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CHLORINE GAS AND FLUORIDE ION IN HOT-SALT STRESS CORROSION CRACKING OF TITANIUM-ALUMINUM ALLOYS

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by

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ABSTRACT

In hot-salt stress corrosion cracking of titanium, chlorine is not the cracking agent at the nominal cracking temperature of 290°C. Above 650°C, however, chlorine does take part in corrosion of titanium. In the cracking process, pyrohydrolytic formation of a hydrogen halide rather than chlorine is indicated. In the salt-titanium reaction at 260 or 400°C, chlorine was not found by mass spectrometry, nor was chlorine observed at 340 or 650°C by ultraviolet spectroscopy. At 650°C, the ratio of HCl/Cl_2 was greater than 105/1, based on the limit of detection by ultraviolet spectroscopy.

Sodium fluoride does not cause hot-salt titanium stress corrosion cracking as do the other sodium halide salts because NaF absorbs much less water, and NaF-coated specimens do not absorb hydrogen generated during corrosion reactions. It is postulated that hydrofluoric acid produced pyrohydrolytically from NaF attacks the metal surface, but both the hydrogen liberated in the attack and the directly affected titanium surface layer are removed from the system by the simultaneous formation and sublimation of TiF_4. Corrosion of titanium by NaCl at 315 and 480°C was due to moisture in the reagents rather than to a "reducible oxide" (TiO_2) as had been proposed by other workers.

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INTRODUCTION

Titanium-aluminum alloys will be used in supersonic aircraft that will operate at skin temperatures as high as 290°C (550°F) while possibly contaminated with sea salt. Laboratory tests showed that titanium-aluminum alloys are susceptible to hot-salt stress corrosion cracking under operating conditions of supersonic aircraft. The Savannah River Laboratory (SRL), sponsored by the National Aeronautics and Space Administration (Contract R-124), is developing fundamental knowledge about the mechanism of hot-salt stress corrosion cracking of these alloys.

Previous work at SRL showed that the reactions between titanium alloys and hot sodium chloride produced significant amounts of HCl[1] and that HCl gas caused cracking.[2] In hot-salt exposures, HCl is produced by the pyrohydrolysis of the chloride salt and water.[1]

Our proposed general mechanism for hot-salt stress corrosion cracking of titanium alloys[3] involves the pyrohydrolytic formation of the hydrogen halide corresponding to the anion of the salt (i.e., HCl from Cl salts), and attack of the metal by the hydrogen halide after penetration of the protective oxide film. Hydrogen is generated by the reaction and is partially absorbed by the metal surface. The hydrogen embrittles the surface, and the crack can then be initiated by residual or applied stresses.

Other workers have postulated that chorine gas is produced and acts as a localized attacking agent;[4] however, the tests they made only identified an oxidizing agent (not specifically Cl_2) at and above 650°C.

In support of our general mechanism for hot-salt stress corrosion cracking of titanium alloys, this report:

a) Describes our attempts to detect chlorine as a corrosion product between 260 and 800°C by mass spectrometry, ultraviolet spectroscopy, and the starch-iodide test.

b) Investigates explanations for the anomalous fact that NaF does not cause hot-salt stress-corrosion cracking while the other sodium halides do.

c) Shows that moisture in the system and an elevated rolling temperature were probably responsible for the salt attack attributed[4] to a "reducible oxide" on the titanium.

SUMMARY

The proposed general mechanism[3] for hot-salt cracking still appears to be valid because:

a) At temperatures of aircraft operation (~300°C), HCl rather than Cl_2 is the principal hot-salt reaction product; even at 650°C, no Cl_2 was detected. Ultraviolet spectroscopy showed less than 3.5 µg of Cl_2 from 500 cm^2 of heated, NaCl-coated titanium chips at 340 and 650°C during 17-hour tests; at 800°C however, 3500 to 18,000 µg of Cl_2 was detected. Mass spectrographic data that showed the presence of HCl but not Cl_2 were used to calculate the molar ratios of HCl/Cl_2, assuming that Cl_2 was generated just below the limit of detection. At 260°C, the HCl/Cl_2 ratio was 11:1; at 400°C the ratio was 159:1.

Earlier evidence of the presence of chlorine was by the starch-iodide test, which was shown to be capable of erroneous results.

Based on the pH change in the starch-iodide test and the ultraviolet spectroscopy limit of detection for Cl_2, the molar ratio of HCl/Cl_2 at 650°C was >105/1, which indicates that the effect of the HCl on the cracking process would have masked any significant influence of Cl_2, if it had been present.

b) The failure of NaF to produce hot-salt stress corrosion cracking is probably due to removal of hydrogen from the metal surface as that surface reacts and sublimes as TiF_4. Experiments with tritiated water also showed that NaF does not adsorb or occlude water as easily as NaCl. NaF-coated test specimens did not absorb hydrogen and did not crack; specimens coated with NaCl, NaBr, and NaI did absorb hydrogen and did crack. The hydrogen halides, intermediates in the formation of H_2, were shown to have attack rates on titanium-aluminum alloys that decrease in the order HF > HCl > HBr > HI. The HF rate is more than 1000 times that of HCl, due to the small size and high electronegativity of fluoride. The very aggressive corrosion of titanium by the pyrohydrolytically generated HF consumes titanium from the surface and removes it from the system so that the remaining surface contains no adsorbed hydrogen.

c) It was very unlikely that a "reducible oxide" (TiO_2) was a factor in causing hot-salt corrosion at 315 and 480°C, as had been reported.[4] The moisture associated with the TiO_2 and the hot rolling operation in the temperature range for Cl_2 production probably were responsible for the observed effects. In our work, reaction products were not formed from NaCl or NaCl + TiO_2 in titanium after 100 hours at 315 or 480°C when: 1) reagents and metal were vacuum dried, 2) test components

were handled in a dry box or vacuum during preparation, and 3) cold rolling rather than hot rolling was used for size reduction. Reaction products were observed at 315 and 480°C only if the metal was not dried and the salt contained brine inclusions.

DISCUSSION

ANALYSIS FOR CHLORINE AS A CORROSION PRODUCT

Several investigators have reported "proof" of chlorine as a corrosion product by the starch-iodide test.[4,5] Others[6] questioned the validity of this test that was conducted as described below except that two very important steps were usually omitted: (1) pH adjustment of the starch-iodide solution before the test, and (2) pH measurement after the test. The starch-iodide test is a test for an oxidizing agent but is not specific for chlorine; it is also pH dependent.[7]

The following sections compare the starch-iodide and spectroscopic methods for the determination of chlorine evolved during the heating of salt-coated titanium alloy chips.

A specific test for chlorine (Reaction 2 below) involves detection of OCl^- in a basic solution and quantitative determination of chlorine by ultraviolet spectroscopy.

Experimental

Samples of Ti-8Al-1Mo-1V chips weighing 3.4 ±0.1 g (surface area: 150 cm^2/g for a total of 500 cm^2) were coated with sodium chloride or stannous chloride by room-temperature evaporation of the appropriate salt solution. The coated chips were placed directly in a mullite (2 moles SiO_2 + 3 moles Al_2O_3) combustion tube heated in a resistance furnace to 340, 650, and 800°C. Uncoated chips were used as blanks.

Filtered compressed air was flowed over the heated chips at 1 cc/sec for 17 hours. The reaction gases were filtered through glass wool and scrubbed by 50 ml of solution in a graduated cylinder. The collection solution was either 45 ml of 0.25M KI plus 5 ml of stabilized starch indicator or 50 ml of 1M NaOH. The pH of the starch-iodide solution was adjusted to 6 with dilute NaOH solution before absorption; the pH was measured after absorption.

Chlorine reacts with both the starch-iodide and the sodium hydroxide solutions:

$$2I^- + Cl_2 \rightarrow 2Cl^- + I_2 \qquad (1)$$

$$2OH^- + Cl_2 \rightarrow OCl^- + Cl^- + HOH \qquad (2)$$

Reaction 1 produces a purple color from reaction of the I_2 with the suspended starch. This reaction is sensitive to ~2 x 10^{-5}M I_2.[7] Reaction 2 produces OCl^-, detectable by ultraviolet spectroscopy at 2925 Å.[8] The detection limit was determined to be 1 x 10^{-5}M OCl^- using 10 cm cells with a Cary Model 14 recording spectrophotometer.

Starch-Iodide Test for Cl_2

Reaction 1 occurs between pH 5 and 8. Bromine reacts equally well. Below a pH of about 4.5, air oxidation also takes place in the starch-iodide solution:

$$2I^- + 2H^+ + \tfrac{1}{2}O_2 \rightarrow I_2 + H_2O \qquad (3)$$

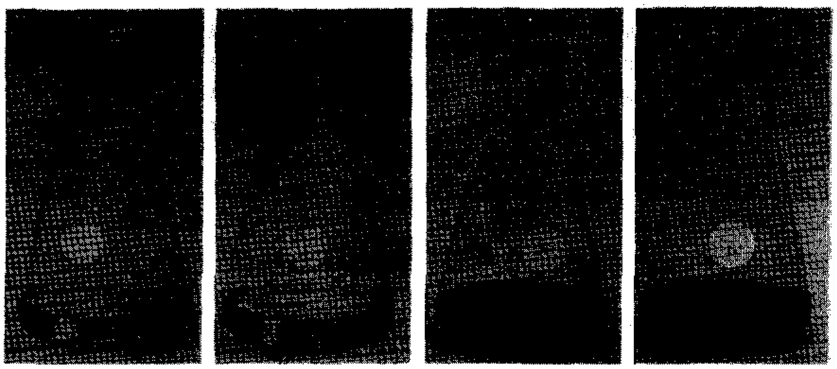
Reaction 3 proceeds with increasing rapidity as the pH of the starch-iodide solution is lowered; light catalyzes the reaction. Therefore a positive test only indicates an oxidizing agent such as Cl_2 or Br_2, or that the air is oxidizing an acidified starch-iodide solution.

The reacted starch-iodide test solutions are shown in Figure 1. At 340°C, the test was slightly positive; at 650°C, definitely positive. In both tests, the starch-iodide solution became more acidic than the blank; therefore, this test could not determine whether the change was due to Cl_2 oxidation or to air oxidation in HCl solution.

The solutions from the NaCl-coated chips were compared to a solution prepared by trapping the gases from heated alloy chips coated with $SnCl_2 \cdot 2H_2O$. $SnCl_2 \cdot 2H_2O$ is known to decompose by the evolution of HCl. The starch-iodide test again showed a definitely positive, but erroneous, indication of Cl_2.

Spectroscopic Analysis for Cl_2

In the test with 1M NaOH as the absorption solution, each solution was analyzed at the end of 17 hours. Results are shown in Table I.



Salt coating on chips	None	NaCl	NaCl	$SnCl_2 \cdot 2H_2O$
Temp of chips, °C	650	340	650	230
Final pH of starch-iodide scrubbing solution	4.8	4.5	3.7	0.7

At low temperatures (230°C), easily hydrolyzable salts ($SnCl_2 \cdot 2H_2O$) that evolve HCl lower the pH of the solution and give a distinct positive test even though chlorine is not a decomposition product. The test cannot determine whether Cl_2 was evolved by NaCl decomposition or whether air oxidation takes place.

FIG. 1 POSITIVE REACTIONS WITH THE STARCH-IODIDE TEST

TABLE I

Determination of Cl_2 by Ultraviolet Spectroscopy

Temp of Chips, °C	Conc of Cl_2, M	Cl_2 Released/Unit Area, μg/cm²
340	$<1 \times 10^{-5}$ [a]	<0.07[a]
650	$<1 \times 10^{-5}$	<0.07
800	$1\text{-}5 \times 10^{-2}$	70-350

a Lower limit of detection

The identification of Cl_2 at 800°C (1470°F) is significant and confirms previously reported results that were based on non-definitive starch-iodide tests.[4,5] However, extrapolation of this data to hot-salt stress corrosion between 290 and 500°C is not valid. Above 500°C, both generalized corrosion and cracking are important, probably because both Cl_2 and HCl are formed above 650°C.

The results on chloride evolution in Table I agree with published mass spectral data,[1] which showed that HCl but not Cl_2 was evolved at 260 and 400°C from NaCl-coated chips. These data were recalculated to determine the possible ratio of HCl/Cl_2, assuming in each case that Cl_2 was generated just below the limit of detection. At 260°C, the molar ratio of HCl/Cl_2 was 11:1 after 2 hours; at 400°C the ratio was 159:1. The ratio increased because more H_2 and HCl were generated at the higher temperature while the sensitivity to Cl_2 remained constant.

The molar ratios of 11:1 and 159:1 HCl/Cl_2 are low. If Cl_2 had been generated at a concentration equivalent to the detection limit of the mass spectrometer at 260°C, it would have been observed at 400°C because of reaction kinetics. In addition, if Cl_2 had been generated in amounts equivalent to the HCl generated (9 micromoles) at 650°C, ultraviolet analysis of the solutions would have easily detected the presence of Cl_2. Nine micromoles of Cl_2 is 315 μg; the Cl_2 detection limit was 3.5 μg.

FLUORIDE ION IN HOT-SALT STRESS CORROSION CRACKING

NaF does not cause hot-salt stress corrosion cracking of titanium-aluminum alloys as do the other sodium halides.[1] The following mechanism to explain this behavior is consistent with our postulated mechanism for hot-salt stress corrosion cracking. The mechanism proposes that crack initiation involves the pyrohydrolytic formation of the hydrogen halide corresponding to the anion of the salt (i.e., HCl from Cl salts), and subsequent attack of the metal by the hydrogen halide after penetration of the protective oxide film. Hydrogen is generated by the reaction and partially absorbed by the metal surface. The hydrogen embrittles the surface, and the crack is initiated by stresses. The following paragraphs present evidence on the behavior of fluorides that provides a theory to explain the observation that fluorides do not cause hot-salt cracking.

All the hydrogen halides should attack titanium-aluminum alloys but at different rates. If H^+ is of primary importance in initiating chemical attack, the most rapid generation of hydrogen should be observed by HI attack because this is the strongest halogen acid. If the halogen ion is the most important because of complex ion formation, HF, a very weak acid should attack the metal at the highest rate. The measured rates of surface attack (Table II) show that attack by HF is more than 1000 times faster than by any other halogen acid.

TABLE II

Attack Rate of 6M Halogen Acids at 85°C on Ti-8Al-1Mo-1V

Acid	Attack Time, min	Penetration Rate, μm/hr
HF	0.13	14,000
HCl	60	11
HBr	60	1.5
HI	120	0.5[a]

---

[a] Lower limit of detection.

Two important conclusions can be drawn from Table II.

- Hydrogen ion concentration is not important in the initial attack rate by hydrogen halides.
- Complexing ability of the anion for the protective oxide and alloy determines the attack rate and therefore the hydrogen production rate at the metal surface.

The very high attack rate by HF is due to the very high electronegativity and small size of the fluoride ion (see Table III).

TABLE III

Size and Electronegativity of Selected Ions

Atom	Electronegativity,[a] ev	Ionic Radius, Å
F	4.0	1.33
Cl	3.0	1.81
Br	2.8	1.96
I	2.4	2.20
O	3.5	1.32
H	2.1	1.54

---

[a] The power of an atom in a molecule to attract electrons to itself.

Radiotracer Tests for Hydrogen Absorption

To resolve the anomalous discrepancy between the high hydrogen evolution rate by HF and the absence of cracking by NaF several experiments were conducted with tritiated sodium halide salt coatings and with absorption of high purity hydrogen gas.

Test specimens were prepared from 3/4- x 3- x 0.050-inch strips of metallographically polished duplex-annealed Ti-8Al-1Mo-1V. The strips were mounted in four-point loading holders and bent to an outer fiber stress calculated to be 85% of the yield strength at 350°C.

Salt coatings were formed on the specimens by putting about 0.2 g of NaF, NaCl, NaBr, or NaI on the stressed metal, adding 0.100 ml of water, and then adding 0.050 ml of 1-Ci/ml tritiated water. The resulting NaF and NaCl solutions were dried in air at 20-25°C for about 20 hours. Because NaBr and NaI solutions dry very slowly in air at room temperature, they were heated to 50°C for 15 minutes.

The salt-coated specimens were first counted for ^3H in a windowless, flow proportional counter. After heating for 75 hours at 350°C, the specimens were rinsed in hot flowing water for one minute to remove the salt and corrosion products. The specimens were air dried then and then recounted for ^3H. The experiment with NaF was repeated twice in duplicate as described above and once in duplicate with a heating time of 25 hours.

The hydrogen absorption results measured by the radiotracer technique are summarized in Table IV.

TABLE IV

Absorption of ^3H by Salt-Coated Titanium-Aluminum Alloy

Salt Coating	^3H in Dried Salt, c/m[a]	Cracking	Corrosion	^3H After Washing, c/min[a]
NaF	4,237	No	Yes	0[b]
NaCl	13,519	Yes	Yes	244
NaBr	58,187	Yes	Yes	110
NaI	58,876	Yes	Yes	239

[a] Represents only surface hydrogen on salt (H_2O) or metal (H) because of the short range of ^3H betas (E_{max}: 18 kev). The 2σ error on counting was 25 c/min.

[b] Results for both 25- and 75-hour exposures. Other specimens exposed 75 hours only.

These experiments showed that even with moisture added, a stressed, heated, NaF-coated strip does not crack, and that diffusion of hydrogen into the metal from the NaF coating is essentially zero. The NaF salt coating retained less moisture (tritium) than did the other salts, as shown in Column 2 of Table IV. NaF does not absorb water as readily as the other halide salts; therefore, the amount of residual tritium present as moisture in NaF is low. This would limit the amount of HF that could be produced initially and would correspondingly limit the amount of hydrogen finally formed from the hydrogen halide - metal reaction. Even when water was subsequently added to a stressed, heated, NaF-coated specimen, to produce more HF, cracking did not occur.

After the samples were heated at 350°C to induce the hot-salt reaction and then washed to remove residual salt, only the fluoride specimen indicated no absorbed tritium; the other halides gave clear evidence of tritium absorption. The absence of hydrogen on the metal surface after exposure to heated NaF would be expected on the basis of the proposed mechanism of cracking, but would not be expected on the basis of the rate of attack by HF in Table II.

Mass spectrographic analyses show that hydrogen is generated by the reaction of NaF and titanium-aluminum alloys in the temperature range of stress corrosion cracking. A portion of the hydrogen produced at the surface of the alloy is normally absorbed by the alloy. Hydrogen would be expected to diffuse into the peaks of metal left in a pitted surface (Figure 2) rather than into the pits because of the slower corrosion rate on the peaks. Previous data with NaCl have shown that after 75 hours, corrosion-produced hydrogen penetrates about 10 μ into the surface.[9]

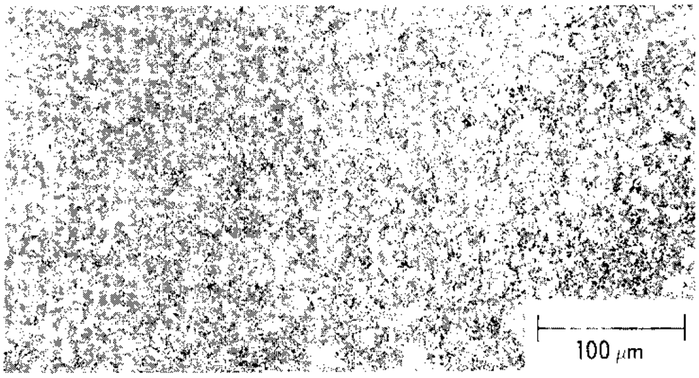


FIG. 2 SURFACE ATTACK OF Ti-8Al-1Mo-1V BY NaF AFTER 20 HOURS AT 350°C (Note fine uniform pitting)

The results in Table IV show that titanium does not absorb hydrogen in the presence of NaF. Two hypotheses can explain the failure of fluoride-generated hydrogen to penetrate the surface of the alloy. First, the hydrogen is transported from the surface as rapidly as it is formed, or second, a fluoride conversion coating[10] can be formed that acts as a diffusion barrier.

Absorption of High-Purity Hydrogen Gas

Specimens of Ti-5Al-2.5Sn foil, 0.010 in. thick, were treated with an aqueous solution of 5 wt % KF - 8 wt % HF to form a fluoride-conversion coating to see if a barrier was formed that would prevent H_2 absorption. Other specimens were treated with NaF from an evaporated solution and heated to 350 or 500°C for one hour. Blanks for both types of specimens were heated in air at the same temperature for the same time. All specimens were again heated while exposed to 1 cc/sec of flowing palladium-diffused H_2. Differences in H_2 absorption were observed.

Specimens treated to form a conversion coating and specimens treated with NaF at 350°C both absorbed the maximum amount of H_2 (3.2 wt %) at 350°C in the same length of time. Specimens heated at 350 and 500°C with NaF actually absorbed H_2 more readily than blanks heated in air. The two 500°C NaF-treated specimens gained an average of 6.6 mg; the blank gained only 3.0 mg. After heating 17 hours at 330°C in purified flowing H_2, the 350°C NaF-treated specimens fractured more severely than the blanks indicating more locations for H_2 penetration (Figure 3). The specimens fractured because of hydriding and residual stresses imposed when the specimens were bent into a V-shaped form prior to test.

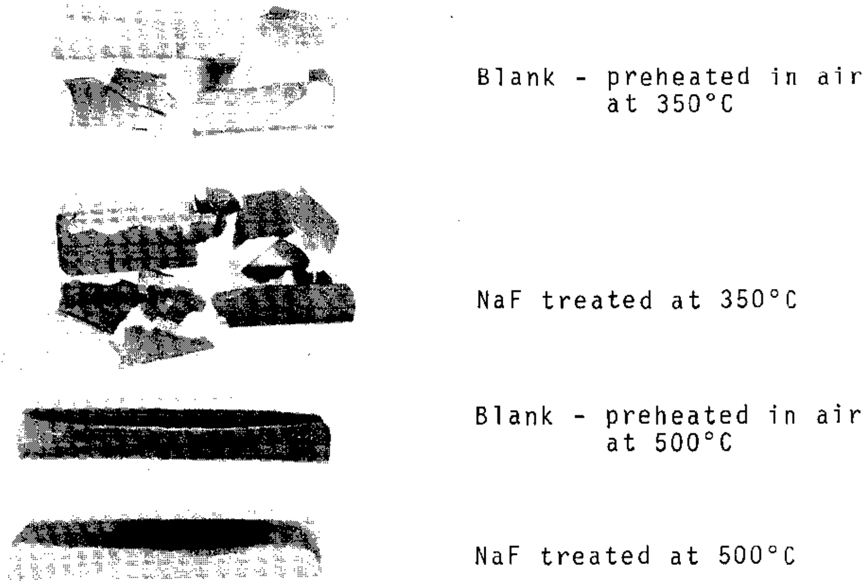


FIG. 3 ABSORPTION OF HYDROGEN GAS BY Ti-5Al-2.5Sn

Specimens treated with NaF absorbed gaseous H_2 more easily than blank specimens during 17 hr in palladium-diffused H_2 at 330°C. NaF treatment at 350°C produced more absorption sites as indicated by greated fragmentation of the specimen. The 500°C NaF-treated specimens gained more weight than the blanks.

Apparently treating the surface with NaF at an elevated temperature allowed hydrogen to be absorbed more rapidly; the protective oxide film thickness was probably reduced by HF attack.

These observations lead to the postulate that heated NaF does not cause hot-salt stress corrosion cracking because the hydrogen formed in the corrosion reaction does not have a chance to penetrate the metal surface. The attack rate by HF is so high that, as the hydrogen is produced on a particular area, the same surface is itself removed by the formation and sublimation of TiF_4,[11] one of the main corrosion products. In the chloride system, the $TiCl_4$ formed as an intermediate hydrolyzes readily with any available moisture to form TiO_2 and HCl. The TiF_4 is much more difficult to hydrolyze; on hydrolysis, $TiOF_2$, another volatile solid, is formed.

EFFECT OF A "REDUCIBLE OXIDE" AND WATER ON TITANIUM CORROSION

A "reducible oxide" was reported to be necessary for the corrosion of titanium alloys and the resultant reaction products that lead to hot-salt stress corrosion cracking.[4] In the experiment described, a mixture of NaCl + TiO_2 was placed in one hole in a block of titanium alloy and NaCl in another; the holes were welded shut in a vacuum arc furnace and the blocks reduced in size 75% by hot rolling at 982°C (1800°F). The specimens were allowed to remain at 482°C (900°F) for 100 hours and sectioned. A reaction product was visually observed in the NaCl + TiO_2 section but not in the NaCl section. The reaction was attributed to the presence of a "reducible oxide."

It is probable that the reaction products observed in those experiments in the cavity that contained TiO_2 + NaCl were formed during hot rolling (982°C) rather than during the test exposure (482°C). At the hot rolling temperature, Cl_2 would have been expected as shown in Table I. Further, it is probable that the reaction products produced by TiO_2 + NaCl can be attributed to the moisture introduced by the TiO_2.

The "reducible oxide" concept is probably incorrect. A "reducible oxide" (presumably TiO_2) requires a reducing agent. A metal (Ti) cannot reduce its own oxide (TiO_2). The process requires a more reactive reducing agent, presumably another metal. All the metals normally used as titanium alloying agents (Cr, Al, Sn, Zr, Mn) are less reactive chemically than titanium and therefore cannot reduce TiO_2.

Preparation of Sealed Corrosion Specimens

To demonstrate that moisture, and not a "reducible oxide" plays the predominant role in hot-salt stress corrosion cracking, blocks of titanium were loaded with specially dried TiO_2 + NaCl, dried NaCl, and NaCl crystallized from aqueous solution. Commercially pure titanium (Ti-55) specimens 1/4 x 3/4 x 3 inch were prepared with 1/8-inch-diameter holes having a 1° taper at the mouth (Figure 4). Special tapered pins were machined for these openings. Sodium chloride and titanium dioxide were dried at 5×10^{-5} torr and 400°C for one hour, and then sealed in glass capsules under vacuum. The machined specimens and pins were semilarly dried and stored. Sodium chloride solutions were evaporated at room temperature to produce NaCl that contained brine inclusions.

The specimens were loaded with the dried salt in a dry box containing nitrogen dried over magnesium perchlorate and having <100 ppm O_2 impurity. The glass capsules containing the dried compounds and specimens under vacuum were opened in the nitrogen dry box. Two specimens were loaded with dry NaCl, and two with mixtures of equal volumes of dry NaCl and dry TiO_2. The salts were tamped into the holes, and the tapered pins were hammered into the blocks. The specimens were removed from the dry box and sealed under vacuum by electron beam welding.

Another pair of specimens that had not been dried were loaded in air with NaCl that contained brine inclusions. These specimens were closed and sealed in the same way as the dried specimens.

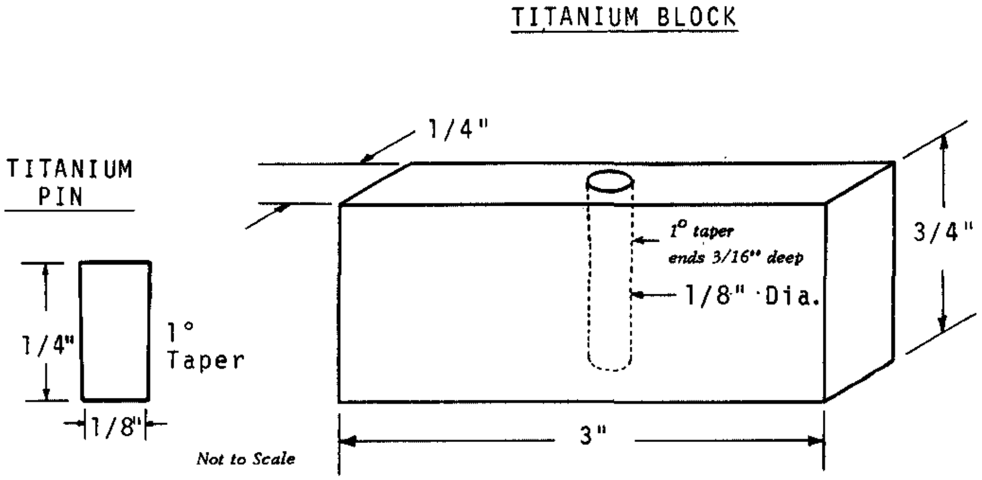
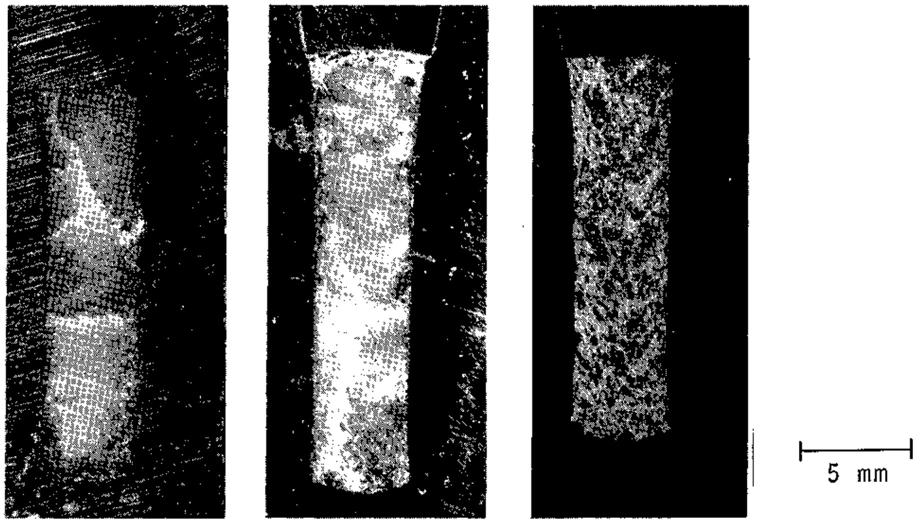


FIG. 4 SEALED CORROSION SPECIMEN
Specimens were dried by heating under vacuum and stored in glass capsules until ready for loading in a nitrogen dry box.

All specimens were cold-rolled to reduce their thickness 25% and produce intimate contact between the reagents and metal. Three specimens, one dry NaCl, one dry NaCl + dry TiO_2, and one NaCl with brine inclusions, were then heated for 100 hours at 315°C (600°F). The other three specimens were heated at 480°C (900°F) for the same length of time. After heating, the specimens were sectioned longitudinally and examined at low magnification.

Results of Examination

The results are shown in Figure 5. The longitudinal sections containing the salt <u>in situ</u> were carefully ground and polished so that any reactions between the salt and the metal would be visible. With undried NaCl, diffusion of dark-colored corrosion products into the salt can be seen around the entire metal-salt interface. In comparison, the lack of corrosion products in the dried NaCl showed that the alloy was not attacked. The same situation is seen with dried NaCl + dried TiO_2 at both 315 and 480°C. Even if a "reducible oxide" is present, corrosion is not observed in the absence of moisture.



Undried NaCl　　Dried NaCl　　Dried TiO_2 + dried NaCl

FIG. 5 DRIED REAGENTS PREVENT HOT-SALT ATTACK AT 480°C

Note attack by undried NaCl and diffusion of dark colored corrosion products into the salt at the salt metal interface compared to dried NaCl after 00 hr at temperature. No attack was observed even in presence of a "reducible oxide" if water is absent. Results were similar at 315°C.

These results confirm that water is necessary for attack of titanium and its alloys in the hot-salt stress corrosion cracking temperature range.[1] This is not to infer that oxygen is unimportant. The protective oxide layer formed on titanium-aluminum is enriched in aluminum.[3] The aluminum oxide acts as an accelerator for the production of HCl by pyrohydrolysis[1] and decreases the incubation time for hot-salt stress corrosion cracking.

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