion cracking. By demonstrating significant similarities between the two processes, it is hoped to establish the relative importance of brittle fracture in stress-corrosion cracking in contrast to theories which describe the cracking as an unusual selective corrosion mechanism.

Delivered by Armour Research Foundation of Illinois Institute of Technology pursuant to Contract No. DA-11-ORD-022-3108. Government's use controlled by the provisions of Articles 26 and 27 of Title II (General Provisions).
The Al 4 1/2% Mg alloy (5083) presents an opportunity to study the interaction between mercury embrittlement and strain-aging. According to Phillips, Swain, and Eborall, alloys of about this composition have the following characteristics:

(a) In the annealed state, the stress-strain curve shows a yield point elongation as in mild steel. The yield point elongation is associated as in mild steel with the formation of readily visible Luders bands. The magnitude of yield point elongation is dependent on grain size, being accentuated by finer grain sizes.

(b) The yield point elongation is not appreciably effected by the temperature of testing between 76° and +20°C.

(c) After prestrain beyond the yield point elongation, strain-aging does not occur (i.e., return of the yield point elongation) on reheating even for long periods of time between 100°-400°C.

(d) The yield point elongation can be suppressed by water quenching from 500°C and can be caused to return by reheating at 100°C for 128 hours. The return is progressive with time.

(e) Beyond the yield point elongation, the stress-strain curve is markedly "stepped" at room temperature over almost the entire range of strain to tensile failure.

(f) The serrated stress-strain curve gradually disappears with decreasing temperature of test and at 68°C, no serrations or discontinuous strain jumps occur.

(g) The existence of the serrated stress-strain behavior is not dependent on grain size.

(h) The rate of strain hardening, yield stress, and total elongation are not significantly different over the...
temperature range +20°C to -76°C.

(i) The yield point elongation is not due to precipitation of a second phase, for when a 7% Mg alloy is deliberately heat treated to cause precipitation, the yield point elongation in the precipitation state is less than in the solution-treated state.

The interpretation of these behavior characteristics requires the condition that Mg atoms segregate to dislocations and dislocation assemblies in the manner that carbon atoms behave in mild steel. Those dislocations along which Mg atoms have segregated require a higher shear stress to displace reversibly than would be the case in the unsegregated or "unpinned" state. Mg atoms can pin fresh dislocations or slip bands very rapidly—not because of their mobility, which is relatively slow, but because of the high population and consequent short distance necessary to reach any dislocation site. In the Al 4 1/2% Mg alloy, there is about one Mg atom for every 22 Al atoms and since the face-centered cubic lattice has a coordination number of 12 (number of nearest neighbors), an Mg atom on the average is only about two atomic distances away from any site on a dislocation wherever it may be in the lattice. This is quite different from the case for iron, where the population of carbon atoms dissolved in the body centered cubic lattice is only about one in 100,000.

The yield point elongation effect signifies that slip initiated in a grain is held back from inducing slip in adjacent grains. Part of the restraint is the barrier effect of grain boundaries enriched with segregated Mg atoms and part by the restraint of Mg atoms all along the slip band. Since the velocity of dislocations increases by orders of magnitude with small changes in stress, the multiplication of slip is very great when grain-to-grain slip is constrained to high stress levels. This leads to the yield point elongation effect.

Since the shear stress at the end of a blocked slip band is higher, the longer is the slip band (i.e., the larger the grain diameter), the restraint to grain-to-grain slip is less in coarse grains and the yield point elongation is proportionately less. This is to say that grain-to-grain slip...
begins at lower stress levels, and consequently the degree of the catastrophic slip action at the yield point is reduced.

The stress magnification at the point of blockage of a slip band produces local intense normal stresses as well as shear stresses. Thus when we lower the critical normal stress for microcracking by introducing mercury at the pile-ups where they occur at the surface, we create the conditions for competition between cracking and macroplastic deformation. Under these conditions it is possible to study those factors in thermal-mechanical history which are conducive to fracture.

A number of experiments have been designed and performed which shed light on the interaction between strain aging and brittle fracture. The first of these is the influence of grain size in the annealed state. Specimens with a range of grain sizes have been prepared by various combinations of cold work and anneal. These are summarized in Table 1. An additional variable was introduced by water-quenching one set from the annealing temperature and slow-cooling a second set. The finer grain sizes were equiaxed, but the coarser ones were elongated in the direction of original rolling and in the axis of tension of testing. For these, the transverse dimension was taken as meaningful for conditions of yielding and fracture.

There was no significant or systematic difference between either the yield stress or the wetted fracture stress of the slow-cooled and water-quenched specimens. The degree of suppression of the yield point elongation produced by quenching is therefore not an important factor. The yield and wetted fracture results as average values (about four tests) are plotted against the Petch Stroh grain size parameter, \( d^{-1/2} \), in Figure 1. A linear relationship was encountered in each case, which signifies that the Petch Stroh models for slip band propagation from grain to grain and the fracture nucleation model are probably operative here. The two lines seem parallel, although in principle they ought to converge to \( d^{-1/2} = 0 \). However, the range of values of \( d^{-1/2} \) encountered is probably too narrow to establish this since the difference between yield and fracture stresses is small.

A series of specimens was plastically prestrained 5% by stretching, unloaded, wetted with Hg, and reloaded to fracture. The results, plotted in...
<table>
<thead>
<tr>
<th>Prestrain, %</th>
<th>Anneal</th>
<th>Grain Diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>550°C-8 hr</td>
<td>0.0125</td>
</tr>
<tr>
<td>8</td>
<td>450°C-7 hr</td>
<td>0.0117</td>
</tr>
<tr>
<td>25</td>
<td>450°C-7 hr</td>
<td>0.0125</td>
</tr>
<tr>
<td>40</td>
<td>425°C-2 hr</td>
<td>0.0069</td>
</tr>
<tr>
<td>65</td>
<td>400°C-2 hr</td>
<td>0.0057</td>
</tr>
<tr>
<td>60</td>
<td>375°C-2 hr</td>
<td>0.0057</td>
</tr>
</tbody>
</table>

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF-B183 12
(Summary Report)
FIG. 1 - INFLUENCE OF GRAIN SIZE ON THE YIELD STRESS AND WETTED FRACTURE STRESS ($\sigma_{yg}$) OF Al 5083 ALLOY.
Figure 2, show a marked and systematic divergence from the results for fracture shown in Figure 1. The 5% prestrain has caused a drop in fracture stress which is greater with finer grain sizes. Although the trend is roughly linear, the slope is now negative which signifies that the Petch-Stroh relationship no longer holds. It must be recognized also that the 5% plastic prestrain has raised the yield point to 40,000-43,000 psi and that these fracture levels correspond to much more emphatic embrittlement by Hg.

In order to explain this, we must realize that by imposing 5% plastic prestrain at room temperature, the grains are now heavily populated by cross hatching slip bands which have been pinned by Mg atoms since strain aging is almost instantaneous. The Petch-Stroh relationship has three terms:

\[ \sigma_F = \sigma_o + Kd^{-1/2} \]

where \( \sigma_F \) = applied tensile stress at fracture

\( \sigma_o \) = stress to propagate slip inside a single grain such that the active tensile stress on a slip band at a grain boundary is \( (\sigma - \sigma_o) \).

\( Kd^{-1/2} \) = the critical tensile stress magnification at the point of a slip band pressing against a grain boundary. The occurrence of fracture signifies that the critical stress for crack nucleation has been reached at the grain boundary by virtue of the active stress \( (\sigma - \sigma_o) \) and the stress magnification produced by a slip band of length, d.

Since K and d are material constants and \( \sigma \) is externally applied, we are forced to consider the influence of plastic prestrain and strain aging on \( \sigma_o \). But this could only act to increase the value of \( \sigma_o \), leading to an elevation of the fracture stress. We are forced again to look for some means for adding rather than subtracting stress from that externally applied.

This leads us to the proposition that certain standing tensile stress fields must exist in the grain as a result of the plastic prestrain and strain aging. This could be developed by the last slip bands produced in the plastic prestrain when they try to relax during unloading of the specimen. It will be recalled that a similar argument was necessary to attempt to account for the influence of plastic prestrain on an age-hardened Al 2024 alloy. This leads to a modified fracture relationship of the form:

ARMOURED RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

- 7 -

ARF-B183-12
(Summary Report)
FIG. 2 - INFLUENCE OF GRAIN SIZE ON THE WETTED FRACTURE STRESS (Hg) OF Al 5083 ALLOY WITH 5% PLASTIC PRE-STRAIN.
where $\sigma_0(\epsilon)$ is the prestrain-dependent slip propagation stress within a grain, $K_1(d,\epsilon)$ is the internal stress field which is a function both of grain size, plastic prestrain and strain aging.

A further set of experiments has been performed to measure the effect of various degrees of plastic prestrain by stretching on the wetted fracture stress. Specimens with an annealed grain size of about 0.0057 mm were stretched by amounts varying between 1 1/2 and 15% at room temperature. These specimens were then wetted with Hg and reloaded to fracture with the results shown in Figure 3. The behavior of plastic prestrain and its associated strain aging at room temperature are very much like that encountered in a precipitation hardened alloy (Al 2024). There is an initial sharp drop in fracture stress with small plastic prestrains, a minimum between 2 and 10% plastic strain, and a small recovery of fracture strength at larger plastic prestrains.

In order to demonstrate that this effect is predominantly due to strain aging, a second set of experiments was performed. In this work, specimens were wetted with Hg, cooled to below the freezing point of Hg, stretched various amounts, unloaded, warmed to the melting point of Hg (-38°C), and stressed to fracture at that temperature. Since strain aging is temperature dependent, the process is partially suppressed by working at the subzero temperatures. In all of this the yield point which is not appreciably temperature dependent is essentially identical with the room temperature values. The results shown in Figure 3 demonstrate that reduced embrittlement is associated with reduced strain aging. Unfortunately, complete suppression of strain aging requires a temperature of 76°C which is well below the freezing point of Hg. Nevertheless these experiments verify that strain aging and not the yield point elongation is associated with the wetted fracture behavior.

These experiments establish that the yield point elongation is not associated with brittle fracture effects. But strain aging, on the other hand, produces effects on embrittlement which are fundamentally the same as produced by precipitation hardening.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

- 9 -

ARF-1'1'12
(Summary Report)
FIG. 3 - INFLUENCE OF TEMPERATURE AND PLASTIC PRESTRAIN ON FRACTURE OF Al 5083 ALLOY WETTED WITH MERCURY.

Plastic prestrain conducted at or below temperature of fracture.
III. ANALYSIS OF STRESS-CORROSION CRACKING

A. An Appraisal Of Stress Corrosion Cracking Theories

There is no shortage of theories to account for stress-corrosion cracking. Rather there is clearly a surplus. Unfortunately, all of these are partially based on reasonable suppositions whose verification has been terminate. Some theories were designed to fit the behavior of only one metal and, while the particular fit seems acceptable in the light of existing information, there is difficulty in broadening the applicability to other metals. There are outright disagreements in the literature on kinetics of highly localized corrosion. All stress-corrosion theories synthesize a cooperative action between chemical and mechanical processes. The details and relative emphasis constitute the nature of the differences. We are also faced with the disagreeable possibility that no one mechanism is applicable to all cases.

The earliest integrated mechanism and still a popular contender was proposed by Means, Brown, and Dix (2). This mechanism presupposes a susceptibility to selective corrosion along more or less continuous paths. There is good experimental evidence that large potential differences can exist between a dispersed phase and its surrounding matrix. Given, therefore, a preferred distribution of precipitate along grain boundaries, the susceptibility of grain boundaries to selective intergranular corrosion is plausible. In fact, intergranular corrosion without the existence of known stresses is a common observation among alloys with segregated grain boundary precipitates.

Under the action of a tensile stress, incipient intergranular or otherwise localized corrosion paths are pulled apart presenting fresh metal at the root of the crack to further attack. Because the freshly exposed metal is more anodic, an increase in the flow of corrosion currents is expected and, hence, an acceleration of corrosion. According to this theory, therefore, stress-corrosion cracking is highly localized corrosion of an electrochemical nature combined with a prying and tearing action of tensile stresses.

This theory seems to fit nicely with the established phenomenology of stress-corrosion cracking in aluminum and magnesium alloys where all of those alloys that are prone possess grain boundary precipitates which are...
decidedly more anodic than the immediate matrix. The stress corrosion environments applied in laboratory synthesis of cracking in aluminum alloys often take many hours and even weeks to develop appreciable penetration. But many stress-corrosion cracking experiments with almost explosive vigor have been demonstrated. There is serious question whether a corrosion process of itself could account for such high velocities of crack propagation.

When we turn from aluminum and magnesium alloys to austenitic stainless steel, some difficulties appear. Although clearly brittle cracks can develop rapidly in boiling MgCl$_2$ solution while the steel is under tensile stress, there is no obvious susceptibility to intergranular or otherwise localized corrosion in the absence of stress. Austenitic stainless steel can be by all examination a homogeneous, single-phase, polycrystalline aggregate. Moreover, stress corrosion cracks generally follow transgranular rather than intergranular cracks. As pointed out by Uhlig,$^{(3)}$ sensitized 18-8 stainless steel, which is prone to intergranular corrosion, will fail nevertheless in a transgranular fashion under conditions conducive to stress-corrosion cracking. This is clearly in conflict with the Mears-Brown-Dix theory.

Faced with the absence of any signs of intergranular corrosion in austenitic stainless steel when immersed in boiling MgCl$_2$ solution, Hoar and Hines$^{(4)}$ proposed another essentially electrochemical theory of stress-corrosion cracking. Here, the initial condition of susceptibility to local corrosion is only a starting phenomenon. The argument is that all metals contain some "disarrayed" regions randomly distributed which will dissolve somewhat more easily than in the more orderly parts. "The galvanic action between cathodic zones on the surface and a small, stressed, disarrayed region may produce a sharp, perhaps submicroscopic pit following the disarrayed region in depth." This localized corrosion is required only to produce a stress-raising micropit. The argument continues that intense elastic or plastic strains at the root of the microcrack or pit create metal which is highly anodic to the surrounding material. The propagation of a crack, therefore, is a cooperative process of localized stress or strain intensification and localized dissolution.
This argument rests on the postulate that the differences in electrochemical potential between highly stressed or highly strained metal at the root of a crack and the surrounding unworked metal can sufficiently account for the known rate of propagation of stress-corrosion cracks. There have been vigorous differences of opinion on this matter. Both Hoar and Hines (4) and Edeleanu (5) agree that a current density of about 1.5 amp/cm² would be necessary to account for the known rates of cracking; but while the former has felt that this current density can be achieved in a deep crack, the latter has taken the same point as an argument against the likelihood of a purely electrochemical mechanism of crack propagation. A considered opinion against a purely electrochemical mechanism has also been given by Harwood. (6)

Considerable support for plastic-strain accelerated electrochemical dissolution as a crack propagating process comes from the work of Hoar and West. (7) In their experiments it was shown that current densities of 0.5 amp/cm² could be produced at potentials of the order of 0.15 volts which is the level of corrosion and cathodic protection potentials. The specific condition for tolerating these anodic current densities is that the specimen is undergoing plastic strain at the same time as the current and potential being measured. The argument therefore is that at the root of a moving crack, plastic straining is in progress which creates the conditions for both rapid and oriented electrolytic dissolution and which, in turn, sustains the active plastic work.

This simultaneous plastic work and stress-directed local corrosion at the root of a crack could be sufficient to account for the crack propagation process. It does not, however, say anything about how a crack starts and, after having been stopped, how it re-starts. The argument that micropits develop by direct chemical or electrochemical action falls back on reasonable supposition because in many instances of stress-corrosion cracking, particularly those which begin quickly, there is no evidence of surface disturbance capable of stress magnification at selected points. One may wonder therefore that if there is a process by which a crack is started, it should also be adequate for propagation and that the Hoar-Hines model, while sufficient, may not be necessary.
Emphasis on the mechanical contribution to stress corrosion cracking has come from direct observations of certain instances of fast discontinuous crack propagation by Edeleanu (8) and Pardue, Beck, and Fontana. (9) Essentially, crack propagation was observed to occur in short bursts separated by periods of apparent inactivity. This character of propagation is clearly incompatible with a purely electrochemical mechanism. Pardue et al. (9) point out, however, that discontinuous crack propagation is not itself a general phenomenon. In a particular Mg alloy under conditions favorable to intergranular corrosion, the crack propagation is not discontinuous. The discontinuous behavior is characteristic only of transgranular cracking.

The various theories of stress corrosion cracking represent three distinguishable viewpoints.

(a) An electrochemical corrosion process, operative on a structure which intrinsically possesses continuous paths of material highly anodic to its surroundings. Stress acts as a prying or tearing agent, intensifying the kinetics of the process and orienting the crack growth in a direction normal to the principal tensile stresses.

(b) An electrochemical process which relies on the stress or strain induced, highly anodic character of material at the root of a sharp crack. The intrinsic structure of the metal and naturally occurring anodic areas are required only for the process of initiating a sharp crack.

(c) An electrochemical process which is responsible for initiation of a sharp crack, propagation of the crack over short distances by purely brittle fracture under triaxial stress conditions, and the dissolution of periodic or random barriers to brittle fracture propagation by the same electrochemical process applicable to initiation.

In considering the validity of any of these basic concepts, certain salient issues are outstanding and certain premises questionable.

The Mears-Brown-Dix model is essentially an extension of intergranular corrosion. A material must have an intrinsic propensity for intergranular corrosion in the absence of stress. However, homogeneous solid solutions do exist which, under specific conditions, exhibit stress-corrosion cracking without proneness to intergranular corrosion. Austenitic stainless steel is a notable example. Moreover, intercrystalline cracking can occur.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

- 14 -

ARF B183-12
(Summary Report)
in alloys under stress where no intercrystalline corrosion will occur in the absence of stress. Cu Au alloys in aqua regia are examples of this.\(^{(10)}\)

There are many instances of transgranular cracking under stress which bear no obvious relationship to the arrangement of distributed phases.

One of the major difficulties has been that for some important metals such as aluminum alloys the existing stress-corrosion media produce cracking whose propagation velocities are of the same order of magnitude as normal intergranular corrosion so that comparing the loss in tensile strength from simple exposure to that from exposure with concomitant applied stress, the values are not very different. See, for example, Sprowls and Brown\(^{(11)}\).

It would be important to study stress corrosion cracking under circumstances where the time to failure is so rapid that normal intergranular corrosion is an unimportant factor. By these remarks the point is made that the Mears-Brown-Dix theory is applicable to too narrow a range of circumstances to be considered a generalized mechanism.

In those instances where associated corrosion is minor or not even observable, the cracks produced by stress-corrosion are by all appearances brittle fractures. There has been for some time a body of opinion that propagation could be regarded as largely a mechanical phenomenon. This opinion has been strongly reinforced by observations of sharp discontinuous bursts of crack movement. It is known that brittle fracture can propagate a limited distance and still be suppressed. The depth to which a brittle microcrack moves before suppression under constant load depends on the strain energy dissipated in unit advance. There has been a tendency to compromise and declare that this may be a dominant factor in certain types of transcrystalline fracture, but even this may only be a temporary position. Brittle fracture need not progress in discontinuous fashion, nor solely by transcrystalline paths. Furthermore, there is no law which demands that brittle fracture proceed only at high speed although this is most commonly observed. Certainly a dominance of brittle fracture as an operative mechanism for propagation more easily accommodates to the many observations of very fast stress corrosion cracking, crack rate dependence on plastic prestrain state of age hardening, and grain size.
Nevertheless, brittle fracture processes can never be divorced from the chemical action of the environment, for unquestionably the cracks will not propagate when removed from the environment except as a terminal condition. Brittle fracture of a purely mechanical nature is not itself sufficient even for part of the model because, for example, austenitic stainless steel cannot be made to propagate a crack in a brittle fashion even for short distances. It seems necessary to regard the environment as instrumental not only to overcome obstacles to discontinuous propagation but also to permit the discontinuous propagation steps themselves.

The cooperative action of chemical processes and mechanical microfracture processes has been suggested by Robertson and Tetelman. Their proposal incorporates two factors: (a) preferential and rapid chemical attack of undetermined nature along planes or surfaces which contain high transverse stresses due to obstruction of slip bands; and (b) the short range propagation of fracture by the release of the strain energy at the head of the blocked slip bands. The term "attack" signifies anything which removes material from the plane or surface or reduces the cohesive energy of that plane or surface. This part of the process is unresolved. Both grain boundaries for the case of intercrystalline cracking and stacking faults for the case of transcrystalline cracking are represented as the barriers to slip which produce local high-intensity transverse or normal stresses. The most impressive justification for this proposition is the correlation between stacking fault energy and propensity for stress-corrosion cracking in austenitic stainless steels and copper base alloys.

Unquestionably the most potent argument for the initial and continuing function of electrochemical processes is the ability of an imposed cathodic potential to prevent cracks from starting and to stop their progress at any arbitrary point.

In summary, it would seem that none of the existing mechanisms for stress-corrosion cracking account for all of the known factors. Cracking solely due to electrochemical processes is not reasonably applicable to all circumstances nor is mechanical brittle fracture, independent of environment, a satisfactory alternative. What seems to be an attractive substitute is the
the proposition that a form of brittle fracture exists which is operative only when the metal is in real contact with specific environments. This point has been suggested in several publications. The difficulty lies in demonstration of the existence and behavior characteristics of an environmental-induced form of brittle fracture.

An Initial Comparison of Liquid Metal Embrittlement With Stress Corrosion Cracking

One of the ways of establishing an argument for environmental brittle fracture is to demonstrate analogy between stress corrosion cracking and other types of environmental cracking. Embrittlement by liquid metals appears to offer opportunity for useful comparison. There is now a strong body of evidence that embrittlement by liquid metals is a form of brittle fracture dominated by changes in interfacial or surface cohesive energies. It is relatively easy in this field of investigation to eliminate intergranular penetration effects unrelated to the existence of stress, and there is no complication with electrochemical processes. Instead, one has the problem of achievement and stability of wetting. From the viewpoint to be presented, the role of electrochemical processes in stress corrosion cracking might be likened to the process of wetting by the liquid metal and the action of imposing cathodic potential likened to the imposition of a de-wetting action.

Let us review the similarities now recognizable. Both liquid metal and stress-corrosion cracking are predominantly intercrystalline but can on occasion be transcrysalline. Both types of cracking occur under static loading, and static fatigue curves can be constructed to show the stress dependence of time to failure. In the case of certain media, stress corrosion cracking will occur in the alloys of Al and Cu but not in the pure metals. This is true also in the case of the action of liquid Hg on Al and Cu. There are many instances where immersion in liquid metals and in aqueous solutions without stress leads to no significant attack but, with the advent of stress, cracking is severe. Both liquid metal and stress corrosion cracking are most severe in precipitation hardened alloys. Furthermore, in both cases the severity of cracking is greatest at similar stages of aging. In both liquid metal and stress-corrosion cracking, only certain specific
media will produce the effect. Moreover, the media are specific to the metal under attack. The crack-branching character on deep penetration observed by Hines and Hugill (14) in austenitic stainless steel stressed in boiling MgCl₂ solution is also observed in Al alloys cracked by Hg.

Finer grain sizes lead to higher breaking stresses or longer times to failure in both liquid metal (13) and stress corrosion cracking (15).

Both liquid metal and stress corrosion cracking are often forestalled in very aggressive media. Thus, for instance, Hg dissolves Mg alloys so rapidly that cracking does not occur. There are recorded observations of the same nature in the literature on stress-corrosion.

Clearly this is a significant beginning but not sufficient to establish the case beyond dispute. There is need for further critical experiments involving the dependence of both cracking processes on material structure, composition and on the conditions of testing. The work of this research program has been directed to these objectives.

One of the characteristics of stress corrosion cracking which ought to distinguish the dominance of either electrochemical dissolution or mechanical processes is the temperature dependence of time to failure. There is very little published information on such trends. There is, however, ample evidence that corrosion or dissolution processes in aggressive media are greatly accelerated by small changes in temperature. Some typical examples are cited in Table II where it is seen that more than ten fold changes in rate of corrosion can be encountered over temperature changes of the order of 50°C. On the other hand, fracture based on mechanical processes will be influenced only by changes in the yield stress over small ranges in temperature, and these, in general, are very small. Therefore, if the temperature dependence of time to crack in a stress corrosion system is small, this may be taken as evidence of the dominance of mechanical processes.

There is one reference to temperature effects on stress-corrosion cracking - that of Hoar and Hines (4). In their work on austenitic stainless steel in hot saturated MgCl₂ solution, a pronounced temperature dependence between 130°C and 160°C was found. Within a 20°C change in solution...
### TABLE II

**TEMPERATURE DEPENDENCE OF THE CORROSION RATE OF SOME METALS IN AGGRESSIVE SOLUTIONS**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solution</th>
<th>Temp, °C</th>
<th>Corrosion Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum 2002</td>
<td>0.20 N NaOH</td>
<td>8</td>
<td>50 mg/hr</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32</td>
<td>360 mg/hr</td>
<td></td>
</tr>
<tr>
<td>Aluminum 5053 T</td>
<td>10% HCl</td>
<td>10</td>
<td>0.005 in/day</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>0.5 in/day</td>
<td></td>
</tr>
<tr>
<td>Cu 29% Zn 1% Sn</td>
<td>3% NaCl</td>
<td>20</td>
<td>0.009 cm/year</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>0.045 cm/year</td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>65% HNO₃</td>
<td>128</td>
<td>100 miles/year</td>
<td>18</td>
</tr>
<tr>
<td>13% Cr 8% Ni</td>
<td></td>
<td>190</td>
<td>5000 miles/year</td>
<td></td>
</tr>
<tr>
<td>Carbon steel</td>
<td>25% NaOH</td>
<td>150</td>
<td>50 miles/year</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>185</td>
<td>300 miles/year</td>
<td></td>
</tr>
</tbody>
</table>
temperature, the time to failure was decreased at the higher temperature limit by a factor of ten. However, the authors’ potential measurements indicate that this effect is primarily in the induction period, i.e., the time to initiate cracking. The time to produce specimen failure after cracking had initiated was too small to make distinctions. We may, therefore, suppose that the temperature effect here is related to the breakdown of passivity and not to the corrosion rate associated with cracking. For a clearer appreciation of temperature effects in cracking, it is necessary to work with solutions in which the metal is not passive. This demands a careful balance of experimental conditions. The aggressive medium must be able to dissolve oxide or passive films rapidly but attack the metal at a much slower rate than cracking proceeds. The latter condition requires testing at high stress levels so that the rate of cracking is as high as possible.

IV. TEMPERATURE DEPENDENCE OF CRACKING IN AN Al 2024 ALLOY

A. Stress-Corrosion Cracking

Exposure of an unstressed alloy in a particular medium can lead to appreciable intergranular corrosion. A failure time in terms of an arbitrary residual load-bearing capacity can be measured or alternatively, and more commonly, loss in apparent tensile strength after finite time of immersion.

The same alloy, in the same medium, under stress can fail in shorter time and, accordingly, the failure is termed stress corrosion cracking. In reality the failure is due to the superposition of the two processes. It is therefore vitally important in any basic study of the stress-corrosion cracking phenomenon that the contributions to failure be separable. This can be accomplished in two ways. By making a separate determination of the rate of penetration by intergranular corrosion, a corrected time to failure by stress-corrosion cracking can be estimated. This is not very satisfactory when the intergranular penetration is of the order of 50% or more of the total loss of supporting section. This is the case for Al alloys in an alternate

—Nominal Composition: 4.5% Cu, 1.5% Mg, 0.6% Mn.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY
immersion and drying test using a simple saline solution. Thus, for example, reference 11 quotes values of 33% loss in tensile strength by intergranular corrosion is compared to about 40% with superimposed stresses.

The other alternative is to find a medium in which cracking rates are very much more rapid than intergranular corrosion penetration. Since a substantial body of information exists now on Hg cracking of the Al 2024 alloy, it seemed important to develop intergranular-free corrosion conditions for that alloy. An aqueous solution was used containing 53 gm/liter of NaCl, 50 gm/liter Na₂CrO₄, and HCl in amount sufficient to lower the pH to about 0.2. The criticality of the HCl addition is illustrated in Figure 4. It was found, however, that the propensity for intergranular corrosion depended on the state of aging of the alloy. It was therefore necessary to define more fully the structure states where stress corrosion cracking could be studied in the practical absence of intergranular corrosion.

Since aging is dependent on both time and temperature, a complete survey of all possible aging cycles presents a very large task. A simple alternative and one which develops every significant structural change in aging is to vary only the aging temperature and hold the aging time constant to 30 minutes. This is essentially making a vertical cut on the time-temperature-transformation diagram for aging.

The results presented in Figure 5 pertain to time to failure at a stress equal to 90% of the yield point. Under these conditions times to failure ranged between 10 and 1500 minutes. Two appraisals of rate of intergranular corrosion rates were made. In one series of tests, the specimens were immersed unstressed in the solution for 8 hours prior to loading and the time to failure clocked after loading. In the second series, the specimens were immersed unstressed in the solution for only that time which was required to produce failure by simultaneous loading and immersion. These latter results permit the conclusions that for stressing to 90% of the yield point, intergranular corrosion is not a significant factor for aging temperatures up to about 190°C. For stress levels of lower magnitude where time to failure must increase, the maximum permissible aging temperature must
FIG. 4 - INFLUENCE OF HCl ADDITIONS TO NaCl-Na₂CrO₄ SOLUTION ON THE TIME TO FAILURE OF AGED Al 2024 ALLOY STRESSED TO 68,000 PSI--after R.C. McCaughey (19)
FIG. 5 - INFLUENCE OF PRIOR IMMERSION IN STRESS-CORROSION SOLUTION ON TIME TO FAILURE OF Al 2024 ALLOY AT VARIOUS STATES OF AGING AND LOADED TO 90% OF THE YIELD STRESS.
be reduced appreciably (see Figure 5). It was therefore decided to confine stress-corrosion cracking studies to specimens aged at 100°-110°C and at stress levels of 90% of the yield point. Under these conditions normal intergranular corrosion penetration is not an interfering factor.

The temperature dependence of time to failure under stress-corrosion conditions wherein cracking rates are much more rapid than intergranular penetration has been explored. The specific conditions were the choice of the Al 2024 alloy aged at 110°C for 30 minutes and stressed to 90% of the yield point in the NaCl-Na₂CrO₄-HCl solution. During these tests, temperatures were controlled at 3°, 25°, 40°, and 60°C. The results are shown in Figure 6 where it is seen that in this temperature range the time to failure is not measurably dependent on temperature.

B  Temperature Dependence of Intergranular Penetration in the Al 2024 Alloy by a NaCl-Na₂CrO₄-HCl Solution

Although it was shown that intergranular penetration as it occurs in unstressed specimens immersed in the stress-corrosion solution did not affect the time to failure under stress provided that a low aging temperature and a high stress level were used, some penetration did occur. In Figure 7 a number of major cracks, clearly separated from each other, exist which are propagating in a direction transverse to the axis of stress. One of these clearly led to final failure. A complex network of intergranular separations may also be observed. This network follows grain boundaries and separates grains from their neighbors. The network advances into the metal more or less as a front. It is of interest to compare the temperature dependence of the rate of advance of this front with the equivalent dependence of cracking time.

A presumably corrosion process is expected to be very temperature dependent. Such measurements were made on small flat coupons about 0.125 in. thick which had been re-solubilized and aged after cutting from the parent stock. The solution was identical with that used in stress-corrosion cracking. A time of 70 minutes' immersion was taken arbitrarily, and the depth of penetration of the front was measured metallographically.
FIG. 6 - INFLUENCE OF TEMPERATURE ON THE TIME TO FAILURE OF Al 2024 ALLOY AT A STRESS OF 90% OF THE YIELD POINT. Aged 110°C-30 minutes, immersed during test in NaCl-Na$_2$CrO$_4$-HCl solution.
Fig. 7

Illustration of intergranular penetration of Al 2024 alloy in the aged state as a result of immersion in the $\text{NaCl-}$ $\text{Na}_2\text{CrO}_4-\text{HCl}$ solution. The intergranular penetration lies between stress-corrosion cracks.
The measurements of penetration for three states of aging and over a span of temperatures from 0° to 300°C are summarized graphically in Figure 8.

The results are intriguing. For the 100°C aged condition, intergranular penetration in 70 minutes is independent of temperature from 0°-60°C. Above 60°C, the rate accelerates abruptly. For the 210°C aged condition, a slight temperature dependence exists between 60°-60°C, and again there is an abrupt acceleration in rate above 60°C. For the annealed condition a sharp temperature dependency exists over the whole range of temperatures. The probable form of true intergranular corrosion for the 100° and 210°C aged states is drawn in Figure 8 as dashed curves.

We may deduce from these results that two processes of intergranular penetration exist—one highly temperature dependent and one temperature independent below 60°C. The temperature-dependent process is surely the intergranular corrosion generally assumed to operate. The absence of the temperature-independent process in the age-hardened states suggests the following model. The process of age hardening generates stress gradients from grain to grain because of the anisotropy of expansion and the high flow stress at the aging temperature. This built-in microstress pattern leads to stress-corrosion cracking in the same manner as externally applied stress. The temperature independence of this form of intergranular penetration, which is really cracking, is consonant with the temperature independence of the time to failure of externally stressed specimens.

C. Temperature Dependence of Delayed Failure

of the Al 2024 Alloy Wetted with Mercury

The mechanical model for brittle fracture which is proposed to apply to embrittlement by liquid metals requires that the conditions for fracture will change with temperature only if the dominant parameters are themselves temperature dependent. In particular, such changes in fracture stress or fracture time require a temperature dependence of the yield stress. Within the temperature range of 0°-80°C, the yield strength of age-hardened Al 2024 alloy is not significantly influenced by temperature. We may, therefore, anticipate that the time to failure in a condition of potential embrittlement should also be independent of temperature provided the mechanical and

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF B183 12
(Summary Report)
FIG. 8 - INTERGRANULAR PENETRATION OF Al 2024 ALLOY IN THREE HEAT-TREATED STATES. SOLUTION NaCl-Na$_2$CrO$_4$-HCl. IMMERSSION TIME, 70 MINUTES.
structural factors govern the fracture process.

The experimental difficulties in conducting delayed failure studies on aluminum alloys wetted with mercury are primarily in terms of the gradual de-wetting by the mercury. It is necessary to develop conditions which prolong wetting as long as possible and to use static stress level which causes failure in times less than will produce de-wetting. Without recounting the wide variety of techniques and stress levels used, it is sufficient to record at this point that the successful combination is the use of a solution of mercuric chloride both as the wetting medium and as the constant temperature bath, and a stress level of 44% of the yield stress. Mercuric chloride both dissolves the intervening oxide film and deposits metallic mercury which readily wets the metal surface. The chloride content introduces some corrosive action which at the higher temperatures is reduced to an insignificant amount by the use of a dilute solution rather than the saturated solution used at lower temperatures. Since both solutions plate out mercury, the solution concentration itself is not a pertinent factor in fracture.

The results of multiple tests at each of five temperatures are graphically presented in Figure 9. The multiple tests were necessary because some scatter in failure times could not be avoided. Nevertheless, the trend indicates no significant temperature dependence of fracture time. This parallels the behavior of the same alloy in the same state of heat treatment immersed in the stress-corrosion solution.

D. Penetration of Mercury into Unstressed Al 2024

In view of the unusual temperature independence of intercrystalline penetration by NaCl-Na₂CrO₄-HCl solution into aged Al 2024 alloy and the probable significance that this reflects microstresses between grains producing a form of microstress corrosion cracking, it seemed useful to examine whether the same sort of effect can be produced by mercury penetration. Mercury penetrates into aluminum very slowly. From 1 to 5 days of exposure are required to produce measurable effects. Moreover, there is a problem in maintaining a state of true wetting because mercury tends to de-wet from aluminum even when the latter is totally submerged.
FIG. 9  - INFLUENCE OF TEMPERATURE ON THE TIME TO FAILURE OF Al 2024 ALLOY WETTED WITH MERCURY.
The problem of de-wetting was solved by the use of sodium amalgam which contains about 0.5% Na in liquid solution. Presumably the sodium chloride oxygen dissolved in the mercury which would otherwise react with the aluminum to form an interfering oxide film. Using sodium amalgam it was possible to preserve wetting for as much as three days or specimens totally submerged.

The specimens themselves were cut into the form of 1/2 in. x 1/2 in. x 0.125 in. thick coupons and then completely solution treated and aged at 100°C for 30 minutes or alternatively, furnace cooled to give the annealed "O" condition. This served to provide a state where, by virtue of aged hardening, grain-to-grain microstresses might exist and a state where they should be absent. Experiments were conducted at two temperatures, room ambient and 60°C. After the exposure to mercury, it was necessary to remove the mercury trapped in the surface penetration zones so that sectioning and polishing itself would not produce cracks. This was accomplished quite simply by heating the specimens to above the boiling point of mercury in a continuously evacuated glass retort for a short period of time.

A comparison of the microstructures produced is given in Figure 3 for the aged condition and in Figure 11 for the annealed "O" condition. A number of points may be noted. Mercury penetrates by apparently intergranular paths. The general penetration is the same in both the aged and overaged condition. The depth of penetration produced at 60°C is about seven times that produced at room temperature. Therefore, there is clearly a strong temperature dependence of penetration rates. In addition to intercrystalline penetration, the aged alloys show a number of fine cracks which have propagated well ahead. The cracks appear only in the aged specimens. We may take this observation as additional evidence that stresses exist between the grains of an aged structure and that these are of sufficient magnitude to produce cracking in the presence of mercury.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF-B183 12
(Summary Report)
Neg. No. 23734 X100
(a) at 25°C after 72 hours

Neg. No. 23733 X100
(a) at 25°C after 72 hours

Neg. No. 23731 X100
(b) at 60°C after 120 hours

Neg. No. 23732 X100
(b) at 60°C after 120 hours

FIG. 10 - MERCURY PENETRATION INTO Al 2024 (AGED 100°C-30 MIN.)

FIG. 11 - MERCURY PENETRATION INTO Al 2024 (ANNEALED. "O" CONDITION.
V. TEMPERATURE DEPENDENCE OF CRACKING IN 70/30 BRASS

A. Stress-Corrosion Cracking

It is well known that 70/30 alpha brass exhibits stress corrosion cracking under stress when in the presence of ammonia vapor or ammonia solutions. Unstressed specimens also show intergranular corrosion but at a much slower rate, i.e., days vs. minutes. Considerable effort was expended in developing suitable conditions for producing cracking over a reasonable temperature range. At room temperature 70/30 brass immersed in concentrated ammonia solution while under stress will only cracking. However, failure will often not occur if the solution is sealed off from the air. It seems quite clear that oxygen is an important factor in the cracking environment. Other gases such as CO\textsubscript{2} which might also be present in the air do not have any recognizable effect. Ammonia solutions, however, are not satisfactory at elevated temperatures because of the high vapor pressure of ammonia. At 45\textdegree C, a concentrated solution loses most of its ammonia in a matter of minutes. A suitable system was developed whereby the test section of the specimen was half immersed in concentrated ammonia solution and ammonia gas and air were bubbled through the solution. The surface of the solution was open to the surrounding air but constructed to help maintain uniform temperature in the test section. Failure occurred consistently above the solution level but not at the solution-gas interface.

In order to shorten the time to failure, the annealed brass specimens were stretched 23\% prior to rupture testing. There was sufficient scatter in the failure times to require about 6 tests at each temperature for a reasonable average value. The results are presented in Figure 12 showing the range of failure times and the arithmetic average values. It will be seen that a small temperature dependence of time to failure does exist over a temperature span of 57\textdegree C.

Intergranular penetration of annealed specimens suspended in an ammonia gas-air mixture above a concentrated ammonia solution is very slow, requiring at least 24 hours for anything measurable under the microscope.
FIG. 12 - INFLUENCE OF TEMPERATURE ON THE TIME TO FAILURE OF 70/30 BRASS (COLD WORKED 23%) IN AMMONIA UNDER A STRESS OF 52,000 PSI.
General attack begins very rapidly as indicated by the change of solution color to blue in a matter of minutes. Many hours, however, are necessary to cause any measurable amount of removal of metal. The brass is therefore not passive to the solution, but the rates of corrosive attack are very small.

B. Temperature Dependence of Mercury Cracking of 70/30 Brass

To provide a comparison with the ammonia cracking of 70/30 brass a similar series of delayed failure tests were conducted using mercuric chloride solution which deposits metallic mercury on the surface of the brass. The specimens were annealed in the machined state and pretrained 23% by stretching. There were then set in the creep stand, and loaded to the required stress level before surrounding by the heated mercuric chloride solution.

It was discovered that the delayed failure curves for brass wetted with mercury are not suitable for comparative studies because of the rapid change from very short failure times to an apparent endurance limit. At stresses of 80-90% of the yield, the failure time was only a few minutes. At 70% of the yield stress, the failure time varied from a few hours to more than a day. Below 70%, failure did not occur at all. It was thus apparent that time to failure was not a feasible parameter.

As a reasonable alternative, the stress for tensile fracture was used as a parameter to compare with varying temperature. As will be shown with plastically pretrained Al 2024 alloy wetted with mercury, the trend of time to failure is essentially the same as the trend of fracture stress in continuous loading. The fracture stress is a quite reproducible property.

The influence of temperature on the fracture stress of cold-worked 70/30 brass wetted with mercury is shown in Figure '3. As in ammonia cracking, there is a small temperature dependence of the cracking process. That is to say, in ammonia cracking, the time to failure decreases by about 28% in a 55-degree span and the fracture stress in mercury cracking decreases by about 11% in the same temperature range.
FIG. 13 - FRACTURE STRESS OF 70/30 BRASS (WITH 23% PRIOR COLD WORK BY STRETCHING) WHEN WETTED WITH MERCURY.
VI. INFLUENCE OF PLASTIC PRESTRAIN ON CRACKING OF AL 2024 ALLOY IN THE AGED CONDITION

In previous work (Summary Report ARF 2183-8, 1961) it was shown that small plastic strains of the order of 1-10% elongation imposed on the aged state before wetting with Hg led to a precipitous loss in the wetted fracture stress. In order to demonstrate that tensile and delayed failure measurements give the same trend, further studies of delayed failure times have been made on specimens aged at 100°C for 30 minutes and given various degrees of plastic prestrain. The results shown in Figure 1 verify that tensile strength and time to failure have the same sharp dependence on small amounts of plastic prestrain.

If our thesis that mechanical fracture processes dominate stress-corrosion cracking is to gain credence, this prestrain embrittlement effect ought also to be found in stress-corrosion cracking of this alloy using the NaCl-Na₂CrO₄-HCl solution as the embrittling medium. These measurements have been performed, and the times to failure at 90% of the yield stress are related to plastic prestrain in Figure 1 where it is clearly seen that the same effect obtains.

VII. SUMMARY

1. The mercury embrittlement of the Al 5083 alloy (4 1/2% Mg), which possesses very rapid strain-aging characteristics at room temperature, shows interesting behavior. It is seen that the conditions leading to a yield point elongation are not an influential factor in mercury embrittlement, for water-quenched structures are not distinguishable from slow-cooled structures. Moreover, the grain size dependence of fracture stress shows a conventional trend for a single-phase material in spite of the fact that the yield point elongation increases with decreasing grain size.

The embrittlement by Hg at -38°C and at +25°C demonstrates that rapid strain aging has a dominant effect on the fracture process. The behavior of the strain-aged condition is similar in character to a precipitation-hardened condition.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF-B183-12
(Summary Report)
FIG. 14 - INFLUENCE OF PRIOR PLASTIC PRESTRAIN ON THE DELAYED FAILURE CURVES OF Al 2024 (ACED 130°C-30 MINUTES) WETTED WITH MERCURY.
FIG. 15 - DELAYED FAILURE BY STRESS-CORROSION OF Al 2024 ALLOY (AGED 100°C-30 MINUTES) AS A FUNCTION OF PRIOR COLD WORK. STRESSED AT 90% OF YIELD STRESS.
The imposition of prior plastic prestrain before wetting on the wetted fracture stress gives a dependence on grain size which is incompatible with a simple Petch-Stroh model for fracture leading to the necessary proposition that internal microstresses of tensile sign are produced by combination of plastic strain and strain aging or precipitation. A term to account for this must be added to the fracture relationships.

2. The temperature dependence of liquid metal and stress-corrosion cracking are similar and small compared to what is normally expected to be the temperature dependence of corrosion processes. This lends support to the proposition that the mechanical fracture mechanisms are dominant in stress-corrosion cracking.

3. The dominance of mechanical fracture mechanisms in stress-corrosion cracking is further supported by the similarity between the dependence of liquid metal and stress-corrosion cracking on prior plastic prestrain.

4. Evidence is presented in terms of the kinetics and appearance of intergranular penetration by aqueous and liquid metal media that large stresses exist between grains in an age hardened polycrystalline aluminum.

VIII. LOGBOOKS AND PERSONNEL

The work herein was conducted by Mr. H. Nichols, Associate Metallurgist, and Mr. R. Sarocco, Technician, under the supervision of the writer. Results are recorded in ARF Logbooks No. C-1091, C-11502, C-12235, and C-12787.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

W. Rostoker

Tech Rev. JFR

jw

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF-B183-12
(Summary Report)
REFERENCES


5. C. Edelcanu, ibid., pp. 126-139.


10. L. Graf, ref. 4, pp. 48-60.


ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY