

NATIONAL BUREAU OF STANDARDS REPORT

9468

FINAL REPORT ON

THE MECHANISMS OF STRESS CORROSION OF THE TITANIUM ALLOY Ti 8-1-1
EXPOSED TO SALT ENVIRONMENTS AT ELEVATED TEMPERATURES

By

Hugh L. Logan

For

Headquarters
National Aeronautics and Space Administration
Requisition No. PR10-2081
May 4, 1964
Contract No. R-130

J.R. Ambrose, C.J. Bechtoldt, M.J. McBee,
B.T. Sanderson, and G.M. Ugiansky, collaborated
in various phases of the investigation.

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An investigation of the mechanisms of the salt stress-corrosion cracking of titanium alloys at elevated temperatures was initiated May 4, 1964, by the Corrosion Section of the National Bureau of Standards with the cooperation of the National Aeronautics and Space Administration. The alloy selected for the study was the Ti-8Al-1Mo-1V. This alloy because of its high strength to density ratio and other good mechanical properties was considered as a wing covering material for the supersonic transport aircraft. It, as well as other titanium alloys, is known to be susceptible to stress-corrosion cracking when subjected to tensile stress in an elevated temperature-sea salt environment. The project was initiated to learn more about the mechanism of this attack so that proper precautions might be taken in the application of this alloy to the above use.

EXPERIMENTAL

Materials - Two different forms of Ti 8-1-1 alloy specimen were used. One type fabricated from sheet material 0.04 inch thick was used in studies of stress cracking susceptibility in tensile and four-point loading tests (see Fig. 2). These also were convenient to use in X-ray diffraction studies of the nature of the corrosion products formed under the environmental conditions studied. The other types were formed from 1-inch diameter rod material and were hollow tensile specimens (see Fig. 5). These were used to investigate the role of atmosphere on susceptibility and to enable an analysis of gaseous reaction products produced during the tests to be made. The chemical composition of the materials used in specimen preparation is given in Table 1.

TABLE 1--Composition of Ti 8-1-1 alloy used in this investigation

Element	Per Cent	
	Rod	Sheet
Aluminum.....	7.7	8.2
Molybdenum.....	1.0	0.97
Vanadium.....	0.7	0.94
Iron.....	0.08	0.10
Nitrogen.....	0.0022	ND ^a
Oxygen.....	0.062	ND
Hydrogen.....	0.010	ND
Carbon.....	0.01	ND

^aND, not determined

TABLE 1--(Continued)

Element	Results of Spectroscopic Examinations ^b	
Chromium.....	vw	vw
Copper.....	vw	vw
Magnesium.....	t	vw
Manganese.....	vw	vw
Nickel.....	...	vw
Silicon.....	w	w
Tin.....	vw	...

^bw, 0.01 to 0.1%; vw, 0.001 to 0.01%, t, <0.001%.

Sheet Material Specimen Preparation - The sheet material was used in the mill annealed condition. Two types of specimens were used: 1-inch by 6-inch bent beam specimens and 1-inch by 10-inch conventional 2-inch by 1/2-inch reduced section tensile specimens. The sheared edges were milled off the bent beam specimens to eliminate possible residual stress from shearing. These specimens were stressed from 40 to 80 Ksi in the outer fibers by four point loading (see Fig. 2). In some cases the convex surface was wet with distilled water and dry salt sprinkled on the surface. In others, a 10% aqueous solution was aspirated onto the surface and dried with a hot air blast. Specimens were exposed at 800°F in a circulating air furnace until failures occurred.

Tensile specimens were mounted in an insulated stainless steel cell wrapped with Nichrome heating wire, fitted with a chromel-alumel thermocouple, and filled with the dry-mixed Kci-LiCl eutectic (mp 670°F). The system was brought to temperature at 750°F, the specimen loaded in tension at 10,000 psi by means of a lever system, and exposed until failures occurred.

Hollow Specimen Preparation - Blanks about 6-inches long were cut from the rod stock and given the following duplex anneal heat treatment: one hour at 1750°F, air cool, then 8 hours at 1050°F and air cool. After heat treatment the rod pieces were machined into hollow specimens as shown in the drawing, Fig. 5. After the specimens had been degreased, a coating of salt was deposited on the inner surfaces in the following manner. Specimens were heated to about 125°C and were then filled with a 10% solution either of NaCl or a salt mixture containing seven parts of NaCl to one part of MgCl₂. After the solution had reached the specimen temperature, it was pipetted out leaving a thin layer of salt on the interior wall. The specimens were then closed with a plug machined from the rod stock.

There was a connection through the plug to the specimen interior so that an atmosphere could be introduced (after the specimens were closed) into the cavity. This connection may also be used to obtain a sample of the gaseous environment in the interior of the specimen. The specimen and plug arrangement are the same as those used previously with stainless steel, Fig. 6. Thermocouples were attached to the shoulders of the specimens and to the centers of the reduced sections. Specimens are placed in conventional creep furnaces heated to 750°F and, after thermal equilibrium has been reached, stressed, using a lever system, through hollow pull rods attached to the ends of the specimens to 73,500 psi.*

RESULTS AND DISCUSSION

Effect of Salt Composition on Susceptibility - Exposure periods for the bent beam specimens generally increased with decreasing stress and ranged from 64 days for specimens stressed to 80 per cent to 91 days for specimens stressed to 40 per cent of their yield strength.

In a check run, specimens coated with NaCl failed in approximately one week compared to the average of 60 days mentioned earlier for specimens exposed at the same stress and under the same condition. Contamination of the NaCl with LiCl was suspected and salt removed from one of the failed specimens was found to contain 1.6ppm of lithium compared to less than 0.1ppm of lithium in the stock NaCl.

The experiment was repeated with known amounts (100 and 1000ppm) of LiCl being added to the 10% spray solution of stock NaCl.

Periodic inspection revealed cracks on one specimen coated with NaCl alone after 5 days exposure. All of the specimens showed cracks on microscopic examination after 9 days. Exact time to initiation of cracks on the different specimens could not be observed, but in general, the severity of cracking increased with increasing Li additions and corrosion products gave a blacker appearance with the greatest addition.

Sheet specimens stressed to 80 Ksi have also been coated with various alkali and alkaline earth chlorides and heated at 800°F in the circulating air furnace. Specimens coated with LiCl or with a LiCl-KCl eutectic mixture (m.p. 670°F) failed in less than 20 hours.**

Preliminary microscopic examinations of the four-point loaded specimens removed from the furnace after 280 days exposure did not reveal any obvious cracking. However, after the specimens were cleaned by pickling in $H_2O + 40\% HNO_3 + 2\% HF$, varying crack patterns were observed on all specimens except one coated with $MgCl_2$ and the blank

*By interpolation of unpublished data of Jenkins and Willard this was considered to be 90% of the yield strength of this alloy at this temperature.

**A cold U-bend specimen dipped into the molten eutectic mixture failed as soon as the surface was wetted.

control. The severity of cracking decreased in the order BaCl_2 , KCl , CaCl_2 , CsCl , SrCl_2 (see Fig. 1). Cracks were associated with pits in specimens coated with KCl and SrCl_2 . No trends that might be expected on the basis of chemical periodicity were found.

Effect of Applied Currents - Failures of the conventional sheet tensile specimens, stressed to 10,000 psi, have occurred in approximately one hour. In one experiment the specimen was made the anode by applying a potential difference of 3 volts between the specimen and cell wall. The exposure period increased slightly, but this may represent scatter in the data. The exposure periods to failure of other specimens exposed under the same conditions except that they were made the cathodes, were approximately doubled. Specimens exposed in the molten eutectic were pitted.

Nature of the Corrosion Products - Fig. 3 shows a crack in a specimen exposed to NaCl for approximately 64 days and the corrosion products formed on the surface of the specimen.

X-ray diffraction patterns taken in order to analyze this product were made directly on the surface. In addition to the pattern of NaCl , lines for three phases, anatase, rutile, and at least one unidentified phase, designated X, were found. The lines of the X-ray diffraction pattern of the X phase are given in Table 2; lines marked A or NaCl under the remarks column are probably due to anatase or NaCl , but there may be overlap. These patterns also indicated a preferred orientation of the $\{101\}$ plane of anatase and the $\{110\}$ plane of rutile with the surface.

Efforts were made to separate the products as to color and other physical characteristics. The following types were found:

- 1) Black particles sticking through surface--principally rutile.
- 2) Clear glassy-like particles--principally NaCl , phase X, and a trace of rutile and anatase.
- 3) White creamy material--sodium chloride, phase X, anatase and a trace of rutile.
- 4) Light yellowish creamy material--weak NaCl , some phase X, strong anatase, and weak lines for rutile.
- 5) Reddish particles on the surface--an ilmenite structure with hexagonal lattice constants $a = 5.03 \text{ \AA}$, $c = 13.81 \text{ \AA}$.

(Could be Ti_2O_3 with some of the titanium replaced by other metal atoms.)

- 6) Metallic-like particles found after washing and filtering-- a $E9_2$ structure (cubic) $a = 10.65$ A, and an apparent FCC structure $a = 4.045$ A (possibly aluminum or the AlTi phase).

Washing or soaking the surface of a specimen removed all the phases with the exception of traces of rutile. However, there remained a black product, often sufficiently thick to mask the lines of the underlying titanium metal, but itself yielding no lines. This would suggest an amorphous structure. The ease in which anatase and rutile were removed suggested they were only lightly held on the surface or entwined with NaCl.

On specimens treated with LiCl, although the surface of the titanium was thickly covered with a black product, no pattern for any corrosion product was found. Using the diffractometer on a similarly treated specimen so that patterns could be obtained while the specimen was heated in place above $1000^\circ F$, with the exception of LiCl lines, only lines for rutile appeared.

Similar X-ray diffraction studies were made at temperature for specimens with LiCl absent. The diffractometer using Cu radiation, was set to oscillate at $2^\circ 2\theta$ per minute over a region containing a group of identifiable lines, except when a slower and more detailed pattern was desired. In this and the other studies, the diffracted beam was monochromated using a doubly bent lithium fluoride crystal. Sheet specimens coated with NaCl and a mixture of 7 parts of NaCl and 1 part $MgCl_2$ (as $MgCl_2 \cdot 6H_2O$) were stressed and heated at temperature up to $1200^\circ F$. Around $800^\circ F$ lines for anatase appeared and only after prolonged heating or a raise in temperature did lines for rutile appear. With reference to the work where X-ray measurements were not made at temperature, the holding times at a temperature were relatively short, never for more than 16 hours. The whole experiment was usually completed in three or four days.

With the specimens exposed to $MgCl_2 \cdot 6H_2O$, no lines for the various hydrate products nor lines for MgO were detected. Specimens were exposed both to 50:50 ratio $MgCl_2$ to NaCl and to 100% $MgCl_2$. The diffraction patterns obtained indicated that the hexahydrate, $MgCl_2 \cdot 6H_2O$ broke down successively to $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 2H_2O$ at temperatures of $190^\circ F$ and $260^\circ F$. At $385^\circ F$, $MgCl_2 \cdot 2H_2O$ decomposed, first yielding a new diffraction pattern, too fleeting or mixed for identification, and then a pattern with amorphous humps for a glassy product which persisted until $680^\circ F$, when lines for MgO appeared. No new lines were obtained on the 100% $MgCl_2$ on further elevation of temperature. The specimen exposed to the 50:50 mixture gave lines for rutile (but not for anatase) which

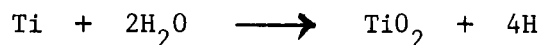
first appeared at 910°F, but faded with time. On each successive raise in temperature, they appeared strongly at first, but then faded on prolong holding as if rutile was going into solution. At 1180°F, the lines for rutile persisted.

In some of the specimens exposed to NaCl, certain lines at high angles were compared after heating and cooling to room temperature to the pattern obtained before heating. No shift was observed, suggesting little or no solid solution of other constituents with NaCl or if such solution occurred at elevated temperature, they were precipitated on cooling.

In addition to looking at the corrosion products formed in the presence of chlorides, a sheet specimen was heated in oxygen for 30 days. A subsequent microscopic examination showed it to be coated with light and dark whiskers, Fig. 4. The light whiskers were NaCl, the dark, rutile. The whiskers suggest that some NaCl existed in the vapor state. NaCl is reported to have a vapor pressure of 2.4 Torr at 1376°F. It is suggested that the black whiskers resulted from the diffusion of the rutile into the NaCl whiskers.

The Effect of Atmosphere - In the first series of experiments utilizing the hollow specimens, a drop or two of water was placed in the interior which had been coated as previously described with NaCl - MgCl₂ mixture. These specimens failed in 227 to 600 hours. Specimens coated with the salt mixture with the cavity subsequently filled with dry argon at a pressure of 4 to 6 psi failed in less than 72 hours. Fig. 7 shows the two halves of a specimen that failed in 18 hours and was subsequently split so that the interior could be examined.

Specimens coated with NaCl (no MgCl₂ added) and filled with dry oxygen failed only after a longer exposure period and several did not fail before the experiment was terminated. As was indicated in the discussion of sheet specimens MgCl₂ · 6H₂O will break down to give off 2 and subsequently 4 molecules of water. Hence, the failures reported with the 7 NaCl, 1 MgCl₂ mixture could be explained. The water conceivably reacts with the titanium to form TiO₂ as follows:



At the temperature of exposure (approximately 750°F) any hydrogen most probably combines with the titanium to form a hydride.

A group of specimens was preoxidized by heating them in tank oxygen at 800°F for 60 to 70 hours. These specimens were coated with NaCl in the usual manner, mounted in the stress-corrosion racks, evacuated to a pressure of less than 10⁻³ Torr and finally filled with purified and dried argon. Specimens failed after exposure periods ranging up to 250

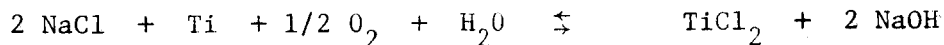
hours. A specimen exposed under the same conditions except that it had not been preoxidized did not fail in 500 hours. Several specimens containing purified argon moistened by bubbling through water before it entered the specimen cavity, failed after exposed periods ranging from 74 to 326 hours. As was suggested earlier, it is believed that the water combines with the titanium to form a thicker oxide in some areas than that on a machined specimen not subsequently heated above 250°F.

Just how the thicker oxide film functions to produce cracking is not clear. It could, of course, occlude water. To investigate this possibility a preoxidized specimen was coated with NaCl crystals by withdrawing the solution, was evacuated to 10^{-7} Torr and heated at temperatures up to 750°F for approximately two days before it was filled with purified argon. This specimen subsequently stressed to 73,500 psi at 750°F failed in approximately 22 hours.

It has been recognized that hydrogen can be absorbed on and diffuse interstitially into rutile films from contact with a water solution. Therefore, instead of coating the interior of a specimen with NaCl from an aqueous solution finely ground dry NaCl was placed in the specimen cavity and scattered on the side walls as far as possible. The specimen was then evacuated using a mechanical fore pump and a liquid nitrogen cold trap and heated to 750°F for approximately two days prior to the introduction of ultrapure dry argon to pressure of 5 psig, and stressing at temperature. The specimen failed in less than 24 hours as the result of a stress-corrosion crack penetrating through the specimen wall. Other stress-corrosion cracks were also found penetrating into the specimen wall from the interior cavity. While these experiments do not eliminate the possibility that water may enter into the reactions causing failures at 750°F they do indicate that if water is present it is in exceedingly minute amounts.

Gas samples were taken from the interior cavities of specimens in which the pressure of oxygen had been reduced to 2×10^{-1} Torr prior to loading. Mass spectrographic analyses did not show the presence of HCl or Cl₂, suggested products in the chemical action leading to stress-corrosion cracking of this alloy. The sensitivity was 1 part in 10⁴, hence, if HCl or Cl₂ was produced in the reaction at all, it was produced only in very small amounts. In subsequent experiments, oxygen flowed over a sheet specimen coated with NaCl and heated to 750°F and was bubbled through a starch-potassium iodide solution. There was no detectable color change. This again indicated that if Cl₂ was produced it was only in minute quantities.

Other workers have suggested NaOH as a product of the reaction that would lead to cracking according to the following reaction:



The interiors of three specimens were subsequently coated in this laboratory with crystals from a solution containing 10% NaCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 10% NaOH. One specimen in which the argon was at atmospheric pressure (and in which an air leak was a possibility) failed in 142 hours. Argon was introduced into the other specimens at 5 psig. They were believed to be leak tight and showed no evidence of cracking when the experiments were terminated after 208 and 570 hours. The specimen exposed for 570 hours had elongated about 1 1/2% indicating that it had been subjected to plastic deformation. As was indicated above, the proposed reaction involving NaOH is reversible.

Hence, the presence of NaOH would tend to make the reaction go to the left and cracking would not be expected. We have found no evidence of NaOH in X-ray diffraction patterns of corrosion products. However, the NaOH could be present in such minute quantities as not to be detected, or may have formed an amorphous glass with other products.

There was a blue film in the interior of the hollow specimens where NaCl crystals had been in contact with the metal at 750°F. We were able to strip some of this film from the interior for examination in the electron microscope. A transmission micrograph is shown in Fig. 8. The spike-like structures are believed to be the beginnings of whiskers found on sheet material after long exposure at temperatures (see Fig. 4). Electron diffraction studies indicated that the film was composed primarily of anatase (TiO_2)

Effect of Concentration Gradients at α - β Grain Boundaries - Metallographic studies were made of specimens containing stress-corrosion cracks. A typical crack is shown in Fig. 9. The cracks tend to follow the grain boundaries or α - β boundaries. An electron probe study was made of the matrix and the precipitate (β phase) of the annealed alloy. Table 3 gives the relative ratios in the α -matrix and the β -phase of titanium, molybdenum and aluminum. It is interesting to note that there is approximately 9 times as much molybdenum in the β -phase as in the α -matrix. The probe analysis also indicates that the region immediately adjacent to the β -phase was depleted in molybdenum, i.e., the molybdenum content was lower than in the β -phase as a whole. Depletion of molybdenum adjacent to the β -phase may be a reason why stress corrosion cracks follow the β -phase. They also follow grain boundaries; it is to be expected that regions of enrichment and impoverishment at the grain boundaries would be too narrow to be detected by the probe in its present state of development.

SUMMARY

1. Stress-corrosion cracking was produced in 4-point loaded bent beam specimens of the Ti 8-1-1 titanium alloy, coated with NaCl and

stressed to 80,000 and 40,000 psi in the outer fiber in 64 to 91 days. In a check run, a coating of NaCl containing 1.6ppm of lithium produced failures in approximately 1 week.

2. Cracking of the bent beam specimens was produced using a number of chlorides. In decreasing order of severity, those investigated were: BaCl_2 , KCl, CaCl_2 , CsCl and SrCl_2 .

3. A molten eutectic mixture of KCl and LiCl (mp 670°F) produced failures in U-bend specimens as soon as the specimen was wetted.

4. Different colored corrosion products found on the surfaces of sheet specimens coated with NaCl were not readily separable and all contained anatase, rutile (both forms of TiO_2) and an unidentified phase. Whiskers of NaCl and rutile were also found on the surface of a sheet specimen, heated for a long period in a stream of oxygen.

5. Sheet tensile specimens subjected to a stress of approximately 10,000 psi in a molten eutectic mixture of KCl and LiCl at 750°F failed after approximately 50 minutes. Making the specimen the anode by applying an external potential of approximately 3 volts had no marked effect on the exposure period to failure. Making the specimen the cathode, with the same applied potential, approximately doubled the exposure period to failure.

6. Considerable data were obtained using hollow specimens. The interiors of the specimen were coated with NaCl or a mixture of 7 parts NaCl and 1 part MgCl_2 (as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). A desired atmosphere could be put into the specimen cavity. The specimens were stressed at 750°F in direct tension to 90% of their yield strength at that temperature.

7. Cracking could be produced in hollow specimens coated with $\text{NaCl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or coated with NaCl and in a moist argon atmosphere.

8. Hollow specimens coated with NaCl and exposed to dry oxygen were quite resistant to cracking. However, if the specimen had been preoxidized (heated 60 hours or more at 800°F in a stream of oxygen) prior to coating with NaCl it could fail in less than 24 hours under stress at 750°F. Further, any water present in these experiments was in exceedingly minute amounts.

9. Experiments to determine whether Cl_2 , HCl or NaOH were reaction products in the stress-corrosion cracking of the alloy, were not conclusive. However, data indicate that in all cases these products, if formed, were present in very minute amounts.

10. Stress-corrosion cracking was intercrystalline or followed the α - β boundaries. An electron probe analysis of the α -matrix and the β - phase indicated that there was approximately 9 times as much molybdenum

in the β as in the α -phase. Also, the matrix was depleted in molybdenum adjacent to the β -boundary.

A major portion of the material presented in this report has been published: H.L. Logan, M.J. McBee, C.J. Bechtoldt, B.T. Sanderson and G.M. Ugiansky, "Chemical and Physical Mechanisms of Salt Stress-Corrosion Cracking in the Titanium 8-1-1 Alloy", Stress-Corrosion Cracking of Titanium", ASTM STP 397, Am. Soc. Testing Mats., 1966, p. 215.

TABLE 2. DIFFRACTION PATTERN FOR "X" PHASE.*

<u>d-spacing</u>	<u>I**</u>	<u>Remarks</u>
4.88	< 5	?
3.91	35	
3.76	35	
3.48	35	A***
3.23	10	NaCl
2.81	100	NaCl
2.63	60	
2.54	< 5	
2.37	35	A
1.992	40	NaCl
1.959	10	
1.882	< 5	A
1.742	30	
1.691	< 5	A
1.623	20	NaCl
1.581	< 5	
1.567	< 5	
1.458	< 5	
1.406	< 5	NaCl
1.263	10	NaCl
1.152	5	NaCl

*Sample taken from washings allowed to dry on glass plate.

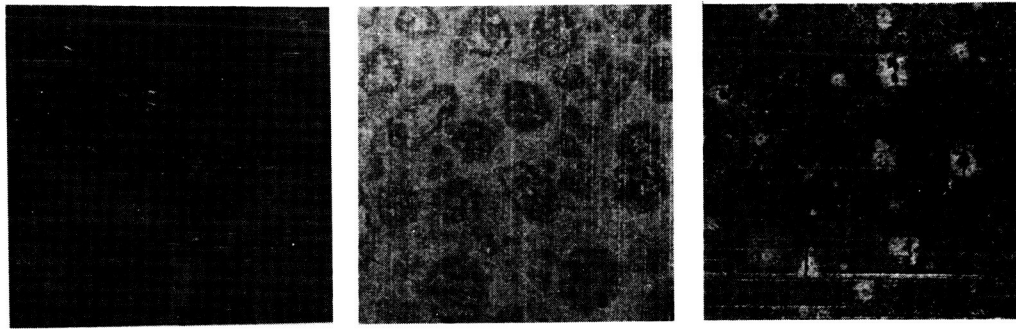
**Relative intensities - visually estimated.

***A stands for anatase (TiO_2). The entries under remarks represents \bar{d} -spacing which may be caused entirely or in part by the substance indicated. ? stands for a \bar{d} -spacing found only in some patterns.

TABLE 3

Ratio of metallic content of α -matrix to β -phase (precipitate
as determined using the electron probe:

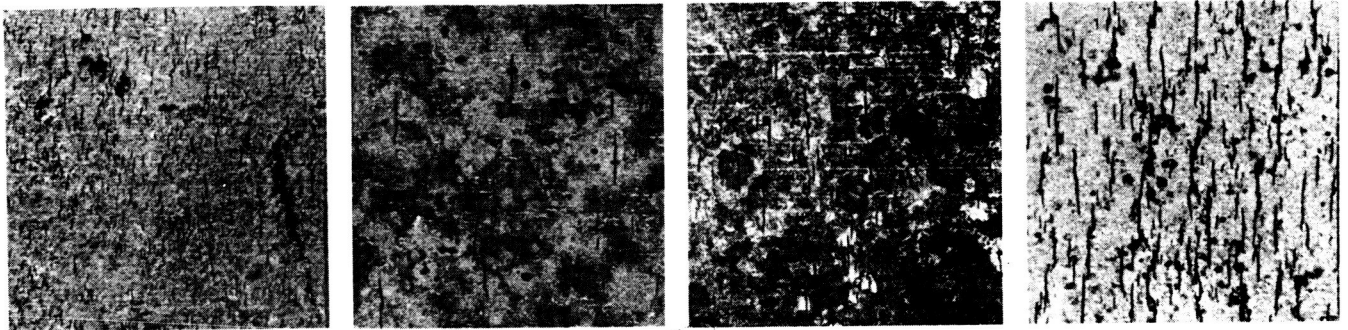
Ti-matrix/Ti- β phase	1.04
Al-matrix/Al- β phase	1.36
Mo-matrix/Mo- β phase	0.11
V-matrix/V- β phase	not determined



Control

MgCl₂

SrCl₂



CsCl

CaCl₂

KCl

BaCl₂

Direction of Stress

Fig. 1. Surfaces of four point loaded (80 Ksi) bend specimens which were coated with representative I and II group chlorides and exposed at 800°F for 280 days. Varying cracking severity is shown after surfaces were cleaned with an acid pickle. X 7

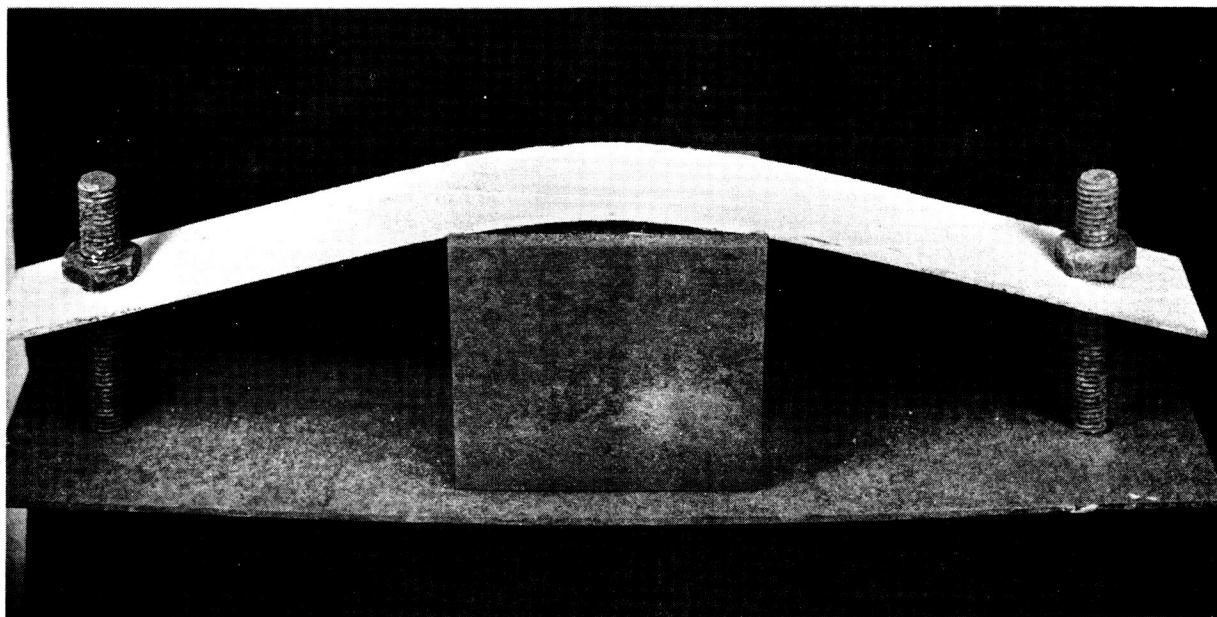


Fig. 2. Sheet specimen subjected to four point loading.
X 3/4

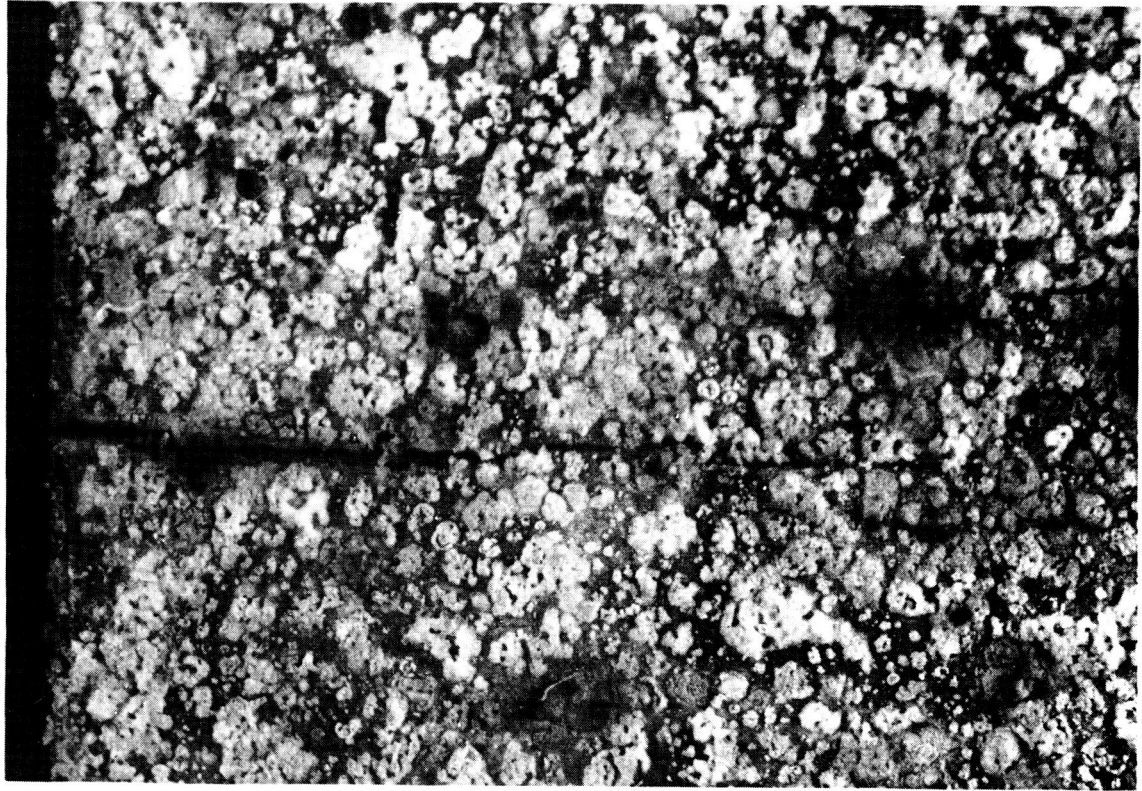


Fig. 3. Cracks in specimen shown in Fig. 2. White translucent material contains NaCl and larger amounts of anatase, rutile and X phase. Light grey contains small amounts of NaCl and rutile and large amounts of anatase and X phase. The dark grey is primarily rutile. X 8

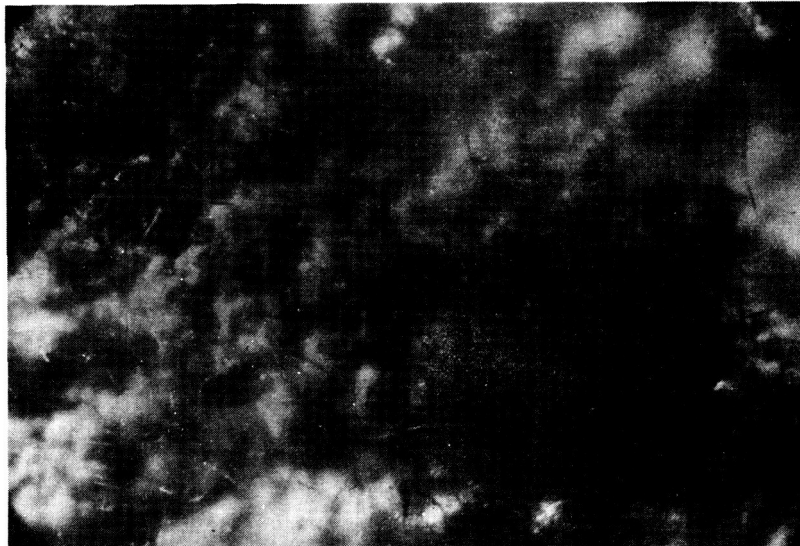


Fig. 4. Surface of sheet specimen with NaCl corrodent after exposure in oxygen atmosphere at 800°F for 30 days. Whiskers are either primarily NaCl (white) or rutile (black). Print from 35mm color slide. X 95

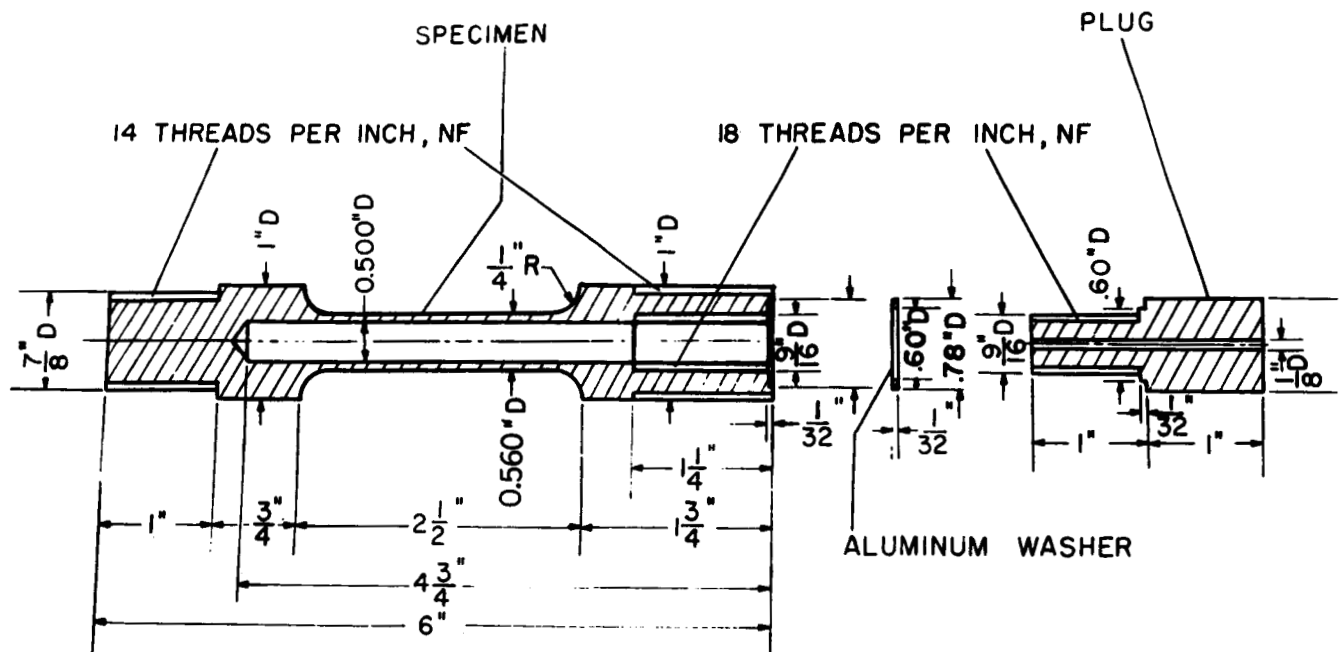


Fig. 5. Drawing of hollow specimen used in this investigation.

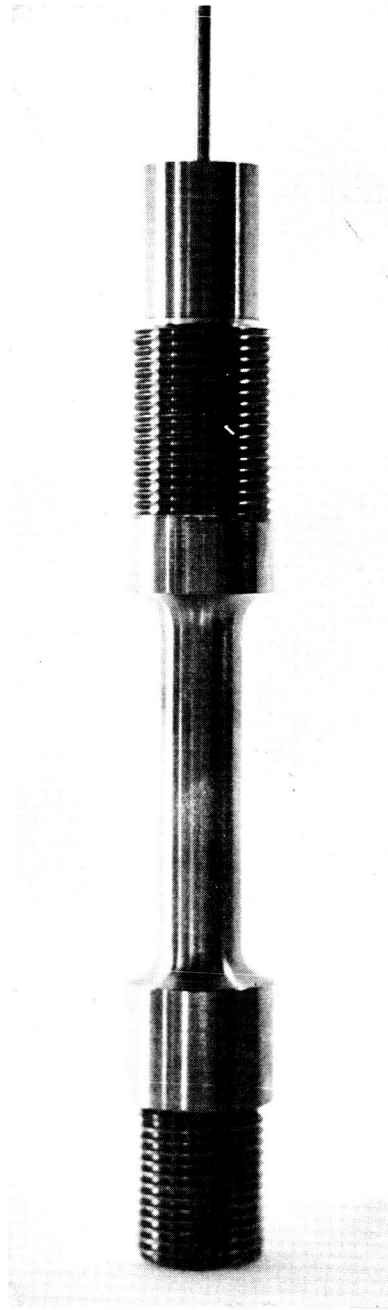


Fig. 6. Specimen assembled with plug and small diameter tube for adding desired atmosphere. Specimen was machined from one-inch diameter rod.

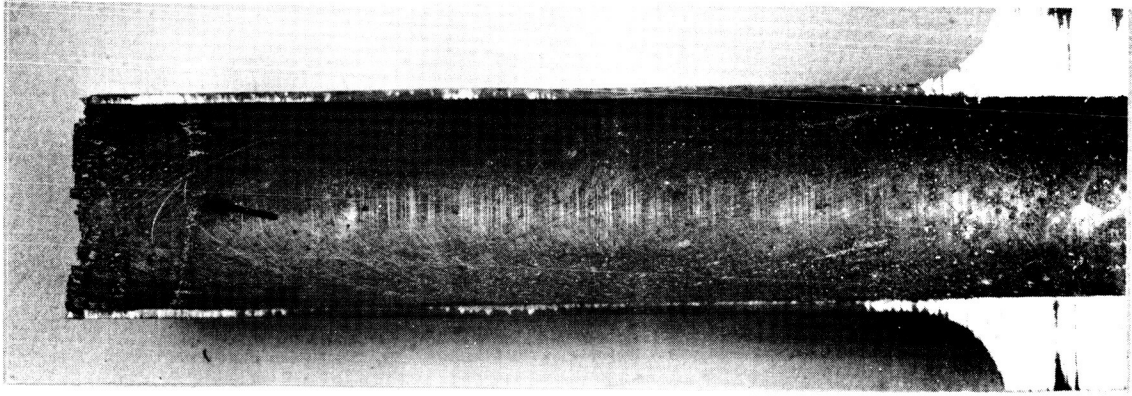


Fig. 7a. Half of specimen split for internal examination.
Area marked by arrow shown much enlarged in Fig. 7b.
X 2

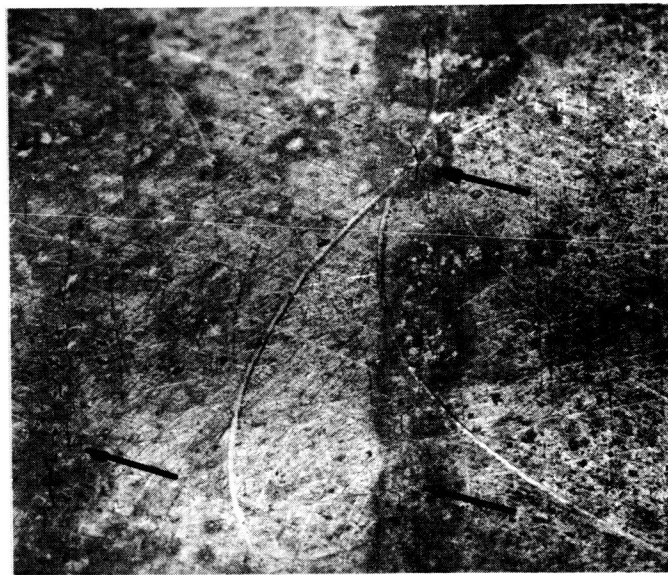


Fig. 7b. Area marked out in Fig. 7a enlarged to show cracks,
marked by arrows, associated with corroded area.
X 13

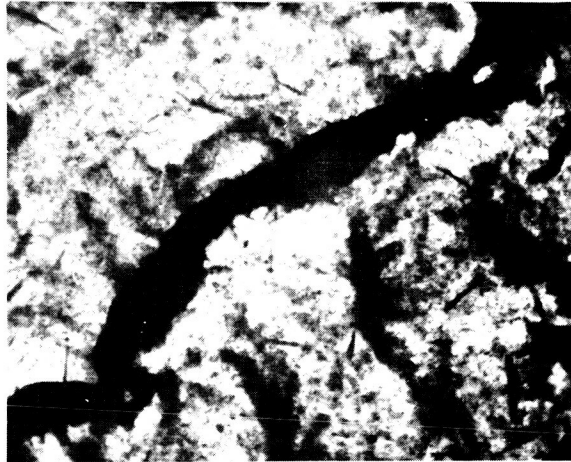


Fig. 8. Electron transmission micrograph of surface film stripped from interior surface of failed specimen. Note dark spike like structures, probably the beginning of whiskers. Dark diagonal band is structure too thick to be penetrated by electron beam. X 18,000



Fig. 9. Intercrystalline stress-corrosion crack in specimen exposed at 750°F under stress of 73,500 psi. Interior of specimen coated with NaCl + MgCl₂ mixture. Specimen cavity filled with dry oxygen. Note textured structure near origin of crack and interior of specimen. Etched same as Fig. 1.
X 500