THE ROLE OF HYDROGEN IN HOT-SALT STRESS CORROSION CRACKING OF TITANIUM-ALUMINUM ALLOYS

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Additional support is presented for the previously proposed role of hydrogen as an embrittling agent in hot-salt stress corrosion cracking of titanium-aluminum alloys. The main source of hydrogen formed during the reactions of titanium alloys with hot salt was identified as water associated with the salt. Hydrogen is produced by the reaction of an intermediate (hydrogen halide) with the alloy rather than from metal-water reactions. The fracture mode of precracked tensile specimens was ductile when the specimens were tested in air, and brittle when tests were made in high-pressure hydrogen. Stressed titanium-aluminum alloys also were cracked by bombardment with hydrogen ions produced in a proton accelerator. The approximate concentrations of the hydrogen ions in the alloys were calculated. The susceptibility of titanium alloys to hot-salt cracking is lower under service conditions than in the laboratory because the concentration of gaseous corrosion products, including hydrogen, is lower in service specimens.
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INTRODUCTION

Titanium-aluminum alloys will be used in supersonic aircraft that operate at temperatures up to 300°C (572°F) while contaminated with sea salt. Laboratory tests have shown that titanium-aluminum alloys are susceptible to hot-salt stress corrosion cracking under the probable operating conditions of supersonic aircraft. Although no cases of cracking that can be specifically attributed to hot salt have been discovered in operating aircraft engines, advanced engine designs using these alloys will require higher temperatures and stress levels, and hot-salt cracking may yet be encountered. The Savannah River Laboratory has carried out a research program to develop fundamental knowledge about the mechanism of hot-salt stress corrosion of these alloys under the sponsorship of the National Aeronautics and Space Administration.

This work has resulted in a proposed mechanism for the hot-salt stress corrosion cracking of titanium alloys which involves the pyrohydrolytic formation of the hydrogen halides corresponding to the anion of the salt (i.e., HCl from Cl⁻ salts) and attack of the metal by the hydrogen halides after penetration of the surface oxide film. Hydrogen is generated by the attack and is partially adsorbed by the metal surface. The hydrogen embrittles the surface, and the crack can then be initiated by residual or applied stress.

This report presents additional experimental verification that hydrogen is the embrittling and crack propagating agent in the hot-salt cracking of titanium alloys. The effects of hot salt in cracking titanium alloys are then compared to the effects of hydrogen on these alloys.
SUMMARY

The amount of hydrogen produced from the corrosion reaction of each of the sodium halide salts and titanium-aluminum alloys was proportional to the amount of water present. The hydrogen was formed from the reaction of an intermediate (hydrogen halide) in the hot-salt cracking process, rather than from a metal-water reaction.

High-pressure hydrogen gas was shown to cause brittle fracture in both Ti-8Al-1Mo-1V and Ti-5Al-2.5Sn tensile specimens; helium did not cause brittle failures. Failures were brittle when specimens were notched and fatigue-cracked; without the fatigue crack, failure was ductile.

Cracks more than 30 μm in depth were caused by hydrogen ions that were accelerated so that they penetrated slightly more than 1 μm into stressed titanium-aluminum. The cracks were intergranular and similar in appearance to hot-salt cracks.

These findings support the proposed mechanism for hot-salt stress corrosion cracking of titanium alloys; in each case hydrogen acts as the embrittling and crack propagating agent. It is proposed that cracking has not been observed in service because the gaseous corrosion products, including H₂, either do not reach a high enough concentration or are lost from the reaction site before they can penetrate the oxide barrier under the influence of very high velocity air. This mechanism is also compatible with the greater susceptibility of alpha or alpha-beta alloys to hot-salt cracking compared to beta alloys because hydrogen is more soluble in beta alloys.
DISCUSSION

DETERMINATION OF HYDROGEN AS A CORROSION PRODUCT

Hydrogen and HCl were identified by mass spectrometry as corrosion products in the hot-salt stress corrosion cracking of titanium-aluminum alloys, as previously reported.\(^3,4\) Chlorine was not observed during reactions between 260 and 650°C by either mass spectrometry or ultraviolet spectroscopy.

Experimental

Volatile corrosion products evolved from chips of titanium-aluminum alloys coated with halide salt at 260 and 400°C were analyzed with a mass spectrometer.* The samples were analyzed as follows. Salt solutions were evaporated to dryness on the chips of both Ti-8Al-1Mo-1V and Ti-5Al-2.5Sn at room temperature; some of the salt-coated chips were then heated to 350°C for one-half hour to remove moisture from the salt. These chips were placed in a reaction vessel (Figure 1), and predetermined amounts of water were pipetted onto the predried salted chips (no water was added to the unheated chips). The vessel was partially evacuated so that at test temperature, without a reaction, the pressure would be approximately one atmosphere. After the reaction vessel was attached to the mass spectrometer, the vessel was heated in a tube furnace to the test temperature, and the gaseous reaction products were sampled periodically. About 2% of the gas in the reaction vessel was removed each time a sample was taken.

Results of Mass Spectrometric Analysis

The amount of hydrogen evolved on heating the coated chips of Ti-8Al-1Mo-1V that were previously dried at room temperature only is shown in Figure 2 (little difference was observed in the amount of hydrogen evolved from the two titanium alloys). The gas was produced by chemical reactions with the metal. Hydrogen initially present in the metal (equivalent to about 0.1 mol % of the hydrogen evolved) would not be released under these conditions. The higher temperature probably drove more water from the salt crystals\(^4\) which produced more HCl and therefore more hydrogen.

* Consolidated Engineering Corporation, Model 21-103.
FIG. 1 HOT-SALT/TITANIUM-ALLOY REACTOR VESSEL
FIG. 2 EVOLUTION OF HYDROGEN IN HOT-SALT CORROSION
Evolution of hydrogen from the salt-covered chips that had been previously dried at 350°C was controlled by the amount of water added. The hydrogen evolved was measured after heating for 1.5 hours (sufficient to reach equilibrium), and the relative concentration is shown in Figure 3 for each of the four sodium halide salts and for a mixture of chips and water alone. These results show that the amount of hydrogen produced was proportional to the amount of water added and was insensitive to the particular halide salt. The amount of hydrogen halide that could be produced by pyrohydrolysis and react with the metal to release hydrogen was limited by the amount of water present. The reaction was not a metal-water reaction, as shown by the blank. Other products observed in the reaction were hydrogen halides.

![Hydrogen Peak Diagram](image)

**FIG. 3 HYDROGEN PRODUCTION AT 350°C**

Small amounts of hydrogen produced in this manner can be absorbed by the metal and thereby embrittle the surface,\(^5,6\) NaF does not cause cracking because of the volatility of TiF\(_4\), the major product of the reaction between HF and titanium, as previously reported.\(^7\)

**EFFECT OF HYDROGEN ON TENSILE SPECIMENS**

The effect of hydrogen on crack propagation in Ti-8Al-1Mo-1V and Ti-5Al-2.5Sn was determined by testing notched specimens containing fatigue starter cracks (Figure 4) in H\(_2\) and He at both atmospheric pressure and 10\(^4\) psi. The strain rate in the high pressure tensile tester was 0.001 min\(^{-1}\). Cellulose acetate-carbon replicas were made of fracture surfaces.
The crack surfaces produced at $10^4$ psi H$_2$ were less ductile than those produced in other atmospheres. The surfaces were characterized by regions of faceted fracture topography typical of low ductility rupture (Figure 5a). This is contrasted with the dimpled structure seen in specimens tested at $10^4$ psi He (Figure 5b). The failures were not brittle if specimens were not precracked.

The crack surfaces produced in both He and H$_2$ at atmospheric pressure were similar and were characterized by dimples typical of ductile rupture (Figure 6). Thus, low pressure H$_2$ in these tests had no effect on the fracture mode.

The change in fracture mode in specimens tested in H$_2$ at high pressure compared to atmospheric pressure suggests that higher pressure was required either to produce a higher surface concentration or to penetrate a surface barrier before the hydrogen could influence crack propagation. Fatigue cracks produced in air would have oxide films at the crack tip when the test was initiated. Oxygen and water vapor, present in tank hydrogen, could have reacted with the titanium preferentially to reform the oxide film when it was ruptured during the test.

The results show that hydrogen at the tip of a propagating crack can change the mode of rupture from ductile to brittle, and are consistent with the hydrogen embrittlement mechanism for the hot-salt cracking of titanium alloys.
FIG. 5 CRACK SURFACES OF Ti-8Al-1Mo-1V PRODUCED IN 10^4 psi H₂ AND He
H⁺ BOMBARDMENT OF STRESSED TITANIUM ALLOYS

To illustrate the effect of hydrogen ions alone (the species of mobile hydrogen believed to exist in metals), stressed titanium alloys were bombarded by H⁺ from an accelerator.

A Texas Nuclear Model 6400 Neutron Generator was converted to a proton accelerator. The neutron generator is designed to ionize deuterium gas and accelerate it at a tritiated target to produce 14.8-Mev neutrons. When the generator is used as a proton accelerator, hydrogen instead of deuterium is introduced into the generator, and the ionizing coils are adjusted for maximum proton production. The protons, partially focused in the stripping tube, are accelerated in a potential field and, after further focusing, drift toward the stressed nontritiated titanium alloy in a specially designed water-cooled holder (Figure 7). The system is normally at a pressure of $\sim 10^{-7}$ torr, but because of the introduction of hydrogen the effective pressure is only $\sim 10^{-5}$ torr.

Because the beam diameter can be measured by its trace on the target (a result of the degradation of organic materials in the vacuum system), and the proton flux can be established from the beam current, the number of ions impinging per unit area can be calculated. Strain gages were used to measure the stress on the alloy surface exposed to protons.
The range of protons in titanium or its alloys has not been measured, but penetration of at least a few hundred angstroms was desired so that the $H^+$ would be injected well into the metal. The range of protons in titanium was calculated from their range in air by the Bragg-Kleeman rule. Data for titanium are shown in Figure 8. The accelerating potential of 150 kev was selected from these data. Protons at 150 kev were calculated to have lost all their energy on traveling through 1.1 μm of titanium.

$R_k = 3.7 \times 10^{-4} \frac{R_A}{P_x} \sqrt{A_k}$

where

- $R_k$ = range in material, cm
- $R_A$ = range in air, cm
- $A_k$ = atomic weight of mat'l., g
- $P_x$ = density of material, g/cm$^3$

Specimens of Ti-5Al-2.5Sn and Ti-8Al-1Mo-1V were stressed to $10^5$ lb/in$^2$ and bombarded with 150-kev protons. The back surfaces of the specimens were water cooled; the outer surfaces were
estimated to be 200°C based on temperature measurements by thermo-
couples located halfway through the target. At a total fluence
of $3.2 \times 10^{19}$ H$^+$/cm$^2$, cracks were observed in Ti-5Al-2.5Sn after
60 minutes. At a fluence of $2.0 \times 10^{19}$ H$^+$/cm$^2$, cracks were
observed in Ti-8Al-1Mo-1V specimens in 40 minutes. Bombardment
at 20% of these fluences did not cause cracking in either alloy.
The fluence was lowered by reducing the flux, rather than by
reducing the irradiation time.

Cracking of Ti-5Al-2.5Sn was more difficult as indicated by
the longer irradiation time required under conditions equivalent
to those for Ti-8Al-1Mo-1V. In addition, the maximum depth of
cracking was only 10 µm in Ti-5Al-2.5Sn compared to 30 µm in
Ti-8Al-1Mo-1V.

The lower H/Ti atom ratio required for cracking and the
greater crack depth in Ti-8Al-1Mo-1V compared to Ti-5Al-2.5Sn
agree with the results in hot-salt cracking. At $10^5$ lb/in.$^2$ outer
fiber stress and 343°C, Ti-8Al-1Mo-1V cracked after about 100
minutes exposure to NaCl, but Ti-5Al-2.5Sn required about 1000
minutes, indicating that some process is occurring that must
continue longer in the 5Al-2.5Sn alloy to cause equivalent damage.
This process is probably the absorption of hydrogen.

Hot-salt and H$^+$-bombarded cracked specimens are compared in
Figure 9. In the as-polished condition, cracks deeper than one
crystal are typically jagged because they are intercrystalline.
In the etched condition, hot-salt cracks are typically blunt-ended
as are cracks produced by H$^+$ bombardment. Hydride structures were
not visible in either alloy at 500X. Occasionally, the grain
structure of the surface of a specimen was very clearly defined
in a portion of the stressed areas as though it had been cathodi-
cally etched or as though hydrides were just forming at the grain
boundaries. The hot-salt cracks in Figure 9 were produced by
30 hours exposure to NaCl at 350°C.

The fluence data were evaluated (as discussed in the Appendix)
to establish the surface concentrations of hydrogen that initiated
cracking and the concentrations near the crack tips that permitted
the cracks to propagate. Estimates are given in Table I.

The hydrogen concentrations calculated for crack propagation
(concentration at crack tip) at $10^5$ lb/in.$^2$ outer fiber stress
agree closely with published data. Gray$^6$ found \textasciitilde 100 ppm H$_2$
by vacuum fusion analyses of specimens taken from titanium alloys
near hot-salt cracks. The value 5.1 cm$^3$ H$_2$/cm$^3$ Ti represents
100 ppm; 3.4 cm$^3$ H$_2$/cm$^3$ Ti represents 67 ppm. As mentioned
in the Appendix, the calculated hydrogen concentrations contain
several uncertainties, but are expected to be accurate within a
factor of 4, equal to \textasciitilde 200 ppm maximum for Ti-5Al-2.5Sn. Tiner
believes this is equivalent to 1200-2000 ppm in the grain bound-
daries for Ti-5Al-2.5Sn.$^{10}$
HOT-SALT CRACKS

As Polished

Etched

Hf BOMBARDMENT CRACKS

As Polished Ti-8Al-1Mo-IV

50μm

FIG. 9 CRACKS PRODUCED IN Ti-Al ALLOYS BY HOT SALT AND H+ BOMBARDMENT

TABLE I

Hydrogen Concentration in Titanium Required to Initiate and Propagate Cracks

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Maximum Concentration at 1 μm, cm³ H₂/cm³ Ti</th>
<th>Concentration at Crack Tip, cm³ H₂/cm³ Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Total</td>
</tr>
<tr>
<td>Ti-5Al-2.5Sn</td>
<td>1.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Ti-5Al-2.5Sn</td>
<td>0.3</td>
<td>3.8</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>1.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>0.2</td>
<td>3.7</td>
</tr>
</tbody>
</table>

a. At 10 μm.
b. At 30 μm.
APPARENT DIFFERENCES IN EXPERIMENTAL RESULTS AND SERVICE APPLICATIONS

Although laboratory studies consistently indicate that hot-salt stress corrosion cracking could be a major problem in the use of these alloys in a supersonic airplane, examination of specimens from field service tests\(^1\) indicates that titanium-aluminum alloys have not cracked. The proposed mechanism of hydrogen embrittlement can explain the difference between laboratory and field experience.

Most laboratory specimens are corroded in static or low-flow systems where the reaction products concentrate close to the metal. In service, especially in compressor turbine blades and on airfoils, high air flows effectively disperse corrosion products.

The corrosion products HCl and H\(_2\), involved in hot-salt cracking between 250 and 600°C, are gases. In the proposed mechanism, water must be very close to the metal-salt mixture when the salt is heated to form a hydrogen halide. In service, most of the hydrogen halides formed will be lost to the atmosphere before they can attack the metal because of the oxide barrier and the high air velocity. If the metal is attacked by the hydrogen halide, the hydrogen too will be lost and will not embrittle the metal, if it is not absorbed immediately. This type of situation will lead to longer incubation times. In addition, airplane flights are often shorter than crack incubation times even in the laboratory; i.e., 1000 min for Ti-5Al-2.5Sn at yield and 343°C.

The \(\beta\) alloys have a much higher solubility for hydrogen than those of the \(\alpha\) or \(\alpha-\beta\) types. Because hydrogen is vital to the cracking process the amount of hydrogen absorbed by a stressed \(\beta\) alloy would have little effect on crack initiation, while the same amount of hydrogen introduced into an \(\alpha\) or \(\alpha-\beta\) alloy could cause rupture under identical conditions. \(\beta\) alloys often lose ductility from attack by hot-salt, but cracks do not always initiate; the \(\alpha\) alloys, on the other hand, usually crack under high static stress.\(^4\)

ACKNOWLEDGMENTS

The assistance of W. L. Pillinger and A. H. Dexter in recommending and evaluating the diffusivity equations and M. E. Epting in performing much of the experimental work is gratefully acknowledged.
APPENDIX - CALCULATION OF FLUENCE DATA

The amount of hydrogen diffusing into the metal from exposure to H\textsuperscript{+} bombardment was the difference between the H\textsuperscript{+} fluence and the fraction of the fluence that was released from the metal by off-gassing. A rigorous mathematical evaluation of the absolute hydrogen concentration profile in the metal is difficult. The main reasons are: 1) hydrogen off-gassing increases as the concentration within the metal increases; 2) the average calculated H\textsuperscript{+} range is valid but range is actually a Gaussian distribution about that average; 3) the diffusivity D depends on temperature, and the temperature decreased with specimen depth, although the temperature gradient was probably small over the depths (0-30 μm maximum) considered.

The method used to calculate the concentration profile C was based on Fick's second law,\textsuperscript{11} with a distributed internal source A(x) and with the diffusivity D treated as constant

\[ \frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} = A(x) \quad (1) \]

The proton injection was treated as a step function source of gas in the metal; to approximate a Gaussian distribution, a square wave centered about the average range was used.

![Diagram](image-url)
The source \( A(x) \) is related to the fluence rate \( P \) of hydrogen ions entering the metal by

\[
P = \int_0^\lambda A(x) \, dx
\]

The boundary and initial conditions for the slab (specimen) were taken as

\[
\begin{align*}
C(0,t) &= 0 \\
C(\ell,t) &= 0 \\
C(x,0) &= 0
\end{align*}
\]

Input data to a computer program in solving the profile are shown below.

<table>
<thead>
<tr>
<th>Alloy:</th>
<th>Ti-5Al-2.5Sn</th>
<th>Ti-8Al-1Mo-1V</th>
</tr>
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<tbody>
<tr>
<td>Results:</td>
<td>Cracks</td>
<td>No Cracks</td>
</tr>
<tr>
<td>Cracks</td>
<td>No Cracks</td>
<td></td>
</tr>
<tr>
<td>( P, \text{ cm}^3 \text{ H/cm}^2\text{-sec} )</td>
<td>( 5.73 \times 10^{-4} )</td>
<td>( 1.15 \times 10^{-4} )</td>
</tr>
<tr>
<td>( t, \text{ sec} )</td>
<td>( 3.60 \times 10^3 )</td>
<td>( 3.60 \times 10^3 )</td>
</tr>
</tbody>
</table>

Diffusivity \( D \) was taken as \( 3.35 \times 10^{-8} \text{ cm}^2/\text{sec} \).

The square wave range \((a-b)\) was taken as both 0.2 and 1.0 \( \mu \text{m} \) entered at the average proton range. The thickness of all specimens, \( \ell \), was 0.0889 cm.

A typical profile is shown for a 0.2 \( \mu \text{m} \) square wave source.
In the region of interest (1 and 10 μm for Ti-5Al-2.5Sn and 1 and 30 μm for Ti-8Al-1Mo-1V), concentration approached steady-state values within 15% or less. Concentrations were relatively insensitive to the width of the square wave (0.2 to 1.0 μm). The major uncertainty is probably the use of a value for D evaluated for the temperature measured at the midplane, although much of the diffusion occurred at the specimen surface. Published values for $D_0$ and $E_d$ were used$^{12}$ to evaluate the equation $D = D_0 \exp(-E_d/RT)$. 
REFERENCES


