

AD 609063

EXPERIMENTAL AND THEORETICAL
ASPECTS OF LIQUID
METAL EMBRITTLEMENT

OR 6317

December 1964

Principal Investigators:

Dr. Henry M. Otte

Dr. Agérico L. Esquivel

COPY	2	OF	3	34P
3 COPY				\$.2 .00
MICROFICHE				\$.1 .50

U. S. Army

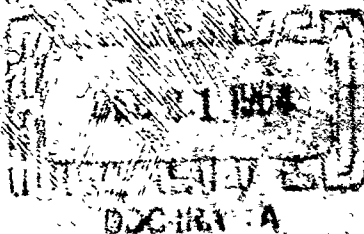
Ballistic Research Laboratories
Aberdeen Proving Ground, Maryland

Project No. AJ-4-A0450-01-A3-AD

AMCMS No. 5549.12.4000.01

Contract DA-36-034-AMC-0065R

Martin Company
Orlando, Florida



ARCHIVE COPY

EXPERIMENTAL AND THEORETICAL
ASPECTS OF LIQUID
METAL EMBRITTLEMENT

OR 6317

December 1964

Principal Investigators:
Dr. Henry M. Otte
Dr. Agerico L. Esquivel

U. S. Army
Ballistic Research Laboratories
Aberdeen Proving Ground, Maryland

Project No. AJ-4-A0439-01-AJ-AD
AMCMS No. 5543.12.46800.01
Contract DA-36-034-AMC-0205R

Martin Company
Orlando, Florida

CONTENTS

Introduction	xi
I. Experimental Procedure	1
A. Materials	1
B. Treatment of Specimens	1
C. Bending Tests	1
D. Tension Tests	3
E. Wetting Procedure	3
F. Preparation of Specimens for Transmission Electron Microscopy	3
G. Preparation of Specimens for X-Ray Diffraction Studies . .	4
II. Results and Discussion	5
A. Embrittlement of Specimens Stressed by Bending	5
B. Embrittlement of Specimens Stressed in Tension	5
C. Transmission Electron Microscopy of Specimens	10
D. X-Ray Diffraction Studies	19
III. Conclusions	23
IV. Acknowledgements	23
References	25
Distribution List	27

ILLUSTRATIONS

1	Effect of Thermal-Mechanical Treatment on Embrittlement by Mercury at Room Temperature of Two Aluminum-Copper Alloys Tested in Tension	6
2	Effect of Heat Treatment on Embrittlement by Mercury of Alpha-Brass (Cu-30% Zn) Tested in Tension.	7
3	Transmission Electron Micrographs of Al-4.3% Cu (2024 Aluminum) After Solution Treatment (540°C, 45 Minutes, Water Quenched to 0°C) and Aging at Room Temperature for More than Two Days	11
4	Transmission Electron Micrographs of Al-6.3% Cu (2219 Aluminum) in As-Received Condition	12
5	Transmission Electron Micrographs of Al-4.3% Cu (2024 Aluminum) and Al-6.3% Cu (2219 Aluminum) Solution Treated in Vacuum for 45 Minutes at 540°C and Quenched in Water at 0°C	13
6	Stacking Faults and Dislocation Networks in Cu-30% Zn Partly Annealed by Heat Treatment at 540°C for 45 Minutes and Water Quenched at 0°C	14
7	Transmission Electron Micrographs of Transcrystalline Microcracks in Cu-30% Zn Exposed to Mercury and Stressed Slightly Beyond its Yield Point	15
8	Transmission Electron Micrographs of Transcrystalline and Intercrystalline Microcracks in Aluminum-Copper Specimens	16
9	Effect of Filing Under Mercury at Room Temperature Instead of in Air on Lattice Parameters of Aluminum (99.99 Percent Pure) and Alpha-Brass (Cu-30% Zn)	20

TABLES

I	Chemical Composition of Alloy Specimens (in Weight Percent)	2
II	Percent Reduction in Fracture Stress and Strain in Cold Worked, Solution Treated and Annealed Specimens Exposed to Mercury	8
III	Yield Point Stresses of Cold Worked, Solution Treated and Annealed Specimens Exposed to Mercury	9
IV	Lattice Parameters of Specimens Filed in Air and in Mercury	21

ABSTRACT

The purpose of the investigation reported here was to examine some of the mechanisms responsible for the premature failure of certain solid metals when stressed and exposed to liquid metals. A feature that appears to be associated with this phenomenon of liquid metal embrittlement, as it is called, is the presence of regions of stress concentration such as precipitates and crystal defects (dislocations, stacking faults, etc.) in the host metal. To determine their effect on the susceptibility to embrittlement of the host metal, the type and density of these regions were varied by subjecting to various mechanical and thermal treatments two commercial, age-hardening aluminum alloys containing 4.3% Cu (2024 aluminum) and 6.3% Cu (2219 aluminum) and an alpha-brass, Cu-30% Zn, with a low stacking fault energy.

The results of tensile and bend tests of the aluminum alloys, when unwetted or wetted with mercury at room temperature, indicate that those specimens subjected to artificial aging (176°C for 19 hours) embrittled more readily than specimens aged at room temperature after solution treatment. Examination by transmission electron microscopy of the heat treated and wetted aluminum alloys revealed a relatively higher density of precipitates present in the specimens which embrittled more easily than in those found less prone to embrittlement. Microcracks, both transcrystalline and intercrystalline, were found in the stressed aluminum alloys exposed to mercury. Dislocation networks and stacking faults, as well as transcrystalline cracks, were observed in the Cu-30% Zn samples stressed in tension and wetted with mercury.

A study was also made of the possible interaction of the liquid metal atoms with the host metal. It was postulated that the liquid metal atoms could sharpen the crack tip, thus reducing the stress necessary to propagate the crack, and that this could be related to a change in lattice parameter. Examination by x-ray diffraction of aluminum, zinc, and Cu-30% Zn filings made in air and in mercury at room temperature revealed lattice parameter changes that seemed to correlate with the embrittling characteristics of mercury.

It may be concluded that:

- 1 Propensity to embrittlement by a liquid metal can be heightened by increasing the density of stress concentration regions in the host metal;

- 2 Transcrystalline cracking in the aluminum specimens indicates that grain boundaries probably play a secondary role in liquid metal embrittlement, although failure can also occur along such boundaries, if present;
- 3 Stacking faults and dislocation networks in the stressed alpha-brass specimens exposed to mercury render the material more susceptible to embrittlement;
- 4 The liquid metal atoms may affect the lattice parameters of the host metal, but the interaction is not fully understood.

INTRODUCTION

When a solid metal is wetted with a liquid metal and stressed below or slightly above its normal yield point, it fails prematurely. The exact cause of this premature failure, or liquid metal embrittlement, is not known; however, certain features associated with the process have been observed frequently. Chief among these features is the requirement that the material exposed to the liquid metal be subjected to a stress (residual or applied), or contain regions of stress concentration, such as precipitates and crystal defects (dislocations, stacking faults, etc.). The type, distribution, and density of these crystal defects as well as of precipitates are influenced by the heat treatment given to the specimen. Thus, heat treatment is expected to affect the mechanical properties of a stressed material exposed to a liquid metal.

To elucidate the mechanism whereby the regions of stress concentration interact with the liquid metal to promote premature failure, it is of consequence to obtain quantitative information about them. Since crystal defects and precipitates in their early stages can be resolved only at magnifications obtainable with the electron microscope, a logical procedure is to use transmission electron microscopy for studying them.

Another feature of liquid metal embrittlement is that a running crack stops propagating once the supply of the liquid metal is cut off (References 1 and 2). This suggests that some form of interaction may take place between the liquid metal and the host metal at the crack tip. One possibility is that the liquid metal atoms may react with the host metal in such a way that a sharpening of the crack tip occurs. This would lead to further propagation of an existing crack or to the growth of an incipient crack. The effect may be related to a reduction of the lattice parameter of the host metal by the liquid metal. Such a reduction, if sufficiently large, could be detected by x-ray diffraction methods.

I. EXPERIMENTAL PROCEDURE

A. MATERIALS

Three commercial alloys known to be embrittled by mercury were chosen for study. Two of these were age hardening aluminum alloys with 4.3% Cu (2024 aluminum) and with 6.3% Cu (2219 aluminum), and the third was an alpha-brass (Cu-30% Zn). The nominal and actual compositions are given in Table I. The Al-4.3% Cu alloy was received in the T4 condition (aged at room temperature after solution treatment), while the Al-6.3% Cu alloy was received in the T81 condition (aged at 175°C for 45 minutes after solution treatment). Besides these alloys, two pure metals, aluminum and zinc, also known to be affected by mercury, were selected for x-ray diffraction studies.

B. TREATMENT OF SPECIMENS

The aluminum alloy specimens were examined in the following conditions, for which the type, density, and distribution of precipitates differed:

- 1 Cold worked (CW) by rolling to 96 percent reduction in thickness from 0.094 inch to 0.004 inch;
- 2 Aged at room temperature (RTA treatment) for more than two days after solution treatment (540°C for 45 minutes in vacuum and water quenched to 0°C);
- 3 Artificially aged (AA treatment) at 175°C for 19 hours after the solution treatment.

The alpha-brass specimens were heat treated (HT) in vacuum at 540°C for 45 minutes and quenched in water at 0°C; this removed most of the cold work (CW) from the material in the as-received condition.

C. BENDING TESTS

For the bending tests on the aluminum alloys, strips 1/4 inch wide by 6 inches long were cut from the as-received material which was 0.094 inch thick. They were then stressed by bending to an angle, $\beta \approx 9$ degrees. Similarly, the alpha-brass, which was received as a foil 0.003 inch thick, was cut into strips (1/4 inch by 2 inches) and stressed by bending to an angle, $\beta \approx 20$ degrees. After the samples were stressed, mercury was

TABLE I
Chemical Composition of Alloy Specimens
(in Weight Percent)

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Pb	Others (total)	Al
Al-4.3% Cu (2024 Alu- minum; No- minal)	0.50	0.50	4.35	0.60	1.50	0.10	-	0.25	-	-	0.15	92.05
Al-6.3% Cu (2219 Alu- minum; No- minal)	0.20	0.30	6.30	0.30	0.02	-	-	0.10	0.06	-	0.15	92.57
Cu-30% Zn (Actual)	-	< 0.05	69.47	-	-	-	-	30.41	-	< 0.07	< 0.15	-

applied to the bent area with the aid of an aqueous acid solution as deoxidizer, and the samples bent till fracture occurred.

D. TENSION TESTS

The complete stress-strain curves (up to fracture) in tension were determined on an Instron machine using flat (0.004 inch thick) test pieces with a gauge dimension of 0.500 inch by 0.095 inch. The test pieces were prepared from the starting material (0.094 inch thick) by cold rolling it, with intermediate anneals, down to a final thickness of 0.004 inch, which was also a suitable starting thickness for the preparation of transmission electron microscopy samples. To remove the cold working introduced into the specimens during the final cold rolling and cutting, the flat tensile pieces were solution heat treated in vacuum for 45 minutes at 540°C and water quenched at 0°C. All specimens were tested at a strain rate of $6.0 \times 10^{-4} \text{ sec}^{-1}$.

E. WETTING PROCEDURE

In all cases, wetting of the samples by mercury was enhanced by using a deoxidizer. In the case of the aluminum alloys, the deoxidizer was 40 percent HF; for the alpha-brass, it was 40 percent HCl. Throughout this report it is to be understood that "wetted by mercury" means that the specimen was "wetted by mercury using a deoxidizer."

For the tensile specimens, deoxidizer and mercury were applied at the gauge section, which was then wiped dry before mounting the specimen on the Instron tester. Both bend and tension tests with deoxidizer only gave the same results as without deoxidizer, showing that the deoxidizer did not affect the mechanical behavior of the materials.

F. PREPARATION OF SPECIMENS FOR TRANSMISSION ELECTRON MICROSCOPY

The specimens for transmission electron microscopy were prepared from 0.004 inch thick foils by electrolytic polishing methods (Reference 3). An electrolyte, consisting of 20 percent perchloric acid and 80 percent absolute alcohol, was used for the aluminum alloys, while a solution of 33 percent nitric acid and 67 percent methanol was used for electropolishing the alpha-brass specimens.

In a number of cases, specimens that had been wetted with mercury were prepared for transmission electron microscope examination by electropolishing from only one side. The wetted side was protected by a lacquer so that the surface areas exposed to mercury remained relatively undisturbed during electropolishing.

A Siemens Elmiskop I, operating generally at 100 kilovolts, was employed.

G. PREPARATION OF SPECIMENS FOR X-RAY DIFFRACTION STUDIES

Specimens from a number of materials (pure aluminum, pure zinc and Cu-30% Zn) were filed at room temperature in air and in mercury. After centrifuging to remove as much excess mercury as possible from those filings prepared under mercury, the filings in both cases were compacted into rods (diameter: 2.2 mm) and examined at room temperature on a General Electric x-ray diffractometer using a Debye-Scherrer geometry and Cu-K α_1 radiation ($\lambda = 1.54050 \text{ \AA}$).

II. RESULTS AND DISCUSSION

This section describes the results obtained from the embrittlement tests of specimens exposed to mercury while stressed by bending and in tension, as well as observations from transmission electron microscopy and x-ray diffraction.

A. EMBRITTLEMENT OF SPECIMENS STRESSED BY BENDING

For the aluminum alloys in the as-received condition, brittle fracture followed almost instantly when specimens were bent and wetted with mercury. These same specimens when unwetted could be bent to $\beta \approx 130$ degrees without fracture. Similar results of premature failure were observed in the alpha-brass foil strips when wetted with mercury. These tests served to confirm the embrittlement by mercury of these materials in their as-received state, in accordance with results reported in the literature (References 1 and 4).

B. EMBRITTLEMENT OF SPECIMENS STRESSED IN TENSION

The results of the tensile tests for the aluminum alloys and the brass specimens, heat treated in various ways and tested in the wetted and unwetted conditions, are shown in the true stress-strain curves of Figures 1 and 2. Critical points from these curves are summarized in Tables II and III, and discussed briefly below.

1. Fracture Stress Observations

The degree of embrittlement of a solid metal may be expressed in terms of the fracture stresses and strains of the wetted specimens as compared with those of the unwetted specimens. Such comparisons of fracture stress and fracture strain values are shown in Table II. The cold worked aluminum alloys exhibit a considerably lower percentage reduction in fracture stress and strain than the solution treated and aged specimens. This effect may be attributed to the higher dislocation density in the cold worked specimens. Thus, under the influence of an externally applied tensile stress, there is a greater likelihood that in the cold worked specimens some of the dislocations could coalesce to form microcracks at the surface, and these could then interact with the liquid metal atoms with resulting embrittlement.

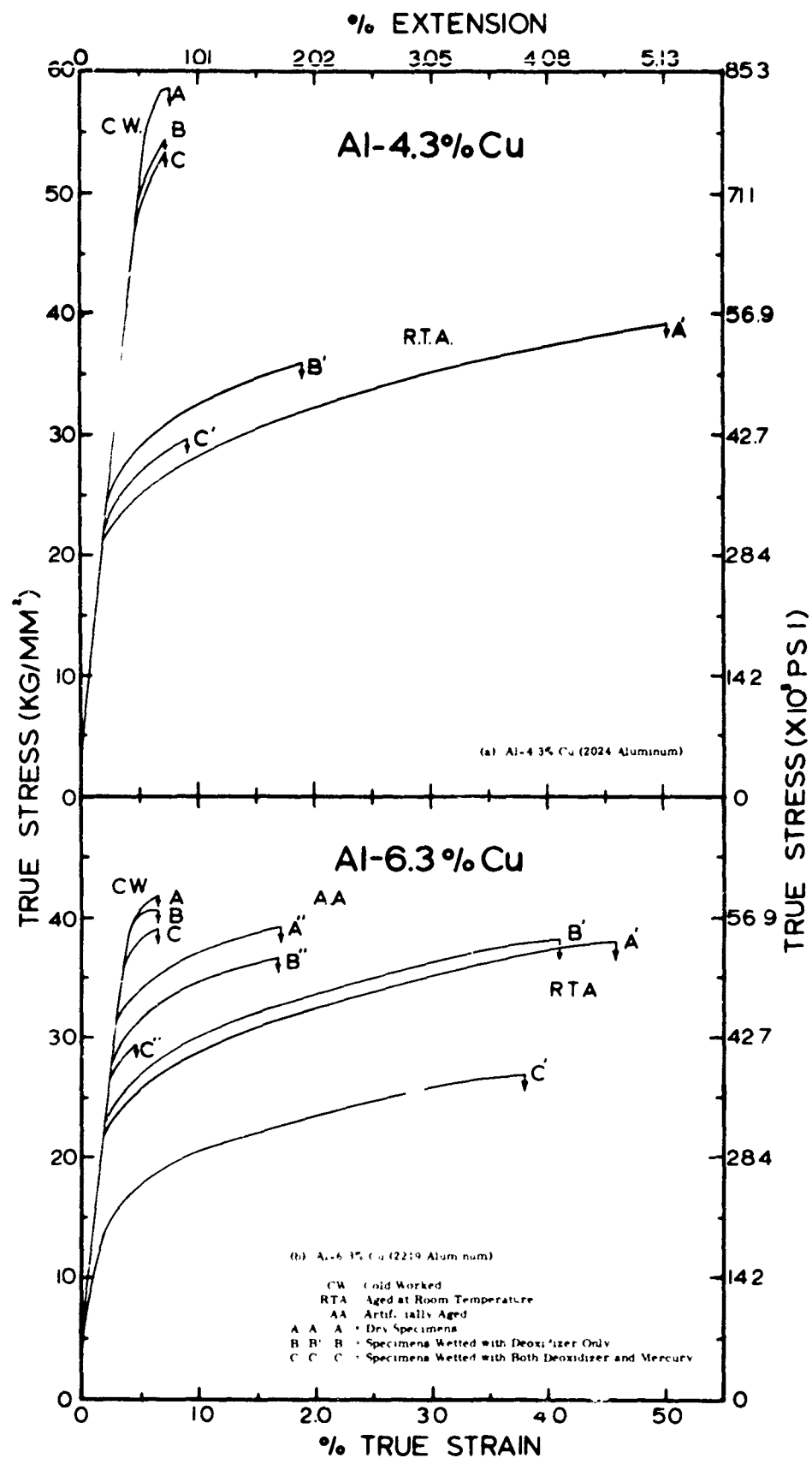


Figure 1. Effect of Thermal-Mechanical Treatment on Embrittlement by Mercury at Room Temperature of Two Aluminum-Copper Alloys Tested in Tension

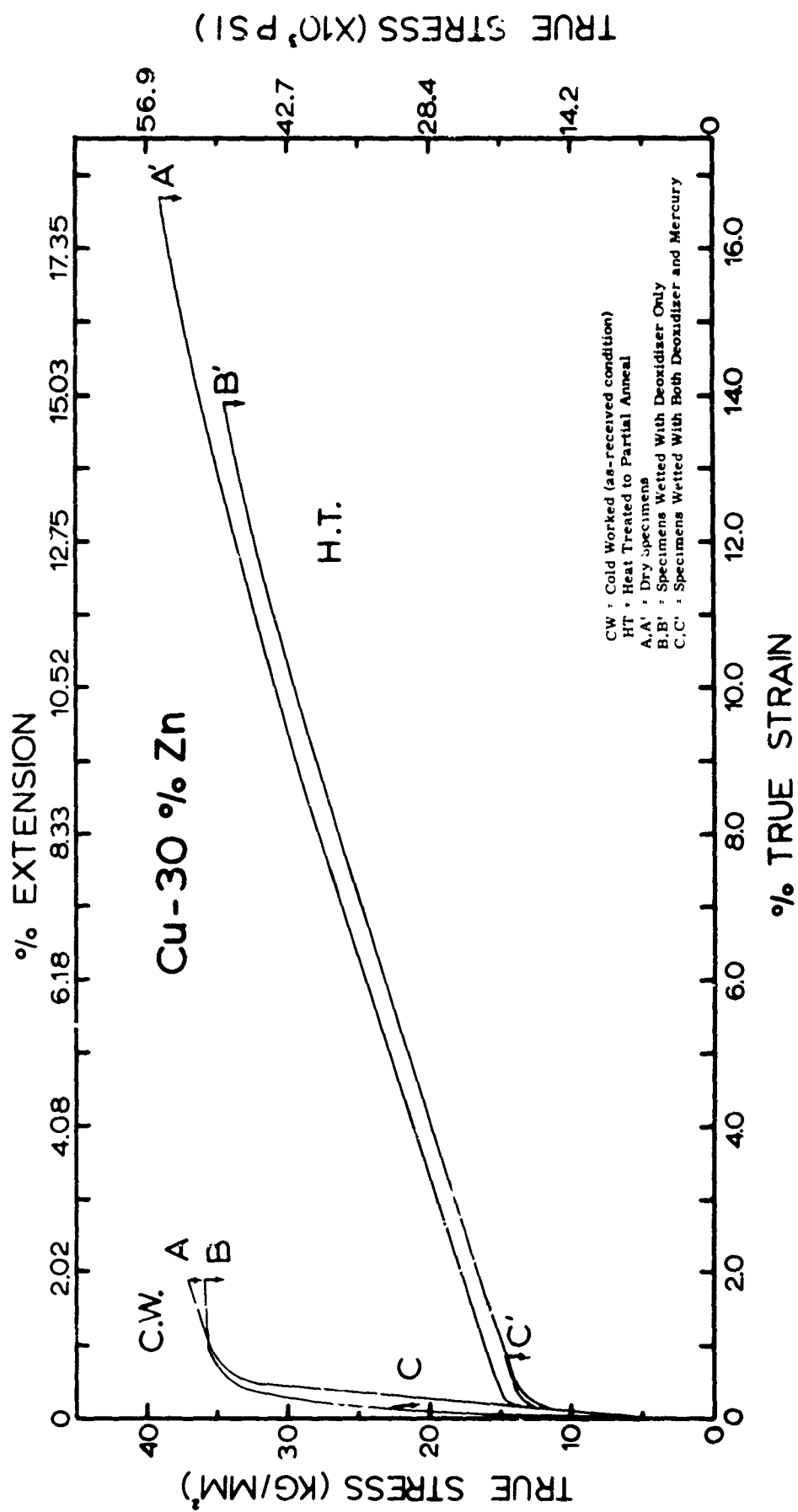


Figure 2. Effect of Heat Treatment on Embrittlement by Mercury of Alpha-Brass (Cu-30% Zn) Tested in Tension

TABLE II

Percent Reduction in Fracture Stress and Strain in Cold Worked,
Solution Treated and Annealed Specimens Exposed to Mercury

Specimen	R (σ_f)				R (ϵ_f)			
	CW	RTA	AA	HT	CW	RTA	AA	HT
Al-4.3% Cu	8.5	24.0	-	-	5.3	87.9	-	-
Al-6.3% Cu	2.9	4.6	25.2	-	3.0	23.5	72.9	-
Cu-30% Zn	33.9	-	-	62.4	91.5	-	-	94.7

Notes:

Specimens are flat tensile test pieces (thickness: 0.004 inch; gauge dimensions: 0.095 inch by 0.500 inch)

R (σ_f) = percentage reduction in fracture stress defined by:

$$\left[\sigma_f (\text{Dry}) - \sigma_f (\text{Wet}) \right] \frac{100}{\sigma_f (\text{Dry})}$$

where σ_f = fracture stress (kg/mm^2)

R (ϵ_f) = percentage reduction in fracture strain defined by:

$$\left[\epsilon_f (\text{Dry}) - \epsilon_f (\text{Wet}) \right] \frac{100}{\epsilon_f (\text{Dry})}$$

where ϵ_f = fracture strain

CW = cold worked by rolling to 96 percent reduction in thickness

RTA = aged at room temperature for more than 2 days after solution heat treatment (45 minutes at 540°C, water quenched at 0°C)

AA = artificially aged for 19 hours at 175°C after solution treatment

HT = heat treated (45 minutes at 540°C, water quenched at 0°C).

TABLE III

Yield Point Stresses of Cold Worked, Solution Treated and Annealed Specimens Exposed to Mercury

Specimen	CW		RTA		AA		HT	
	σ_f (d)	σ_o (w) $\Delta \sigma_o$	σ_o (d)	σ_o (w) $\Delta \sigma_o$	σ_o (d)	σ_o (w) $\Delta \sigma_o$	σ_o (d)	σ_o (w) $\Delta \sigma_o$
Al-4.3% Cu	5.8	SYF -	23.0	28.0 -5.0	-	- -	-	- -
Al-6.3% Cu	4.2	4.1 +0.1	22.6	24.3 -1.7	31.8	27.0 +4.8	15.0	- -
Cu-30% Zn	3.3	SYF -	-	- -	-	- -	15.0	13.5 +1.5

Notes:

Specimens are flat tensile test pieces (thickness: 0.004 inch; gauge dimensions: 0.095 inch by 0.500 inch)

Yield point stress was measured at 0.1 percent plastic strain

 σ_o (d) = yield point stress (kg/mm²) of a dry (unwetted) specimen σ_o (w) = yield point stress (kg/mm²) of a specimen wetted with mercury (and aqueous HF or HCl as deoxidizer)

$$\Delta \sigma_o = \sigma_o$$

SYF = subyield point fracture

CW, RTA, AA, and HT are defined as in Table II.

In the aged samples the dislocation density appears to be quite low. During deformation, dislocations are generated and interact with the precipitate. Clearly it takes more deformation in these cases to build up a situation susceptible to embrittlement, and the exact amount is dependent on the aging treatment, which determines largely the size and distribution of the precipitate (Section C).

In the alpha-brass specimens, which do not form precipitates, other mechanisms, such as dislocation networks and stacking faults introduced by heat treatment and deformation, must be invoked to account for the slight increase in propensity to embrittlement as indicated by the increase in percentage reduction of fracture stress and strain shown in Table II.

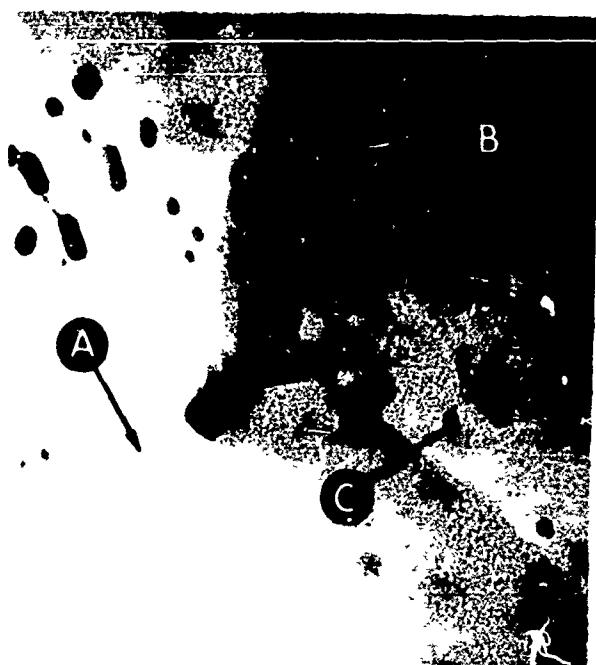
2. Yield Point Observations

The slight variations between the yield points of wetted and unwetted specimens subjected to the same heat treatment (Figures 1 and 2, and Table III) must be viewed with reserve. The results are preliminary since they are based on an insufficient number of tests. To establish a standard of deviation for the yield point values, further tests are necessary, which will determine whether or not the differences observed are within the experimental scatter. Other investigators (References 4 and 5) have reported no effect on the yield point of materials exposed to liquid metal. Although the difference in the yield point is sometimes positive and sometimes negative (Table III), the effect, if real, could be discussed in terms of the liquid metal influencing the release or unpinning of dislocations at the yield point (Reference 6). Such a discussion is best delayed till more data are gathered.

C. TRANSMISSION ELECTRON MICROSCOPY OF SPECIMENS

Transmission electron micrographs of the aluminum alloy and alpha-brass specimens are shown in Figures 3 through 8. These illustrations show the microstructural features and crystal defects arising from the heat treatments given the specimens, exposure to mercury, and deformation by tensile stress.

The solution treated and age hardened aluminum alloys were characterized by the presence of precipitates and dislocations while the partially annealed alpha-brass was found to contain dislocation networks, pile-ups at grain boundaries, and stacking faults.



(a) Typical grain boundaries (A), and precipitates (B, C), lying at different orientations relative to foil surface

0.5 μ



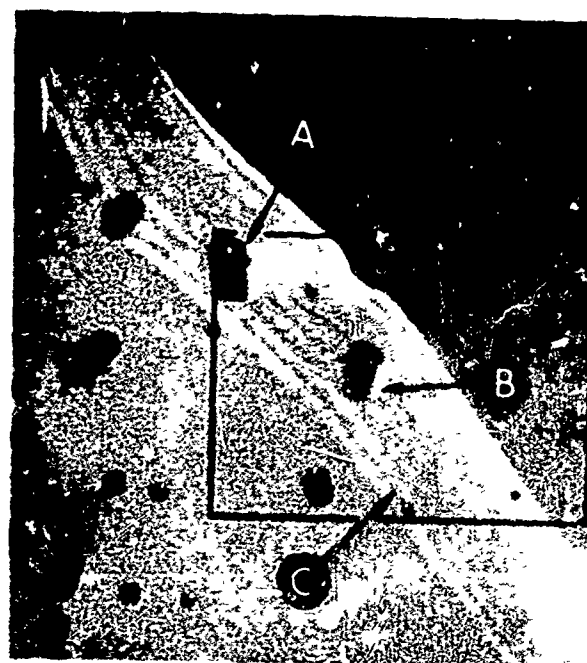
(b) Helical dislocations (A), and precipitates (B)

0.25 μ



(c) Bright-field transmission electron micrograph of precipitates (A) and (B) lying within a high-angle grain boundary (C)

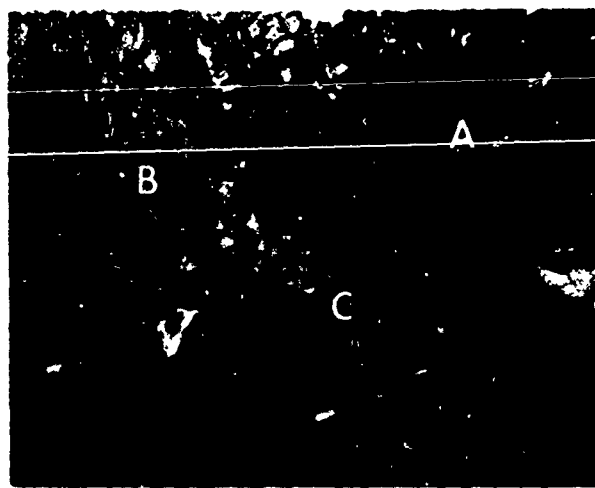
0.5 μ



(d) Dark-field image of Figure 3(c). (A), (B), and (C) represent by a reversal of phase contrast, the dark field image of the correspondingly labeled objects in Figure 3(c)

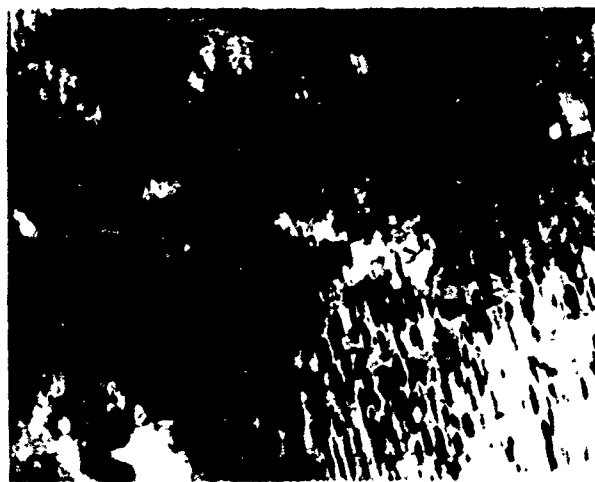
0.5 μ

Figure 3. Transmission Electron Micrographs of Al-4.3% Cu (2024 Aluminum) After Solution Treatment (540°C, 45 Minutes, Water Quenched to 0°C) and Aging at Room Temperature for More Than Two Days



(a) Region showing junction of three grains with precipitation virtually up to grain boundaries (A). Strain field (C) around precipitate (B).

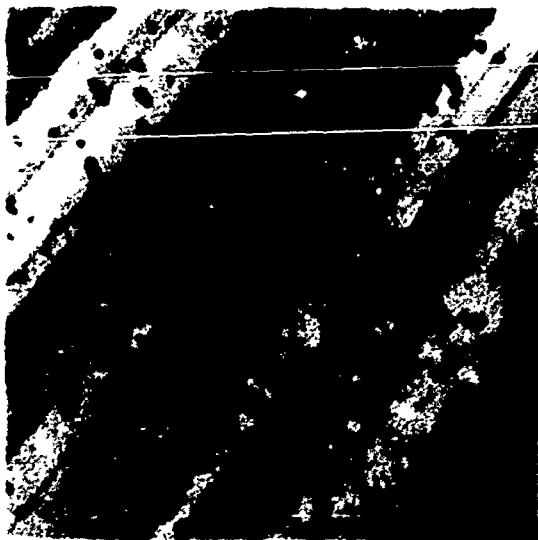
0.5μ



(b) Grain oriented so as to reveal plate-like character of the precipitates, density of precipitates: $\sim 3.0 \times 10^{10} \text{ cm}^{-2}$

0.5μ

Figure 4. Transmission Electron Micrographs of Al-6.3% Cu (2219 Aluminum) in As-Received Condition



(a) Al-4.3 percent Cu aged at room temperature after solution treatment
Precipitate density $\sim 5.0 \times 10^9 \text{ cm}^{-2}$

0.5 μ



(b) Al-4.3 percent Cu aged at 0°C after solution treatment
Precipitate density $\sim 5.0 \times 10^9 \text{ cm}^{-2}$

0.5 μ



(c) Al-6.3 percent Cu (as-received, T81 condition) artificially aged for 19 hours at 176°C after solution treatment
Precipitate density $\sim 10^{10} \text{ cm}^{-2}$

0.5 μ



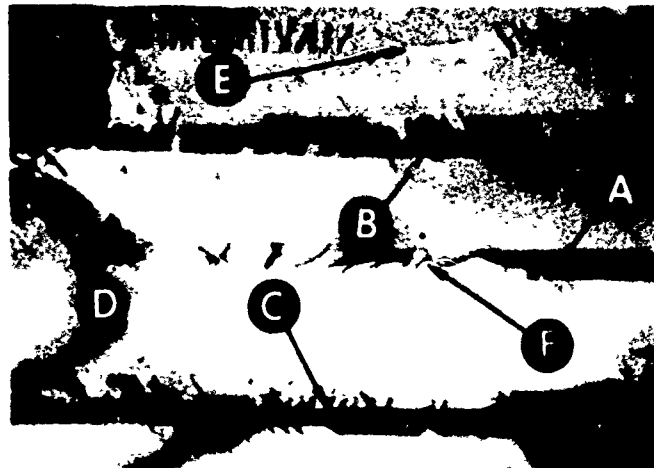
(d) Al-6.3 percent Cu aged at 0°C after solution treatment
Precipitate density $\sim 2 \times 10^7 \text{ cm}^{-2}$

0.5 μ

Figure 5. Transmission Electron Micrographs of Al-4.3% Cu (2024 Aluminum) and Al-6.3% Cu (2219 Aluminum) Solution Treated in Vacuum for 45 Minutes at 540°C and Quenched in Water at 0°C

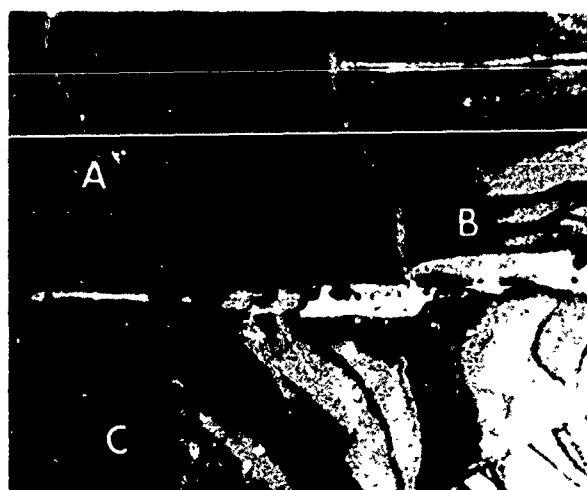


(a) Typical high-angle grain boundaries showing interference fringes (A), dislocation networks (B), and pile-ups of dislocations at a grain boundary (C)



(b) Typical interference fringes characteristic of stacking faults (A, B), other features (C), dislocation interaction with stacking fault (C), dislocation networks (D), possible Frank-Read source (E), and dislocation node (F)

Figure 6. Stacking Faults and Dislocation Networks in Cu-30% Zn Partly Annealed by Heat Treatment at 540°C for 45 Minutes and Water Quenched at 0°C



(a) Relatively thin area (A) is possibly related to a microcrack. Lines such as (B) are probably microtwins. Dark fringes (C) are extinction contours due to foil buckling.

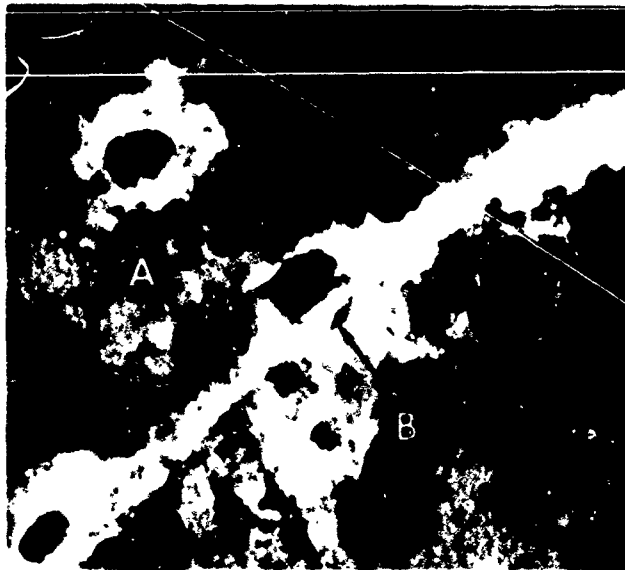
0.5 μ



(b) Transcrystalline crack (A) about 250 Å wide. Foil buckling indicated by intersection of extinction contour lines at (B).

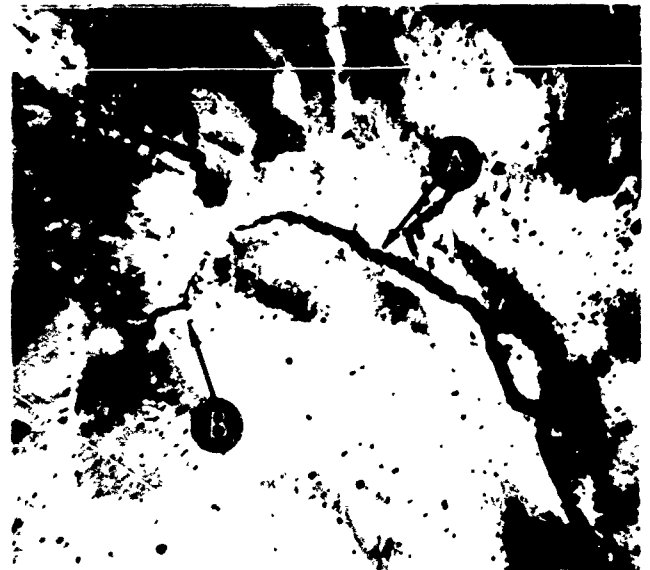
0.5 μ

Figure 7. Transmission Electron Micrographs of Transcrystalline Microcracks in Cu-30% Zn Exposed to Mercury and Stressed Slightly Beyond its Yield Point



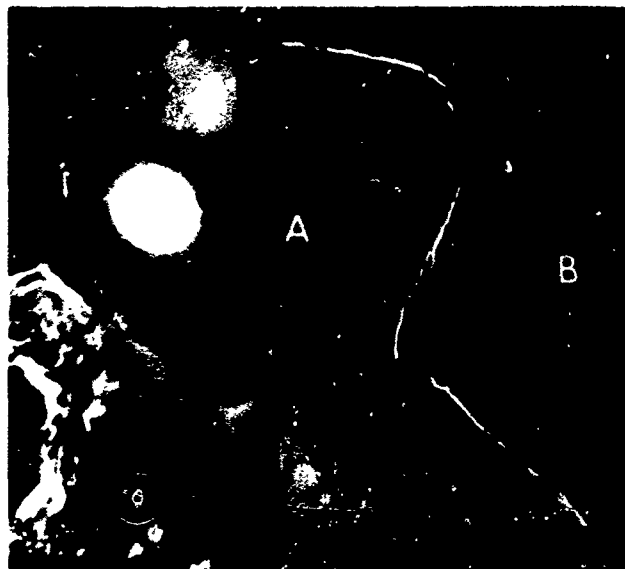
(a) Microcrack (A) about 300 Å wide probably passing along a grain boundary and propagating around a precipitate (B) in the Al-4.3 percent Cu (2024 aluminum) specimen.

0.5 μ



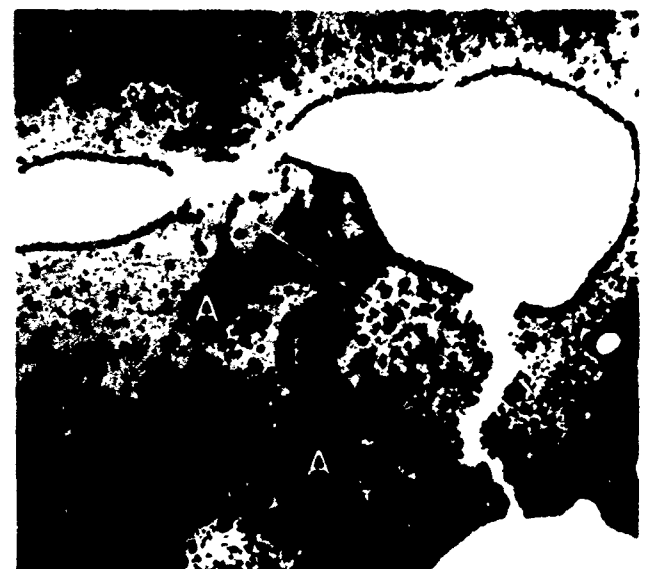
(b) Transcrystalline crack (A) about 2400 Å wide: propagating across a grain defined by boundary (C) in the Al-4.3 percent Cu (2024 aluminum) specimen. Dark spots like (B) are probably precipitates.

2.0 μ



(c) Intercrystalline crack (A) about 800 Å wide in the Al-6.3 percent Cu (2219 aluminum) specimen stressed but not wetted. Crack seems to propagate along a precipitate (B). Bright spot on upper left corner is a hole.

1.0 μ



(d) Transcrystalline crack (A) about 6000 Å wide in the Al-6.3 percent Cu (2219 aluminum) specimen. Dark spots such as (B) are due to surface contamination during electropolishing.

2.0 μ

Figure 8. Transmission Electron Micrographs of Transcrystalline and Intercrystalline Microcracks in Aluminum-Copper Specimens

1 Correlation of Embrittlement with Precipitation in the Aluminum Alloys

Figure 3 shows transmission electron micrographs of Al-4.3% Cu after the AA treatment. The precipitates appear to be cylindrical in shape, as may be seen from (B) and (C) in Figure 3(a). Figure 3(b) shows, in addition to the precipitates (B), helical dislocations such as (A), which have been interpreted as resulting from condensation, during quenching, of vacancies onto dislocation lines.

Although precipitates in the Al-4.3% Cu alloy, such as those shown in Figure 3(a) and 3(b), have been observed in aluminum-copper alloys of similar composition (Reference 7), the possibility that these structures may be due to surface contamination was investigated by taking bright- and dark-field micrographs of the same area (rectangle in Figures 3(c) and 3(d)) containing the precipitates. A partial reversal in contrast for the precipitates marked (A) and (B) in Figures 3(c) and 3(d) indicates strongly, but not conclusively, that these structures are probably true precipitates and not surface contamination. However, other experimental tests are available and will be applied in future experiments to determine the true nature of the precipitates.

The Al-6.3% Cu alloy (Figure 4) also exhibits, in the as-received T81 condition, a considerable amount of precipitation. The precipitate density varied from $\sim 0.8 \times 10^{10} \text{ cm}^{-2}$ (Figure 5(c)) to $\sim 3.0 \times 10^{10} \text{ cm}^{-2}$ (Figure 4(b)). Figure 4(a) shows grain boundaries (A) and strain fields (C) around precipitates (B).

The two aluminum alloys subjected to the same heat treatments behaved differently with regard to the formation of precipitates. Typical electron micrographs of these precipitates are shown in Figure 5. Precipitates were always present in the Al-4.3% Cu (Figures 5(a) and 5(b)) whether held at room temperature or at 0°C after solution treatment and quenching. The micrograph shown in Figure 5(a) was obtained from a specimen aged at room temperature, while Figure 5(b) was from one aged at 0°C . No difference in precipitate density ($\sim 5.0 \times 10^9 \text{ cm}^{-2}$) was observed between the two specimens.

In contrast to this, the Al-6.3% Cu alloy showed relatively fewer precipitates when aged at 0°C than when aged at higher temperatures, indicating that precipitation is more readily inhibited in this alloy. Although Table I indicates that both alloys have almost the same amount of aluminum as solvent, the proportion of solute elements is not the same. The Al-6.3% Cu has 2 percent more copper, in place of magnesium for the most part,

and some silicon, iron, and manganese. This suggests that the replacement of these elements by copper makes the Al-6.3% Cu less supersaturated and thus slightly less prone to precipitation.

The Al-6.3% Cu in its as-received, T81 condition with a precipitate density of about 10^{10} cm^{-2} (Figure 5(c)) embrittles drastically. When aged at 0°C immediately after a similar solution treatment, a lower precipitate density ($\sim 2.0 \times 10^7 \text{ cm}^{-2}$) was observed (Figure 5(d)) and an almost total loss of embrittlement behavior when exposed to mercury. This indicates a strong correlation between precipitate density and susceptibility to embrittlement by liquid metals (References 8 and 9).

2. Observations on the Alpha-Brass

Electron micrographs of the alpha-brass specimens are shown in Figures 6 and 7. Figure 6 is from a specimen wetted with mercury and stressed to 10.3 kg/mm^2 , slightly beyond its yield point (10.2 kg/mm^2). Figure 6(a) shows grain boundaries meeting at (A), dislocation networks (B), and dislocation pile-ups at a grain boundary (C). A number of features visible in Figure 6(b) are: stacking faults (A) and (B), dislocation interactions with a stacking fault (C), some dislocation networks (D), what appears to be a Frank-Read source (E), and a dislocation node (F). Of these, stacking faults have been suggested as influencing stress corrosion cracking in alpha-brass (Reference 10). They probably also influence the susceptibility to embrittlement of this material by mercury. Other micrographs (Figure 7) show the type of microcracks found in alpha-brass exposed to mercury.

3. Microcracks in Specimens Exposed to Mercury

Electron microscopic evidence from alpha-brass (Figure 7) and the aluminum alloy specimens (Figure 8) shows that both transcrystalline cracking (Figures 7(b), 8(b), and 8(d)) and intercrystalline microcracks (Figures 8(a) and 8(c)) can be observed in specimens exposed to mercury.

Transmission electron micrographs of the alpha-brass specimens (Figure 7) stressed in tension and wetted with mercury reveal heavily distorted regions ((A) and (C) in Figure 7(a); (B) in Figure 7(b)) probably due to foil buckling. Intercrystalline crack formation is frequently described in terms of dislocation pile-ups at a grain boundary or some form of dislocation coalescence (Reference 11); however, so far no evidence of this was obtained in the electron micrographs of either the stressed, dry specimens or the stressed, wetted specimens. Since transcrystalline cracks such as those found in alpha-brass (Figure 7(b)) and in the aluminum alloys (Figures 8(b) and 8(d)) have been observed in materials ex-

posed to mercury, the role of grain boundaries in liquid metal embrittlement is probably secondary, although failure can also occur along such boundaries, if present.

D. X-RAY DIFFRACTION STUDIES

Current theories (References 12 and 13) describe the stress, σ_f , necessary to extend a crack as proportional to $\sqrt{\rho}$ where ρ is the radius of curvature of the crack tip. The fracture stress could thus be reduced if the liquid metal atoms were to "sharpen" the crack as might be conceivable if they reduced the lattice parameter of the host metal.

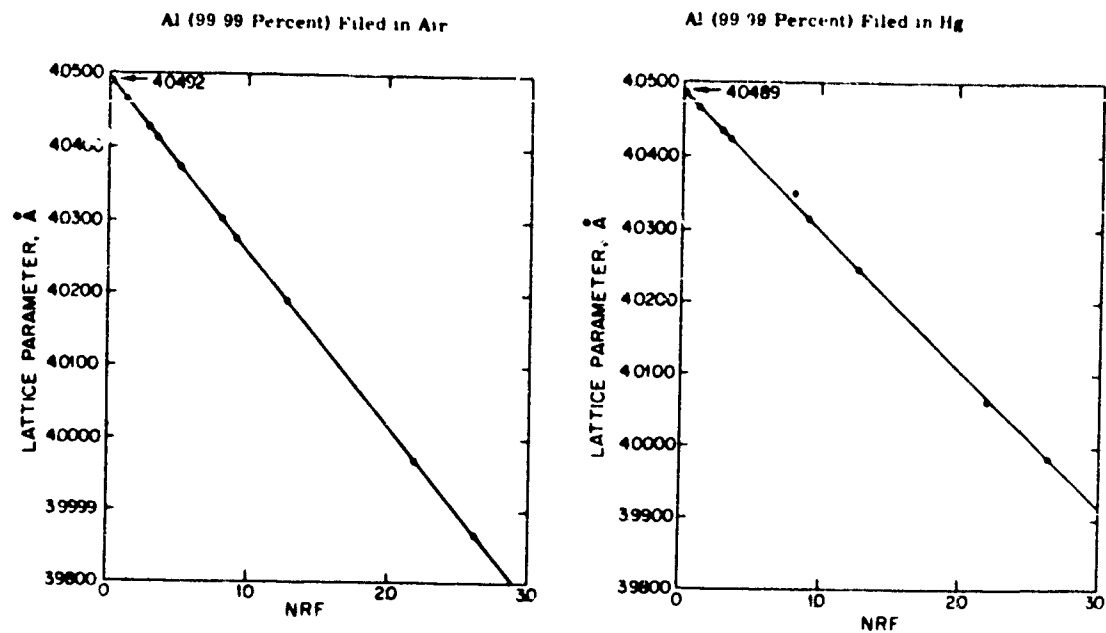
To test this hypothesis, the lattice parameters of aluminum, zinc, and alpha-brass filings made in air and in mercury were measured by x-rays. Analysis of the resulting diffraction patterns is shown, for aluminum, in Figures 9(a) and 9(b) and for Cu-30% Zn in Figures 9(c) and 9(d). The results are also summarized in Table IV.

In Figure 9, the lattice parameter calculated from each diffraction peak has been plotted against the Nelson-Riley extrapolation function to correct for absorption effects (Reference 14). This function is defined by:

$$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$

where θ is the Bragg angle. The corrected lattice parameter is obtained by extrapolation to zero for this function. In the case of zinc, two lattice parameters, a_0 and c_0 , are involved, and their calculation is less straightforward. A least squares analysis (Reference 15) was therefore adopted and programmed on an IBM 7094 computer to calculate from the observed diffraction peak positions the lattice parameters of the zinc specimens filed in air and in mercury.

While the lattice parameters of aluminum and alpha-brass appear to have been reduced by an amount outside the range of experimental error, those of zinc seem to have increased. The zinc data were obtained from a pattern that also included reflections from a hexagonal zinc-mercury compound formed when zinc is filed in mercury. Of the total of 22 reflections, only seven could, with reasonable confidence, be identified as belonging to zinc. Hence, the relatively large lattice parameter changes calculated from the zinc data are considerably less reliable than those obtained from the other two FCC materials, which exhibited lattice parameter changes in the direction postulated. However, there is a possibility that cannot be dismissed at present that the observed changes may have been caused by the mercury atoms entering into solid solution with the

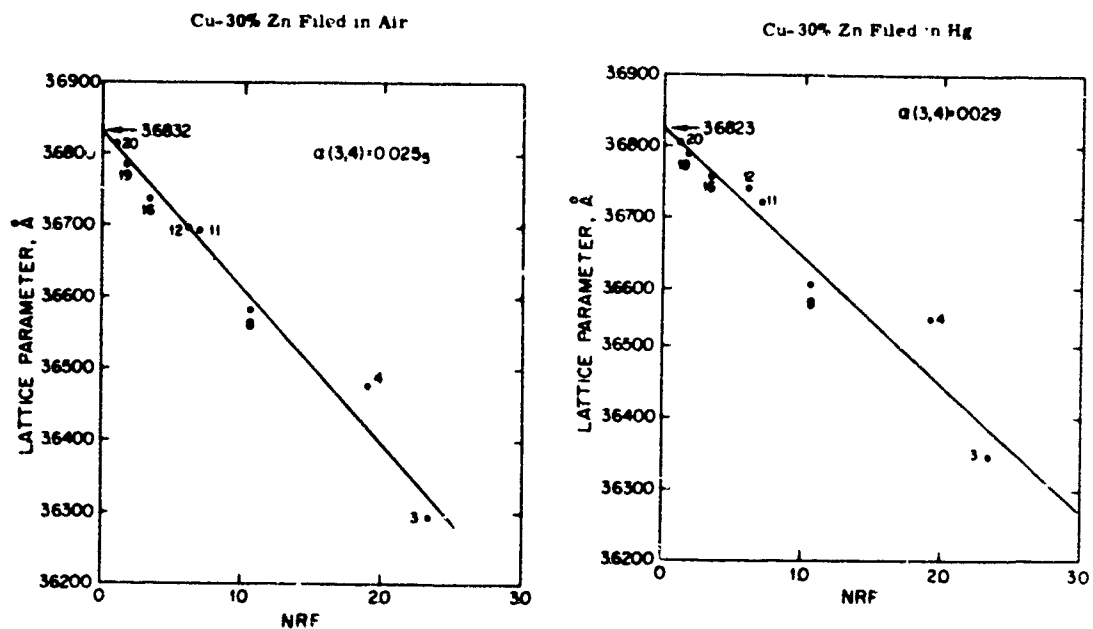


(a)

(b)

$$\text{NRF} = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$
 is the extrapolation function; θ is the Bragg angle

$\alpha(3,4)$ = Stacking fault probability obtained from the change in separation of lines 3 and 4



(c)

(d)

Figure 9. Effect of Filing Under Mercury at Room Temperature Instead of in Air on Lattice Parameters of Aluminum (99.99 Percent Pure) and Alpha-Brass (Cu-30% Zn)

TABLE IV

Lattice Parameters of Specimens
Filed in Air and in Mercury

Specimen	Filed in Air		Filed in Hg		$\Delta a_o (\text{\AA}) = \Delta a_o (\text{Hg}) - \Delta a_o (\text{Air})$ $\Delta c_o (\text{\AA}) = \Delta c_o (\text{Hg}) - \Delta c_o (\text{Air})$
	$a_o (\text{\AA})$	$\delta(1) = \pm \text{\AA}$	$a_o (\text{\AA})$	$\delta(1) = \pm \text{\AA}$	
Aluminum	4.0492 ₅	0.00005	4.0489 ₀	0.0002 ₀	-0.0003 ₅
Cu-30% Zn	3.6832 ₀	0.00005	3.6823 ₀	0.0005 ₀	-0.0009 ₀
Zinc	$\delta(2) = \pm \text{\AA}$		$\delta(2) = \pm \text{\AA}$		$\Delta a_o = + 0.007_0$ $\Delta c_o = + 0.007_0$
	$a_o = 2.6650_7$ $c_o = 4.9467_2$	0.0002 ₅	$a_o = 2.6657_9$ $c_o = 4.9537_2$	0.009 ₁	

Notes:

 $\delta(1)$ represents estimated reproducibility of measurements. $\delta(2)$ represents the minimum average deviation obtained by a least squares fit of lattice parameter values, plotted against the Nelson-Riley extrapolation function.

zinc; this could also apply to the other two cases where a decrease in lattice parameter was obtained. Further investigation will be necessary to verify this possibility.

III. CONCLUSIONS

From the above results and discussion, the following preliminary conclusions may be drawn:

- 1 Propensity to embrittlement in aluminum-copper alloys exposed to a liquid metal can be heightened by increasing, through appropriate heat treatment and aging, the density of stress concentration regions associated with precipitates.
- 2 Transcrystalline cracking in the aluminum-copper alloys exposed to mercury suggests that grain boundaries probably play a secondary role in liquid metal embrittlement, although failure can also occur along such boundaries, if present.
- 3 Stacking faults and dislocation networks in the stressed α -brass specimens exposed to mercury probably render the material more susceptible to embrittlement.
- 4 The liquid metal atoms may affect the lattice parameters of the embrittled host metal, but the interaction is not fully understood.

IV. ACKNOWLEDGEMENTS

The authors have benefited greatly from stimulating discussions with Dr. S. Amelinckx of the Nuclear Research Center, Belgium.

REFERENCES

1. Rhines, F. N., Alexander, J. A., and Barclay, W. F., "Transactions of the ASM," Volume 55, pp 22-44, 1962
2. Stoloff, N. S., and Johnston, T. L., "Acta Metallurgica, Volume II, pp 251-256, 1963
3. Thomas, G., "Transmission Electron Microscopy," John Wiley and Sons, New York, 1962
4. Rosenberg, R. and I. Cadoff, "Fracture of Solids," Volume 20, pp 607-636, 1963
5. Rostoker, W., McCaughey, J. M., and Markus, H., "Embrittlement by Liquid Metals," Reinhold Publishing Corporation, New York, 1960
6. Cottrell, A. H., "Transactions of AIME," Volume 212, pp 192-203, 1958
7. Doherty, R. D., and Martin, J. W., "Third European Regional Conference on Electron Microscopy," Czechoslovak Academy of Sciences, Prague, pp 141-142, 1964
8. Levine, E., and Cadoff, I., "Transactions of the Metallurgical Society AIME," Volume 230, pp 1113-1115, 1964
9. Levine, E., and Cadoff, I., "Transactions of the Metallurgical Society AIME," Volume 230, pp 1116-1119, 1964
10. Tromans, D., and Nutting, J., "Fracture of Solids," Volume 20, pp 637-655, 1963
11. Cottrell, A. H., in "Fracture," B. L. Averbach, D. K. Felbeck, G. T. Hahn, and D. A. Thomas, ed., John Wiley and Sons, Inc., New York, pp 20-24, 1959
12. Gilman, J. J., in "Fracture," pp 193-221, 1959
13. Nichols, H., and Rostoker, W., "Acta Metallurgica," Volume 9, pp 504-509, 1961
14. Nelson, J. B., and Riley, D. P., "Proceedings of the Physical Society" (London,) Volume 57, pp 160, 1945
15. Otte, H. M., and Esquivel, A. L., "Program and Abstracts of the American Crystallographic Association," pp 27-28, July 1964

DISTRIBUTION LIST

1. Technical Supervisor (2 copies and one reproducible)
Dr. Coy M. Glass, Chief
Metallurgy Section
Ballistic Research Laboratories
Aberdeen Proving Ground
Aberdeen, Maryland
2. Contracting Officer (1 copy)
Birmingham Procurement District
U. S. Army
Orlando Branch Office
P. O. Box 5837
Orlando, Florida
Attn: Mr. John R. Lemna, Chief Operations Branch
3. Commander (10 copies)
Defense Documentation Center
Cameron Station
Alexandria, Virginia
Attn: TIPDR
4. Commanding Officer (1 copy)
Diamond Ordnance Fuze Laboratory
Washington 25, D. C.
Attn: Technical Reference Section, ORDTL 06.33
5. Defense Metals Information Center (DMIC) (1 copy)
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio

OR 6317	Martin Company, Orlando Division EXPERIMENTAL AND THEORETICAL ASPECTS OF LIQUID METAL EMBRITTLEMENT December 1964 Contract No. DA-36-034-AMC-0205R 39 p. UNCLASSIFIED REPORT This report describes the investigation of the premature failure of a solid metal wetted with a liquid metal and stressed below or slightly above its normal yield point. Conclusions are: 1) Propensity to embrittlement by a liquid metal can be heightened by increasing the density of stress concentration regions in the host metal; 2) Grain boundaries probably play a secondary role in liquid metal embrittlement; 3) Stacking faults and dislocation networks render the material more susceptible to embrittlement; and 4) Liquid metal atoms may affect the lattice parameters of the host metal.	UNCLASSIFIED	1. Embrittlement 2. Liquid Metals 3. Electron Microscopy I. Contract Number DA-36-034-AMC-0205R II. Project No. AJ-4-A0439-01-AJ-AD III. Esquivel, A. L.	UNCLASSIFIED	1. Embrittlement 2. Liquid Metals 3. Electron Microscopy I. Contract Number DA-36-034-AMC-0205R II. Project No. AJ-4-A0439-01-AJ-AD III. Esquivel, A. L.
OR 6317	Martin Company, Orlando Division EXPERIMENTAL AND THEORETICAL ASPECTS OF LIQUID METAL EMBRITTLEMENT December 1964 Contract No. DA-36-034-AMC-0205R 39 p. UNCLASSIFIED REPORT This report describes the investigation of the premature failure of a solid metal wetted with a liquid metal and stressed below or slightly above its normal yield point. Conclusions are: 1) Propensity to embrittlement by a liquid metal can be heightened by increasing the density of stress concentration regions in the host metal; 2) Grain boundaries probably play a secondary role in liquid metal embrittlement; 3) Stacking faults and dislocation networks render the material more susceptible to embrittlement; and 4) Liquid metal atoms may affect the lattice parameters of the host metal.	UNCLASSIFIED	1. Embrittlement 2. Liquid Metals 3. Electron Microscopy I. Contract Number DA-36-034-AMC-0205R II. Project No. AJ-4-A0439-01-AJ-AD III. Esquivel, A. L.	UNCLASSIFIED	1. Embrittlement 2. Liquid Metals 3. Electron Microscopy I. Contract Number DA-36-034-AMC-0205R II. Project No. AJ-4-A0439-01-AJ-AD III. Esquivel, A. L.