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HOT SALT STRESS CORROSION OF TITANIUM ALLOYS IN AN ADJUSTABLE DEFLECTION, MULTI-SPECIMEN BENT BEAM TEST APPARATUS

ANTHONY K. WONG and MILTON LEVY

METALS RESEARCH DIVISION

March 1973



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ABSTRACT

Susceptibility of titanium alloys to hot salt stress corrosion was first discovered in 1955. This unexpected phenomena was manifested by the presence of surface cracks in a high temperature test specimen which was accidentally contaminated by salt residue from a finger print. Since elevated temperature titanium components, such as gas turbine compressor blades, may be exposed to salt-laden, atmospheric environments, catastrophic failure of such components remains as a potential problem requiring resolution.

An adjustable deflection, multi-specimen, bent beam test fixture was devised for conditioning sheet specimens used in the investigation of hot salt stress corrosion effects in titanium alloys. Initial tests were conducted with a Ti-5Al-2.5Sn titanium alloy at a temperature of 900°F and a stress just below the yield strength. Crack developments on salt-treated surfaces were observed to increase with exposure time of 150, 500 and 1000 hours. In addition, deleterious effects of orientation and overstress were also observed. Later, efforts were made to evaluate a proprietary boron carbide coating at exposure time up to 500 hours. Preliminary results indicated the potential of the coating.

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INTRODUCTION

The susceptibility of titanium alloys to hot salt stress corrosion was first revealed¹ in 1955. This unexpected phenomenon was manifested by presence of cracks in the post-test surface of a high temperature test specimen which was accidentally contaminated by salt residue from a finger print. Following this earlier discovery, many research endeavors have since been conducted to elucidate the mechanism of attack and to determine crack related parameters since premature failure of the structural titanium alloys in aircraft high temperature applications could be highly catastrophic. At least one field service report* has attributed the failure of a titanium component, in the compressor section of a Navy aircraft engine, to the hot-salt, stress phenomena.

Therefore, in addition to protecting not jet engine components such as compressor blades and impellers, from the familiar debilitating effects of erosion engendered by sand and dust particle ingestion, stress corrosion, corrosion fatigue, creep, and oxidation, efforts must be also undertaken by the designer to insure against precipitant failures due to the added presence of hot salt.

Hence, the overall objective of this investigation was to develop multi-purpose surface protection for titanium alloys in structural members operating in hot, salt-rich environments. However, the immediate objective of the work cited in this report was to develop a simple test method for rapidly and economically screening candidate coatings, surface treatments and titanium alloys with potential for utilization as tensile-loaded structural members exposed to hot salt environments.

TEST MATERIALS

An alpha type, 5Al-2.5Sn; titanium alloy sheet, with a nominal thickness of 1/32" was selected for initial testing in the new hot salt stress corrosion constant deflection test fixture. This alloy is a weldable grade which normally possesses good oxidation resistance, stability and strength at elevated temperatures and thus is a candidate material for structural applications at high temperatures. Table I lists some of the typical tensile properties of annealed Ti-5Al-2.5Sn titanium alloy at temperatures up to 1000°F, along with the actual room-temperature properties of the sheet material used in this study. Additionally, the chemical composition, as determined by the manufacturer, is listed in Table II.

*Private Communication: Mr. S. Goldberg, Naval Air Systems Command

¹HADLEY, B.F., BAUER, G.W., and EVERS, D., "Effect of Various Heat Treatment Cycles Upon the Mechanical Properties of Titanium Alloys with Various Interstitial Levels," Mallory-Sharon Titanium Corp., Report No. WADC TR 56-580, March 1957.

Tests were conducted on this material both to obtain base-line crack phenomena data and to evaluate the efficacy of the newly-devised test fixture. The titanium alloy was utilized in the mill-annealed condition.

Several promising coatings were considered for preliminary evaluation. However, one leading candidate for applications in hot, erosive, engine environments is boron carbide with its attendant melting point of about 4450°F and good oxidation resistance up to 1800°F. Hence, for this initial investigation a proprietary NRC vacuum deposited B₄C overlay was selected. Maximum thickness of the coating on the 1/32" thick titanium alloy specimens was 1.8 mils.

Substrate deposition temperature for this proprietary process is maintained² within the 700-1050°F range. However, full annealing of 5Al-2.5Sn titanium alloys is usually conducted at a higher temperature in the 1325-1550°F range.³ Furthermore, stress relief processing is generally carried out at temperatures somewhere between 1000° and 1200°F. Therefore, the lower temperature of the proprietary coating process is not expected to appreciably affect the mechanical properties of the base alloy. Yet, at these deposition temperatures, some changes in physical, metallurgical and mechanical properties are sure to be manifested. Thus, in critical applications, further consideration must be given to the individual characteristics of the substrate alloy and the accompanying interacting effects of the deposition process.

The boron carbide coating is reported² to possess an extremely fine equiaxed microstructure with an average boron content varying from 74 to 77 percent by weight. Close control of coating thicknesses is another capability claimed by the manufacturers for this process. Potential production volume scale-up feasibility with concomitant moderate production cost is another advantage cited.

As stated earlier, coatings for advanced engine components must also be capable of withstanding other harmful environments such as that created by sand and dust particle ingestion. Enhanced erosion resistance of several titanium alloys has been exhibited by specimens covered with the proprietary boron carbide coating, as disclosed by the data in Table III. Improvements in erosion resistance of as much as 27-fold have been reported. Thus it appeared logical to further evaluate the capabilities of the boron carbide coating against other potential hazards including hot salt stress corrosion. For background information, Table IV contains data pertaining to other physical properties of the proprietary boron carbide coating.

²ANON., "Boron Carbide Erosion Resistant Coatings," National Research Corporation, January 1971.

³ANON., "Basic Design Facts about Titanium," #1000-6502, RMI Titanium, Reactive Metals Inc.

TABLE I
TENSILE PROPERTIES Ti-5Al-2.5Sn ALLOY SHEET

	Ultimate Strength ksi	(0.2% Offset) Yield Strength ksi	Elongation (in 2") %	*Note
Transverse	133.3	121.2	14.0	(1)
Longitudinal	134.6	122.7	14.3	(1)
RT	120.0	115.0	10.0	(2)
600°F	82.0	65.0	18.0	(2)
800°F	78.0	59.0	18.0	(2)
1000°F	67.0	55.0	19.0	(2)

*NOTE: (1) Manufacturer's Data: Hot Rolled and Annealed, Specification MIL-T-9046F, Type II, Comp. A, Annealed.

(2) Typical minimum properties³

TABLE II
CHEMICAL COMPOSITION Ti-5Al-2.5Sn ALLOY SHEET

Manufacturer's Data

COMPOSITION (%)						
Al	Sn	Fe	C	N	Mn	Ti
5.4	2.5	.36	.02	.016	.01	Bal

TABLE III

EROSION RESISTANCE PROPERTIES OF BORON CARBIDE COATING

(based on 30 μ sand particle jet abrader
tests on standard 1 mil coating)

Improvement Factor for 1 mil B ₄ C Coating*					
<u>Base Metal</u>	<u>Particle Impingement Angle</u>				<u>References</u>
	<u>90°</u>	<u>60°</u>	<u>30°</u>	<u>20°</u>	
Ti (A-40)	12X			16X	2
Ti-6Al-4V	7-10X			20X	2
Ti-5Al-2.5Sn	10X			16X	2
Ti-6Al-2Sn-4Zr-2Mo	10X			27X	2
Ti-6Al-6V-2Sn	3-5X	5-8X	13X		AMMRC
403 s.s.	3.0-3.5X			10-12X	2
410 s.s.	3X			10X	2
AM-355	3-5X			12X	2
Greek Ascoloy (Fe-13Cr-2Ni-3W)	3.5X			9X	2

*Improvement factor represents the erosion rate ratio of bare metal surface to B₄C coated surface.

TABLE IV

PHYSICAL AND MECHANICAL PROPERTIES OF BORON CARBIDE COATINGS²

Hardness	3300 Knoop
Tensile Strength	100-150 x 10 ³ psi
Elastic Modulus	62 x 10 ⁶ psi
Color	black to grey
Adherence (Specific Adhesion Strength)	
to stainless steel alloys	1000-1500 psi
to titanium alloys	2500-4000 psi
Density	2.33 - 2.35 g/cc (Bulk density of B ₄ C is 2.51 g/cc)
Salt-Spray Corrosion Resistance	Excellent
Chemical Stability	Excellent to 725°C (1330°F)

TEST SPECIMEN

Static surface stresses in a rectangular beam of finite length with a fixed deflection are strongly dependent upon the length and thickness of the structure. Using methods proposed by Loginow et al,^{4,5} calculations were made to establish a specimen length and deflection which would effectively generate a maximum tensile stress of 50 ksi, at 900°F, in a sheet 1/32" thick. This maximum tensile fiber stress was determined from the following relationship:

$$\sigma = 4E_m [2E(k) - K(k)] \left[\frac{k}{2} - \frac{2E(k) - K(k)}{12} \left(\frac{t}{H} \right) \right] \frac{t}{H}$$

wherein $K(k)$ and $E(k)$ are the complete elliptical integrals of the first and second kind, respectively, and k is the modulus of these integrals. Further, σ is the maximum tensile strength, E_m is Young's modulus, t is the specimen thickness, and H is the distance between the two ends of the deflected specimen as shown in Figure 1a. Additionally, the length of the specimen, L , was derived from the following ratio:

$$\frac{L-H}{H} = \frac{2[K(k) - E(k)]}{2E(k) - K(k)}$$

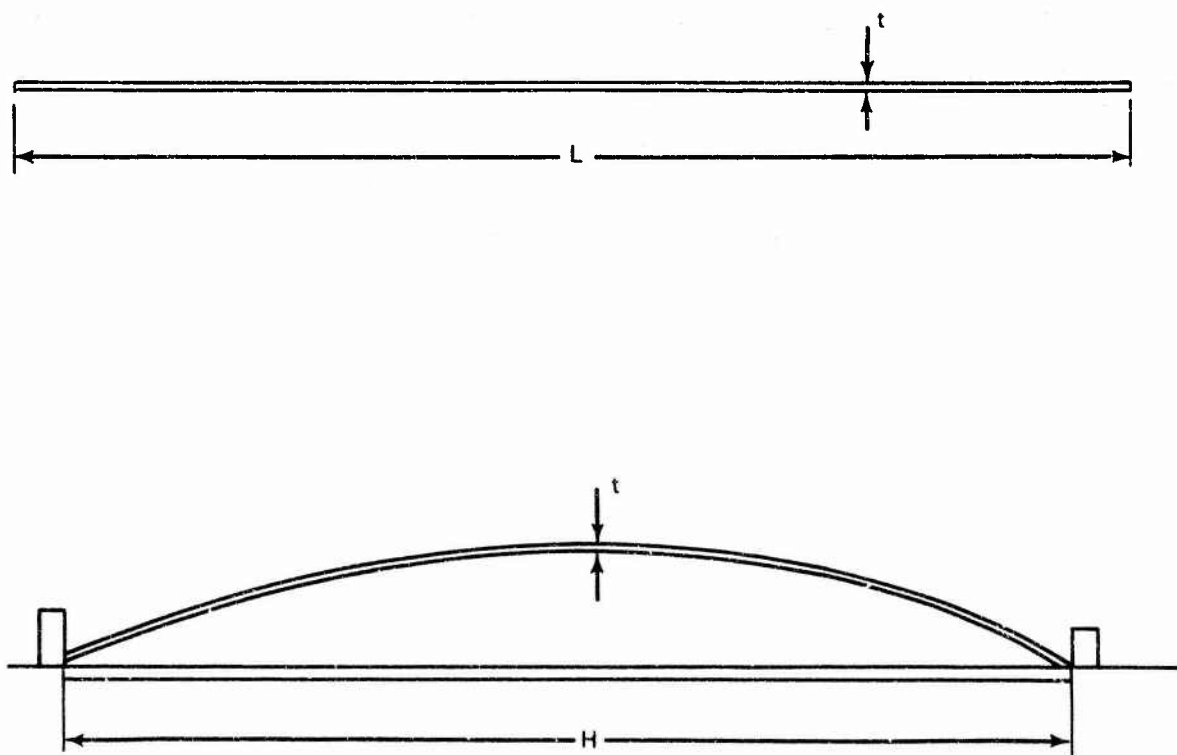
Assuming a high temperature Young's modulus of 11.6×10^6 psi, it was calculated that a specimen 6.0" long, deflected to a span length of 5.6", would produce the prescribed stress condition. But for more accurate determinations of prestresses, actual measured values of high temperature Young's moduli and effects of thermal expansion should be employed in the calculations. Figure 1b shows an illustration of the 6.0" long specimen used in this study.

It may be noted in the properties listing of Table I that the typical minimum yield strength of the Ti-5Al-2.5Sn titanium alloy at 900°F should be in the vicinity of 57 ksi. Therefore, assuming no residual stress to be present, the experimental prestress of 50 ksi should not cause any appreciable initial yielding. However, related data³ further states that a tensile stress of only 48 ksi, at 800°F, will produce 1% creep in 100 hours. Consequently, in this fixed deflection test, relaxation of stresses, due to creep, will serve to reduce the initial prestress loading as the exposure time increases.

Also used in a limited experiment was a specimen essentially identical to that shown in Figure 1b except for the longer length of 6.8". Calculations

⁴PHELPS, E. H., and LOGINOW, A. W., "Stress Corrosion of Steels for Aircraft and Missiles," Corrosion-National Association of Corrosion Engineers, Vol. 16, July 1960, p. 97.

⁵HAAIJER, G., and LOGINOW, A. W., "Stress Analysis of Bent-Beam Stress Corrosion Specimens," Corrosion-National Association of Corrosion Engineers, Vol. 21, No. 4, April 1965.



$$\sigma = 4E_m \left\{ 2 E(k) \cdot K(k) \right\} \left\{ \frac{k}{2} \cdot \frac{2 E(k) \cdot K(k)}{12} \left(\frac{t}{H} \right) \right\} \frac{t}{H}$$

$$\text{and } L = H \left\{ \frac{2 [K(k) \cdot E(k)]}{2 E(k) \cdot K(k)} + 1 \right\}$$

by Loginow et al^(4,5)

Figure 1a. Stressing of Bent-Beam Test Specimen

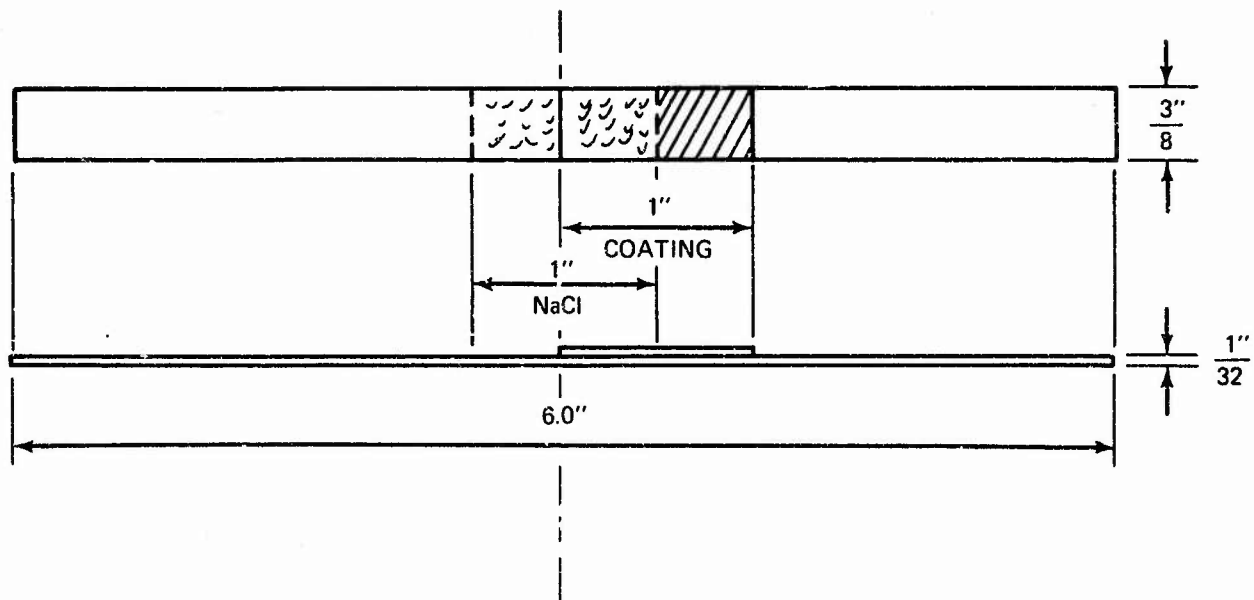


Figure 1b. Constant Deflection Bend Test Specimen

disclosed that this longer specimen, deflected to the same bend span length as the shorter specimens, would result in an outermost fiber stress of over 60 ksi at 900°F, a value somewhat in excess of the yield strength of the material. Thus, a means was provided for observing effects of initial over-stressing at elevated temperatures, utilizing the same test fixture settings and exposure conditions experienced by the shorter specimens.

Some test specimens were prepared by the National Research Corporation to include a proprietary refractory boron carbide coating in thicknesses up to 1.8 mils. As indicated in Figure 1b the coated test section was about 1 inch in length and offset at one side of the specimen midlength. This was done so that salt-treating a 1 inch long test section at midlength would allow four different test conditions to be present on a single specimen; namely, (1) untreated titanium, (2) salt-treated titanium, (3) salt-treated coating, and (4) untreated coating. Hence, means for comparison of time-temperature effects were conveniently provided for in adjacent segments.

TEST PROCEDURE

A variety of specimens have been employed by various investigators in the study of the hot salt stress corrosion phenomena of titanium. Specimen type include specially-developed tubular tensile^{6,7} and self-stressed specimens,⁸ as well as the more conventional tensile and creep specimens. However, for less sophisticated evaluations, Pratt and Whitney Aircraft Company has utilized a constant deflection bent beam test for screening sheet materials.

Based on this latter concept, a stainless steel fixture, with added provisions for adjusting the specimen deflection, was designed and fabricated. This multi-specimen fixture was designed to hold over a dozen sheet metal specimens at a constant deflection in a high temperature environment. A photograph of the test fixture, as it appeared immediately after removal from a temperature-controlled furnace, is shown in Figure 2. Also appearing in the photograph are the first groups of specimens used to both test out the efficacy of the new fixture and to establish base-line reference data on Ti-5Al-2.5Sn exposed to a temperature of 900°F for durations up to 1000 hours. A conventional muffle-type furnace was used in this study.

Specimens were first wiped with emery cloth, cleaned with acetone (reagent grade) and then rinsed in distilled water. Later, it was demonstrated that

⁶LOGAN, H. L., "A Specimen for Use in Investigating the Stress Corrosion Cracking of Metals at Elevated Temperatures," Materials Research & Standards, February 1962.

⁷GRAY, HUGH, R., "Relative Susceptibility of Titanium Alloys to Hot-Salt Stress-Corrosion," Lewis Research Center, Report No. NASA TN D-6498, November 1971.

⁸HEIMERL, G. J., "A Stress Corrosion Test for Structural Sheet Materials," Materials Research & Standards, January 1965.

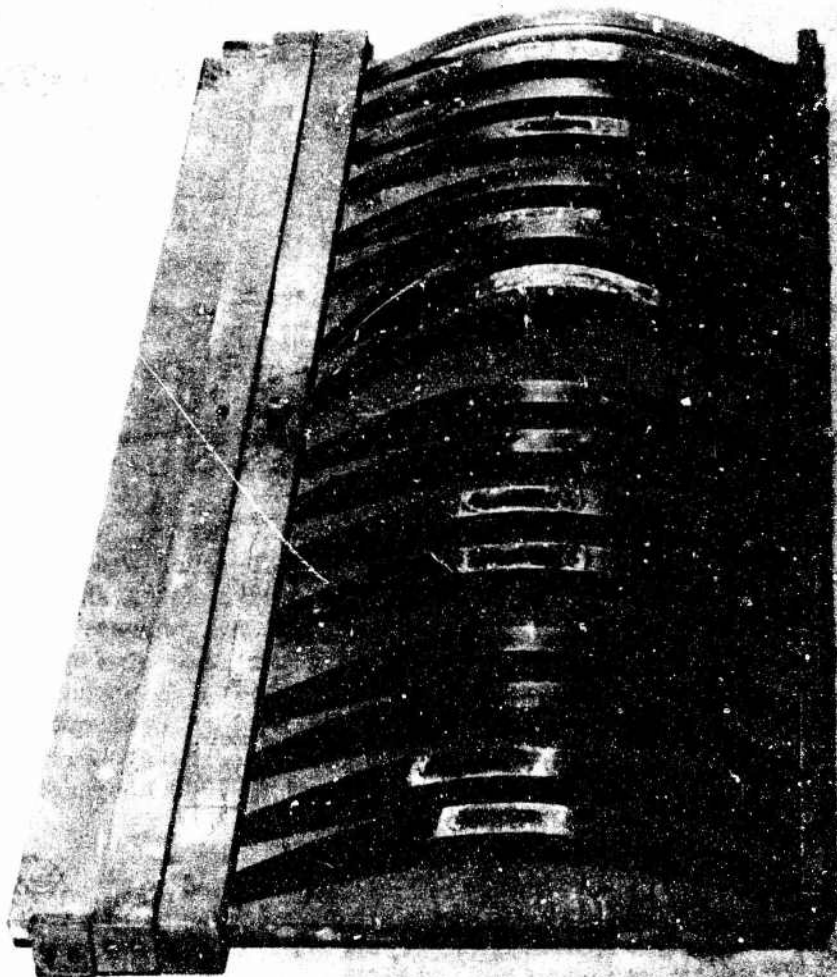


Figure 2. Specimens Mounted for Hot Salt Stress Corrosion Test - Side View
19-066-888/AMC-72

preliminary purging with a laboratory detergent enhanced the wettability of the surface with the salt solution. This cleaning procedure was used to prepare the coated specimens for test. A 3% sodium chloride solution was applied to the central section of selected sheet metal specimens and spread evenly over a one-inch span, as shown earlier in Figure 1b. The specimens then were air-dried under a heat lamp. Weight measurements indicated that the density of salt deposit was about 5 milligrams per square inch. This areal density was consistent with actual amounts of salt observed to be deposited on aircraft engine components.⁹

Titanium alloys are susceptible to hot salt stress corrosion cracking at temperatures ranging up from 400°F. In this study, an initial test temperature of 900°F was selected as representative of temperatures which may be encountered in the compressor section of future high performance gas turbine aircraft engines.

In the initial trial of the new test fixture, sixteen of the aforementioned specimens, in the salt-treated and untreated condition, were carefully flexed and emplaced into the fixture. Table V lists the conditions of each test. All of the specimens were exposed to quiescent air at 900°F for durations ranging from 150 to 1000 hours. Moreover, all but two of the end-supported bent beam specimens were designed to incorporate an initial flexural stress of 50,000 psi at 900°F.

In addition, every one of the specimens, except for another pair, were fabricated with their lengths parallel to the rolling direction of the sheet material. Furthermore, to evaluate reproducibility of test results, duplicate test specimens were utilized in Test Series I, IV, and V.

As inferred in Table V, Test Series I's objective was to establish base-line data on the behavior of Ti-5Al-2.5Sn, cut parallel to the rolling direction and herein referred to as "longitudinal," exposed for 150 hours with an initial maximum tensile prestress of 50 ksi. Meanwhile, the effect of sheet rolling direction was to be distinguished by the "transverse" specimens of Test Series II. Furthermore, the deleterious effect of applying a stress above the yield point was expected to be revealed by the overstressed specimens of Test Series III. In each of these base-line reference test series, at least one control specimen was left untreated with salt so that better comparisons of the debilitating actions of the hot salt could be made. However, later experience indicated that separate untreated control specimens were not necessary since comparisons of damage could be made between the treated and untreated sections of the same specimen.

The influence of longer exposure time was expected to be disclosed by the specimens of Test Series IV and V after test durations of 500 and 1000 hours, respectively.

⁹ASHBROOK, RICHARD L., "A Survey of Salt Deposits in Compressors of Flight Gas Turbine Engines," National Aeronautics and Space Administration, Report No. TN D-4999, January 1969.

TABLE V
STRESS CORROSION TESTS

TEST SERIES	SPECIMEN NO.	SPECIMEN SURFACE CONDITION	FURNACE TEMPERATURE °F	NOMINAL EXPOSURE HOURS	INITIAL STRESS PSI	ORIENTATION
I	A1	CLEAN	900	150	50,000	L
I	A2	SALT	900	150	50,000	L
I	A3	CLEAN	900	150	50,000	L
I	A4	SALT	900	150	50,000	L
II	B2	CLEAN	900	150	50,000	T
II	B3	SALT	900	150	50,000	T
III	AX	CLEAN	900	150	60,000+	L
III	A15	SALT	900	150	60,000+	L
IV	A5	CLEAN	900	500	50,000	L
IV	A6	CLEAN	900	500	50,000	L
IV	A8	SALT	900	500	50,000	L
IV	A9	SALT	900	500	50,000	L
V	A10	CLEAN	900	1000	50,000	L
V	A11	CLEAN	900	1000	50,000	L
V	A12	SALT	900	1000	50,000	L
V	A14	SALT	900	1000	50,000	L
VI	A17	NRC COAT/SALT	900	150	50,000	L
VI	B4	NRC COAT/SALT	900	150	50,000	T
VII	A18	NRC COAT/SALT	900	500	50,000	L
VII	B5	NRC COAT/SALT	900	500	50,000	T

Specimens with a proprietary boron carbide coating were introduced into these experiments later as Test Series VI and VII. As indicated in Table I, the test variables also included specimen sheet orientation and exposure time.

Loading and removal of the individual test specimens at the appropriate time intervals was accomplished by withdrawing the bend test fixture from furnace, performing the required action with short handle tongs, and then returning the fixture to the furnace in as short a time as possible. The thermal cycling involved was deemed insignificant to the results of this test. However, an experiment also demonstrated that, if necessary, this interchange action could be performed with long handle tongs, with the fixture remaining permanently in the furnace for the full duration of testing. Upon removal from the test fixture, each specimen was visually examined for breaks and obvious cracks. Subsequently, the specimens were cleaned by means of wet abrasive blast techniques and reexamined at magnifications up to 10x. But in order to fully appreciate the extent of damage to the surface, it was necessary to chemically etch the specimens.

An etchant composed of 50 ml nitric acid, 10 ml hydrofluoric acid, and 10 ml sulfuric acid was adequate for revealing the cracks attributable to stress corrosion. The specimens were immersed in this solution for 60 seconds at room temperature or until excessive red fumes were liberated. An alternate method was to immerse the specimens for only 30 seconds at a temperature of 140°F. Photomacrographs were taken to record the surface damage.

RESULTS AND DISCUSSION

Ti-5Al-2.5Sn Alloy

Constant deflection bend test specimens were removed from the test fixture after exposure to 900°F for 150, 500 and 1000 hours as required by the test plan. Generally, the oxidation and salt reaction products on the surface masked the damage on the surfaces. Representative of this phenomenon were three of the specimens tested in Series I after exposure for 150 hours, as shown by the photomacrographs (5x) in Figure 3. These photographic enlargements show the appearance of the central sections of one non-salt-treated and two salt-treated titanium specimens.

Although not apparent in the photograph, the surface of the untreated (no-salt) specimen was covered with a typically smooth oxidation coating in various shades of blue, purple, and straw. Moreover, the surface was obviously striated in the direction of the length of the specimen, as shown in Figure 3a. As mentioned previously, this series of specimens was cut from sheets with the specimen length parallel to the direction of rolling.

Islands of white on the temperature-exposed, salt-treated specimens appeared, under higher magnification, to be composed of conglomerated crystals



a. (A3) UNTREATED CONTROL



b. (A2) SALT-TREATED



c. (A4) SALT-TREATED

Figure 3. Test Series I - (900°F - 150 Hours) - Central Test Section of
Longitudinal Specimens After Removal from Furnace (X5)
19-066-142 MC-72

of sodium chloride. However, an earlier investigator¹⁰ reported that X-ray diffraction patterns of translucent white particles on titanium, exposed to 800°F for 64 days, revealed the presence of at least four phases: anatase, rutile, NaCl, and an unknown phase. Meanwhile, surrounding the aforementioned islands of white substances were other islands composed of dark, amorphous forms of reaction products. Another investigator¹¹ of hot salt stress corrosion of titanium has indicated that intermediate solid corrosion products of reaction may include various compounds of titanium chlorides, and aluminum chloride. Although Figures 3b and 3c are photographs of specimens prepared and tested in nearly-identical fashion, the patterns of salt agglomeration are different and may be partially attributable to differences in the wettability of the specimen surfaces. Similar reaction products were present on the surface of the transverse specimens of Test Series II, as shown by the macrograph in Figure 4b. In addition, transverse striations, indicative of rolling direction, were clearly displayed within the surface of the untreated control specimen as evidenced by Figure 4a. Inadvertent contamination of the surface was also manifested in the control specimen by the presence of clearly identifiable spot pitting.

After removal from the furnace, agglomerations of white salt crystals were observed to be present on the surface of the specimens even after exposures up to 1000 hours, as shown by the duplicate specimens in Figure 5. Similar appearances were also exhibited by the specimens exposed for only 150 hours and shown earlier in Figures 3b, 3c, and 4b. The locations and sizes of the islands of white substance were closely related to the wettability of the original surface by the saline solution.

The wet abrasive blast cleaning method employed to remove the previously mentioned corrosion products was adequate for revealing the presence of pitting and incipient cracking as exhibited in the photographs of paired, salt-treated specimens from Test Series V in Figure 6. In the 2x magnification photographs, the relative severity of the pitting was clearly evident. On the other hand, the presence of cracks in both the 2x and 5x magnification photographs were less well-defined.

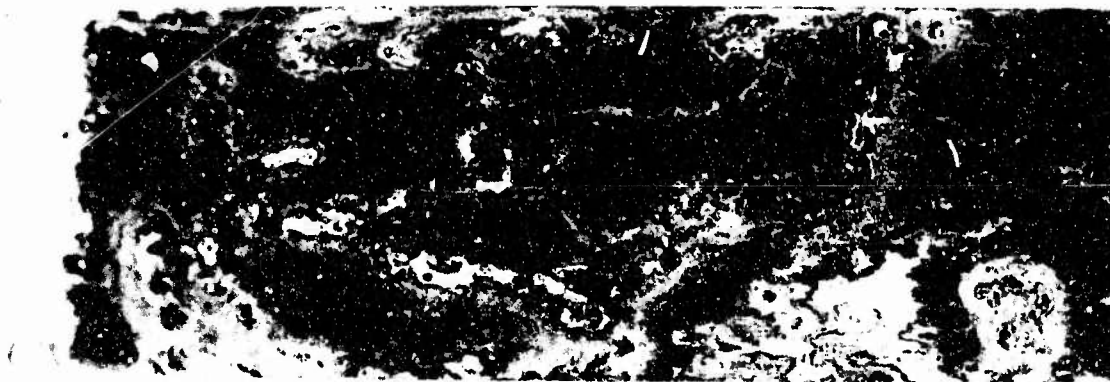
Hence, to fully assess the damage, an etchant proved necessary to fully develop the surface cracks. As shown in Figure 7, crack formation at 900°F for 1000 hours was quite severe. In contrast to Figure 6, etched specimens in Figures 7a and b explicitly exhibited multi-numbers of cracks on the surfaces which were exposed to the salt-treatment. Characteristically, the crack lengths are all positioned in a pattern arrangement perpendicular to the direction of stress.

¹⁰ LOGAN, HUGH L., "Studies of Hot Salt Cracking of the Titanium 8Al-1Mo-1V Alloy," Proceedings of the Conference on Fundamental Aspects of Stress Corrosion Cracking, Ohio State University - 1967, Publication of National Association of Corrosion Engineers, 1969.

¹¹ ORDREJCIN, R. S., RIDEOUT, S. P., and LOUTHAN Jr., M. R., "The Hot-Salt Cracking of Titanium Alloys," Savannah River Laboratory, DP-MS 70-24, 1970.

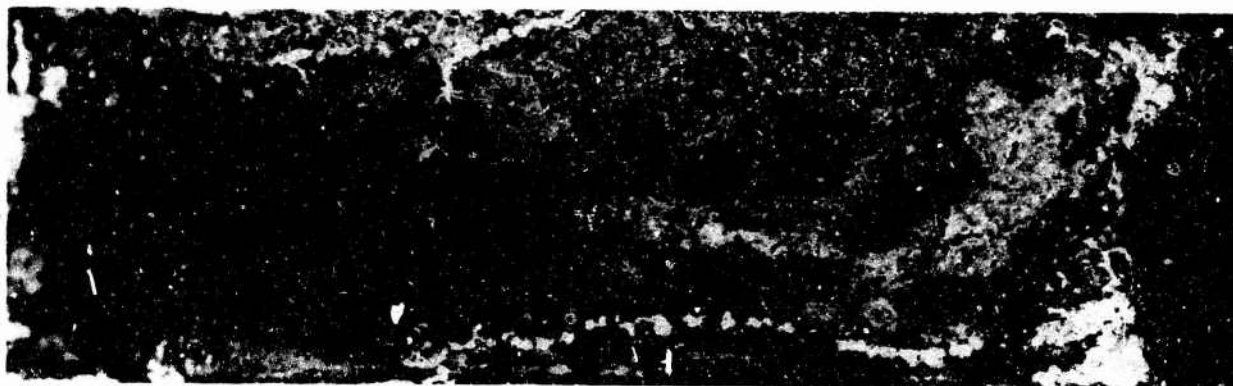


a. (B2) UNTREATED CONTROL



b. (B3) SALT-TREATED

Figure 4. Test Series II - (900°F - 150 Hours) - Central Test Section of
Transverse Specimens After Removal From Furnace (X5)
19-066-1424/AMC-72



a. (A12)



b. (A14)

Figure 5. Test Series V - (900°F - 1000 Hours) - Salt-Treated
Longitudinal Specimens After Removal from Furnace (X5)
19-066-1425/AMC-72



a. (A12)
(X2)



b. (A14)
(X2)

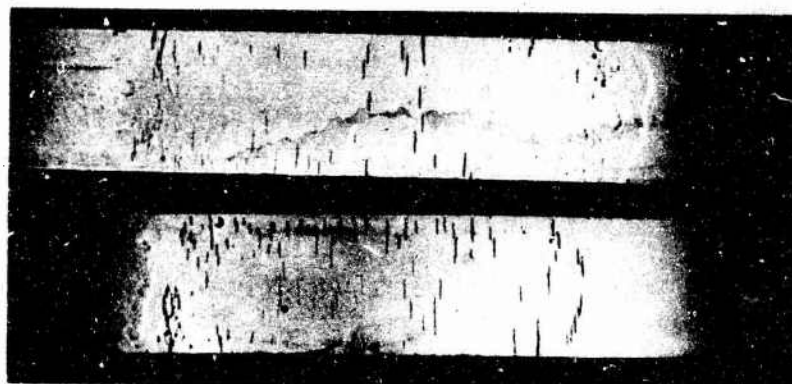


c. (A12)
(X5)



d. (A14)
(X5)

Figure 6. Test Series V - (900°F - 1000 Hours) - Salt-Treated Specimens
Cleaned by Wet Abrasive Blast Method
19-066-1426/AMC-72

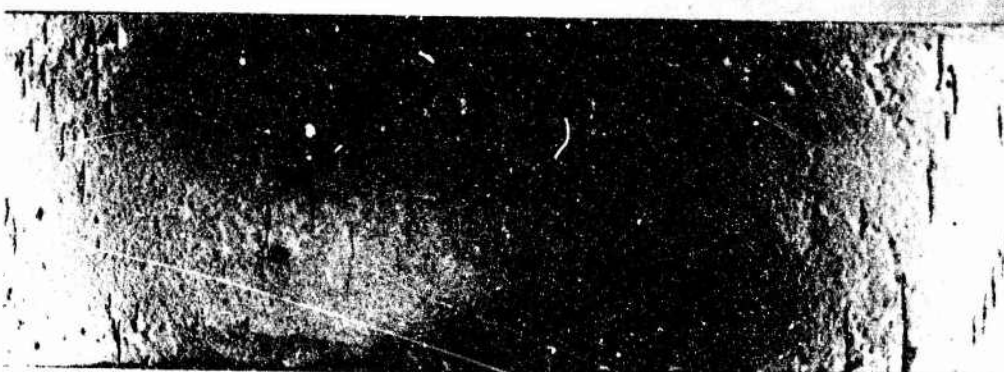


a. (A12)
(X2)

b. (A14)
(X2)



c. (A12)
(X5)



d. (A14)
(X5)

Figure 7. Test Series V - (900°F - 1000 Hours) - Etched Salt-Treated Specimens
19-C66-1427/AMC-72

Pits existing on the surface are more completely revealed by the 5x photographic enlargements shown in Figures 7c and 7d. It may be noted that the pits and cracks groupings coincide remarkably well with the white salt patches found on the surface of these same specimens, shown earlier in Figure 5. But the pitting and cracking phenomena appeared to occur independently as manifested by the paucity of intersection of the cracks with the pits. Nevertheless, despite the lack of interaction, the presence of corrosion pits are quite harmful since their existence decreases the volume and load carrying ability of the base metal. Furthermore, these small craters serve as focal points for the initiation of other damage due to stress corrosion and fatigue stresses.

Meanwhile, inspection of the untreated control specimens, exposed to an identical test condition, revealed no damage, neither in the form of cracks nor pits, on their surfaces. Figure 8, shows the appearance of three relatively unharmed, untreated control specimens, etched after cleaning, following exposure for durations up to 1000 hours. Hence, impairment of the surface of the salt-treated specimens was directly attributable to the attendant hot salt and duration of exposure.

Cracking was also severe after 500 hours, as indicated by Figures 9c and 9d. Also shown for comparison, in Figures 9a and 9b, are two specimens held at temperature for only 150 hours. In these cases, the deleterious effect of longer holding times was clearly demonstrated. More cracks were definitely present after the 500 hour incubation period as compared to the 150 hour test. Thus, these tests have shown that the Ti-5Al-2.5Sn alloy was indeed susceptible to hot salt-stress corrosion after exposure to only 150 hours at 900°F. Furthermore, increased exposure times up to 1000 hours increased the amount of surface damage.

In order to determine any effects of sheet orientation on hot salt stress corrosion, one transverse specimen was prepared. Earlier, it was shown in Figure 4a that the transverse striations on the surface of the unetched, untreated control specimen were clearly visible after exposure to the Test Series II condition of 900°F for 150 hours. In the etched condition, the effect of rolling direction was still apparent as evidenced by Figure 10a. As shown in Figure 10b the etched transverse salt-treated specimen was more severely cracked than its counterpart Test Series I, longitudinal, specimens shown previously in Figures 9a and 9b. However, whether to attribute the obvious difference in magnitude of cracking to mechanical factors or metallurgical factors remains as a problem to be resolved. One investigator¹² has found that the properties deteriorated more in the transverse direction for specimens of a particular Ti-8Al-1Mo-1V titanium alloy sheet. Later, in

¹² ROYSTER, DICK M., "Hot-Salt-Stress-Corrosion Cracking and its Effect on Tensile Properties of Ti-8Al-1Mo-1V Titanium-Alloy Sheet," Langley Research Center, Report No. NASA TN D-4674, August 1968.



a. (A3) - 150 HOURS



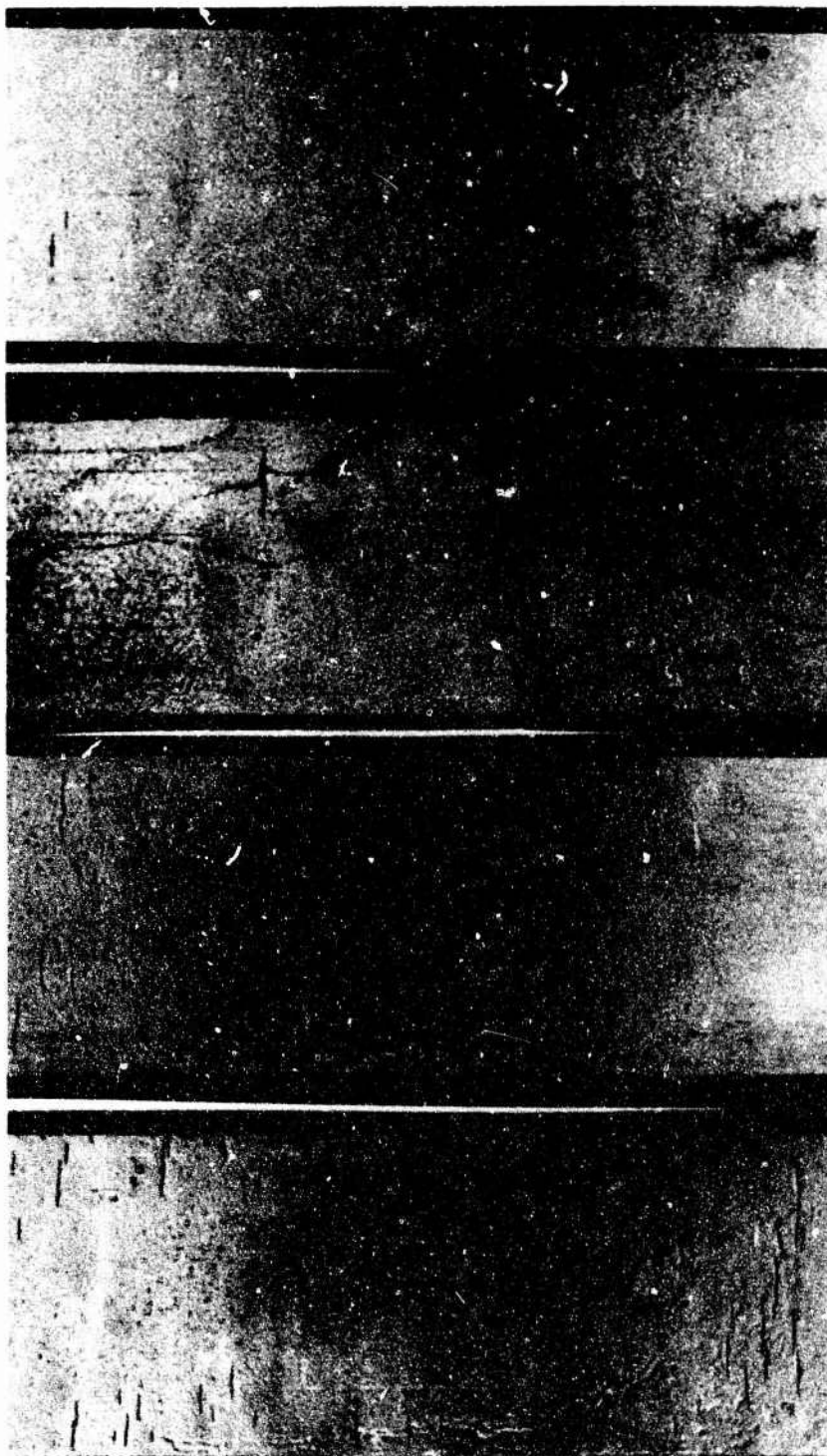
b. (A5) - 500 HOURS



c. (A10) - 1000 HOURS

Figure 8. Etched Untreated Control Longitudinal Specimens After Exposure to 900°F Temperature (X5)

19-066-1428/AMC-72



a. (A2)
150 HOURS

b. (A4)
150 HOURS

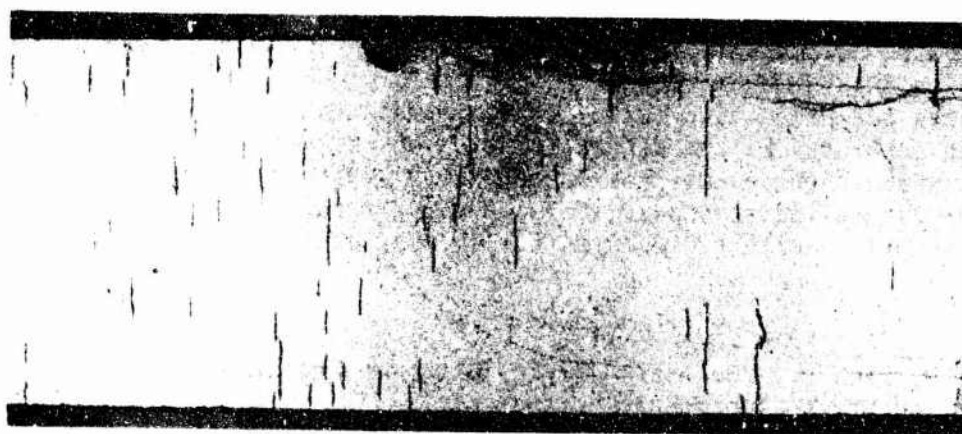
c. (A8)
500 HOURS

d. (A9)
500 HOURS

Figure 9. Test Series I - (900°F - 150 Hours) and IV - (900°F - 500 Hours) -
Etched Salt-Treated Specimens (X5)
19-066-1429/AMC-72



a. (B2) UNTREATED CONTROL



b. (B3) SALT-TREATED

Figure 10. Test Series II - (900°F - 150 Hours) Etched Transverse Specimens (X5)
19-066-1430/AMC-72

another report,¹³ the same investigator disclosed no differences in cracking due to orientation in his evaluation of a sheet of Ti-6Al-4V titanium alloy.

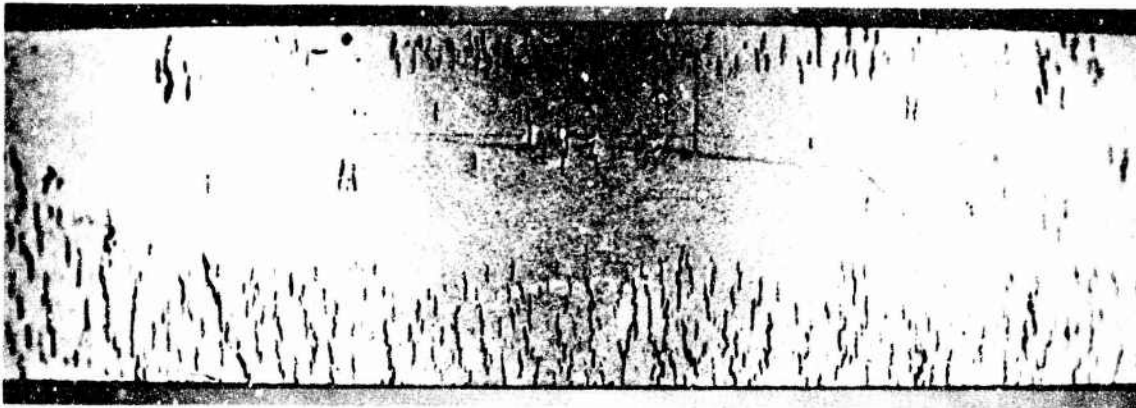
But, further experimentation¹⁴ by other workers with smooth and pre-cracked specimens revealed that the effects of hot salt were relatively insensitive to the existence of initial surface flaws, as determined by stress-rupture tests. Their results disclosed that small cracks selectively initiated and grew on the external flat, stressed surfaces despite the inviting presence of large initial fatigue precracks. Thus it would appear that the surface striae do not necessarily promote the formation of surface cracks. Nevertheless, the Ti-5Al-2.5Sn sheet alloy used in this study was more susceptible to stress corrosion cracking when exposed to the test environment in the form of transverse specimens.

Increased stresses should also naturally engender more damage. This was verified by a test of specimens deflected to yield an outermost fiber stress of over 60 ksi at 900°F, a value somewhat over the projected 57 ksi yield stress of this alloy at the test temperature, in contrast to the calculated 50 ksi prestress used in the other specimens. The higher density of short cracks in the highly stressed, salt-treated specimens of Test Series III after only 150 hour exposure, is evident in Figure 11. A comparison may be made with other specimens prestressed at a lower level for various time periods, such as those shown earlier in Figures 7 and 9. cursory inspection discloses that the quantity of cracks present in the overstressed specimen exposed to 150 hours to be greater than in the normally-stressed specimen exposed to 1000 hours. However, the degree of severity of cracking was not determined in this study wherein the prime intention was to validate the use of this bent beam deflection test method as a convenient means for screening candidate coatings.

Many explanations have been proposed to elucidate the mechanism of hot salt stress corrosion. One current exposition^{11,14} suggests that the cracking phenomena involved the pyrohydrolytic formation of the hydrogen halide corresponding to the anion of the salt. For example, HCl, formed from Cl salts, penetrates the protective oxide film to attack the underlying metal. Meanwhile, hydrogen generated by the diffusion reaction is partially absorbed by the metal surface which then becomes embrittled. Cracks are subsequently initiated by residual or applied stresses. Subsequently, these cracks are propagated by stress sorption, with hydrogen as the sorbing species.

¹³ ROYSTER, DICK M., "Hot-Salt-Stress-Corrosion Cracking and its Effect on Tensile and Stress Rupture Properties of Ti-6Al-4V Titanium-Alloy Sheet," Langley Research Center, Report No. NASA TN D-5417, Sept. 1969.

¹⁴ LISAGOR, W. BARRY, GARDNER, JAMES E., and ROYSTER, DICK M., "The Effect of Dynamic and Static Environments and Surface Flaws on the Hot-Salt Stress-Corrosion Cracking of Titanium Alloys," Langley Research Center, Presented at the International Symposium on Stress Corrosion Mechanisms in Titanium Alloys, Atlanta, Georgia, January 1971.



(A15)

Figure 11. Test Series III - (900°F - 150 Hours) - Etched Overstressed
Longitudinal Salt-Treated Specimen (X5)

19-066-1431/AMC-72

As mentioned earlier, a tensile stress of only 48 ksi at 800°F was expected³ to produce about 1½ creep in annealed Ti-5Al-2.5Sn titanium alloys in 100 hours. Consequently creep of a higher order of magnitude was expected to be exhibited by the specimens used in this study since they were designed to be stressed at 50 to 60 ksi at the higher temperature of 900°F. Creep of these specimens did indeed occur and was manifested by permanent curvatures of the specimen after high temperature exposure. Examples of the permanent set experienced by the specimens are shown by the profiles in Figure 13. These photographs disclose the magnitude of creep, represented by specimen curvature, increased with increasing exposure time. Although the relaxation phenomena tended to reduce the prestress load on the specimens in these tests, the conditions were still quite adequate for delineating the deleterious cracking effects as a function of exposure time, specimen orientation, and overstress. Thus the bent beam test method appeared to be a satisfactory vehicle for screening candidate materials.

Incidentally, examination of the profile of the etched specimens shown in Figure 12 also revealed the presence of cracks to be limited to the salt treated areas. Later efforts will be directed toward correlating density and depth of cracks with specimen curvature and residual strength.

Boron Carbide Coating

To validate the test method described herein, the work was continued to evaluate the proprietary boron carbide coating referenced earlier in this report. The one inch long test section of coating was applied, by the producer, to the specimen surface adjacent to the midlength of the specimen as indicated in Figure 1b. Further, the thickness of the coating was measured and determined to be less than 2 mils. Moreover, the tensile strength of the coating was claimed by the producers to exceed 100,000 psi. Thus, overt cracking of the coating surface was not expected to occur in view of the projected substrate prestress of only 50,000 psi and the presence of the relatively thin coating. In fact, no visible cracks were observed on the surfaces of coatings during the initial flexing of the specimens.

Subsequently, the salt solution was applied to the midlength test area such that it covered one-half of the proprietary coating and a half-inch length of titanium alloy surface. Thus on one test specimen, it was planned to observe the effects of time-temperature on the untreated titanium, salt-treated titanium, salt-treated coating and untreated coating surfaces.

These various test segments are evident in Figure 13, which includes photomacrographs of longitudinal and a transverse specimen after 900°F exposure for 150 hours and 500 hours. Inspection of the 150-hour specimens after removal from the furnace disclose the fact that the untreated coated area



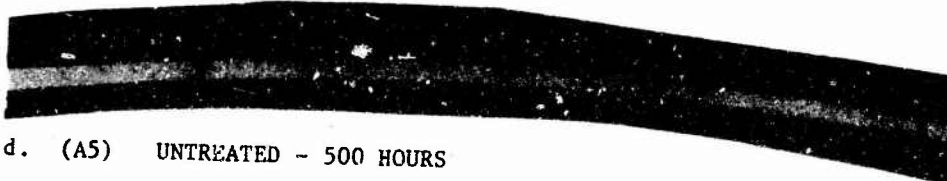
a. (A15) SALT-TREATED - 150 HOURS - OVERSTRESSED



b. (A3) UNTREATED - 150 HOURS



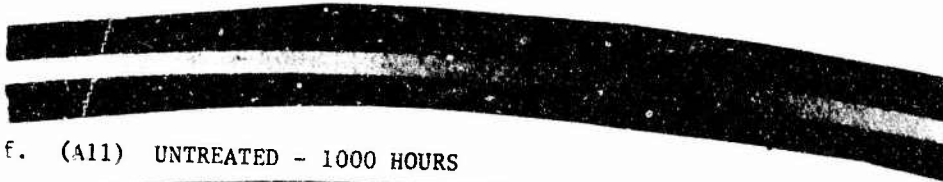
c. (A4) SALT-TREATED - 150 HOURS



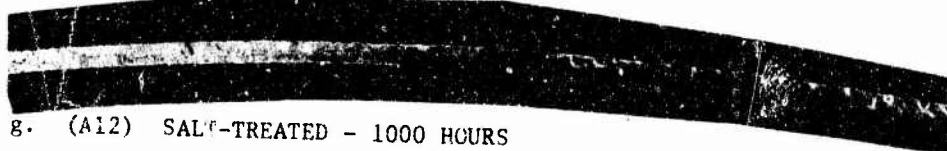
d. (A5) UNTREATED - 500 HOURS



e. (A8) SALT-TREATED - 500 HOURS

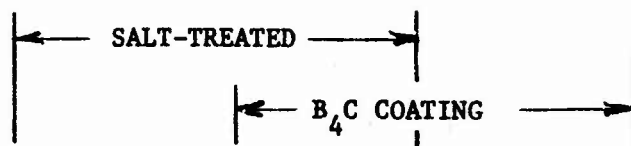


f. (A11) UNTREATED - 1000 HOURS



g. (A12) SALT-TREATED - 1000 HOURS

Figure 12. Etched Profile Sections of Specimens Exposed to 900°F Temperature (X5)
19-066-1432/AMC-72



a. (A17) - 150 HOURS - LONGITUDINAL



b. (B4) - 150 HOURS - TRANSVERSE



c. (A18) - 500 HOURS - LONGITUDINAL



(B5) - 500 HOURS - TRANSVERSE

Figure 13. Test Series VI - (900°F - 150 Hours) and Test Series VII (900°F - 500 Hours) - Salt-Treated Boron Carbide Coated Specimens (X2)
19-066-1433/AMC-72

appeared to be relatively unaffected by the stress-heat treatment combination except for a conversion in color from the original grey hue to a golden tan. On the other hand, the salt-treated coated areas had darkened considerably, as shown in Figures 13a and 13b. White salt crystals were also present in the treated areas. However, more blobs of reacted salt compounds were observed within the treated titanium area than on the treated coated surface. Thus, the boron carbide coating appeared to have inhibited some of the salt reactions. Furthermore, the coating appeared to be still firmly attached to the titanium alloy surface after the long-term exposure tests.

Shown in Figures 13c and 13d are macrographs of similar coated specimens which were exposed at temperature for 500 hours. In this longer-term test, untreated coated specimens had turned to a darker bronze color. In addition, striations in the coatings became clearly evident. Macrographs of the salt-treated regions may be seen in Figure 14. The geometric shapes of the salt crystals are revealed more explicitly on the transverse specimen. In addition, some of the black spots present on the surface were observed to erupt and flow upon removal of the specimens from the hot furnace. Apparently some of the high temperature reaction products were unstable at room temperature. Absorption of moisture from the air may have also hastened the transformation to a more stable structure.

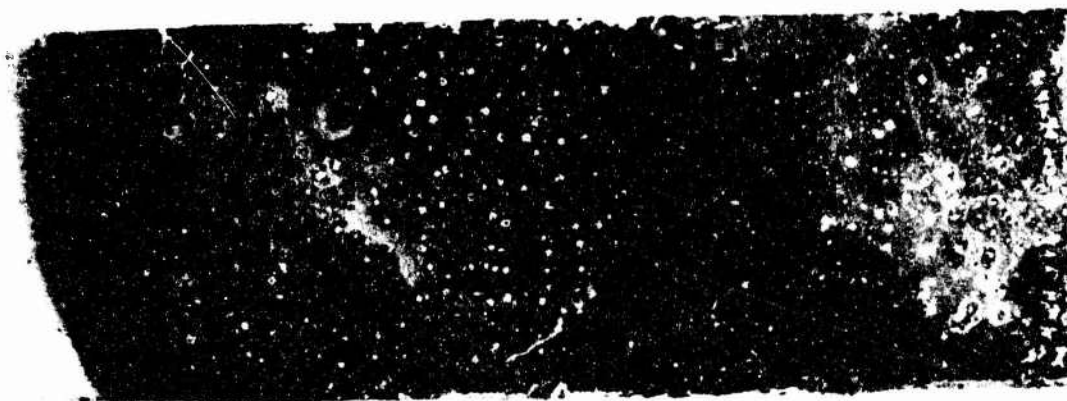
To further evaluate the coating, the 150-hour specimens were subjected to the wet abrasive blast cleaning procedure. Surprisingly, the untreated boron carbide coating was easily removed while the salt-treated segment of coating exhibited a high degree of tenacity. As shown in Figures 15a and 15b, a significant portion of the reacted coating remained on the surface of the specimen after the initial cleaning effort. This residual coating was hard and adherent could not be scraped off with a knife.

Exploratory X-ray diffraction examinations of the substrate below the black residual coating did not reveal any gross diffusion of chemical species into the titanium alloy structure. Similar effects to identify the composition of the residual coating proved to be negative. Nevertheless, it was speculated that the black, adherent substance was composed of some forms of boron oxide produced by unidentified chemical reactions between B_4C and oxygen at elevated temperatures, catalyzed by the presence of sodium chloride and its constituents or its reaction products.

A qualitative measure of the effect of the test-environment on the boron carbide coating was made by comparing its tenacity with that of the virgin coating. Following controlled exposure to a wet abrasive blast treatment, the as-received refractory coating of an untested specimen was observed to have essentially retained its structural integrity, with the exception of some limited material loss at the coating periphery, a condition exhibited in the photograph in Figure 15c. In contrast to this demonstration of abrasion resistance, the non-salt-treated, 500-hour-exposure segment of the coating was readily removed by an equivalent wet blast treatment. On the other hand, the non-salt-treated, 150-hour, boron carbide coating proved to be slightly more abrasive-resistant although it too was readily detached from the substrate.



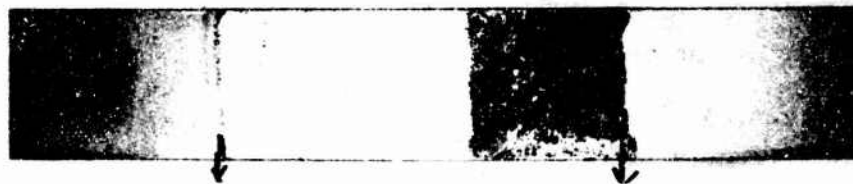
a. (A18) LONGITUDINAL



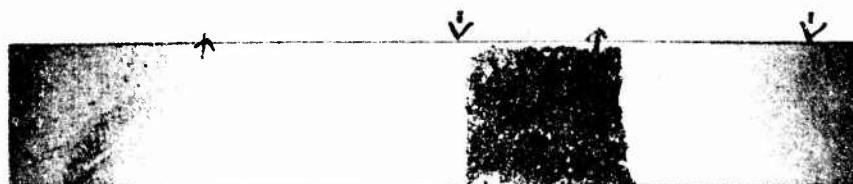
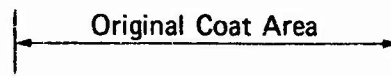
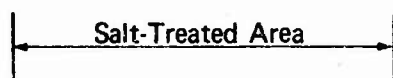
b. (B5) TRANSVERSE

B_4C COATING

Figure 14. Test Series VII - (900°F - 500 Hours) - Salt-Treated Test Section of
Boron Carbide Coated Specimens (X5)
19-066-1434/AMC-72



a. (A17) - Longitudinal Specimen - Tested



b. (B4) - Transverse Specimen - Tested



c. (B7) - Transverse Specimen - Untested

Figure 15. Test Series VII - (900°F - 150 Hours) - Salt-Treated Specimens and One Untested Coated Specimen - After Initial Exposure to Wet Abrasive Blast Treatment (X2)

19-066-1435/AMC-72

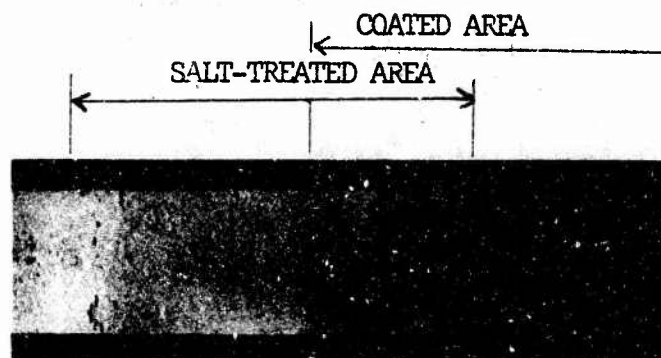
As shown by the specimens photographs in Figures 15a and 15b, the non-salt-treated segments of the coating were cleanly removed from the respective substrates. Therefore, it was tentatively concluded that exposure to tensile stresses at 900°F temperatures in quiescent atmospheres reduced the room-temperature efficacy of the boron carbide coating.

But subsequent attempts to remove the black residual coating, clearly evident on the specimens in Figures 15a and 15b, by the same technique and effort which handily remove the heat-affected, non-salt-treated boron carbide coating, were not successful, attesting to greater tenacity of the reacted coating. Hence, longer durations of wet abrasive blasting of the residual coating, were required to clean the specimen surfaces. However, under these conditions, the black, adherent coating still managed to selectively protect the substrate. Thus, the removal of the black coating resulted in the generation of cratered, pocked, undercut surfaces, as shown on certain portions of the specimens photographed in Figure 16. Areas adjacent to the aforementioned segments were more uniformly cleaned by the process.

Moreover, as alluded to by the magnitude of roughened areas, the residual coating present after 150 hours was more adherent, and consequently more difficult to remove, than that remaining after 500 hours. The differences in surface roughness may be observed by comparing the 150-hour specimens shown in Figures 16a and b, with the 500-hour specimen shown in 16c. Therefore, it was also concluded that increased exposures at elevated temperatures may potentially degrade the residual coating, manifested by a decrease in tenacity.

To further evaluate the efficacy of the proprietary refractory coating in retarding the debilitating effects of hot salt on titanium alloys, the substrate below the coating, along with adjacent areas, were chemically etched. As exhibited by the specimens shown in Figure 16, the test conditions were capable of generating many cracks within the salt-treated titanium alloy test segments. However, in comparison to the crack patterns described earlier in this report, the crack distributions in these coated test specimens were more uniform. This uniformity was attributed to the changes in surface cleaning techniques which enhanced the wettability of the specimen surfaces prior to the application of the saline solution.

Moreover, close scrutiny of the etched specimens also disclosed the presence of a limited number of cracks within the coating substrate area. These cracks, along with other surface phenomena, are clearly evident in Figure 17. Therein, it may be observed that the substrate cracks were few in number and confined to the edge periphery of the salt-treated coating only. It may be recalled that the coating integrity along the edges of the specimens was minimal as shown earlier in Figure 15c. Consequently, many of these edge cracks may have initiated because of the inadequate protection offered by the boron carbide coating at the periphery. On the other hand, slightly higher edge



a. (A17) LONGITUDINAL - 150 HOURS



b. (B4) TRANSVERSE - 150 HOURS



c. (A18) LONGITUDINAL - 500 HOURS

Figure 16. Test Series VI (900°F - 150 Hours) and Test Series VII -
(900°F - 500 Hours) - Etched Salt-Treated Specimens (X2)
19-066-1436/AMC-72



a. (A17) L
150 Hours



b. (B4) T
150 Hours



c. (A18) L
500 Hours

COATED FIBER

Figure 17. Test Series VI - (900° - 150 Hours) and Test Series VII - (900°F - 500 Hours) Etched Salt-Treated Specimens (X5)
19-066-1437/AMC-72



stresses encountered in this type of configuration⁵ may also have contributed to the presence of edge cracks.

However, no cracks were observed on the non-salted titanium alloy surfaces, nor in the substrate below the major portion of the salt-treated boron carbide coating. Thus, the corrosion-crack-inhibiting potential of this proprietary coating was positively demonstrated on both longitudinal and transverse specimens exposed to a 900°F air environment for 150 and 500 hours.

Additionally, the black residual coating was not completely removed by the wet abrasive action even though the erosive action produced severe under-cutting of the metal specimens. Closer inspection of the specimens under higher magnification, as represented by the macrograph in Figure 17, verified the existence of some retained black patches on the surface of the otherwise clean, though roughened, segments. These patches were remnants of the residual coating which survived the attempts to abrasively clean the surface thereby again testifying to the endurance of the salt-reacted boron carbide coating. Incidentally, it was also noted, as revealed in Figure 17a, that the fissure-like surface cracks, created by the hot-salt stress corrosion phenomena, were essentially short and discontinuous in nature. There did not appear to be any tendency for the cracks to merge.

A recapitulation of the post-test examinations of the flexure specimens utilized for the evaluation of the efficacy of the proprietary boron carbide coating revealed that:

- a. No damage, as evidenced by cracks or pits, was present
 - (1) on the non-salt-treated titanium alloy surfaces
 - (2) under the non-salt-treated boron carbide coating
 - (3) under a major portion of the salt-treated boron carbide coating
- b. Cracks were present,
 - (1) along with pits, on the surfaces of the salt-treated titanium alloy segments
 - (2) though few in number, on the substrate at the edge periphery under the boron carbide coating

Therefore, the results of this screening test indicated that the proprietary boron carbide coating did indeed possess desirable characteristics

with potentials for protecting titanium alloys against hot salt stress corrosion and therefore warranted consideration for further evaluation.

GENERAL CONSIDERATIONS

In summary, base-line comparison data on the hot-salt stress corrosion cracking characteristics of a Ti-5Al-2.5Sn titanium sheet alloy exposed to a temperature of 900°F for durations up to 1000 hours have been obtained in this study utilizing the new deflection bent beam test apparatus. Clear distinctions in the cracking characteristics were observed to have been manifested by varying exposure times, orientation and overstress as indicated in the earlier figures. However, further work is necessary for quantifying these observations relative to factors such as crack initiation parameters, crack growth, creep, stress rupture, and residual strengths.

Moreover, many other interrelated factors affecting the failure phenomena must also be considered. Some of the complex materials and environmental variables include⁷ microstructural characteristics, processing methods including fabrication and heat treatment, alloy composition, surface condition such as machining and shot-peening, and air velocity. Also of importance are other interacting variables^{11, 15} such as moisture content, salt composition, salt deposition temperature, pH, and cyclic heating and stress. Thus it is well-recognized that supplementary studies must also be conducted in the complete investigation of protective mechanisms for titanium alloys exposed to complex environments.

Nevertheless, this exploratory investigation has demonstrated the feasibility of employing a simple bent beam deflection-type apparatus for economically screening sheet-type candidate materials and coatings for resistance to hot salt stress corrosion. A proprietary boron carbide coating investigated by this technique appeared to have promise and warranted further evaluation.

CONCLUSIONS

1. The bent beam test apparatus and procedures developed are adequate for screening candidate titanium alloys and coatings in conjunction with investigations of damage attributable to hot salt stress corrosion. This exploratory

¹⁵ONDREJCIN, R. S., "The Hot-Salt Stress Corrosion Cracking of Titanium Alloys," E. I. DuPont De Nemours Co., National Aeronautics and Space Administration, Report No. Cr-1829, October 1971.

study verified that a Ti-5Al-2.5Sn titanium alloy was susceptible to cracking and pitting while subjected to tensile stresses in the presence of hot salt at 900°F. Moreover, pitting, crack initiation and crack growth were observed to increase with incubation times up to 1000 hours. Increased stresses also produced more harmful effects.

2. Screening tests conducted with a proprietary boron carbide coating indicated that further evaluation of this class of materials as a means for protecting titanium alloy substrates from hot salt corrosion was warranted.