

27
664299
DP(NASA) - 961

STRESS CORROSION CRACKING OF TITANIUM ALLOYS

PROGRESS REPORT: OCTOBER 1 - DECEMBER 31, 1964

S. P. Rideout, M. R. Louthan, Jr., and C. L. Selby

RECORD
COPY

DO NOT RELEASE
FROM FILE



ISSUED BY

Savannah River Laboratory

Aiken, South Carolina

UNCLASSIFIED

664299

DP(NASA)-961
Special Distribution

STRESS CORROSION CRACKING OF TITANIUM ALLOYS
PROGRESS REPORT: OCTOBER 1 - DECEMBER 31, 1964

by

Sheldon P. Rideout
McIntyre R. Louthan, Jr.
Clifford L. Selby

Approved by

P. H. Permar, Research Manager
Nuclear Materials Division

March 1965

Prepared for

National Aeronautics and Space Administration
Work performed under NASA Purchase Order No. R-124,
Issued to the United States Atomic Energy Commission

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA

CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

ABSTRACT

Results are described for the third quarter of research on the mechanism of hot-salt stress corrosion cracking of the Ti-8Al-1Mo-1V alloy.

Initiation of stress corrosion cracking by chemical, rather than mechanical action was indicated by corrosion of alpha-beta phase boundaries in polished, unstressed specimens exposed to NaCl at 650°F for one hour.

Very slow cooling from the annealing temperature (1450°F) increased susceptibility to stress corrosion cracking, possibly because of segregation of alloy or impurity elements.

"Self-stressed" samples cracked within 24 hours in anhydrous HCl gas at 650°F.

Tests with radiotracers ^{36}Cl and ^{22}Na showed that chloride ions are readily adsorbed on the alloy surface at room temperature and apparently are absorbed into the oxide on heating. Sodium was not adsorbed, and was retained only at spots where salt adhered due to salt-metal reaction.

Aluminum in the alloy appears to be selectively corroded during attack by NaCl at 650°F.

Chloride salts are not unique in causing cracking. Both sodium iodide and sodium bromide caused initiation of cracking within 3 days at 650°F.

Electron microscopy studies revealed that hydrogen was charged into the foils during thinning, resulting in precipitation of titanium hydride on the $\{10\bar{1}0\}$ planes. Hydride precipitation was particularly noticeable near grain and phase boundaries, suggesting a higher affinity for hydrogen in these regions.

CONTENTS

	<u>Page</u>
List of Tables and Figures	4
Introduction	5
Summary	5
Review	5
Summary of Third Quarter	6
Discussion	8
Procurement	8
Experimental Procedure	8
Experimental Results	9
Effects of Stress and Temperature on Cracking	9
Effect of Heat Treatment on Cracking	11
Role of Surface Oxide	13
Role of HCl Gas	13
Tests with Radiotracers ^{36}Cl and ^{22}Na	15
Identification of Corrosion Products	20
Cracking by NaI and NaBr	21
Role of Hydrogen	23
Electron Microscopy Studies	24
References	28

LIST OF TABLES AND FIGURES

<u>Table</u>		<u>Page</u>
I	Effects of Stress and Temperature on Hot-Salt Cracking	10
II	Comparison of Crack Propagation in Mill- and Duplex-Annealed Ti-8Al-1Mo-1V Alloy	11
III	Effect of Cooling Rate from 1450°F on Crack Propagation in Ti-8Al-1Mo-1V Alloy	12

<u>Figure</u>		
1	Corrosion Etching of Beta Phase Particles by NaCl Deposit on Unstressed Ti-8Al-1Mo-1V Exposed 3 Hours at 650°F	10
2	Distribution of ³⁶ Cl Activity (Counts per Minute) on Samples Exposed to Saturated NaCl Solution at Room Temperature for 15 Minutes	15
3	Ti-8Al-1Mo-1V Exposed to Na ³⁶ Cl for 3 Days at 650°F	17
4	Ti-8Al-1Mo-1V Exposed to ²² NaCl for 3 Days at 650°F	19
5	Microcrack in Ti-8Al-1Mo-1V Exposed to Na ³⁶ Cl 3 Days at 650°F	20
6	Hot-Salt Cracking of Ti-8Al-1Mo-1V Alloy by Various Halide Salts	22
7	Spotty Contrast in Titanium Foil Resulting from Titanium Hydride Precipitation	24
8	Series of Photomicrographs Showing Precipitation of Titanium Hydride on the (1010) Plane	26
9	Association of a Fine Precipitate with Dislocation	27
10	Precipitation of the Hydride Phase at Grain Boundaries and Alpha-Beta Interfaces	27

STRESS CORROSION CRACKING OF TITANIUM ALLOYS
PROGRESS REPORT: OCTOBER 1 - DECEMBER 31, 1964

INTRODUCTION

The Savannah River Laboratory is engaged in a program of NASA-sponsored research to develop fundamental knowledge about the mechanism of hot-salt stress corrosion cracking of titanium alloys. Emphasis is being placed on study of the Ti-8Al-1Mo-1V alloy because it is a prime candidate as a structural material for the proposed supersonic transport (SST). This alloy is known to be susceptible to hot-salt cracking in laboratory tests under conditions that may occur during SST operation; i.e., skin temperature in the range of 550-650°F with sea salt contamination acquired during transoceanic operations.

Knowledge and techniques developed by SRL during studies of stress corrosion cracking of stainless and carbon steels are being used in this research. In particular, radiotracers such as ^{36}Cl , ^{22}Na , and ^3H are being used to investigate the role of these elements in the stress corrosion cracking phenomenon. Electron microscopy techniques are being used to study crack morphology and to determine the effects of heat treatment and alloy structure on cracking.

This research was started April 1, 1964, and this third quarterly progress report covers the period October 1 - December 31, 1964. Some incomplete or unconfirmed data may be included in these progress reports.

SUMMARY

REVIEW

Results reported prior to this period are summarized below for convenience.^(1,2)

Tests demonstrated that HCl gas is given off during dehydration of sea salt at 650°F. This raised the possibility that HCl gas and/or resultant hydroxides in the salt deposit are involved in initiating stress corrosion. Tests comparing the degree of cracking caused by each of the four principal salts in sea salt (NaCl, KCl, MgCl₂, and CaCl₂) showed that NaCl and KCl produced severe cracking during two weeks exposure at 650°F, while MgCl₂ and CaCl₂ produced only a few tiny cracks. It was suggested that this difference might be related to the fact that sodium and potassium form strong reactive hydroxides while magnesium and calcium form stable, less reactive hydroxides.

In metallographically polished samples having an extremely thin oxide film (stressed to yield), both sea salt and pure sodium chloride caused cracks to initiate within 3 to 5 hours at 650°F. A thick oxide film delayed crack initiation. Spark-source mass spectrometer analyses gave qualitative evidence that the oxide film on Ti-8Al-1Mo-1V alloy contains a higher ratio of aluminum to titanium than the base metal.

Cracks propagated along alpha grain boundaries and alpha-beta phase boundaries. Beta phase particles appeared to be unattacked during stress corrosion cracking.

Electron microscopy comparing the inner surface of a stress corrosion crack (produced at 1200°F) with a fracture surface produced by mechanical rupture indicated that stress corrosion cracking occurred primarily by chemical attack. Structural details of the alloy matrix and beta particles were visible on the stress corrosion surface, whereas the mechanically ruptured surface appeared to have formed by ductile mechanisms with no preference for rupture along beta-phase boundaries.

Thin foils of Ti-8Al-1Mo-1V alloy suitable for electron transmission microscopy were prepared and studies of fine structure were begun.

SUMMARY OF THIRD QUARTER

Corrosion of alpha-beta phase boundaries initiated within one hour on polished, unstressed Ti-8Al-1Mo-1V samples exposed to NaCl at 650°F, which indicates that stress corrosion cracking initiates primarily by chemical corrosion rather than mechanical means.

Stress corrosion cracks propagated faster in samples cooled very slowly from the annealing temperature of 1450°F than in samples cooled very rapidly. Very slow cooling should promote segregation to grain boundaries. The rapid cracking of slow-cooled samples suggests that segregation of alloy or impurity elements along grain boundaries may increase susceptibility to cracking.

HCl gas was given off from pure NaCl and titanium alloy chips coated with NaCl heated at 650°F, but the amount was considerably less than in previous tests with sea salt. The greater amount of HCl gas given off from sea salt was probably due to the presence of water of hydration in components of sea salt such as $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot xH_2O$. "Self-stressed" samples of Ti-8Al-1Mo-1V alloy heated at 650°F in an atmosphere of anhydrous HCl gas (no salt) cracked to complete rupture within 24 hours.

Tests with radiotracer ^{36}Cl demonstrated that chloride ions from saturated Na^{36}Cl solutions were very readily adsorbed on unstressed, polished samples of titanium alloy exposed only 15 minutes at room temperature. The chloride ions were fairly evenly distributed in the area of initial contact and could not be rinsed off with hot water. On samples heated at 250 and 650°F to produce deposits of solid salt, chloride ions were absorbed into the oxide film. Similar tests with radiotracer ^{22}Na showed that significant amounts of sodium were retained only on heated samples at spots where solid NaCl adhered to the metal because of the salt-metal corrosion reaction. Attempts to show chloride or sodium concentrations in cracks by autoradiography were unsuccessful.

Evidence of selective corrosion of aluminum during attack by NaCl was observed by analysis of pure water used to wash salt-corroded areas of samples exposed 2 weeks at 650°F. The ratio of aluminum to titanium in the wash water was as great as 0.5 whereas the ratio in the base metal is only 0.089. This is consistent with the previous report of aluminum enrichment in the oxide film, and indicates that preferential attack of aluminum in the alloy may be involved in stress corrosion cracking.

Tests during this quarter demonstrated that chloride salt is not unique in causing stress corrosion cracking of titanium alloys. Deposits of NaI and NaBr both produced cracking, but to a lesser extent than NaCl .

Electron microscopy studies revealed that spotty contrast in some areas of transmission micrographs is due to precipitation of titanium hydride which is induced by absorption of hydrogen in the foils during thinning. A thinning procedure recommended by Boeing will be used in future work.

The habit plane of the hydride was shown to be the $\{10\bar{1}0\}$ plane. The hydride precipitate appeared to be concentrated along alpha grain and beta-phase boundaries, suggesting that diffusion of hydrogen into the metal occurs preferentially along these boundaries. This may be related to the cracking phenomenon.

DISCUSSION

PROCUREMENT

Additional quantities of ^{36}Cl (as HCl solution) and ^{22}Na (as NaCl in HCl solution) were purchased for preparation of saturated solutions of NaCl (pH 5 to 7) having higher specific radioactivity than solutions used previously. Higher activities were needed to facilitate use of autoradiography for determining the distribution of Cl and Na with respect to cracks in salt-corroded areas. Specific radioactivities of old and new solutions are shown below.

Solution	Specific Radioactivity, disintegrations per minute per ml	
	$^{22}\text{NaCl}$	Na^{36}Cl
Old	9.14×10^7	0.87×10^7
New	16.7×10^7	9.97×10^7

Pure water containing approximately 1 curie of ^3H (tritium) activity was also purchased for experiments to investigate the role of hydrogen in stress corrosion.

EXPERIMENTAL PROCEDURE

Three different types of samples were used during this quarter in studies of the cracking phenomenon. The type used in each specific test is stated in the discussion, and the designations and descriptions are given below.

Designation	Description
Four-point loaded	Strips $3/4$ inch by 3 inches mounted in four-point loading holders. Stress level calculated using beam deflection formula.
Three-point loaded	Strips 0.45 inch by 1.40 inches mounted in three-point loading holder. Stressed to produce plastic deformation and maintain samples at the yield point during exposures.
Self-stressed ^(a)	Two strips $1/4$ inch by 4 inches bent to angle of 25° , $3/4$ inch from each end; strips spot welded together at both ends such that the strips bow away from each other in the center portion.

Except where noted, all samples were metallographically polished on the surface bearing the salt deposit. Two different heats of Ti-8Al-1Mo-1V alloy were used: one initially mill-annealed sheet 0.030 inch thick, and one initially duplex-annealed sheet 0.050 inch thick. Heat analyses were given in a previous report.⁽²⁾

Salt deposits were applied as droplets of a saturated neutral solution. Pure sodium chloride solutions with and without radiotracers ^{36}Cl and ^{22}Na were used in most cases instead of sea salt in order to simplify the investigation of corrosion reactions and products. Solutions of NaI and NaBr were used in tests to determine the effect of anion species on stress corrosion.

Radiation counting and autoradiography were used to study the retention of radiotracers ^{36}Cl and ^{22}Na after various stages of exposure to saturated salt solutions.

EXPERIMENTAL RESULTS

Effects of Stress and Temperature on Cracking

In the investigation of the mechanism of stress corrosion cracking, it is important to establish the relative influence of localized corrosion and tensile stress on the initiation and propagation of cracks. If cracks propagate along paths that are preferentially corroded in the absence of stress, corrosion usually plays the dominant role in the cracking phenomenon. Alternatively, when corrosion is minimal, oxide film rupture by stress may be required to initiate and sustain cracking.

In order to determine if hot-salt corrosion of Ti-8Al-1Mo-1V alloys occurs in the absence of applied stress, polished and unstressed strips of mill-annealed alloy were exposed with NaCl deposits at 650°F for periods of 1 to 4 hours. Microscopic examination after removal of the salt showed that corrosion had started within 1 hour, and corrosion etching of beta-phase boundaries was evident. This is illustrated in Figure 1. This observation combined with a previous one⁽²⁾ that cracks in stressed samples were not detected until 3 to 5 hours exposure is evidence that corrosion initiates cracking; or conversely, that oxide film rupture by stress is not an essential part of crack initiation.

An apparent threshold temperature of 550°F for hot-salt cracking of titanium alloys has been reported.⁽⁴⁾ During this quarter an investigation of the effects of temperature and stress level on initiation of cracking was begun. Four-point loaded samples with NaCl deposits were exposed at various stress levels at temperatures of 400, 550, and 650°F. Results are summarized in Table I. These tests are continuing. The threshold stress and temperature for initiation of cracking will be determined by microscopic examination of samples exposed with polished surfaces.



FIG. 1 CORROSION ETCHING OF BETA PHASE PARTICLES BY NaCl DEPOSIT ON UNSTRESSED Ti-8Al-1Mo-1V EXPOSED 3 HOURS AT 650°F. (Dark Field Illumination, 750X)

TABLE I

Effects of Stress and Temperature on Hot-Salt Cracking

Temperature, °F	Stress, psi ^(a)	Exposure Time, weeks	Cracks
400	75,000	3	No
	50,000	4	No
550	50,000	3	Yes
	75,000	2	Yes
	100,000	2	Yes
650	25,000	1	No
	50,000	1	Yes
	75,000	1	Yes
	100,000	1	Yes

(a) Calculated at room temperature

Effect of Heat Treatment on Cracking

Studies of the effect of heat treatment on susceptibility to cracking have been complicated somewhat by erratic results. In one previous test⁽²⁾, a maximum crack depth of 0.022 inch was observed in a four-point loaded sample of duplex-annealed material after 14 days at 650°F. This result was not duplicated during this quarter in tests comparing crack propagation in duplex- versus mill-annealed alloys. The results of this comparison are presented in Table II. The maximum crack depth observed in duplex-annealed material was 0.007 inch after 14 days. This particular series of tests shows no significant difference between duplex- and mill-annealed materials.

TABLE II

Comparison of Crack Propagation in Mill-
and Duplex-Annealed Ti-8Al-1Mo-1V Alloy

Heat Treatment (a)	Sheet Thickness, inch	Crack Depth, inch				
		Days Exposure at 650°F				
		.3	1	3	7	14
Mill-annealed	.050	.0011	.0015	.0050	.0098	.0076
Duplex-annealed	.050	.0015	.0017	.0037	.0038	.0070
Duplex-annealed	.030	.0015	.0020	.0025	.0040	.0050

(a) Standard mill-anneal: 8 hours at 1450°F followed by
furnace cool

Standard duplex-anneal: Same as mill-annealed plus 1/4 hour
at 1950°F followed by air cool

The propagation of stress corrosion cracks appears to be influenced by the manner in which the salt deposit spreads over the surface during application. When the deposit spreads over a relatively large area, cracking is usually more severe than when the deposit covers a smaller area. This is probably related to the fact that cracking occurs primarily at the edges of the deposit. In order for a crack to propagate in depth, it must also propagate along the surface. Surface propagation apparently is hindered when the salt has not spread over a large area. The technique of applying the salt deposit to give uniform and reproducible spreading is being perfected. This should eliminate some of the variance and permit a more definitive study of the effects of heat treatment on crack propagation.

Some evidence that crack propagation is influenced by heat treatment was obtained in other tests in spite of the uncertainties described above. The tests indicated that material rapidly quenched from 1450°F is more resistant to cracking than furnace-cooled materials. Samples of initially duplex-annealed sheet (0.050 inch thick) were heated at 1450°F for 1 hour and cooled in various ways. Strips were polished, stressed in a three-point loading holder, salted, and exposed at 650°F for 24 and 72 hours. Crack depths observed for each method of cooling are given in Table III.

TABLE III

Effect of Cooling Rate from 1450°F
on Crack Propagation in Ti-8Al-1Mo-1V Alloy

Method of Cooling(a)	Crack Depth, inch	
	Hours Exposure at 650°F	
	24	72
Quenched in acetone - dry ice -80°C	.002	.003 .004
Quenched in liquid nitrogen -195°C	.002	.004 .004
Air blast	.003	.006 .007
Static air	.003	.006 .008
Furnace cooled 1450°F to room temp in 4 to 6 hr	.005	.010
Furnace cooled 1450°F to room temp in ~16 hr	-	.050 ^(b)

(a) Initially duplex-annealed sheet .050 inch thick,
heated 1 hr at 1450°F

(b) Complete rupture

After 72 hours exposure, crack depths in quenched and air-cooled material are comparable to data from other tests on standard mill- and duplex-annealed alloys (Table II this report and Figure 2 in Ref. 2). However, in furnace-cooled material, crack propagation was considerably faster; complete fracture occurred in the sample cooled from 1450°F to

room temperature in 16 hours. These observations may be especially significant to the mechanism of cracking. Cracking along alpha grain and alpha-beta phase boundaries may be caused by segregation of certain alloy or impurity elements along these boundaries, and very slow cooling would be expected to promote such segregation. No differences in the structures of samples cooled at different rates have been observed to date by either optical or electron microscopy, however. Studies of the effects of heat treatment are continuing, and electron transmission microscopy of thin foils will be used to search for structural differences.

Role of Surface Oxide

An oxide film produced either by heating in air or by anodizing Ti-8Al-1Mo-1V alloy reduces susceptibility to hot-salt stress corrosion cracking.⁽²⁻⁵⁾ The investigation of the effect of oxide film composition on cracking, which was begun last quarter, was not continued during this quarter. Analyses of the oxide are very difficult because the films are extremely thin. Results obtained with the spark-source mass spectrometer are only qualitative because the oxide is diluted with base metals due to penetration of the spark. Methods of overcoming this difficulty are being explored. The possibility of using an electron microprobe for film analysis is also being considered.

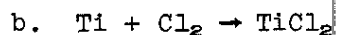
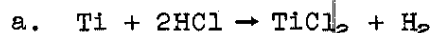
Role of HCl Gas

Previous tests⁽²⁾ demonstrated that HCl gas is given off during dehydration of sea salt heated at 650°F either alone or as salt-coated chips of titanium alloy. Similar tests were performed during this quarter to compare the release of HCl gas from pure sodium chloride, because the pure salt is equally effective in producing cracks.

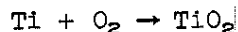
The amount of HCl gas given off in tests using NaCl alone and as salt-coated metal chips was considerably less than in previous tests with sea salt. The maximum rate of chloride ion accumulation in the water trap in tests with sea salt on metal chips was about 1200 parts per million per hour, whereas the rate was only about 260 parts per billion per hour with pure sodium chloride on metal chips. The results are reliable even though the level of chloride was extremely low in the case of pure sodium chloride on metal chips. The analytical method used is capable of determining chloride ion concentrations as low as 10 parts per billion. The significance of the results is that there must be some moisture present either on the metal or NaCl to produce HCl. The greater amount of HCl released from sea salt probably is due to the presence of extra water of hydration in some of the chlorides, such as $MgCl_2 \cdot 6H_2O$ or $CaCl_2 \cdot xH_2O$.

In order to determine if HCl gas alone can cause cracking, two self-stressed samples of the type used by Braski and Heimerl⁽³⁾ were encapsulated in anhydrous HCl gas such that the gas pressure was about 1 atmosphere at 650°F. The stress level was calculated to be 100,000 psi at room temperature and therefore would be at the yield point of 650°F. No salt was used. Both samples cracked to complete failure within 24 hours exposure. The ruptures occurred at the ends of the samples near the spot welds and between the straight and bent portions where the metal had been cold worked during sample fabrication. Braski⁽⁵⁾ reported failures at the same place in similar samples exposed to moist chlorine gas. Cracking of U-bend samples in air containing 1% chlorine gas was also reported by Cox.⁽⁶⁾ It is possible that in the tests performed by both Braski and Cox some HCl gas was formed by reaction of the chlorine with moisture in the air.

Reaction of either HCl or chlorine gas with titanium is possible, as follows:



However, for either of these reactions to occur the oxide film must be mechanically ruptured or the Cl_2 or Cl^- must penetrate the film. The oxide film probably is ruptured on a sample stressed to the yield point at 650°F, but when oxygen is present in the atmosphere the film may tend to repair itself by the reaction



If this reaction fails to heal the film, corrosion of the base metal will continue as long as Cl_2 or HCl are available.

The fact that a thick oxide film retards the initiation of cracking but does not prevent it entirely is strong evidence that diffusion of the reactant through the oxide film does occur. In this situation, where the protective oxide film is not ruptured, it seems likely that chloride ions would penetrate the film more readily than chlorine atoms or molecules. Even though the chloride ion is larger than the atom, the mobility of the ion in an oxide should be much greater. Evidence that chloride ions are readily absorbed into the oxide film on Ti-8Al-1Mo-1V alloy was obtained in experiments with radiotracers ^{36}Cl in sodium chloride, as described in the following section.

Tests with Radiotracers ^{36}Cl and ^{22}Na

Radiotracers ^{36}Cl and ^{22}Na were used separately in saturated solutions of NaCl (pH 5-7) to study salt corrosion reactions under various exposure conditions. The presence and distribution of the radiotracers was determined by radiation counting and microautoradiography.

The tests demonstrated that chloride ions were very readily adsorbed on the surface of samples at room temperature and could not be washed off. On samples heated at 250 and 650°F, the chloride ions were apparently absorbed into the oxide film. The chloride ions were distributed fairly uniformly in the area of initial contact. Significant amounts of sodium were retained only on heated samples at spots where solid NaCl adhered to the metal or where salt-metal corrosion occurred. Attempts to show chloride or sodium concentrations in cracks by autoradiography were unsuccessful. Results are discussed in detail below.

Saturated solutions of $^{22}\text{NaCl}$ and Na^{36}Cl with high specific radioactivities were deposited as droplets on unstressed strips of duplex-annealed alloy, some of which had mill-finished oxide surfaces degreased only and some of which were metallographically polished. On both polished and oxide-coated samples, a substantial concentration of chloride ion was retained on the surfaces when the solution was washed off after only 15 minutes exposure at room temperature. The distribution of the chloride as determined by scanning the surface with a radiation counter is shown in Figure 2. The radioactivity on these samples represented about 24 to 27 micrograms of total chloride ions ($^{36}\text{Cl} + ^{35}\text{Cl}$) retained on each sample (1 count per minute = 15×10^{-9} gram total chloride ion). Similar tests using $^{22}\text{NaCl}$ solution to determine sodium retention gave such low count rates that it was not possible to show definitely that even a trace of sodium remained on the surface.

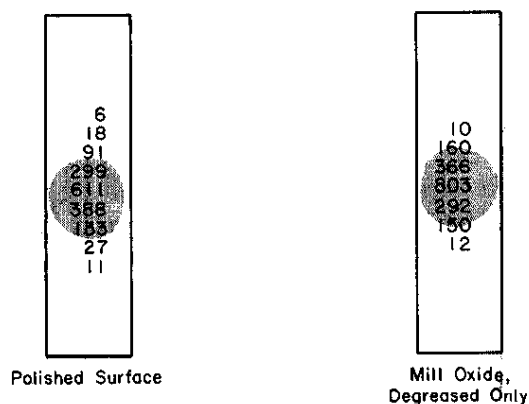


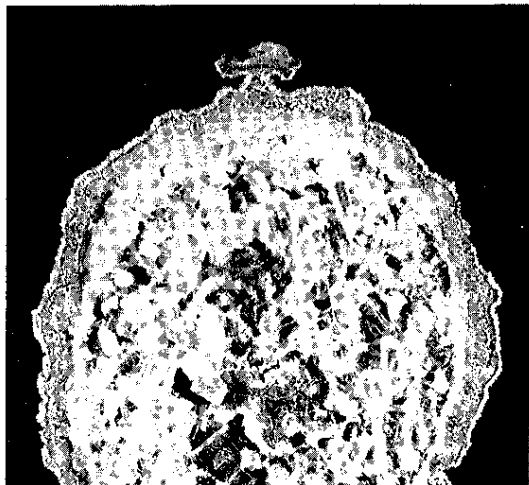
FIG. 2 DISTRIBUTION OF ^{36}Cl ACTIVITY (COUNTS PER MINUTE) ON SAMPLES EXPOSED TO SATURATED NaCl SOLUTION AT ROOM TEMPERATURE FOR 15 MINUTES. Drops of the solution were applied (shaded areas) and then washed off with hot water prior to counting.

An additional test was performed to determine the retention of chloride and sodium ions on polished, unstressed samples on which the salt solutions were evaporated to produce solid salt deposits. One sample was exposed to Na^{36}Cl and one to $^{22}\text{NaCl}$. The test sequence and results were as follows:

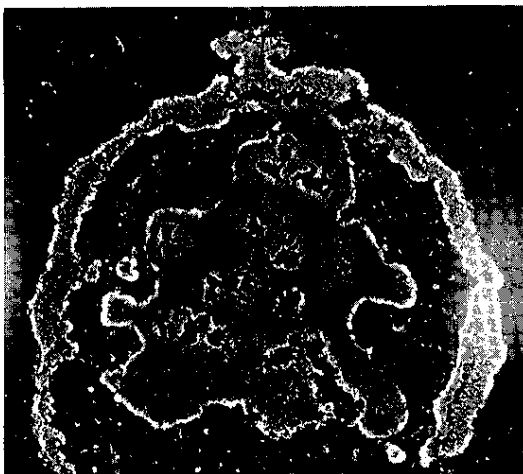
Sample Treatment	Radioactivity Detected, counts/min from area $3/16 \times 3/4$ "	
	^{36}Cl (± 7 counts/min)	^{22}Na (± 3 counts/min)
Salt deposited by evaporation at 250°F for 40 minutes, then removed by hot water rinse	665	27
One additional hot water rinse	632	24
Sample stored at room temperature for 2.5 days, no further rinse	523	28
Sample heated at 650°F for 5 hours, cooled, and rinsed in hot water	464	31

In this test, a detectable amount of sodium was retained on the sample. In the small area counted ($3/16" \times 3/4"$), the ^{22}Na activity represented about 0.14 microgram sodium (1 count per minute = 5×10^{-9} gram total Na). The amount of chloride indicated in the equivalent area was about 7 to 10 micrograms (1 count per minute = 15×10^{-9} gram total Cl^-). The apparent reduction of ^{36}Cl radioactivity during storage at room temperature and subsequent heating to 650°F may be due to partial shielding by the oxide film as it thickens or as the chloride diffuses into it, or to loss by effusion of volatile chloride compounds.

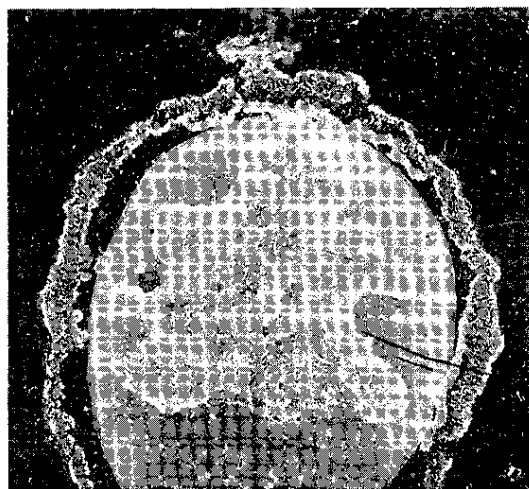
Autoradiography was used to determine the distribution of ^{36}Cl and ^{22}Na on prepolished and stressed samples exposed with salt deposits at 650°F for 3 days. The salt deposits were produced by evaporating drops of saturated solution on the sample surfaces. After exposures the salt deposits were rinsed off and the samples were coated with a liquid photographic emulsion sensitive to beta radiation. The emulsions were dried, exposed, and developed in situ. Figure 3 illustrates this sequence on a sample exposed to Na^{36}Cl . The area covered by the salt deposit before and after the salt was rinsed off is shown in Figures 3a and 3b, respectively. During evaporation of the saturated solution, a fringe of fine crystals formed around the circumference of the deposit as a result of efflorescence. As shown in Figure 3a, the final deposit contained a wide range of crystal sizes. Figure 3b shows some Na^{36}Cl



a. Salt before rinsing (4X)



b. After rinsing (4X)



c. Autoradiograph in situ (4X)



d. High magnification view of
autoradiograph with emulsion
partially removed to reveal metal
surface. (200X)

Emulsion
removed

FIG. 3 Ti-8Al-1Mo-1V EXPOSED TO Na^{36}Cl FOR 3 DAYS AT 650°F.
Note nonuniform salt attack in Figure b, and distribution of chloride ions in auto-
radiograph (c and d).

(confirmed by X-ray diffraction) adhering to the surface in a non-uniform pattern after the deposit was rinsed off. This is indicative of a salt-metal reaction in these areas. Over much of the area covered by the deposit there was no evidence of reaction, probably because the salt bridged over during crystallization. Figure 3c shows the sample with the autoradiographic emulsion developed in situ after a 7-day emulsion exposure. (Because of the lighting used in this photograph, the areas darkened by the radiotracer ^{36}Cl appear as light areas.) In addition to the obvious pattern due to residual Na^{36}Cl , the autoradiograph shows a uniform distribution of chloride ions in the area of original contact between the metal and the drop of saturated solution, even in those areas where no visible reaction occurred. However, the chloride ions were not uniformly distributed in the outer fringe of the deposit formed by efflorescence. This indicates that the chloride ions were absorbed into the surface oxide film when they were present as free ions in solution. Figure 3d shows a higher magnification of the autoradiography in an area where the emulsion was partially removed to reveal the underlying metal surface (area at lower right of Figure 3c). Darkening of the emulsion due to uniformly absorbed chloride ions in an area where no visible reaction with the metal occurred is shown at the left, and intense darkening due to Na^{36}Cl adhering at spots of salt-metal reaction are shown at the right. Figure 3d also shows that emulsion darkening was not entirely uniform on a microscale in areas of no reaction. This may be because of discontinuities in the thin film of emulsion. Further study should clarify this point.

Autoradiographs of samples exposed to $^{22}\text{NaCl}$ showed that sodium was present only in those spots where NaCl adhered to the surface, as shown in Figure 4.

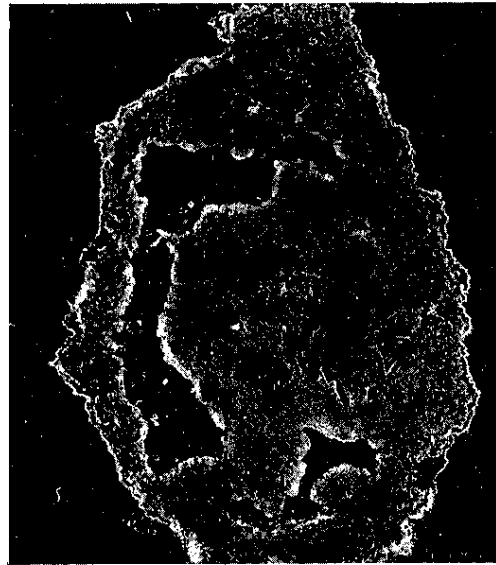
No evidence of chloride or sodium ion concentrations at crack sites has been observed in autoradiographs to date. However, all of the cracks examined have been quite small. An example is illustrated in Figure 5, which shows the same area on a sample exposed to Na^{36}Cl before and after autoradiography. The autoradiographic emulsion in this case was very thin and was developed after 1 day of emulsion exposure so that the tiny cracks (arrows in Figure 5) would be visible. Some darkening of the emulsion occurred, but no intensified darkening at the cracks. Samples with larger cracks are being prepared for further autoradiographic studies.



a. Salt before rinsing

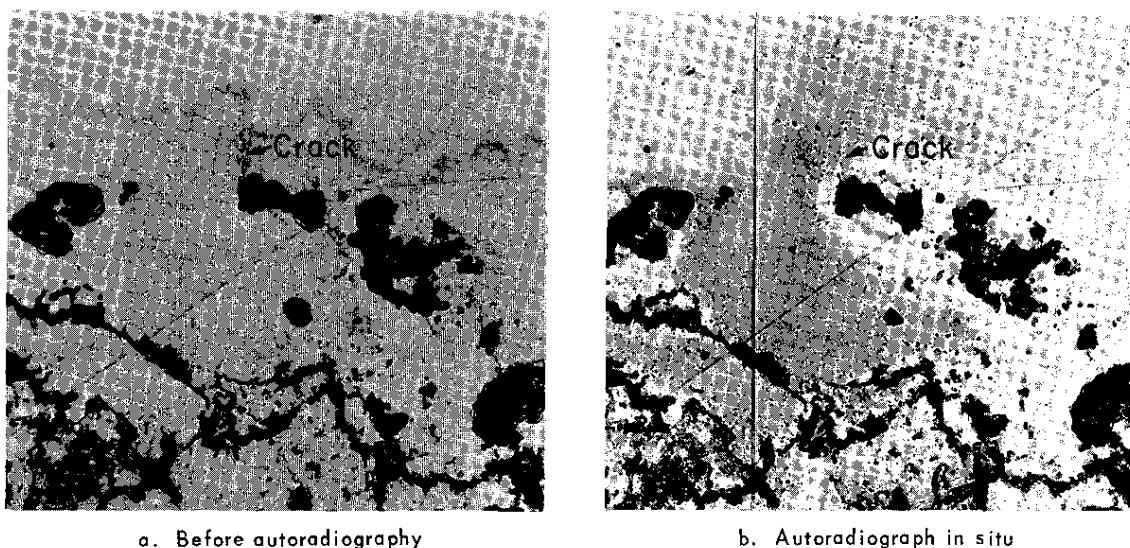


b. After rinsing



c. Autoradiograph in situ

FIG. 4 Ti-8Al-1Mo-1V EXPOSED TO $^{22}\text{NaCl}$ FOR 3 DAYS AT 650°F.
 Autoradiographic emulsion (c) was exposed 7 days. ^{22}Na was present only where
 residual $^{22}\text{NaCl}$ adhered. (4X)



a. Before autoradiography

b. Autoradiograph in situ

FIG. 5 MICROCRACK IN Ti-8Al-1Mo-1V EXPOSED TO Na^{36}Cl 3 DAYS AT 650°F . Emulsion exposed only one day. No preferential darkening of emulsion around crack. (150X)

Identification of Corrosion Products

Attempts to identify corrosion products by X-ray diffraction have been unsuccessful. Diffraction patterns of material scraped from salt-exposed samples after excess salt was washed off have shown only NaCl. The program for future work includes hot-stage X-ray diffraction studies to attempt identification of products in situ.

The major products of salt corrosion on titanium alloys may be soluble in water. During this quarter, experiments were begun to determine if analyses of water used to wash salt-exposed samples would reveal the nature of corrosion products. Preliminary results provided evidence that selective corrosion of aluminum (and possibly vanadium) occurs during hot-salt attack on Ti-8Al-1Mo-1V alloy.

Two four-point-loaded samples with NaCl deposited on the polished surfaces were exposed 2 weeks at 650°F . After exposure the samples were washed with pure water which was saved for analysis. On one sample the loose salt was removed by tapping prior to washing, and on the other sample the entire salt deposit was washed off. The water samples were then evaporated and the residue was spectrographically analyzed. The residue was NaCl with traces of titanium, aluminum, and vanadium. The concentrations, expressed as parts per million of NaCl residue, were as follows:

Sample	Analysis, ppm in NaCl			
	Ti	Al	V	Mo
Entire salt deposit washed off	100	15	<5	Not detected
Loose salt removed by tapping prior to washing	1000	500	25	Not detected

In both cases the Al/Ti ratio was higher in the salt residue than in the base metal; i.e., salt-residue Al/Ti ratios of 0.15 and 0.5 versus Al/Ti ratio in base metal of 0.089.

The V/Ti ratio was 0.025 in the water which contained the least residual NaCl, and this ratio is also significantly greater than the base metal ratio of 0.011. These results are consistent with the previous report of aluminum enrichment in the oxide film.⁽²⁾ Preferential attack of aluminum in the alloy may be involved in stress corrosion cracking through the formation of aluminum chloride, aluminum oxychloride or other low-melting compounds. Vanadium forms unstable chlorides, the tetrachloride having a melting point of about -28°C. Data on the relative susceptibility to cracking of titanium alloys reported by Braski and Heimerl⁽³⁾ provide some evidence that cracking is influenced by aluminum content. Although these authors did not relate cracking to aluminum concentration, their data suggest that resistance to cracking increases with decreasing aluminum concentration. The alloys in order of increasing resistance to cracking at 550°F were

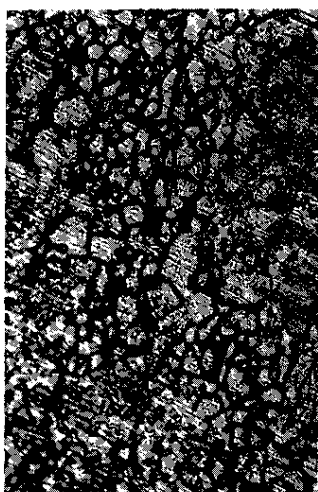
- a. Ti-8Al-1Mo-1V (most susceptible)
- b. Ti-6Al-4V (cracked at 100,000 psi)
- c. Ti-4Al-3Mo-1V (no cracking at 100,000 psi)

The alloy Ti-13V-11Cr-3Al cracked at 100,000 psi but was more resistant than Ti-6Al-4V and Ti-8Al-1Mo-1V alloys.

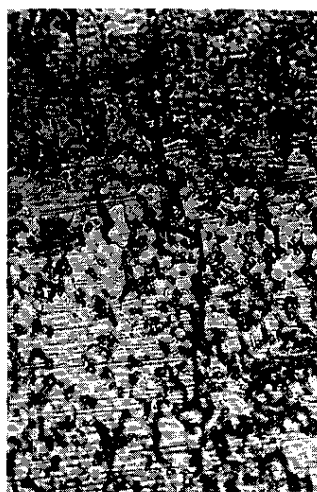
Studies of corrosion products are continuing.

Cracking by NaI and NaBr

Tests performed during this quarter demonstrated that NaCl is not unique in causing stress corrosion cracking of titanium alloys. Deposits of NaI and NaBr both produced cracking. Polished samples of duplex-annealed Ti-8Al-1Mo-1V alloy stressed in three-point loading jigs were exposed with deposits of NaI, NaBr, and NaCl for 3 days at 650°F. The samples were exposed in the same muffle furnace together with a control sample having no salt deposit. Metallographic examination of the surfaces after removal of the salts revealed intergranular cracking on all samples except the unsalted control. Cracking caused by the NaCl was most severe, as shown in Figure 6. Sectioning revealed crack depths as follows:



NaCl

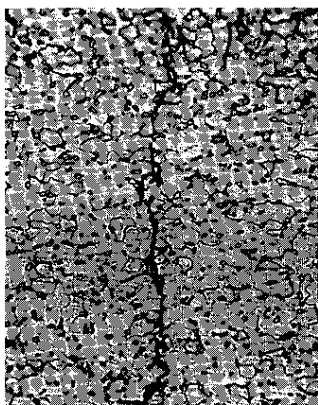


NaBr

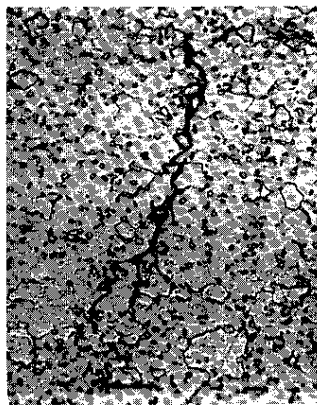


NaI

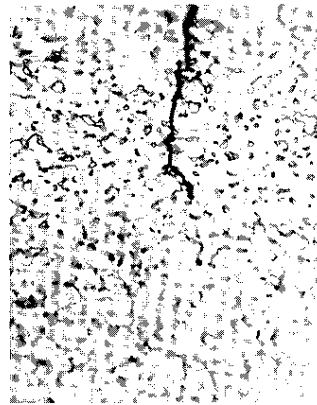
a. Surface view (salt removed from surface and specimens examined)



NaCl



NaBr



NaI

b. Transverse view (specimens sectioned, polished, and etched)

FIG. 6 HOT-SALT CRACKING OF Ti-8Al-1Mo-1V ALLOY BY VARIOUS HALIDE SALTS. Samples were exposed for 72 hours at 650°F. (425X)

<u>Salt</u>	<u>Crack Depth, inch</u> <u>(3-day exposure at 650°F)</u>
NaCl	.006
NaBr	.003
NaI	.003
None ^(a)	No cracks
<u>(a) Control sample</u>	

The absence of cracks in the control sample proves that gas-phase transport of chlorine from the NaCl did not cause the cracking observed on NaI and NaBr samples.

These results expand the list of chemical environmental factors known to cause stress corrosion cracking of titanium alloys. Any mechanism proposed to explain the phenomenon must account for these factors. The fact that cracking occurs in moist chlorine gas,⁽⁵⁾ in air with 1% chlorine gas,⁽⁶⁾ and in HCl gas (this report) demonstrates that the cation in salt deposits must not play a vital role in cracking. It is also possible that anions other than chloride, iodide, and bromide can cause cracking. Work is continuing to further define environmental factors that influence cracking.

Role of Hydrogen

Radiotracer ^3H (tritium) is being used in studies to determine if hydrogen is involved in stress corrosion cracking of titanium alloys. There are at least three possible ways that hydrogen could be involved:

1. Diffusion of corrosion-produced hydrogen into the alloy causing localized embrittlement.
2. Reduction of hydrogen ion at cathodic areas sustaining the cathodic half-cell reaction, or intensifying it if another reaction is occurring simultaneously, thereby stimulating the anodic half-cell reaction.
3. Prevention of oxide film healing at corrosion sites by making a reducing atmosphere and creating a metallic surface condition favorable for nucleation of dislocations and cracks at the surface.

Experiments with autoradiography to demonstrate the presence of hydrogen (^3H) have been unsuccessful to date. The energy of beta radiation from ^3H is very low (0.018 Mev) and therefore ^3H is difficult to detect. Tests of long exposure times to increase salt corrosion damage are in progress. These samples should be more suitable for autoradiography. Also, radiation counters capable of detecting lower levels of ^3H will be evaluated for use in these studies.

Electron Microscopy Studies

The transmission electron microscopy studies of the duplex-annealed Ti-8Al-1Mo-1V alloy (heat D-5657) were continued during this quarter. Particular emphasis was placed on determining if hydrogen was picked up during foil preparation because work at Boeing had indicated that hydride contamination could cause contrast effects in the foils which would lead to erroneous conclusions about the titanium substructure.⁽⁷⁾

These studies revealed that spotty contrast (Figure 7) observed in many areas in the foils resulted from titanium hydride precipitation in certain regions. The hydride was identified by selected area electron diffraction.

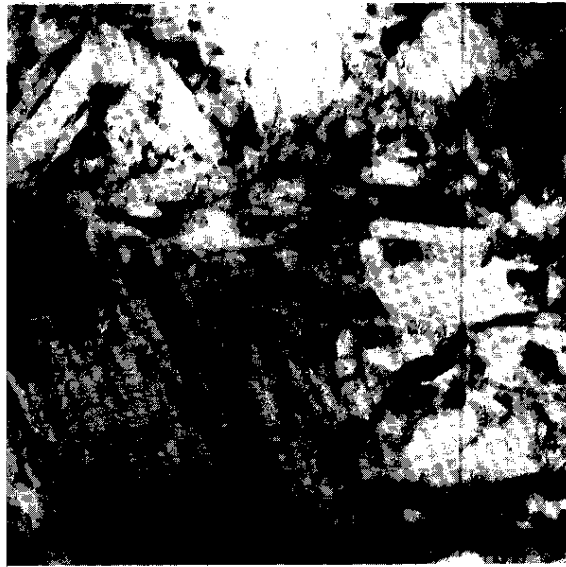


FIG. 7 SPOTTY CONTRAST IN TITANIUM FOIL RESULTING FROM TITANIUM HYDRIDE PRECIPITATION. (37,000X)

Additional study revealed that the habit plane for the hydride phase was $\{10\bar{1}0\}$, which is the same as reported for hydride in pure titanium.⁽⁸⁾ The habit plane was identified as follows:

- a. An area showing the hydride precipitate (Figure 8a) was selected.
- b. An electron diffraction pattern from that area was indexed (Figure 8b) showing that the $(10\bar{1}0)$ plane gave maximum diffraction intensity.
- c. The area shown in Figure 8a was then viewed using the beam diffracted from the $(10\bar{1}0)$ plane. The fact that the hydride precipitate was visible, but with reversed contrast, is proof that the hydride was on the $(10\bar{1}0)$ plane. If the hydride were on some other plane, the contrast reversal would not be observed.

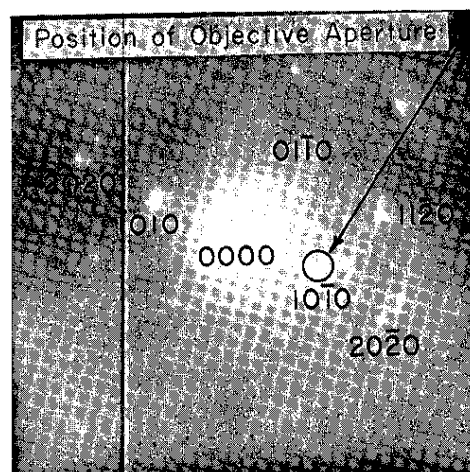
The $\{10\bar{1}0\}$ planes are also the slip plane in α -Ti⁽⁹⁾ and analysis of several foils confirmed that the dislocations were also in these planes. A fine precipitate was often associated with the dislocations (Figure 9). Such precipitates should inhibit dislocation movement and, if it is assumed that the phase is titanium hydride, the association with dislocations could cause hydrogen embrittlement.

The introduction of hydrogen into the foils and subsequent hydride precipitation during preparation could clearly affect interpretations of the substructure. Therefore, the thinning procedure will be changed to eliminate, or at least reduce, the possibility of hydrogen contamination. A thinning procedure using perchloric acid electropolishing solutions has been recommended by Boeing⁽⁷⁾ and foils thinned in such solutions will be examined in the future.

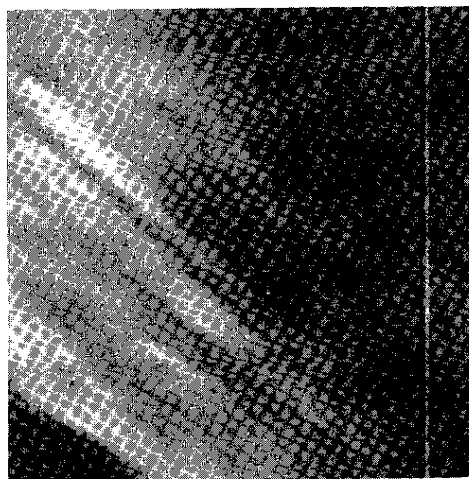
The morphology of the hydride in the contaminated foils was such that most of the precipitation occurred in regions near alpha-beta phase boundaries (Figure 10a) and along α grain boundaries (Figure 10b). This association may be due to a tendency for the hydrogen to enter the foil at such boundaries because of higher affinity for hydrogen in these regions. If one assumes that other interstitial impurities would behave similarly to hydrogen, then impurity segregation to grain boundaries would be expected. Such segregation should change the activity of the boundary and could be a contributing factor in the susceptibility to hot-salt cracking. Since the impurity segregation is generally enhanced by slow cooling rates, these results may have some bearing on the effect of cooling rate on the susceptibility to hot-salt cracking, described earlier in this report. Also if hydrogen embrittlement is involved in the cracking phenomena the affinity of the boundaries for hydrogen would explain why cracking is generally intergranular.



a. Bright field image (60,000X)



b. Selected area diffraction



c. Dark field image from $(10\bar{1}0)$ plane. (60,000X)

FIG. 8 SERIES OF PHOTOMICROGRAPHS SHOWING PRECIPITATION OF TITANIUM HYDRIDE ON THE $(10\bar{1}0)$ PLANE. Plane of the foil is (0002) .

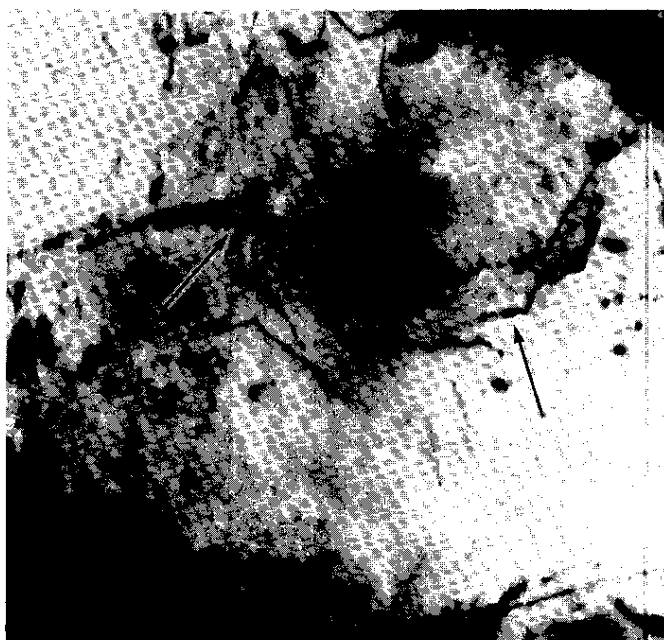
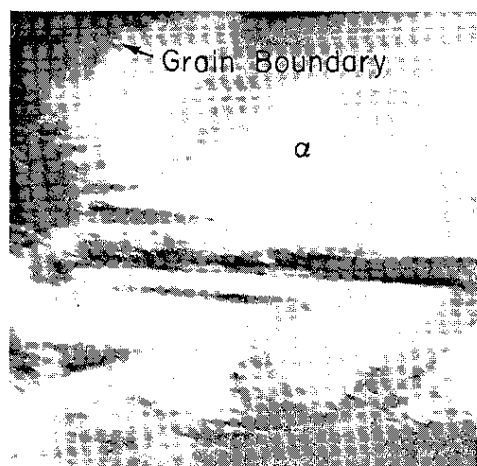


FIG. 9 ASSOCIATION OF A FINE PRECIPITATE WITH DISLOCATION. Arrows point to the phase which may be hydride phase. (50,000X)



a. Hydride at grain boundary. Note the more or less continuous hydride precipitate along the boundary. (70,000X)



b. Hydride at α - β interface. Note the continuous nature of the hydride precipitate along the interface. (50,000X)

FIG. 10 PRECIPITATION OF THE HYDRIDE PHASE AT GRAIN BOUNDARIES AND ALPHA-BETA INTERFACES

REFERENCES

1. S. P. Rideout, M. R. Louthan, Jr., and C. L. Selby. Stress Corrosion Cracking of Titanium Alloys, Progress Report - April 1 - June 30, 1964. DP(NASA)-917, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).
2. S. P. Rideout, M. R. Louthan, Jr., and C. L. Selby. Stress Corrosion Cracking of Titanium Alloys, Progress Report - July 1 - September 30, 1964. DP(NASA)-941, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).
3. D. N. Braski and G. J. Heimerl. The Relative Susceptibility of Four Commercial Titanium Alloys to Salt Stress Corrosion at 550°F. NASA TN D-2011, Langley Research Center, Langley Station, Hampton, Va. December 1963.
4. The Salt Corrosion of Titanium Alloys at Elevated Temperature and Stress - Progress Report. TML-88, Battelle Memorial Institute, Titanium Metallurgical Laboratory, Columbus, Ohio (1957).
5. D. N. Braski. Preliminary Investigation of Effect of Environmental Factors on Salt Stress Corrosion Cracking of Ti-8Al-1Mo-1V at Elevated Temperatures. NASA Technical Memorandum NASA TM-X-1048, December 1964.
6. H. D. Cox. Stress Corrosion Mechanisms, Progress Report No. 2. Henderson Laboratory, Titanium Metals Corporation of America, July 27, 1964.
7. M. J. Blackburn. The Boeing Company, Private discussion.
8. M. J. Blackburn and R. M. N. Pelloux. "Precipitation of Hydride Phase in Pure Titanium," Progress Review Solid State Physics Laboratory, First Six Months, 1964. Boeing Scientific Research Laboratories, Seattle, Washington, p. 164, August 1964.
9. A. D. McQuillan and M. K. McQuillan. Titanium. Academic Press, Inc., New York, p. 291 (1956).