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by R. S. Ondrejcin and M. R. Louthan, Jr.

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E. I. DU PONT DE NEMOURS & COMPANY
Aiken, S. C.
for

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ABSTRACT

The reactions of titanium-aluminum alloys with anhydrous HCl gas were studied, and the reaction products were found to be $TiCl_2$, $TiCl_3$, $TiCl_4$, Al_2Cl_6, and H_2. These products are considered to be intermediates in the hot-salt stress corrosion cracking of titanium-aluminum alloys. These products are not normally identified because they oxidize and hydrolyze in the presence of oxygen, moisture, and heat. Fractographic examination of Ti-8Al-1Mo-1V specimens cracked by hot salt and HCl showed the same fracture mechanism in both cases — mechanical rupture accompanied by dislocation movement. It is proposed that stress-sorption is the mechanism of cracking, and that atomic hydrogen is the species sorbed.

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INTRODUCTION

Titanium-aluminum alloys are important in the design of supersonic aircraft which will operate at skin temperatures as high as 290°C (550°F) while contaminated with sea salt. In laboratory tests, titanium-aluminum alloys are susceptible to hot-salt stress corrosion cracking that might also occur during operation of supersonic aircraft. The Savannah River Laboratory is engaged in a research program sponsored by the National Aeronautics and Space Administration to develop fundamental knowledge about the mechanism of hot-salt stress corrosion cracking of these alloys.

Previous work[1] had shown that the reactions between titanium alloys and hot salt produce significant amounts of HCl, and that HCl gas caused cracking.[2] In hot-salt exposures, HCl is produced by the pyrohydrolysis of the chloride salt and water between 260°C (500°F) and 400°C (752°F).[1] Other workers have postulated that chlorine gas is produced and acts as a localized attacking agent;[3] however, they were able to identify chlorine only above 650°C (1202°F).

This report describes the reactions of titanium and its alloys with anhydrous HCl and moist HCl. Possible intermediates and final products were identified in the hot-salt cracking process. In addition, fractography was used to identify the process for crack propagation.

SUMMARY

Titanium reacts with double-distilled anhydrous HCl to produce $TiCl_2$, $TiCl_3$, $TiCl_4$, and H_2 at 350°C (662°F). Aluminum, when present as an alloying agent, reacts to produce Al_2Cl_6. In the presence of moist air, hydrated aluminum chloride was formed. $TiCl_4$ was hydrolyzed, and $TiCl_2$ and $TiCl_3$ were hydrolyzed and oxidized to form TiO_2, HCl, and H_2. Fractographic analyses

of specimens cracked with NaCl, HCl, and $SnCl_2$ showed that the fracture mechanism was the same in all cases and was consistent with a stress-sorption process. The sorbing species is postulated to be hydrogen.

DISCUSSION

EXPERIMENTAL PROCEDURES

Specimen Exposure to Anhydrous HCl

Metallographically polished specimens (3 x 0.25 x 0.050 inch) of duplex-annealed Ti-8Al-1Mo-1V were used. The strips were mounted and stressed in 4-point loading holders. A standard beam deflection formula was used to calculate stress.[4] The specimen and holder were vapor degreased in isopropyl alcohol and placed in a glass capsule.

The capsules containing the stressed specimen were filled with double-distilled HCl gas. Figure 1 shows the vacuum manifold used to fill the capsules. After the system was evacuated to $<10^{-5}$ torr, commercially available "anhydrous" HCl gas (99%) was frozen in Trap 1 with liquid nitrogen coolant. Noncondensable gases were pumped off until $<10^{-5}$ torr was attained; then the HCl was distilled into the second trap by changing Trap 1 coolant to solid CO_2 in trichloroethylene and cooling Trap 2 with liquid nitrogen. Water remained frozen in Trap 1, and the system was again evacuated to $<10^{-5}$ torr to remove the last traces of noncondensable gases. The specimens and their capsules were then baked in a tube furnace at 400°C (752°F) for 30 minutes to remove the last traces of moisture while the HCl remained frozen in Trap 2. The pumping system was closed off and the specimen cooled. HCl was then distilled into the specimen capsules by partially removing the liquid nitrogen from Trap 2. Pressure was measured on the manometer, and the specimen capsule was sealed off with a torch when the desired pressure was obtained.

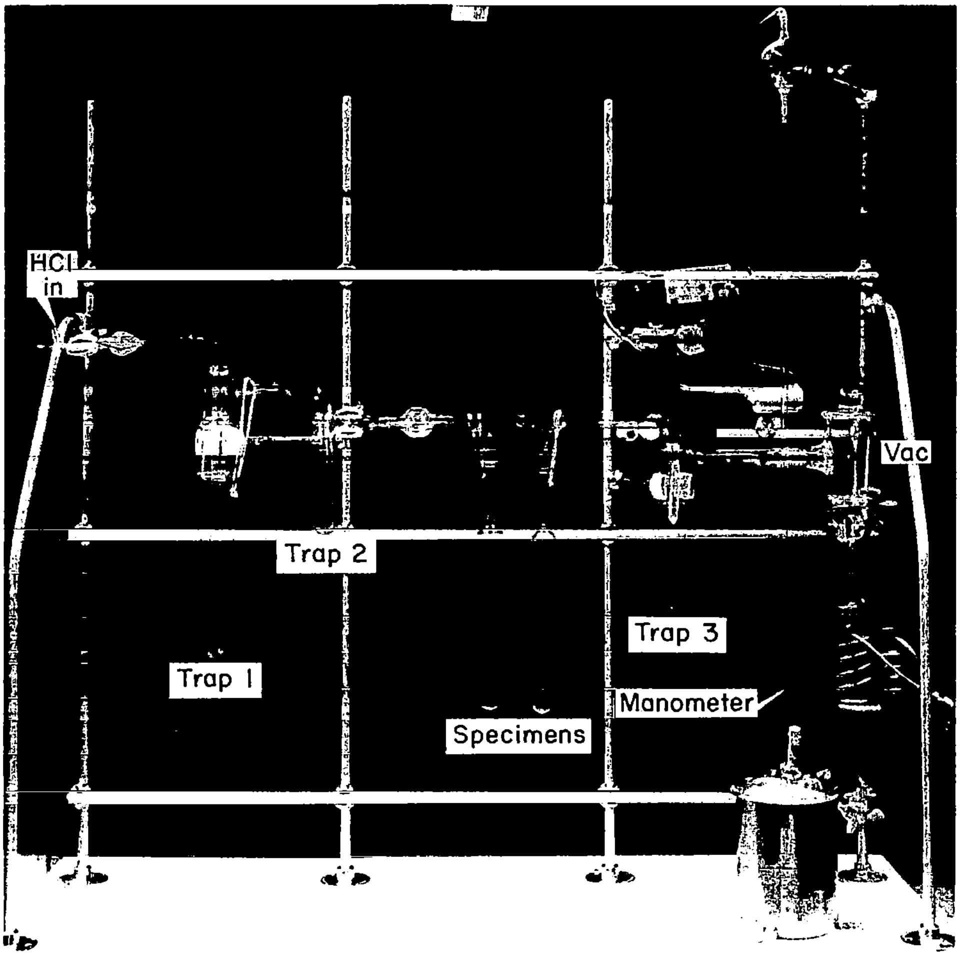


FIG. 1 VACUUM MANIFOLD FOR LOADING CAPSULES CONTAINING STRESSED SPECIMENS WITH ANHYDROUS HCl GAS

To prevent mercury vapors and diffusion pump oil from backstreaming into the specimen capsule, Trap 3 was cooled with solid CO_2 in trichloroethylene.

Sealed specimen capsules were placed in tube furnaces at various temperatures. The capsules were filled and the specimens stressed so that, at test temperature, HCl pressure was 1 atmosphere and stress was 85% of yield.[5]

Specimen Preparation for Fractographic Analyses

Five types of specimens were prepared for fractographic analyses:

1. Cracked with NaCl
2. Cracked with $SnCl_2 \cdot 2H_2O$
3. Cracked with Anhydrous HCl
4. Cracked with HCl containing 5 mole % H_2O
5. Charged with H_2 and cracked mechanically

All specimens were tested until complete failure occurred.

The salt-coated samples were cracked at 343°C (650°F). The NaCl-treated specimen was a stressed U-bend rather than a 4-point loaded specimen in order to attain complete fracture in a reasonable time. The stannous-chloride-treated specimens were 4-point loaded to 10^5 lb/in^2 calculated stress in the outer fibers. Detailed specimen preparation for hot-salt stress corrosion cracking studies is described in Reference 1. One stannous-chloride-coated specimen was allowed to crack at room temperature after the crack was initiated at elevated temperature.

The specimens cracked in HCl gas were treated as described in the preceding section. Water was added to one capsule before loading with HCl gas. Cracking temperature was 350°C (662°F).

Metallographically polished, unstressed specimens were charged in a modified Sieverts Apparatus[6] with H_2 purified by diffusion through palladium. The specimens were charged for about 1 hour at 650°C (1202°F) with H_2 at 400 mm pressure, cooled to room temperature, and bent to fracture.

Cellulose acetate-carbon replicas were made of the fracture surfaces.

REACTIONS OF TITANIUM

Previous results[1] have shown that crack initiation in the hot-salt stress corrosion cracking of titanium-aluminum alloys was associated with the pyrohydrolytic reaction of a halide salt and water. The halogen acid produced by pyrohydrolysis reacted with the metal to form hydrogen. Reactions between halogen acids and titanium (Table I) are numerous. In addition, a few reactions(9-14) are included that could form the extremely protective oxide found on titanium metal and its alloys.

TABLE I

REACTIONS OF TITANIUM OR ITS CHLORIDES AT 327°C (600°K, 621°F)

	$Ti(c) + HCl(g)$	ΔF (kcal/mole of Ti or salt)
(1)	$Ti + 2HCl \rightarrow TiCl_2 + H_2$	-55.9
(2)	$Ti + 3HCl \rightarrow TiCl_3 + \frac{3}{2}H_2$	-70.4
(3)	$Ti + 4HCl \rightarrow TiCl_4 + 2H_2$	-67.9
	$Salt(c) + HCl(g)$ or $Ti(c)$	
(4)	$TiCl_2 + HCl \rightarrow TiCl_3 + \frac{1}{2}H_2$	-14.5
(5)	$TiCl_2 + 2HCl \rightarrow TiCl_4 + H_2$	-12.0
(6)	$TiCl_3 + HCl \rightarrow TiCl_4 + \frac{1}{2}H_2$	+2.5
(7)	$TiCl_3 + \frac{1}{2}Ti \rightarrow \frac{3}{2}TiCl_2$	-13.5
(8)	$TiCl_4 + Ti \rightarrow 2TiCl_2$	-43.9
	$Ti(c) + O_2(g)$ or $H_2O(g)$	
(9)	$Ti + \frac{1}{2}O_2 \rightarrow TiO$	-109.9
(10)	$Ti + \frac{3}{4}O_2 \rightarrow \frac{1}{2}Ti_2O_3$	-160.9
(11)	$Ti + O_2 \rightarrow TiO_2$	-199.1
(12)	$Ti + H_2O \rightarrow TiO + H_2$	-58.7
(13)	$Ti + \frac{3}{2}H_2O \rightarrow \frac{1}{2}Ti_2O_3 + \frac{3}{2}H_2$	-84.1
(14)	$Ti + 2H_2O \rightarrow TiO_2 + 2H_2$	-96.7

The direct combination of titanium to form the di-, tri-, and tetrachlorides is quite favorable, and would be expected to proceed at 327°C (621°F) in an anhydrous system. The dihalide would probably go to the tri- or tetrahalide. The trihalide would not be expected to convert to the tetrahalide. Also if the higher halides come in contact with titanium metal they could be reduced to the dihalide.

Since such a large number of reactions are possible between titanium or its chlorides and HCl, the actual end products will be primarily dependent on reaction kinetics rather than on the free energies of formation.

In practical applications, titanium is highly resistant to corrosive attack because of the stability of the protective oxide on its surface. Table I infers this stability from the extremely high negative heat of formation (about 200 kcal/mole for TiO_2). Note that in the absence of oxygen but in the presence of water, titanium will form an oxide, and hydrogen will be liberated.

CRACKING WITH ANHYDROUS HCl

Purity of HCl

Commercially pure (99%) "anhydrous" HCl was analyzed by mass spectrometry; H_2, O_2, N_2, H_2O and organics were detected. After double distillation, the only detectable impurity was 0.1 mole % N_2, which does not influence Ti-HCl reactions.

Effect of Surface Oxide Films on Time to Cracking

A series of specimens were polished, stressed, encapsulated in an HCl atmosphere, and heated in tube furnaces. The stress on the outer fibers was calculated to be 85% of yield, and the HCl pressure was one atmosphere at test temperature. Duplicates were heated to 250, 300, 350, and 400°C (482, 572, 662, and 752°F). Time to cracking was plotted against temperature in Figure 2.

The time to cracking consists of the time required to penetrate the protective film and the time required to attack the metal and cause cracking. To minimize the time required to

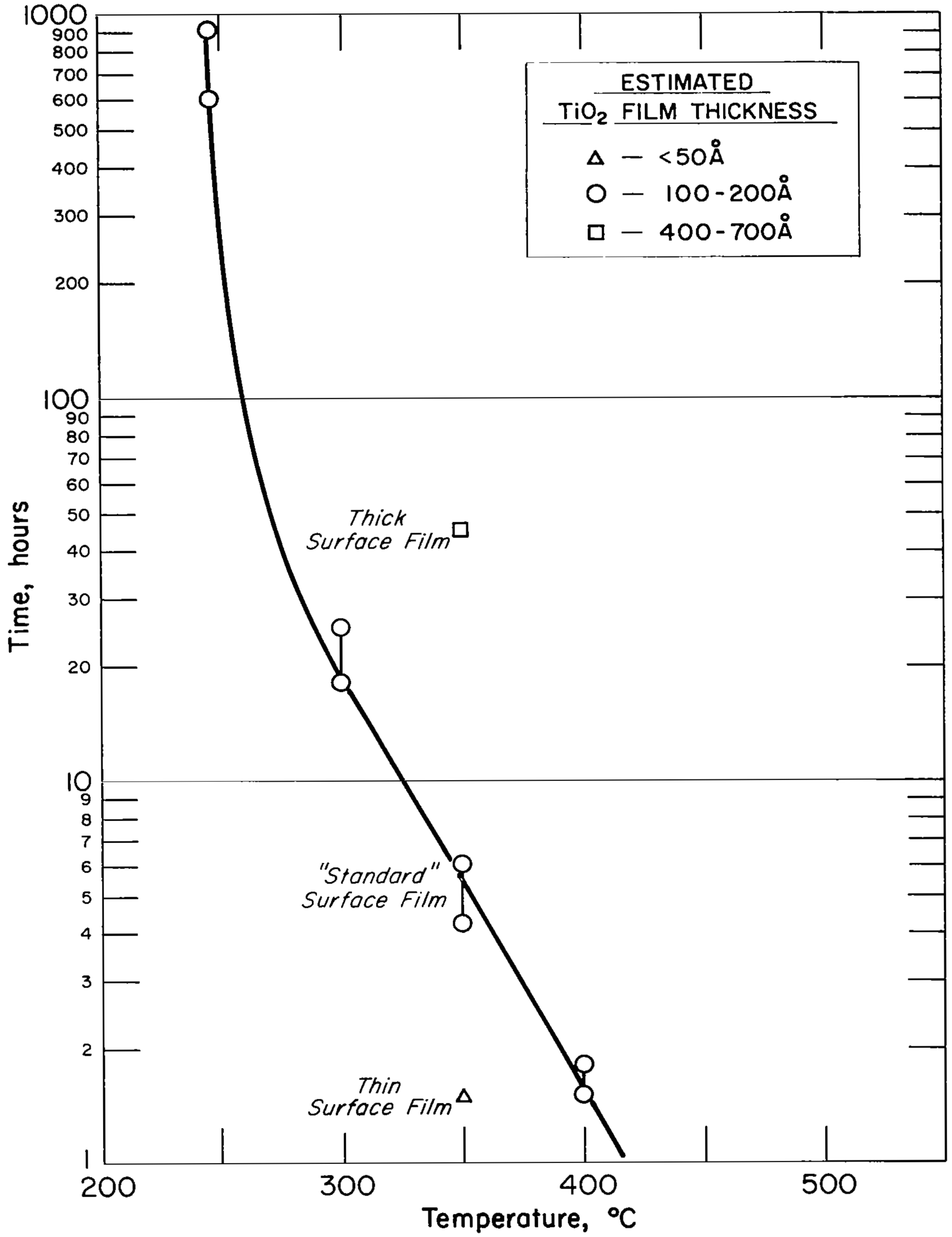


FIG. 2 TIME TO CRACKING OF TI-8Al-1Mo-1V LOADED AT FIBER STRESS OF 85% OF YIELD STRENGTH IN ANHYDROUS HCl

penetrate the protective oxide, specimens were given a final polish with 1μ diamond abrasive just before loading. The time between the final polish and insertion of the specimen in the manifold under vacuum was 1.5 to 2 hours.

To show the effect of protective oxide thickness on cracking times, two special specimens with different oxide thicknesses were encapsulated. One was allowed to stand at room temperature for 18 hours prior to testing. The other had been initially oxidized in air until a relatively thick blue oxide film had formed. The times required to crack these two specimens were compared to the time required to crack a standard specimen (~100Å of oxide). Times to cracking were longer as oxide thickness increased (Figure 2). These differences prove that the mechanism for penetration of HCl is diffusion-controlled because HCl gas cannot react with TiO_2, the protective oxide, to form a chloride and water; in fact, the reverse reaction occurs.

The threshold temperature required to produce cracking in samples exposed to anhydrous HCl gas was approximately 245°C (473°F), Figure 2. This closely corresponds to the previously reported threshold temperature for hot salt cracking, 232°C (450°F), and therefore provides additional experimental evidence that hot-salt and HCl cracking of Ti-8Al-1Mo-1V occurs by the same mechanism. The chief difference in HCl and hot-salt cracking is that crack propagation is much more rapid in HCl than in hot salt. The more rapid crack propagation in the HCl environment is attributed to the continuous supply of HCl, whereas in hot-salt attack, HCl must be generated by the pyrohydrolytic reaction.

Reactions and Cracking of Ti-8Al-1Mo-1V

Titanium specimens exposed to anhydrous HCl became generally corroded prior to cracking. The surface of the specimens turned a dark violet and gradually adsorbed water on exposure to air. The corrosion product was water soluble, and formed purple solutions that were air oxidized. X-ray diffraction of the product showed only $TiCl_3$, but several percent of other compounds may have been present. The following reaction shows the oxidation and hydrolysis of $TiCl_3$ with moist air:[7]

$$2TiCl_3 + 7H_2O + \frac{1}{2}O_2 \rightarrow 2TiO_2 \cdot 2H_2O + 6HCl$$

In addition to the corrosion products on the specimen, there were several solid condensates in transluscent bands on the cooler portions of the tubes, plus one colorless liquid condensate. As soon as the glass capsule was cracked, the liquid began to react with the moist air and gave off dense white fumes. The liquid was $TiCl_4$ and the fumes, minute particles of TiO_2 together with water droplets. $TiCl_4$ is known to hydrolyze rapidly according to the reaction

$$TiCl_4 + 4H_2O \rightarrow TiO_2 \cdot 2H_2O + 4HCl$$

to produce the dense white smoke used in smoke screens and skywriting. The bands of solid condensates from the highest to the lowest temperature portions of the capsule were pink, white, and yellow-green. After dissolution in hydrochloric acid, emission spectroscopy showed the pink to be primarily associated with Ti, the white with Al, and the yellow-green with Al and Fe. On the basis of reactions with HCl, relative vapor pressures, color, and cations present, the compounds were identified as $TiCl_3$ (pink), Al_2Cl_6 (white), and Al_2Cl_6 contaminated with $FeCl_2$ (yellow-green).

The identification of $TiCl_3$ and $TiCl_4$ as end products does not exclude $TiCl_2$ as a product. $TiCl_3$ is a violet solid and $TiCl_2$ is a black solid; therefore, small amounts of $TiCl_2$ in $TiCl_3$ would not be observed. In addition, when exposed to air, $TiCl_2$ oxidizes and hydrolyzes very rapidly as follows:

$$TiCl_2 + 3H_2O + \frac{1}{2}O_2 \rightarrow TiO_2 \cdot 2H_2O + 2HCl$$

In the absence of oxygen, water will oxidize $TiCl_2$ to $TiCl_3$ with release of hydrogen.

Reaction of Pure Titanium

Pure titanium is known to be immune to hot-salt stress corrosion cracking, and because HCl forms during exposures to hot salt, pure titanium should not crack in HCl gas. Specimens of commercially pure titanium, stressed to 85% of yield at temperature and loaded with HCl gas in a capsule, did not crack at 343°C (650°F) after 2 weeks exposure.

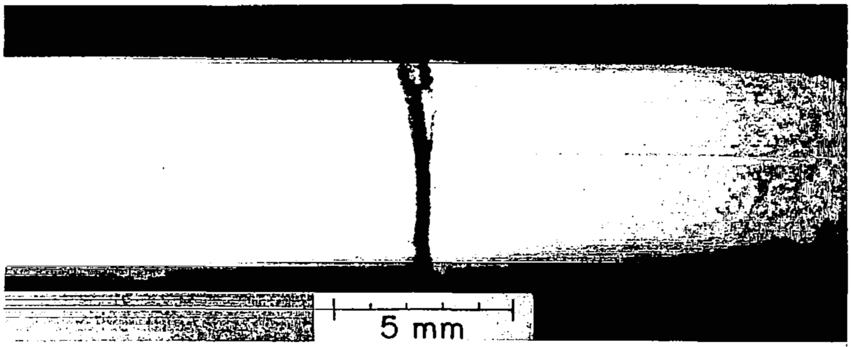
Corrosion of the stressed titanium specimens was severe, and the reaction products were identified as liquid $TiCl_4$ and crystallized $TiCl_3$ on the walls of the tube. A black solid remained on the surface of the specimen. The capsule was opened in a dry box containing nitrogen having <10 ppm H_2O and <100 ppm O_2 impurities. The surface was scraped and the scrapings loaded in a capillary for X-ray diffraction analysis. The compound $TiCl_2$ was identified.

The formation of $TiCl_2$, $TiCl_3$, and $TiCl_4$ as final products in the corrosion of titanium by anhydrous HCl requires the formation of hydrogen with probable hydrogen absorption by the metal. Reactions 1 through 3 in Table I are not necessarily the reactions producing the final products. If $TiCl_2$ had not been identified, direct combination of Ti and HCl to form $TiCl_3$ and $TiCl_4$ would have been a logical conclusion.

CRACKING OF TITANIUM ALLOY BY HCl IN THE PRESENCE OF H_2O

All of the corrosion products formed under anhydrous conditions could be postulated as intermediate products when moisture was present. The titanium chlorides hydrolyzed, and the anhydrous aluminum chloride could not form. If oxygen were also present, the titanium chlorides would oxidize and hydrolyze to titanium dioxide and HCl.

The surface appearance of specimens cracked in the presence of water vapor, but without oxygen, differed entirely from those cracked under anhydrous conditions. In the presence of moisture, the surface of the specimen is bright and shiny (Figure 3) in



a. HCl containing 5 - 6 mole % H_2O

b. Anhydrous HCl

FIG. 3 STRESS CORROSION CRACKING OF Ti-8Al-1Mo-1V BY HCl
Specimens loaded to 85% of yield at 350°C (662°F). Note the general corroded appearance in b when water vapor was not available to form protective oxide.

contrast to the corroded dark violet surface produced under anhydrous conditions. Cracking was complete in both cases. At 350°C (662°F), the time to initiate cracking was about doubled due to a thicker protective oxide formed by the following reaction when the HCl gas contained 5-6 mole % H_2O:

$$\mathrm{Ti} + 2\mathrm{H_2O(g)} \rightarrow \mathrm{TiO_2(C)} + 2\mathrm{H_2(g)}$$

The surface oxide produced under hot-salt stress corrosion cracking conditions was identified by X-ray diffraction as a mixture of rutile and anatase (polymorphs of TiO_2).

When the capsules containing stressed specimens were loaded with 100 μl (2 drops) of 12M hydrochloric acid but with no gaseous

HCl, corrosion was severe, but cracking did not occur. Specimen areas covered by condensed liquid corroded during the early stages of attack at 350°C (662°F) as seen in Figure 4. Cracking did not occur because of 100 μl of acid was probably insufficient. More acid could not be added because of pressurization of the capsule by water at 350°C (662°F).

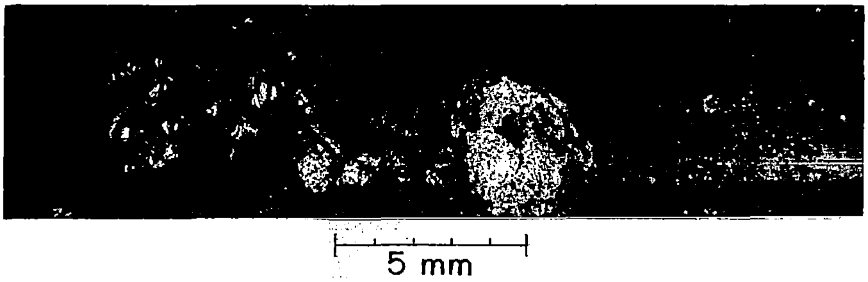


FIG. 4 ATTACK OF STRESSED Ti-8Al-1Mo-1V BY 12M HCl AT 350°C (662°F). Specimen loaded to 85% of yield at temperature. Cracking did not occur, probably because of insufficient acid.

RELATION BETWEEN CRACKING AND SELECTIVE CORROSION OF ALLOYING AGENTS

Exposure of titanium alloys to hot-salt stress corrosion conditions resulting in the pyrohydrolytic formation of HCl requires the production of the corresponding oxide or hydroxide. The HCl or basic oxide produced from the decomposed salt would be expected to attack selectively the impurities or alloying elements in the metal surface. Evidence of such selective attack has been observed.[2] The following experiments were designed to investigate this attack.

A series of alloys was corroded with hot sodium chloride at 343°C (650°F) and 427°C (800°F) to determine which alloying agents were selectively attacked. Corrosion products were analyzed by atomic absorption spectroscopy. The amount of a given metal in the corrosion product was calculated as a weight percent of the total metal present in the product. Results are given in Table II. The same selective attack observed at 343°C (650°F) was also observed at 427°C (800°F).

TABLE II

SELECTIVE ATTACK OF ALLOYING ELEMENTS BY HOT SALT AT 343°C (650°F)

	Wt % of Element in Oxide and Metal											
	Al		Mo		V		Sn		Mn		Fe	
Base Metal	Oxide	Metal[a]	Oxide	Metal[a]	Oxide	Metal[a]	Oxide	Metal[a]	Oxide	Metal[a]	Oxide	Metal[a]
99% Ti	-		-		-		-		-	-	12.9	0.3
Ti-8Mn	-		-		-		-		16.9	7.3	9.3	0.25
Ti-8Al-1Mo-1V	28.6	7.7	1.2	1.0	0.7	1.0	-		-		4.9	0.08
Ti-6Al-4V	7.8	5.9	-		2.5	4.0	-		-		1.3	0.13
Ti-5Al-2.5Sn	13.9	5.2	-		-		0.8	2.3	-		7.0	0.28
Ti-4Al-3Mo-1V	11.6	4.3	1.2	3.2	0.6	1.1	-		-		2.7	0.14

(a) Wt % of element in metal by analysis.

Significant differences were observed in the proportion of given alloying elements in the oxide and in the base metal. The oxide on the Ti-Al alloys was generally enriched in aluminum by a factor of 2-3 over the content in the metal. Molybdenum was either enriched or depleted depending on the alloy. Vanadium and tin were depleted in the oxide compared to the metal. Manganese in the Ti-8Mn alloy was always enriched in the oxide. Iron, present at comparatively low concentrations as an impurity in the metal, was consistently enriched in the oxide by factors larger than any of the alloying elements.

The enrichment of aluminum in the hot-salt corrosion product is related to the corrosion mechanism. Since aluminum oxide acts as an accelerator in the pyrohydrolysis of difficultly hydrolyzable salts such as NaCl,[8] the more aluminum present in the alloy, the more easily HCl is formed under a given set of conditions. Hot-salt cracking of titanium-aluminum alloys has been shown to be more severe with increasing aluminum content.[9] This increase in cracking severity is at least partially due to the ease of formation of HCl, and provides additional experimental evidence for the similarity between HCl and hot-salt cracking.

Sodium hydroxide was not a cracking agent although it is produced by pyrohydrolysis of sodium chloride. Surfaces treated with NaOH are more resistant to cracking by both NaCl and HCl;[2] cracking was delayed but not eliminated. The solid NaOH corroded the Ti-Al alloy specimens and selectively removed aluminum. The metal surface of the Ti-8Al-1Mo-1V specimen was apparently converted to a form closely approaching that of pure Ti, which is not cracked by hot salt or HCl.

FRACTOGRAPHIC STUDIES

Several processes such as electrochemical attack, stress sorption, and hydrogen embrittlement have been suggested to describe hot-salt cracking of titanium alloys.[1] Fractures produced by each of these possible processes should have certain topographic characteristics which are distinguishable by fractography. Fracture mechanisms, such as cleavage, void coalescence, fatigue, glide plane decohesion, and others, have been identified by their fractographic appearances. Illustrations of typical topographic characteristics and descriptions of the mechanism of their formation have been published[10-15] and will not be discussed in detail.

A fractographic analysis of the ruptured surfaces of Ti-8Al-1Mo-1V alloy samples cracked by exposure to moist and dry HCl, $SnCl_2$, and NaCl revealed that in all cases cracking occurred by the same mechanism. The fractures were predominately intergranular with limited regions of transgranular cleavage. Little evidence of ductile failure was noted in any of the samples, while corroded regions were often found. Evidence of dislocation movement and, therefore, of plastic deformation accompanying fracture was also observed.

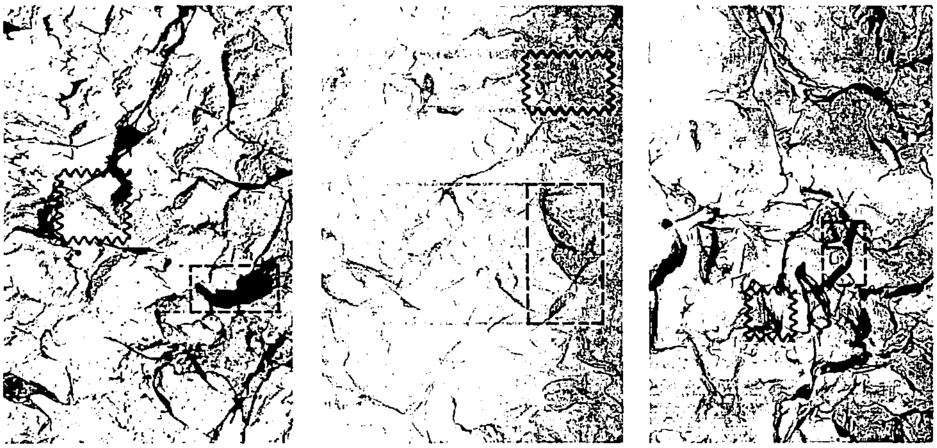
Typical fractographs of samples cracked under five different conditions are shown in Figure 5. The topography of the fracture surfaces is quite similar, and several features are found in common in most of the samples.

A. Intergranular cracking, shown by grain shapes revealed on the fracture surface. Little evidence of ductile failure is apparent.

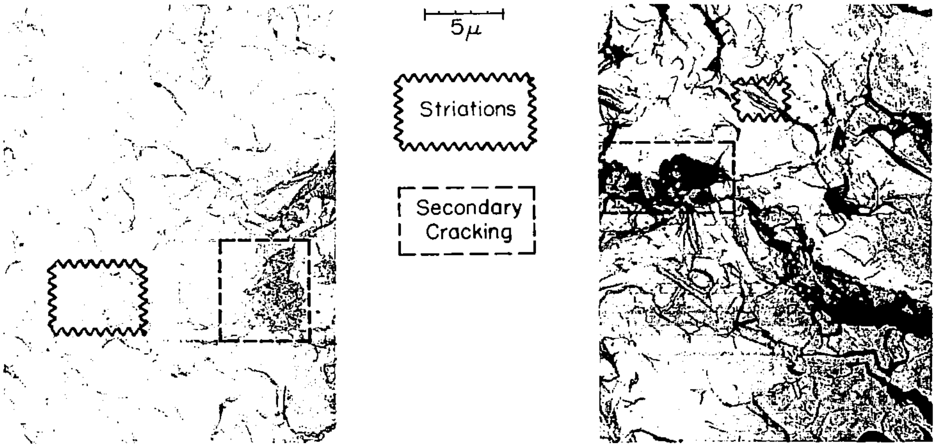
B. Secondary cracking.

C. Rough grain surfaces with areas of more or less regular striations, steps, or folds.

D. Surface roughening, probably resulting from corrosion after cracking was also observed in some samples (Figures 5a, b, c), while others did not show the roughening (Figures 5d, e).



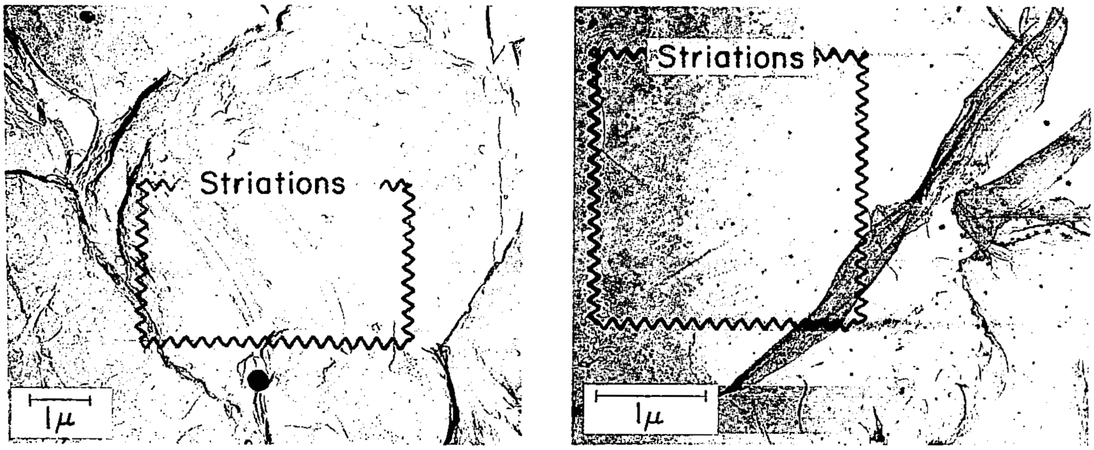
a. $SnCl_2$ at 343°C (650°F) b. NaCl at 343°C (650°F) c. Anhydrous HCl at 343°C (650°F)



d. Moist HCl at 343°C (650°F) e. $SnCl_2$ at 25°C (77°F)

FIG. 5 TYPICAL FRACTOGRAPHS OF HOT-SALT CRACKS IN Ti-8Al-1Mo-1V
Intergranular cracking is shown by the presence of grain shapes in the above fractographs. Note general roughening or pitting of grain surfaces (a, b, c) compared to smooth surfaces (d, e).

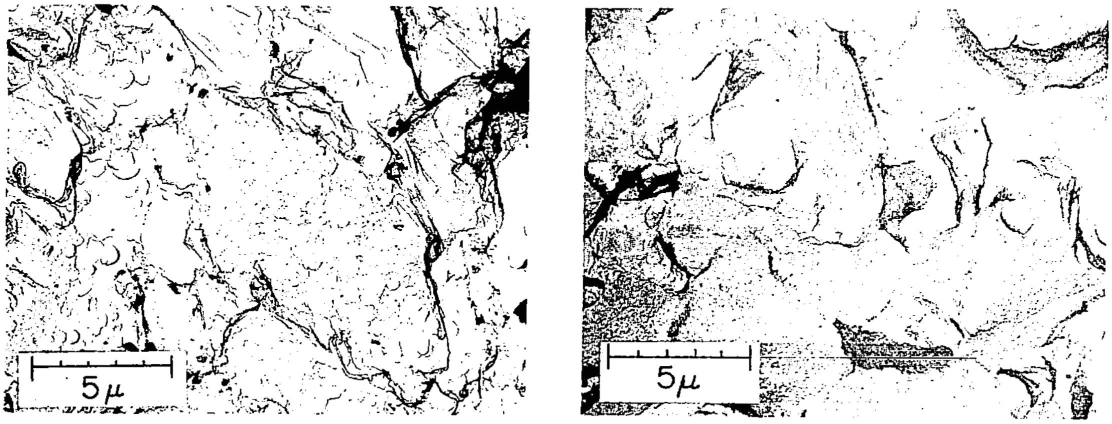
The regular striations are shown in more detail in Figure 6. These regions probably result from serpentine glide, glide plane decohesion, and stretching, and are interpreted as evidence of dislocation movement during the formation of the fracture.



a. NaCl at 343°C (650°F) b. Anhydrous HCl at 343°C (650°F)

FIG. 6 FRACTOGRAPHS SHOWING EVIDENCE OF DISLOCATION MOVEMENT ACCOMPANYING FRACTURE

Severely corroded regions are shown in Figure 7 to emphasize the extent to which roughening can occur.



a. Anhydrous HCl at 343°C (650°F) b. $SnCl_2$ at 343°C (650°F)

FIG. 7 FRACTOGRAPHS SHOWING EVIDENCE OF CORROSION OF FRACTURE FACES
Note extremely pitted and roughened grain surfaces.

River patterns, Figure 8, characteristic of transgranular cleavage were observed in limited regions of most of the samples. There was no evidence that the hot-salt and HCl failures occurred by the coalescense of microvoids. The relatively smooth grain surfaces, the topographic detail, and the evidence of cleavage fracture indicate that the failures must have been mechanical, and that the fracture surfaces corroded after fracture.

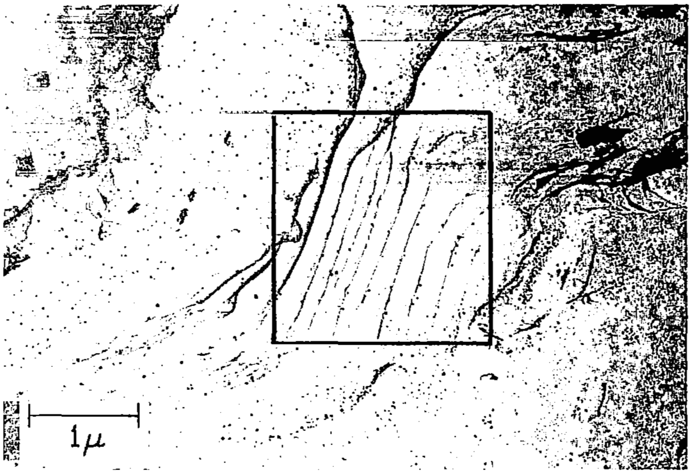
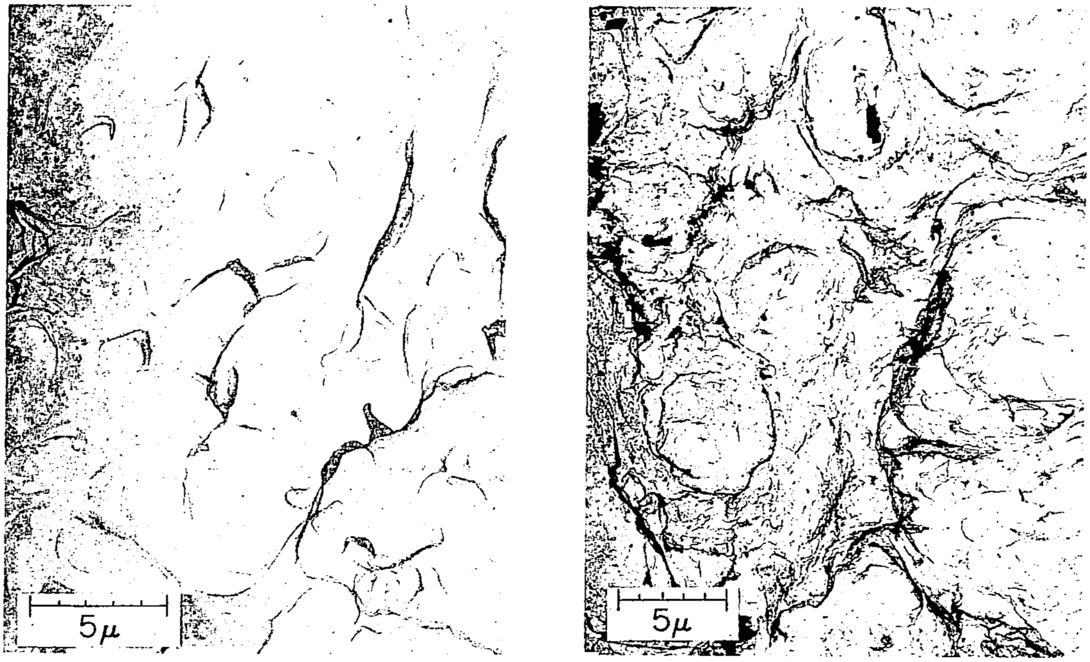


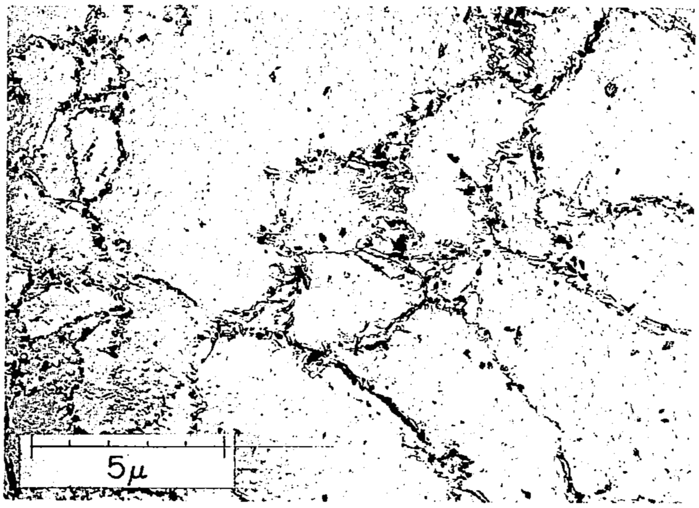
FIG. 8 FRACTOGRAPH SHOWING TYPICAL RIVER PATTERN FOUND IN LIMITED REGIONS OF BOTH HOT-SALT AND HCl CRACKS

Samples containing 1400 and 4000 ppm hydrogen were mechanically ruptured to provide a fractographic comparison with hot-salt and HCl fractures. The sample containing 1400 ppm hydrogen failed by both brittle and ductile mechanisms, but mainly by ductile mechanisms (Figure 9a); the sample with the higher hydrogen content failed almost entirely by brittle mechanisms (Figure 9b). The rough appearance of the fracture surface was due to the twisting path required for the crack to follow the almost continuous network of hydrides lying along the α-α and α-β grain and phase boundaries, shown in the polished microstructure (Figure 9c). These observations show that fracture near a metal-hydride interface was brittle and had a very rough surface due to hydride precipitation. The fractographic appearance of these samples was quite different from that of cracks caused by hot-salt and HCl (compare Figure 5), although isolated regions with



a. Fractograph Showing Ductile Characteristics of Sample Containing 1400 ppm H_2.

b. Fractograph Showing Brittle Characteristics of Sample Containing 4000 ppm H_2.



c. Microstructure of Surface of Sample containing 4000 ppm H_2.

FIG. 9 EFFECT OF HYDROGEN CHARGING ON STRUCTURAL CHARACTERISTICS similar features were observed in one crack produced by exposure to $SnCl_2$ at 343°C (650°F). These studies indicate that hot-salt cracking does not occur by hydride formation and subsequent fracture along or through the hydride platelets.

Because the fractographic studies described above effectively eliminate chemical attack by HCl, and hydrogen embrittlement by hydride platelets, the data indirectly but strongly suggest that stress-sorption is the mechanism of hot-salt cracking of titanium alloys.

SIMILARITY OF HCl CRACKING AND HOT-SALT CRACKING

There is a strong similarity in the cracking processes observed for hot-salt cracking and for HCl cracking, as shown in Table III.

TABLE III
CHARACTERISTICS OF HCl AND HOT-SALT CRACKING OF TITANIUM ALLOYS

Characteristic	Hot-Salt Cracks	HCl Cracks
Fracture Path	Predominately Intergranular	Predominately Intergranular
Fracture Mode	Mechanical	Mechanical
Crack Threshold Temp.	232°C (450°F)	245°C (473°F)
Effect of Oxide Film	Delays Crack Initiation	Delays Crack Initiation
Crack Propagation Rate(a)	Relatively Slow	Rapid

(a) The difference is due to the availability of HCl to react to form atomic hydrogen.

HYDROGEN AS THE SORBING SPECIES

If the sorbing species were either HCl or solid corrosion products, some evidence of their presence would be a common characteristic of all fractures. If the sorbing species were HCl, the clean titanium surface would react vigorously to form titanium chlorides (Reactions 1-3, Table I). Therefore, it is unlikely that HCl as such would be sorbed on a metal surface and not react. In addition, the titanium chlorides formed by the reactions are not stable in the presence of moisture and oxygen; they would react to form titanium oxide. Many fracture surfaces were observed to be free of corrosion.

These observations strongly suggest that the sorbing species is hydrogen. Cracking of Ti-Al alloys follows surface corrosion. The observed incubation time for crack initiation is explained by the need for pyrohydrolysis to progress sufficiently to provide the HCl and in turn the atomic hydrogen. Atomic hydrogen would rapidly combine to form molecular hydrogen and be lost unless adsorbed on the metal and would account for the corrosion-free fracture faces. Because hydrogen is first formed as an atom with an unshared electron (free radical) it will scavenge the nearest available mobile electron such as normally found in a metal lattice. The weakened lattice then becomes more susceptible to cracking.

The fracture mechanism was different from that observed in specimens that were hydrided and then mechanically ruptured. The cracking process is therefore not fracture along hydride platelets formed ahead of the crack tip.

The sorbing species has not been definitely identified but is believed to be atomic hydrogen.

PROPOSED MECHANISM FOR HOT-SALT STRESS CORROSION CRACKING

The following mechanism is proposed for hot-salt stress corrosion cracking of titanium-aluminum alloys.

- Pyrohydrolytically produced HCl penetrates the protective oxide film on titanium-aluminum alloys and reacts to form metal chlorides plus hydrogen.[1]

  With anhydrous HCl, the observed corrosion products were $TiCl_2$, $TiCl_3$, $TiCl_4$, Al_2Cl_6, and H_2.

  Anhydrous HCl reaction products are not usually observed because they hydrolyze ($TiCl_4$), oxidize and hydrolyze ($TiCl_2$, $TiCl_3$), or hydrate (Al_2Cl_6) in the presence of moist air.

- The products formed in anhydrous HCl attack can be intermediates in hot-salt stress corrosion cracking.

  The intermediates form TiO_2, HCl, and H_2 in contact with moisture and oxygen.

  The hydrogen can be absorbed by the alloy.

  The hydrogen chloride can attack the metal, form more hydrogen, and again form chlorides. These chlorides hydrolyze to form TiO_2, HCl, and H_2 to begin the cycle again.

- The fracture mechanism for hot-salt and HCl cracking was stress-sorption.

  The fracture mechanism was the same for samples cracked with NaCl, $SnCl_2 \cdot 2H_2O$, moist HCl, and dry HCl, but different for mechanically cracked hydrogen-charged specimens.

Fracture by hot-salt and HCl was mechanical and accompanied by dislocation movement.

Classical electrochemical and hydrogen embrittlement mechanisms were eliminated as processes.

- Hydrogen is the most likely sorbing species.

  Evidence of HCl or solid corrosion products would be common to all fracture faces if these were the sorbing species; this evidence was not present.

  Hydrogen would account for corrosion-free fracture faces.

  Cracking occurred only after the alloy surface corroded.

  All stages of the corrosion reactions produce hydrogen which is absorbed by the alloy.

  Delay between corrosion and cracking could be due to the time required to produce adequate hydrogen. Corrosion controls the extent of hydrogen formation.

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