[redacted] [redacted]

2483

AD 661 463

NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Washington, D.C. 20007

Embrittlement of Titanium in Seawater

This document has been approved for public release and sale; it's distribution is unlimited.

MARINE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT REPORT

October 1967 Report 2483

NDW-NSRDC-3960/15 (648) (Rev. 4-67)

The Naval Ship Research and Development Center is a U.S. Navy center for laboratory effort directed at achieving improved sea and air vehicles. It was formed in March 1967 by merging the David Taylor Model Basin at Carderock, Maryland and the Marine Engineering Laboratory at Annapolis, Maryland.

Naval Ship Research and Development Center
Washington, D. C. 20007

Embrittlement of Titanium in Seawater

By
J. L. Cavallaro

October 1967

ABSTRACT

Sea-water stress-corrosion tests on notched cantilever-beam specimens of Alloy Ti-7Al-2Cb-1Ta (Ti-721) demonstrated that it has a transition in behavior with increasing notch sharpness. Sea-water tests on Alloy Ti-721 indicate that a threshold stress level exists below which stress corrosion does not occur.

Sea-water stress corrosion is dependent on the presence of embrittling constituents in the alloy. Alloy chemistry and heat treatment are the most significant factors which control sensitivity. The results of tests made on a series of Ti-Al binary alloys indicate that aluminum in solid solution does not cause stress corrosion, but that it is caused by a finite amount of a coherent Ti_3Al. A decrease in aluminum and oxygen contents and the addition of isomorphous beta stabilizers improve the resistance of Ti-Al alloys to sea-water stress corrosion by suppressing the formation of Ti_3Al.

A stress-sorption cracking mechanism is suggested as a general model for the embrittlement of titanium and titanium alloys in seawater.

ADMINISTRATIVE INFORMATION

This investigation is supported by Sub-project S-F020 01 01, Task 0721, and augmented by Sub-project S4607, Task 11896. The work was done under Assignments 87 115 and 87 113.

TABLE OF CONTENTS

LIST OF FIGURES

TABLE OF CONTENTS (Continued)

NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

EMBRITTLEMENT OF TITANIUM IN SEAWATER

By
J. L. Cavallaro

INTRODUCTION

This report covers one phase of the Navy's program to provide the technology for use of titanium as a marine structural material. The report concerns the fracture behavior of titanium alloys in seawater, andis the second report to cover this subject. The investigation was undertaken to obtain a better understanding of the metallurgical and mechanical variables which lead to stress corrosion, so that the problem can be avoided in service.

BACKGROUND

Since December 1964 the results of laboratory tests on the effect of seawater on specimens containing stress concentrations have been well documented.[1,2,3,4] Even though it has been demonstrated that under certain conditions some titanium alloys have reduced fracture strength in seawater, it has not been proved that a problem exists relative to in-service applications. The reasons for this situation are summarized as follows:

- Knowledge of the variables associated with the stress-corrosion behavior of titanium is incomplete.

- There have been few in-service sea-water applications, as well as incomplete knowledge of the variables encountered in these applications.

Therefore, it is assumed that a problem exists until it is proved otherwise, and the approach has been taken that a candidate titanium-alloy hull material should show immunity to laboratory sea-water stress-corrosion tests.

The first report on this investigation covered evaluation of a spectrum of titanium alloys for loss of fracture resistance in seawater.[3] Sensitivity in titanium-aluminum alloys was found to be related to aluminum content, isomorphous beta

---

[1] Superscripts refer to similarly numbered entries in Appendix A.

stabilizer content, and heat treatment. A later paper on the subject concluded that sea-water stress corrosion is associated with the presence of an embrittling constituent in the structure of the metal.[4] Circumstantial evidence indicated that there is a relationship between this behavior and the titanium-aluminum embrittlement reaction. Data developed by the Marine Engineering Laboratory and others led to the suspicion that interstitial content, presence of eutectoid phase, and presence of omega phase also have a relationship to sea-water stress corrosion. The most significant observation was that the stress corrosion of titanium alloys can be circumvented by compositional control and careful attention to thermal treatment.

The first phase of the investigation led to development of Alloy Ti-6Al-2Cb-1Ta-0.8Mo (Ti621/0.8), a compositional variation of Alloy Ti-7Al-2Cb-1Ta (Ti-721). This alloy has been found to be completely resistant to sea-water stress corrosion even after severe thermal treatments designed to induce sensitivity.[5]

SCOPE

The current phase of the investigation included a study of the effect of mechanical and metallurgical factors associated with the stress-corrosion cracking of titanium in natural seawater. The mechanical factors considered were: (1) the effect of notch acuity, and (2) the existence of a threshold stress. The metallurgical considerations included: (1) compositional effects, including the substitutional alpha stabilizers aluminum (Al) and tin (Sn); the interstitial alpha stabilizer oxygen, (O_2); the isomorphous beta stabilizers molybdenum (Mo), vanadium (V) and columbium (Cb); the beta eutectoid formers nickel (Ni), iron (Fe) and manganese (Mn); and palladium (Pd) as a minor noble metal addition; and (2) the fracture path.

MATERIAL DESCRIPTION

The material used was in plate form with thicknesses ranging from 1/2 to 1 inch. The binary alloys, which were 2-inch-thick bar forgings were an exception. The material represented 15 to 30-pound research heats, 100-pound pilot heats, and 1500- to 500-pound production heats. Identification data, including chemical composition, of all materials are presented in Appendix B.

RESEARCH HEATS

Research heats consisted of titanium alloys made especially for this investigation, and excess material generated in previous research contracts.[6, 7, 8]

PILOT HEATS

One-hundred-pound pilot heats of Alloy Ti-621/0.8, Heats X2345 and X2343, were made by the consumable electrode arc-melting technique. They were beta fabricated to 1-inch-thick plate and delivered to MEL in the as-rolled condition.

PRODUCTION HEATS

Ti-7Al-2Cb-1Ta (Ti-721)

One production ingot of Alloy Ti-721, approximately 5000 pounds (Heat 30935), was beta fabricated to 2-inch thickness. The plate was supplied by the mill in the beta-annealed condition.

Ti-6Al-4V (0.16 Oxygen)

Alloy Ti-6Al-4V was obtained as 2-inch-thick plate from the DOD sheet rolling program. No information is available on its past history, but the appearance of the microstructure indicates that it was rolled and annealed in the alpha-beta field.

---

*Abbreviations used in the text are from the GPO Style Manual, 1967, unless otherwise noted.

METHOD OF TEST

NRL cantilever-beam stress-corrosion tests were used throughout this study.[2] The tests were similar to those described in the first phase of the investigation.[3] Notched specimens 0.420-inches square x 5-inches long were tested in air and in seawater obtained from Harbor Island, North Carolina. The notch, containing a 45-degree included angle, was machined at the mid-length of the specimen perpendicular to the rolled surface to a depth of 20 percent of the specimen thickness. The machined notch contained a root radius of 0.002 inch. Some specimens were tested with only the machined notch. However, the majority were fatigue cracked, using a modified Manlabs fatigue precrack machine, to achieve a total defect depth (machined notch plus fatigue crack) of 25 to 35 percent of the specimen depth.

Specimens were exposed to seawater and then step-loaded in increments to produce nominal stress increases of 10 to 15 ksi at the notch. These incremental stress increases were made at 5-minute intervals until rupture. Specimen loading was accomplished by adding lead shot to a bucket fixed at the end of a moment arm. Tests in air used the same step-loading technique. Companion samples were tested in air and in seawater for each alloy and heat treatment. Duplicate tests were made whenever possible.

A nominal bending stress to fracture was calculated at the notch root according to simple beam theory, $S_n = \frac{Mc}{I}$. A ratio of the fracture stress in seawater to the fracture stress in air was used as a parameter of the sensitivity of a material to embrittlement.

Notch Acuity Investigation

A study was made of the effect of notch acuity on the sea-water stress-corrosion behavior of production heats of Alloys Ti-721 (Heat 30935) and Ti-6Al-4V containing 0.16 weight-percent 0_2. Alloy Ti-721 was tested as received in the beta-fabricated plus beta-annealed condition. Alloy Ti-6Al-4V was heat treated at 1600 F for 1 hour and air cooled, then aged at 1200 F for 2 hours and air cooled.

A series of 0.420- x 0.420 - x 5-inch specimens was prepared with notch-root radii of 0.035, 0.020, 0.010, 0.007, and 0.002 inches and a fatigue crack.

Long-Term Tests

A conventionally processed Alloy Ti-721 (Heat 291488) was held at various stress levels below the threshold breaking stress for periods up to 500 hours. Specimens containing 0.002-inch root-radius notches and specimens with fatigue cracks were used in this study. A metallographic sample was sectioned 1/8 inch from each side of the specimen through the notch to determine if there was any corrosive damage.

RESULTS

MECHANICAL FACTORS

Notch Acuity

A plot of notch acuity versus fracture stress for Alloy Ti-721 in air and seawater appears in Figure 1. The alloy displayed, essentially, no notch sensitivity when tested in air. However, when exposed to seawater, it displayed a sharp transition from insensitive to sensitive behavior at a notch-root radius of approximately 0.007 inch. These data also show that a notch-root radius of 0.002 inch is as effective in inducing stress corrosion as a fatigue crack in this material. However, another heat of Alloy Ti-721 (D-8288) tested in the as-received condition (beta-fabricated and quenched from the rolling mill) showed increased stress-corrosion sensitivity between a 0.002-inch notch and a fatigue crack, with the stress-corrosion ratio changing from 0.67 to 0.44.

Figure 2 shows the fracture strength versus notch acuity for Alloy Ti-6Al-4V. This alloy, in the condition tested, displayed notch sensitivity both in air and in seawater. However, the fracture strength in seawater was only slightly less than than that in air for all notches, with the greatest fall-off of strength being in the fatigue-cracked condition.

Threshold Stress

Alloy Ti-721 (Heat 291488) conventionally processed (beta-fabricated plus beta-annealed) was tested at several stress levels less than, but approaching, the sea-water fracture stress as previously determined from the standard short-time step-loaded tests. These tests were run up to 500 hours with both a 0.002-inch root radius machined notch and with a machined notch plus a fatigue crack. Specimens tested at 5 to 10 ksi less than the indicated threshold stress (85 to 90 ksi) did not fail after 500 hours exposure as shown in Figure 3.

Metallographic examination (up to 500X) of sections taken perpendicular to the notch showed no evidence of pitting or slow-crack extension, indicating that a detectable incubation period apparently does not precede stress-corrosion failure.

METALLURGICAL FACTORS

Compositional Effects

Titanium-Aluminum Binary Alloys

A series of binary titanium-aluminum alloys containing 3, 5, 6, 7, and 8 weight-percent aluminum was studied to determine the effect of aluminum content on stress-corrosion tracking. These alloys were homogenized by an anneal in the beta field at 2200 F for 1 hour and water quenched prior to subsequent thermal treatment. The alloys were then tested in the alpha-annealed and in the alpha-annealed and aged conditions.

Stress corrosion was correlated with the presence of Ti_3Al on the basis of the titanium-rich end of the titanium-aluminum phase diagram determined by Crossley,[9,10] (Figure 4). Alloy Ti-8Al was the only alloy quenched from above the alpha plus Ti_3Al phase field which was sensitive to seawater. Aging at 1100 F rendered all compositions sensitive except Alloy Ti-3Al which, according to the phase diagram, does not contain Ti_3Al. Alloys Ti-5Al through Ti-8Al showed an approximate linear decay of nominal fracture stress in seawater for the aged condition. A fall-off of the fracture stress in air, starting at the Ti-7Al composition, is also noted from Figure 5, which indicates that alloys in this composition range are notch sensitive.

Ti-(7-8)Al-XCb[6]

Alloys Ti-(7-8)Al-XCb with 0.07 and 0.12 weight-percent O_2 (where X = 1, 3, 5, and 7 weight percent) were tested in the beta-annealed and beta-annealed and aged conditions. The data in Figures 6 and 7 show that the alloys increased in resistance with increasing columbium content. Alloy Ti-7Al-7Cb was completely resistant at the 0.07 weight-percent oxygen level in both the annealed and the annealed plus aged conditions. However, the columbium contents were not sufficient to overcome the increased sensitivity promoted by 0.12 weight-percent oxygen. Alloy Ti-7Al-7Cb (0.12-percent oxygen) in the annealed plus aged condition also displayed a significant degree of notch sensitivity in air.

Alloys Ti-8Al-XCb at 0.07 percent oxygen showed increased sensitivity in the annealed plug aged condition compared to the annealed condition, except for alloy Ti-8Al-7Cb which showed no additional sensitivity on aging. These data are presented in Figure 8.

The Effect of Oxygen on Alloys Ti-6Al-2Sn-1Mo-V and Ti-6Al-4Zr-V

The influence of increasing the oxygen content from 0.08 to 0.4 weight percent on the stress corrosion of Alloys Ti-6Al-2Sn-1Mo-(1-2)V and Ti-6Al-4Zr-(1-2)V in the beta-annealed condition is shown in Figures 9 and 10. The 0.2 weight-percent oxygen concentration rendered Alloy Ti-6Al-2Sn-1Mo-1V alloy extremely sensitive, but Alloy Ti-6Al-2Sn-1Mo-2V showed no reduction in fracture stress at this same oxygen level. Both alloys were notch sensitive at 0.4-percent oxygen in both the air and sea-water environment. However, the alloy containing 1-percent vanadium showed the larger reduction in fracture stress in seawater.

Oxygen influenced the stress-corrosion behavior of Alloy Ti-6Al-4Zr-(1-2)V more than Alloy Ti-6Al-2Sn-1Mo-(1-2)V. Alloy 6Al-4Zr-1V was sensitive at 0.08-oxygen concentration, and the sensitivity increased with increasing oxygen content. Notch sensitivity was developed in this alloy at 0.4-percent oxygen. Alloy Ti-6Al-4Zr-2V was not sensitive at 0.08-percent oxygen;however, it became sensitive with an increase in oxygen concentration. It was also determined that Alloy 6Al-4Zr-2V was not as notch sensitive as Alloy 6Al-4Zr-1V.

Modified Alloy Ti-7Al-2Cb-1Ta

Preliminary work on the effect of minor molybdenum additions (0.2 and 0.8 weight-percent Mo.) to Alloy Ti-7Al-3Cb alloy showed promise in rendering the alloy resistant to stress-corrosion, particularly at the 0.8-percent Mo level.[3] Additional small research-size heats of Alloy Ti-7Al-3Cb, 0.8 Mo (Heat X2357) and two similar alloys with slight compositional variations, Alloys Ti-6Al-3Cb, 0.8 Mo (Heat X2356) and Ti-6Al-2Cb-1Ta, 0.8 Mo (Heat 2345), were evaluated for their sea-water resistance. All three alloys were not significantly embrittled, although Alloy Ti-7Al-3Cb, 0.8 Mo, showed a 30-percent loss in strength after a 10-hour age at 1100 F. The other two alloys retained their strength after a similar aging cycle.[5] Following these tests, Alloy Ti-6Al-2Cb-1Ta, 0.8 Mo, was scaled up and evaluated as 1- and 2-inch thick plate made from production size heats (292555 and 292596). This material was found to be resistant (Figure 11) to sea-water stress corrosion after a 20-hour, 1100 F aging treatment.[5]

Minor additions of beta eutectoid formers (0.09 and 0.2 weight-percent nickel) were added to research-size heats of a high-purity Alloy Ti-721 and to Alloy Ti-721 containing 0.3-percent Mn plus 0.18-percent Fe plus 0.01-percent Si to determine how they would alter the stress-corrosion sensitivity of the alloy. Figure 12 shows that these small additions of nickel render the alloy more sensitive, even in the beta-annealed condition. The 0.2-percent nickel addition to the high-purity Alloy Ti-721 reduced the sea-water fracture stress of the alloy from 146 to 84 ksi. The data also show a slight reduction in fracture stress in seawater due to the manganese, iron, and silicon additions when compared to the high-purity Alloy Ti-721.

A minor addition of 0.09 weight-percent palladium was also added to the high-purity and Mn/Fe/Si - bearing Alloys Ti-721 to determine the effect of noble metal additions. The high-purity Alloy Ti-721 plus palladium alloy showed complete resistance in the beta-annealed condition, while Alloy Ti-721-X plus palladium showed only nominal improvement. Both alloys had a stress-corrosion ratio of 0.80 in the as-received condition (beta-fabricated plus 1650 F alpha anneal). These results appear in Figure 13.

Unalloyed Titanium

Several production grades of unalloyed titanium (Ti-35A, Ti-55A, Ti-75A, and RS-70) were tested in the as-received, beta-annealed and beta-annealed and aged conditions. The results of these tests appear in Table 1. Alloys Ti-35A and Ti-55A were not sensitive to stress corrosion. Alloy Ti-75A was made sensitive after aging at 1200 F for 4 hours, with a seawater/air ratio of 0.73. Alloy RS-70 was sensitive for all conditions tested.

If the oxygen content were critical in rendering Alloy Ti-75A sensitive, then aging of the alloy should not have made a difference; but since aging rendered the alloy sensitive, it suggests that some other constituent, such as the relatively high-iron content (0.17 weight percent) responded to aging. The treatment possibly formed omega or a compound, and thereby induced stress-corrosion cracking. Alloy RS-70, on the other hand, displayed sensitivity for all conditions tested, and the fracture stress in seawater increased for each subsequent heat treatment ($Sn_{seawater}/Sn_{air} = 0.4$ for the as-received condition).

It has been suggested by Goode, et al, [11, 12] that hydrogen influences sea-water embrittlement in titanium. The hydrogen content of the alloy, as shown in Appendix B, is for the as-fabricated condition. Each subsequent heat treatment was conducted in a vacuum; hence, the hydrogen content for each of these conditions should have become increasingly less than the as-received condition. This might explain the increasing values of the fracture stress in seawater ($Sn_{seawater}/Sn_{air} = 0.4$ to 0.7) for Alloy RS-70. Nevertheless, the alloy still had a ratio of 0.70 after aging. It appears that the oxygen concentration of approximately 0.25 weight percent, or the iron content, or both, may have accounted for the stress-corrosion sensitivity of the unalloyed titanium.

Heat Treatment

Short-Time Aging Effect

Very rapid heating and cooling rates with short dwell times at temperature were achieved by programming thermal cycles with a modified Duffers-Gleeble apparatus.[13]

Table 1
Sea-water Embrittlement of Unalloyed Titanium

Titanium Grade	1800F, 2 Hr, AC			1800F, 2 Hr, AC +1200F, 4 Hr, AC		
	Nominal Fracture Bend Stress, Sn (ksi)		$\frac{Sn_{sw}}{Sn_{air}}$	Nominal Fracture Bend Stress, Sn (ksi)		$\frac{Sn_{sw}}{Sn_{air}}$
	Air	Seawater		Air	Seawater	
Ti-35A	94	89	0.95	-	-	-
Ti-55A	120	121	1.00	118	127	1.00+
Ti-75A	145	131	0.90	138	100	0.72
Ti-RS70	128	80	0.62	122	85	0.70

AC = Air Cooled
SW = Seawater

Three thermal cycles were used, consisting of a 2000 F peak temperature followed by aging at 1100 or 1200 F for 10 minutes and rapid cooling to room temperature. These cycles are shown diagrammatically in Figure 14. The effects of these heat treatments on the stress-corrosion behavior of several alloys are listed in Table 2. The data indicate that sensitivity is a function of heat treatment. Alloy Ti-6.5Al-5Zr-1V demonstrated very rapid transition from insensitive to sensitive behavior. Ten minutes at either 1100 or 1200 F rendered the alloy sensitive.

The effect of these heat treatments on Alloy Ti-7Al-2Sn-1Mo-1V at 0.08, 0.2, and 0.4 weight-percent oxygen concentrations is shown in Figure 15. The 1200 F aging temperature seemed to have a greater effect on this alloy than the 1100 F temperature.

The effect of aging temperature and time on the stress-corrosion behavior of Alloy Ti-6Al-4V (0.16-percent oxygen) is shown in Figure 16. The data indicate that the 1200 F temperature is more effective in rendering the alloy sensitive, and that the extent of embrittlement is increased slightly with time at temperature.

Long-Time Aging Effect

Alloys Ti-6Al-2Sn-1Mo-1V, Ti-6Al-5Zr-1V, and Ti-6Al-2Cb-1TaX, 0.8Mo, alloys were tested as received and after aging. These data are shown in Figures 11 and 17. Alloy Ti-6Al-2Cb-1Ta, 0.8Mo showed no loss of fracture stress in seawater after aging up to and including 20 hours. Alloy Ti-6Al-2Sn-1Mo-1V was rendered sensitive to stress corrosion in 10 hours, and Alloy Ti-6Al-5Zr-1V in 2 hours.

Table 2
Effect of "Gleeble" Heat Treatments on the Sea-water Embrittlement
of Several Titanium Alloys

Titanium Alloy	As-Received Condition			Nominal Fracture Bend Stress in Seawater, ksi		
	Nominal Fracture Bend Stress, ksi		$\frac{Sn_{air}}{Sn_{SW}}$	Heat Treatment*		
	Air	Water		A	B	C
			Alpha			
5A1-2.5Sn	170	65	0.32	138	128	125
6A1-2.5Sn	225	110	0.49	151	118	125
			Near Alpha			
7A1-3Cb (0.10_2)**	235	144	0.61	145	148	140
7A1-3Cb-2.5Sn	205	110	0.53	135	122	128
6.5A1-5Zr-1V	186	186	1.00	175	158	130
			Lean Beta, Alpha-Beta			
6A1-4V (0.1560_2)**	145	137	0.95	195	205	212
6A1-4V (0.080_2)**	206	198	0.96	224	210	220
6A1-2Sn-1Mo-1V (0.080)	200	180	0.90	230	215	233

*Thermal Cycles: A-2000F peak temperature; B-2000F peak temperature +1100 F for 10 minutes; C-2000F peak temperature +1200 F for 10 minutes.

**0.156 0_2 for example.

Stress-Corrosion Fracture Path

Metallographic examination of a partially failed Alloy Ti-721 containing a Widmanstatten microstructure showed that the fracture path contained a branching crack network that propagated transgranularly with respect to the prior beta-grain boundaries. The advancing cracks generally crossed the alpha platelets and changed direction when leaving one group of platelets of similar orientation, and entering another group of different orientation. Some groups of platelets contained cracks which appeared to parallel one another.

An equiaxed unalloyed titanium alloy, RS-70, failed by what appeared to be an intergranular path, and both transgranular (relative to alpha grains) and intergranular stress-corrosion cracking have been observed in Alloy Ti-5Al-2.5Sn which also has an equiaxed microstructure. These microstructures are shown in Figures 18, 19, and 20.

DISCUSSION

It is generally accepted that the breakdown of the passive oxide film and the kinetics of its repair are the controlling factors in the stress-corrosion cracking of titanium in seawater. Mechanical rupture by a slip step at the notch surface[14] has been suggested as the most likely mechanism for exposing an active titanium surface to the sea-water environment. Some mechanical, metallurgical, and theoretical aspects of this phenomenon will now be considered with respect to this premise.

MECHANICAL FACTORS

A sharp notch in a bulk specimen such as the cantilever specimen is a necessary requirement for stress corrosion of a susceptible titanium alloy in seawater. The critical notch sharpness to initiate stress-corrosion cracking varies with the sensitivity of the alloy. This sensitivity is related to the deformation characteristics of the material. These characteristics in turn are dependent on the alloy composition, heat treatment, and processing history.

The work of Wald[15] and Feige[16] on tensile sheet specimens of solution treated and aged Alloys Ti-8Al-1Mo-1V and Ti-6Al-4V with a constant notch sharpness (fatigue crack), show that there is a transition from insensitive to sensitive stress-corrosion behavior with increasing sheet thickness. It is suspected that the concentration and distribution of strain in the plastic zone beneath the notch affect the initiation and propagation stages of the stress-corrosion process.

METALLURGICAL FACTORS

Alloy Chemistry

Alloy chemistry is the most important factor affecting stress-corrosion behavior in a titanium alloy. An earlier investigation[3] on a spectrum of alloys, as well as this one, indicates that stress corrosion in seawater is dependent on the presence of embrittling constituents in the alloy. There is strong evidence that stress corrosion in titanium-aluminum alloys is induced by the coherent Ti_3Al phase. Other data suggest that interstitial content, presence of eutectoid compound, or presence of omega phase may also have a direct relationship to the sensitivity of titanium in seawater.

Aluminum

When Ti-Al binary alloys containing 5 to 8 weight-percent aluminum were aged at 1100F for 2 hours, they displayed an increase in sea-water stress-corrosion sensitivity with an increase in aluminum content. When these alloys were alpha annealed and quenched through the alpha plus Ti_3Al region, all were resistant to stress corrosion except for the 8-percent aluminum composition.

The data correlate well with the latest information that Crossley[9] has developed on the titanium-aluminum system. It confirms the earlier conclusion that aluminum in solid solution is not responsible for stress corrosion, but that such behavior is due to the presence of coherent Ti_3Al.

Homogeneous alloys containing less than approximately 4 weight-percent aluminum contain no Ti_3Al and thus are not susceptible to stress corrosion. Alloys containing between 4 and 8 weight-percent aluminum and with identical thermal histories within the Ti_3Al field are sensitive to stress corrosion, and the sensitivity is proportional to the Ti_3Al content which in turn is proportional to the aluminum content.

Crossley[10] has also reported that a hexagonal close pack (hcp) phase forms by shear transformation in the 8.4 to 11 weight-percent aluminum range when quenched from the alpha field. The lattice strains induced by this martensitic phase, and also the clustering of some titanium and aluminum atoms associated with the prenucleation kinetics of the Ti_3Al precipitation process, may have been sufficient to cause embrittlement, and thereby account for the sensitivity of the nominal Alloy Ti-8Al in the alpha-annealed and water-quenched condition.

The fracture-stress-in-air versus aluminum-content curve in Figure 5 indicates that the amount of Ti_3Al which induces stress-corrosion cracking is less than the amount causing notch sensitivity in air.

Isomorphous Beta Stabilizers

The addition of isomorphous beta stabilizers (Mo, V, Cb) to Alloys Ti-Al, Ti-Al-Sn, and Ti-Al-Zr has significantly improved or rendered the alloys completely resistant to seawater. The addition of Mo and V to the Ti-Al system retards the Ti_3Al precipitation reaction[17]. Figures 6 and 7 show the effect of increasing columbium content in Alloy Ti-7Al in the beta-annealed and the beta-annealed and aged conditions. The data show that the alloys had an increase in stress-corrosion resistance with increasing columbium content. Alloy Ti-7Al-7Cb was completely resistant at the 0.07 oxygen level in the annealed and in the annealed and aged conditions. It is suspected that the amount of coherent Ti_3Al in the alloy decreased with increasing columbium content.

Tests were run on Ti-2Mo, Ti-8Mo, Ti-4V, Ti-12V, Ti-6Cb, and Ti-17Cb binary alloys in the beta-annealed and quenched condition and the beta-annealed-quenched and aged conditions to determine if the omega phase would also induce stress corrosion of titanium in seawater. Only Alloy Ti-8Mo showed a reduced fracture stress in seawater (ratio of 0.85). An alloy containing an extensive amount of omega is very brittle and therefore would be notch sensitive in air. It is suspected that the notch-bend strength in air would be low enough that sensitivity to seawater would not be apparent. However, some intermediate amount of omega phase may induce stress corrosion in a manner similar to that in which small amounts of coherent Ti_3Al cause stress corrosion without affecting air toughness.

Beta Eutectoid Formers

A limited number of tests were made on hypoeutectoid compositions Ti-2Ni and Ti-5Fe, and a hypereutectoid composition Ti-7Ni in the beta-annealed and quenched condition and in the beta-annealed-quenched and aged condition. These alloys demonstrated a high degree of brittleness and notch sensitivity by failing at the same low stresses, both in air and seawater. This indicates that major additions of eutectoid formers such as iron and nickel lead to brittleness and notch sensitivity to such a degree that embrittlement in seawater is not detectable. However, it has been reported that Alloy Ti-8Mn was sensitive in seawater.[16, 18] Manganese is a more sluggish eutectoid former than either iron or nickel, and this may account for the behavior.

Minor additions of nickel, iron, and manganese to Alloy Ti-721 markedly increased the seawater sensitivity of the alloy. Minor additions of beta eutectoid formers, especially nickel, to titanium and titanium-aluminum alloys are very effective in promoting and/or increasing the stress-corrosion sensitivity of the alloy. These additions may affect the formation of Ti_3Al in the alloy by influencing the reaction kinetics of the precipitate. It also should be noted that the beta decomposition of these alloys results in the omega phase as well as compound plus alpha, and that the omega phase forms more readily on beta decomposition than compound in most alloys.[20] Omega may thus influence sea-water embrittlement more than compound.

Noble Metal Addition

The addition of 0.075 weight-percent palladium to Alloy Ti-721 rendered the alloy insensitive in the beta-annealed condition, while the alloy was slightly sensitive in the as-received condition, having a ratio of 0.80. It is believed that the beta anneal resulted in retention of more palladium in solid solution than was the case in the alpha annealed, as-received material.[20] The low-temperature alpha anneal may have caused precipitation of some Ti_2Pd, and the embrittling effect of this precipitation may have offset any beneficial effect of palladium in the alloy.

Oxygen Content

Unalloyed titanium containing a low amount of residual Fe, C, N, and H, was made sensitive to sea-water stress corrosion by oxygen contents above approximately 0.250 weight percent. Oxygen also indirectly influenced the stress-corrosion sensitivity of titanium-aluminum alloys by affecting the solubility of aluminum in primary alpha and by affecting the kinetics of the Ti_3Al precipitation reaction.

Heat Treatment

Those heat treatments that promote loss of toughness in air in titanium alloys also tend to sensitize the alloy to sea-water stress corrosion.[21] Heat treating promotes embrittlement in alpha plus compound or beta plus compound two-phase fields by precipitating compounds such as Ti_3Al in the Ti-Al system. The alpha plus compound phase field is significant, in that most of the experimental and commercial alloys of interest are heated and cooled through this region and are occasionally heat treated in this range to achieve certain mechanical properties. It should be noted that the omega transition phase can also be promoted in this temperature range.

The sea-water sensitivity of titanium-aluminum alloys is therefore largely dependent on thermal history. Titanium alloys containing up to 4-percent aluminum and annealed in the beta field or the alpha field are homogeneous in composition. Ti_3Al is not developed in the structure because these low aluminum compositions are not within the alpha plus Ti_3Al field at any temperature. Any composition between approximately 4 and 8 weight-percent aluminum will be insensitive to seawater if it is given a fast cool through the alpha plus Ti_3Al field subsequent to a higher-temperature anneal.

An anneal within the alpha plus beta field results in partitioning of aluminum between the alpha and the beta phases. Aluminum-rich and aluminum-lean mixed alpha structures then exist at room temperature. A titanium alloy of nominal 4 percent or less aluminum could therefore contain areas of aluminum content of 5 percent or greater. If subsequent thermal treatment be in the alpha plus Ti_3Al field, Ti_3Al could be developed in the aluminum-rich areas. The critical nominal aluminum content for stress-corrosion sensitivity could therefore be less than the 4-percent criterion if care is not taken in thermal treatment.

The kinetics of the formation of other intermetallic compounds are equally important regarding heat treatment effects. However, since most of the alloys studied have been titanium-aluminum alloys, the following discussion will continue to be restricted to the Ti_3Al phase.

Crossley[17] found that overaging a Ti-7Al binary alloy containing Ti_3Al resulted in a significant recovery of the conventional Charpy V-notch toughness (from 13 ft-lbs at 650 C for 120 hours to 84 ft-lbs at 650 C for 500 hours). This tends to confirm the coherent nature of the phase. At present there are no sea-water fracture data for alloys in the overaged condition, but it is suspected that resistance to stress corrosion would increase with overaging and that an alloy may become completely resistant if the Ti_3Al phase is completely incoherent. If this be true, lattice strains resulting from coherent precipitated phases and from other sources are significant with respect to the sea-water stress-corrosion mechanism. Crossley[17] has also reported that formation of Ti_3Al is retarded by ternary additions of Mo, V, Cb, Sn and Zr to the Ti-Al system.

Seawater stress-corrosion experiments on alloys containing Mo, V, Cb, Sn, and Zr show a relationship between sea-water sensitivity and the effect of the ternery additions on the formation of Ti_3Al. Alloy Ti-6Al-2Sn-1Mo-1V was tested as received and after aging at 1100 F for 2, 4, and 10 hours. The fracture stress in seawater remained constant at approximately 220 ksi for the as received, and for the 2- and 4-hour aging treatments. However, the 10-hour aging reduced the fracture stress to 120 ksi, indicating the sluggish formation of Ti_3Al in the presence of Mo and V. Hence, the low oxygen content titanium-aluminum alloys of commercial interest, containing 5 to 7 weight-percent aluminum and containing Mo and/or V, can be fabricated and heat treated without causing formation of sufficient Ti_3Al to induce stress corrosion in seawater.

Stress-Corrosion Fracture Path

The macroscopic fracture appearance of sensitive alloys shows a distinct zone associated with stress corrosion in seawater. The corrosion zone usually contains brittle facets, varying in size up to the grain size of the material. Beachem and Meyn[22, 23] have shown by fractography studies that the fracture zone of Alloy Ti-721 in the beta-fabricated and beta-annealed condition (Widmanstätten microstructure) has a cleavage-like appearance (quasi-cleavage) and that the fast-fracture zone (air) has a dimpled rupture appearance. The fracture path determined metallographically was found to be transgranular, with some dependency on the alpha-platelet colonies. It is believed that the distribution of the Ti_3Al precipitate influences the stress-corrosion fracture path. Crossley[17] has shown that Ti_3Al forms in the grain boundaries and in the matrix of equiaxed alpha structures, and Brauer[24] also has shown the presence of Ti_3Al in alpha cell boundaries and in the alpha-platelet boundaries of Alloy Ti-8Al (weight percent).

The fracture path in unalloyed titanium (RS-70), on the other hand, appears to follow an intergranular path, and the macroscopic fracture appearance of the sea-water embrittled zone has a tunnel-like appearance.

THEORETICAL CONSIDERATIONS

The general corrosion resistance of titanium in seawater is unsurpassed by any other structural metal. Although titanium is a very reactive metal, it has excellent corrosion resistance due to the presence of a passive film on its surface. The film is extremely difficult to break, and if broken by mechanical action, such as by abrasion, repair in seawater is rapid so that corrosion does not occur. Sea-water stress corrosion therefore must involve a breakdown of the passive film plus some condition that prevents repair of the film.

It has been questioned whether the embrittlement phenomenon displayed by titanium alloys in laboratory sea-water tests should be categorically classified as stress-corrosion cracking. This is because of the requirement of a sharp notch in the specimen. The concept as set forth by Brown[2] that the mechanical notch in the cantilever-beam test simulates the corrosion initiation phase (corrosion crevice) of the stress-corrosion process may not strictly apply to titanium alloys exposed to seawater. Nevertheless, the phenomenon of sea-water stress corrosion of titanium does, in general, agree with one of the classical definitions of stress corrosion as set forth by Sutton[25], i.e., "stress-corrosion cracking implies a greater deterioration in mechanical properties through the simultaneous action of static stress and exposure to corrosive environment than would occur by the separate but additive action of those agencies." The actual embrittling mechanism may be of the hydrogen-cracking or stress-sorption-cracking type[26] rather than chemical dissolution. Nevertheless, in relatively thick test samples, a notch imposes a localized stress intensity which is considered a necessary condition for sea-water stress corrosion.

MEL and other stress-corrosion investigators have found that not all titanium alloys are susceptible to sea-water embrittlement, and those that are, contain an embrittling constituent in the structure, such as the coherent Ti_3Al precipitate. The critical amount of the embrittling constituent is usually less than that which can be detected by conventional techniques for measuring mechanical toughness.

The following significant observations have been made by various investigators:

- Crack propagation is rapid and generally transgranular.[3, 27]

- Failure is by a brittle fracture mode with the fracture surface displaying striated quasi-cleavage facets approximately 16 degrees off the basal plane.[22, 23, 27, 28]

- A sharp notch in a bulk-test sample is a necessary condition to render a susceptible alloy sensitive to stress corrosion.

- A threshold tensile stress resulting in a sufficient amount of plastic deformation in the notch root must be applied to initiate the stress-corrosion process.

- There appears to be a selected phase attack, in that stress-corrosion cracks have only been identified to propagate through a structurally embrittled alpha phase.[29]

- Dislocations tend to form long coplanar arrays in susceptible alloys, while dislocation tangles form in nonsusceptible pure titanium.[30]

- There is no apparent pitting, etching, or development of corrosion products.

- The stress-corrosion process can be suppressed by cathodic protection.[31]

- If the chloride ion concentration is low, inhibitors such as silver nitrate, potassium nitrate and sodium sulfate are effective in suppressing stress corrosion.[29]

- Sound emission has been detected during the stress-corrosion process by special techniques.[32]

In an attempt to establish the mechanism of sea-water embrittlement of titanium, it would be most helpful if one could postulate the general type of embrittlement, based on existing experimental data, such as stress corrosion, stress-sorption cracking, or hydrogen cracking.

Scully's[33] proposed mechanism for stress-corrosion cracking in stainless steel may be partially applicable to titanium. Scully suggests a mechanically assisted anodic dissolution model in which a coarse slip step associated with long coplanar dislocation arrays emerges at the stress concentration. This ruptures the oxide film and reacts preferentially with the hydroxyl (OH^-) ion to passivate the slipped surface. The long-slip step exhausts the supply of OH^- ions in the liquid in contact with the surface. The last part of the slip step reacts with the available Cl^- ions and initiates the stress-corrosion process. The attack at the root of a stress concentration may be influenced by the crevice conditions of the notch. That is, the supply of passivating ions are used up faster than they can be replenished by diffusion into the close quarters of the crevice. An alternate argument can also be made that the emerging slip step reacts with the aqueous environment to decompose the water to OH^- and hydrogen (H^+) ions, and the hydrogen then reacts with titanium to induce premature failure. However, limited experimental evidence[11, 12, 29, 31] tends to discount a purely hydrogen-cracking mechanism.

The crack-growth rate during sea-water stress-corrosion cracking of titanium has been measured at 0.17-inch per minute (25 centimeters per hour).[27] This fast rate appears to rule out dissolution as the sole mechanism.[34,35] Cathodic protection in this case can alter the rate of crack initiation and growth by increasing the pH and favoring adsorption of OH^- ions in place of other ions.

It is also believed that a mechanical model of the type proposed by Nielson[36] for austenitic stainless steel is not applicable, since no extensive corrosion products have been observed in the notched region that could cause a possible wedging action.

It seems possible that all of the observations on the sea-water stress corrosion of titanium could be satisfied by a stress-sorption-cracking mechanism similar to that proposed by Westwood[37,38] for liquid metal embrittlement and for the embrittlement of silver chloride in aqueous environments.[39,40] Westwood suggests in the latter cases that the embrittlement is caused by the adsorption and interaction of specific species with strained bonds. This causes a localized reduction in cohesive strength and allows rupture at reduced stress levels. Sea-water stress corrosion of titanium could possibly involve the adsorption of the chloride (Cl^-) ion which causes a reduction in cohesive strength. This proposed film-dependent-adsorption mechanism is suggested to proceed in the following manner:

> The passive oxide film is mechanically ruptured by a coarse slip step developed in the highly strained region just beneath the notch. Coarse slip is believed to be promoted either by coherent Ti_3Al or by short-range order.[29,33] Either process restricts slip and in turn promotes coarse slip. The Cl^- ion is then adsorbed on the fresh titanium metal surface in a manner similar to that suggested by Scully for austenitic steel, causing a localized reduction of the cohesive strength. This results in the development or the extension of a stress-corrosion crack. The crack is then arrested by more stress-corrosion resistant alpha. The Cl^- ion adsorption process could start again, either prior to the passive film reformation and leading directly to further crack extension, or if a passive film has reformed, the plastically strained region at the crack tip would again cause mechanical rupture of the film and thus allow the process to continue. In either case, this model could account for the striated cleavage markings revealed by replica microscopy.[22,23] The existence of striations on the fracture surface does not necessarily indicate that the fracture involved the rupture of a brittle film as was found in the case of AgCl.[35]

Titanium alloys susceptible to stress corrosion in sea-water have also been shown to be susceptible to stress corrosion in distilled water.[3,4] Beck[29] believes that residual Cl^- ion present in titanium may be leached out by distilled water and be active in the stress-corrosion process. He has also noted slight increases in crack velocity with additions of sodium chloride to the water. It seems possible that the concentration of Cl^- ions, within some concentration limit in the solution, may affect the extent to which the cohesive strength of the material is lowered. Westwood, et al[41] have also suggested from their work on lithium fluoride (LiF) that the presence in solution of certain strongly adsorbing species may be responsible for the tunneling found in materials exposed to environments which cause stress corrosion. In this regard, the adsorption of the Cl^- ion may have caused the macroscopic tunneling observed in the unalloyed titanium Alloy RS-70.[3]

It appears from the information developed up to this time that a film-rupture, adsorption-dependent mechanism could be responsible for embrittlement of titanium in seawater, and that it is very likely that the Cl^- ion is the adsorbing species. The intensive work now being conducted toward understanding the mechanism should confirm or refute this argument.

CONCLUSIONS

- A sharp notch is a necessary mechanical condition for sea-water stress corrosion of susceptible titanium alloys.

- A threshold stress level exists in susceptible alloys. It is believed that the plastic strain associated with this stress level generates sufficient coarse slip to rupture the passive film. Below this stress, no stress corrosion occurs. At or above this stress, the stress-corrosion process requires only a few minutes for failure of the test sample.

- The presence of a critical minimum amount of the coherent Ti_3Al precipitate will cause sea-water stress corrosion of titanium. As the quantity of Ti_3Al increases, the sensitivity of the alloy increases. Thus, if the precipitation of Ti_3Al is suppressed, the resistance of the alloy is improved. The reduction of aluminum and oxygen contents and the addition of isomorphous beta stabilizers suppress the formation of Ti_3Al, thereby improving the resistance of Ti-Al alloys in seawater.

- Minor additions (<0.5 weight-percent total) of eutectoid formers Ni, Fe, and Mn increase the sea-water sensitivity of Alloy Ti-721. Minor additions of palladium (0.09 weight percent) render Alloy Ti-721 resistant.

- A critical minimum oxygen concentration of approximately 0.250 weight percent induces sea-water embrittlement in unalloyed titanium.

- The stress-corrosion fracture path appears to be related to the amount and distribution of the embrittling constituent.

FUTURE WORK

Work will continue toward achieving a more complete understanding of the structural factors that influence the sea-water stress corrosion of titanium. Additional effort will be placed on an interpretation of the engineering significance of the phenomenon. This knowledge will lead to the development of titanium alloys that can be used effectively for marine applications.

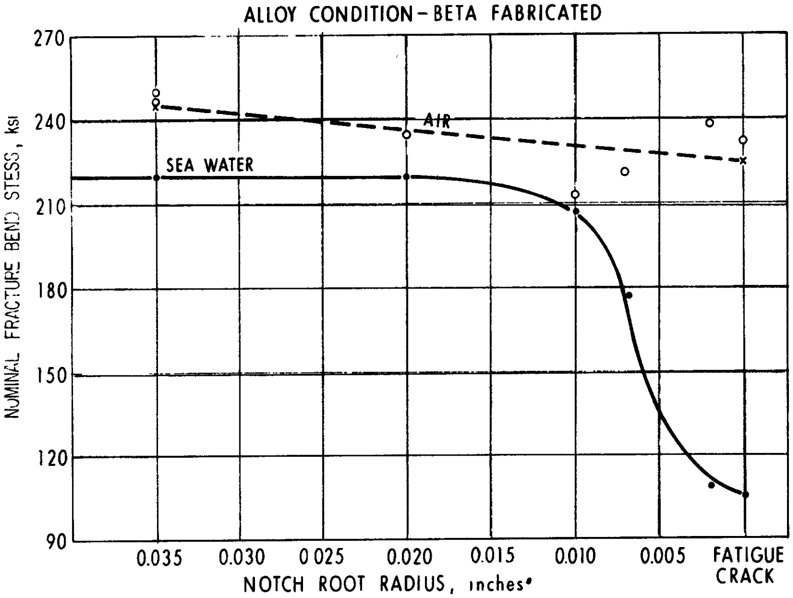


Figure 1
Effect of Notch Acuity on Nominal Fracture Bend Stress of Ti-721 Alloy

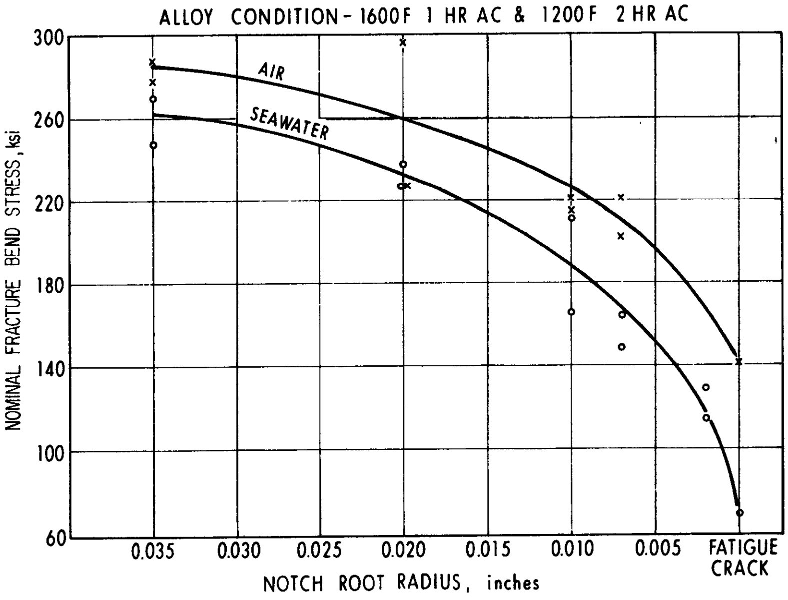


Figure 2
Effect of Notch Acuity on the Nominal Fracture Bend Stress of Ti-6Al-4V (0.160$_2$)

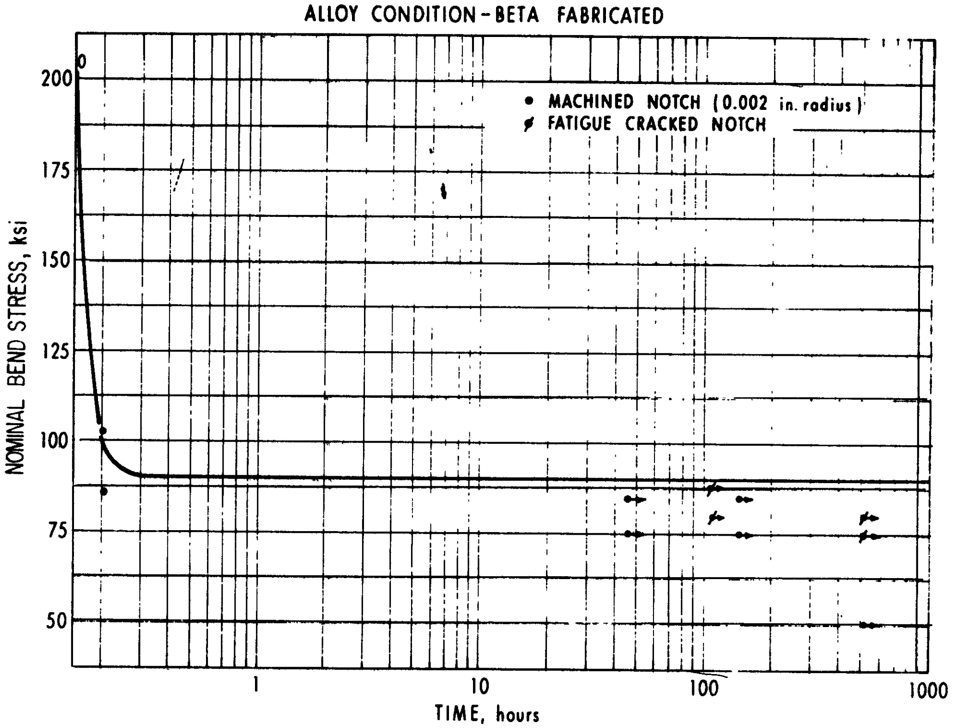


Figure 3
Threshold Stress Curve for Ti-7Al-2Cb-1Ta Alloy in Sea-Water

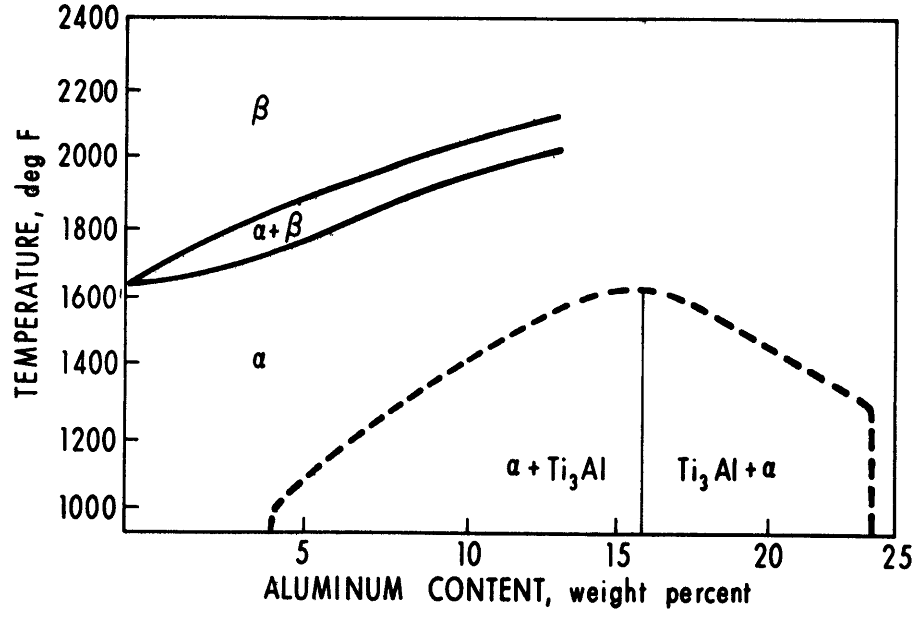


Figure 4
Titanium-rock End of the Titanium-Aluminum Binary Phase Diagram Determined by Crossley[9, 10]

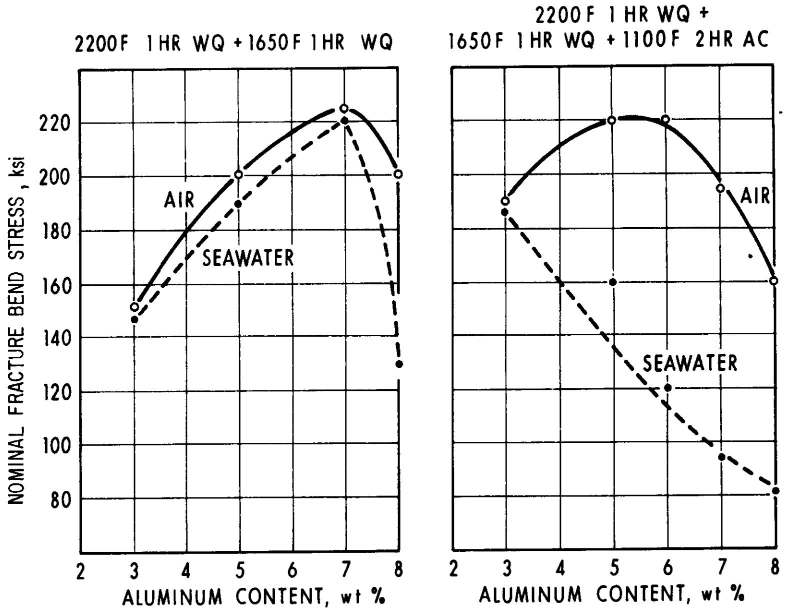


Figure 5
Sea-Water Embrittlement of Titanium-Aluminum Binary Alloys

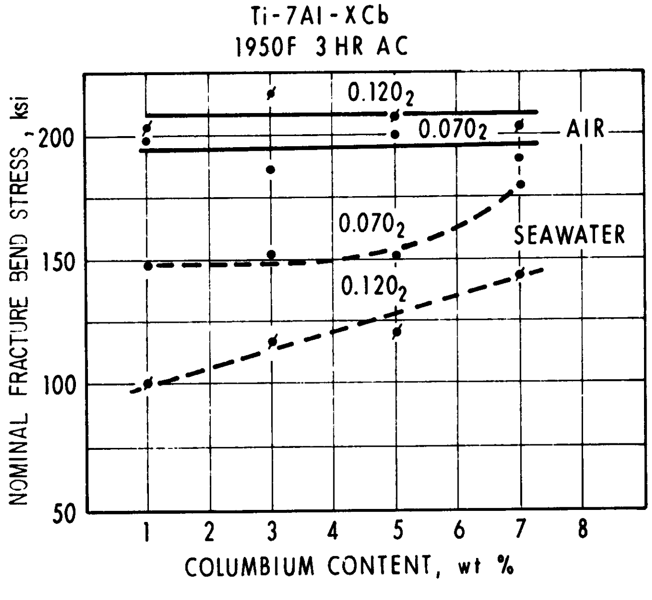


Figure 6
Effect of Columbium Additions on the Sea-Water Embrittlement of Ti-7Al Alloy at Two Oxygen Levels (0.07 and 0.12 wt percent oxygen) in the Beta-Annealed Condition.

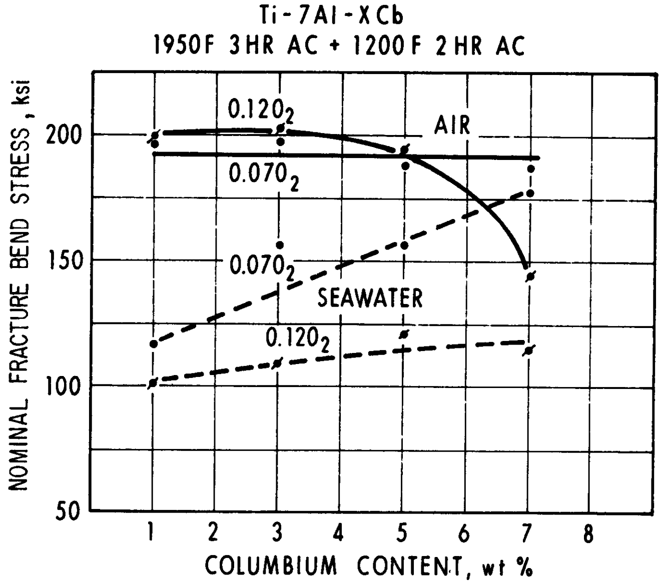


Figure 7
Effect of Columbium Additions on the Sea-Water Embrittlement of Ti-7Al Alloy at Two Oxygen Levels (0.07 and 0.12 wt percent oxygen) in the Beta-Annealed and Aged Condition

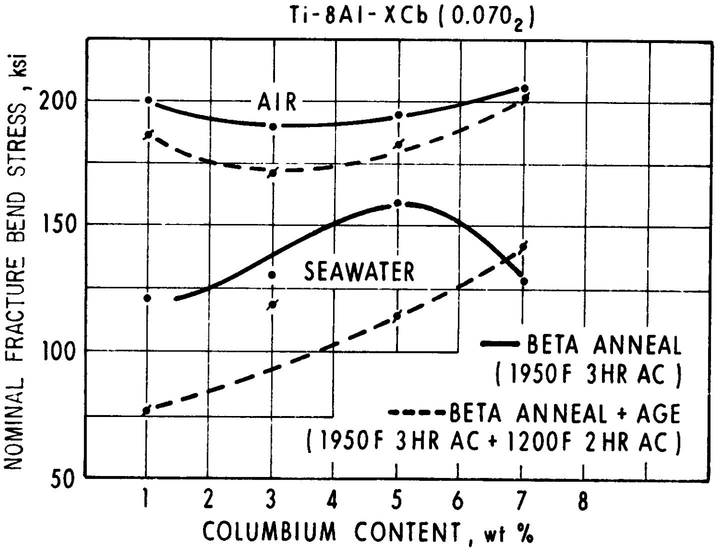


Figure 8
Effect of Columbium Additions on the Sea-Water Embrittlement of Ti-8Al Alloy in the Beta-Annealed and Aged Conditions

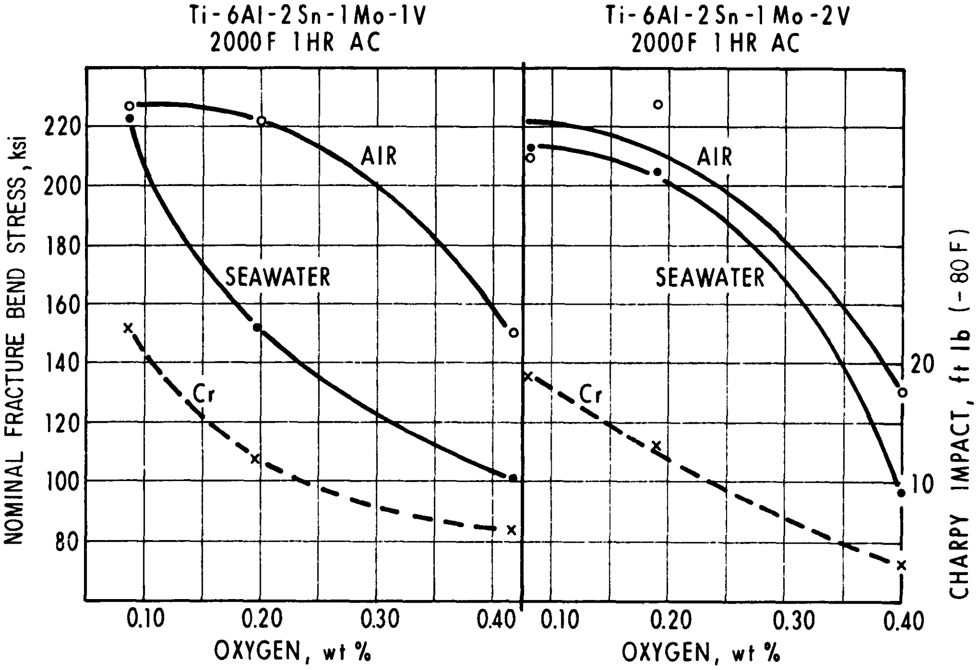


Figure 9
Effect of Oxygen on the Sea-Water Embrittlement of Ti-Al-Sn-Mo-V Alloys

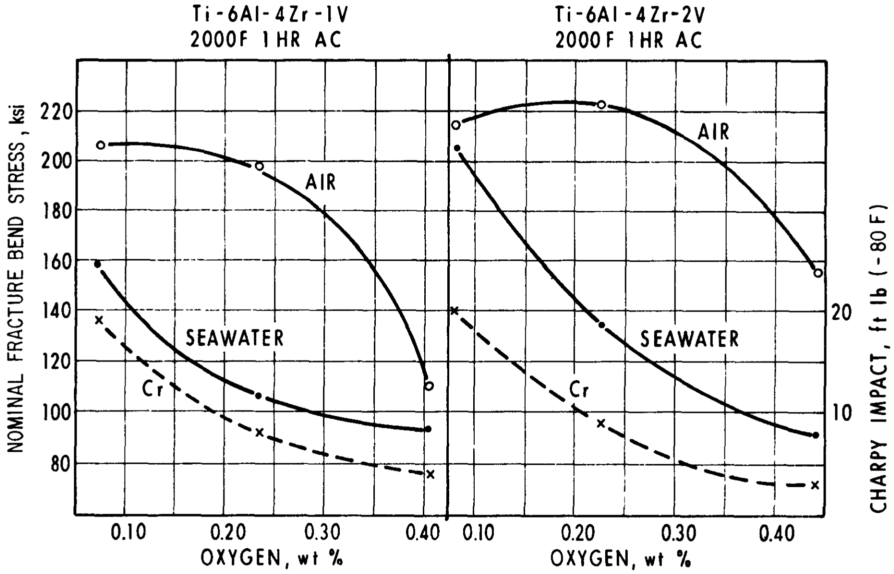


Figure 10
Effect of Oxygen on the Sea-Water Embrittlement of Ti-Al-Zr-V Alloys

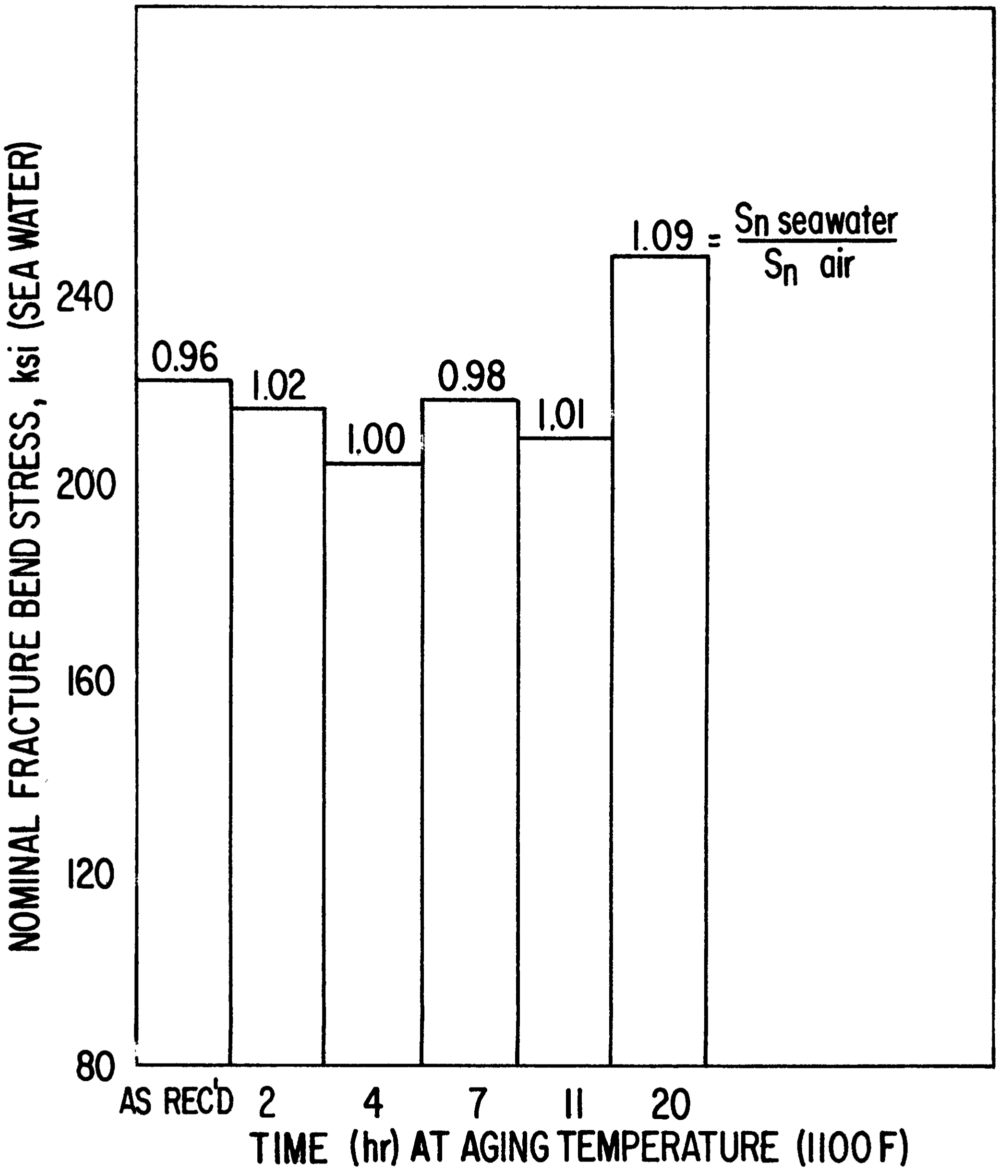


Figure 11
Effect of Aging on the Sea-Water Embrittlement of
Ti-6Al-2Cb-1Ta-0.8Mo (292555) Alloy

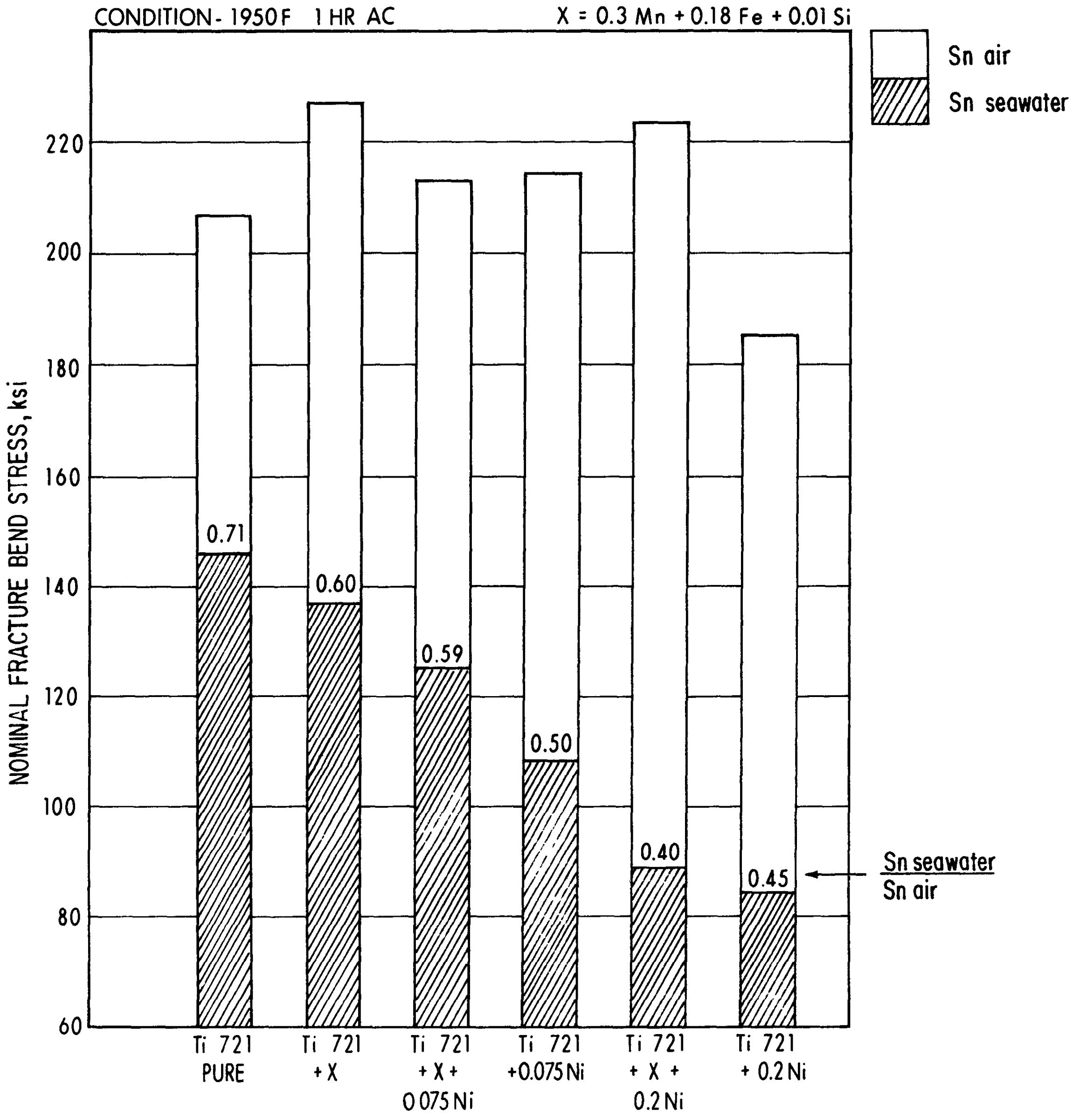


Figure 12
Effect of Minor Nickel Additions on the Sea-Water Embrittlement of Ti-7Al-2Cb-1Ta Alloy

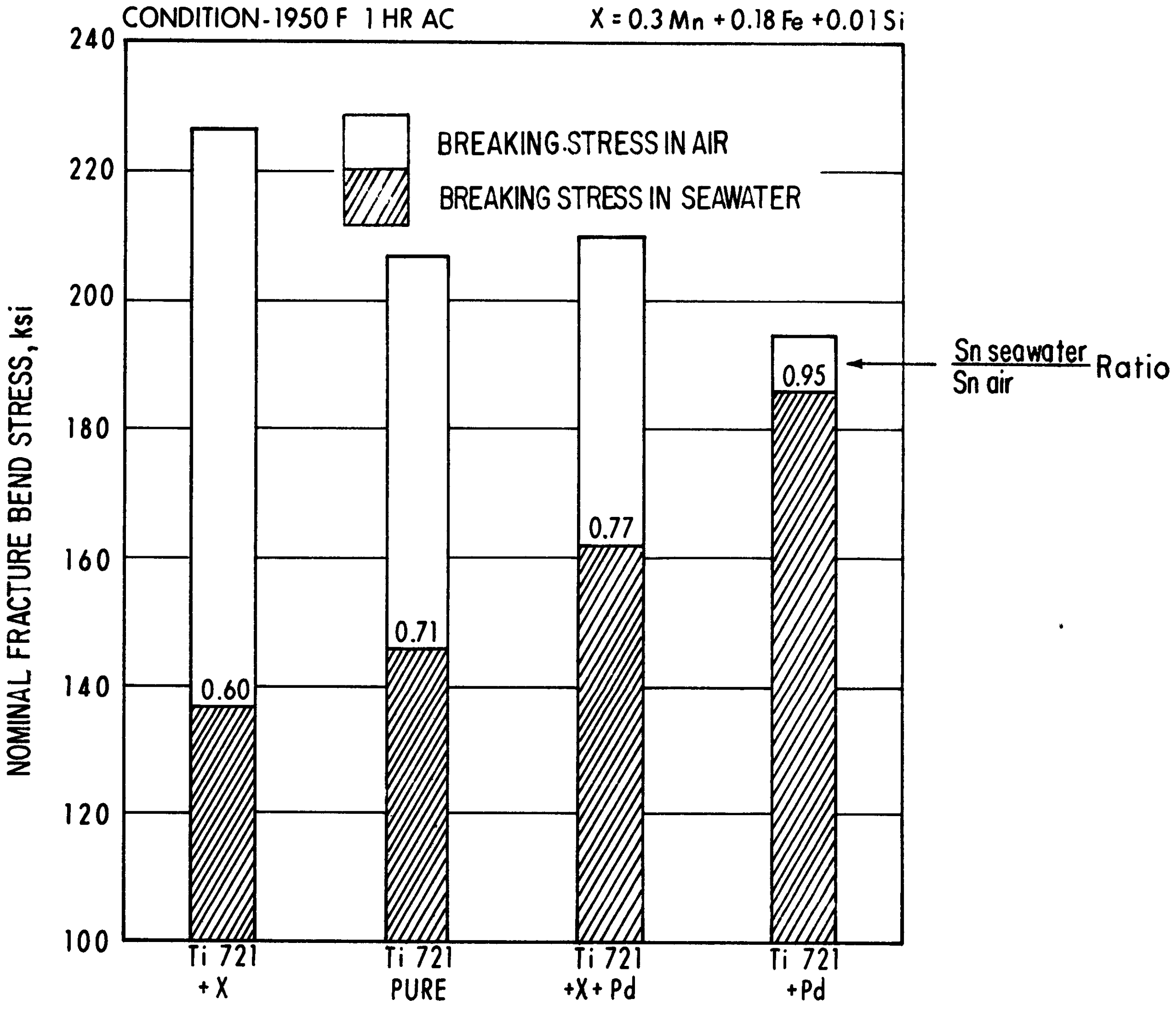
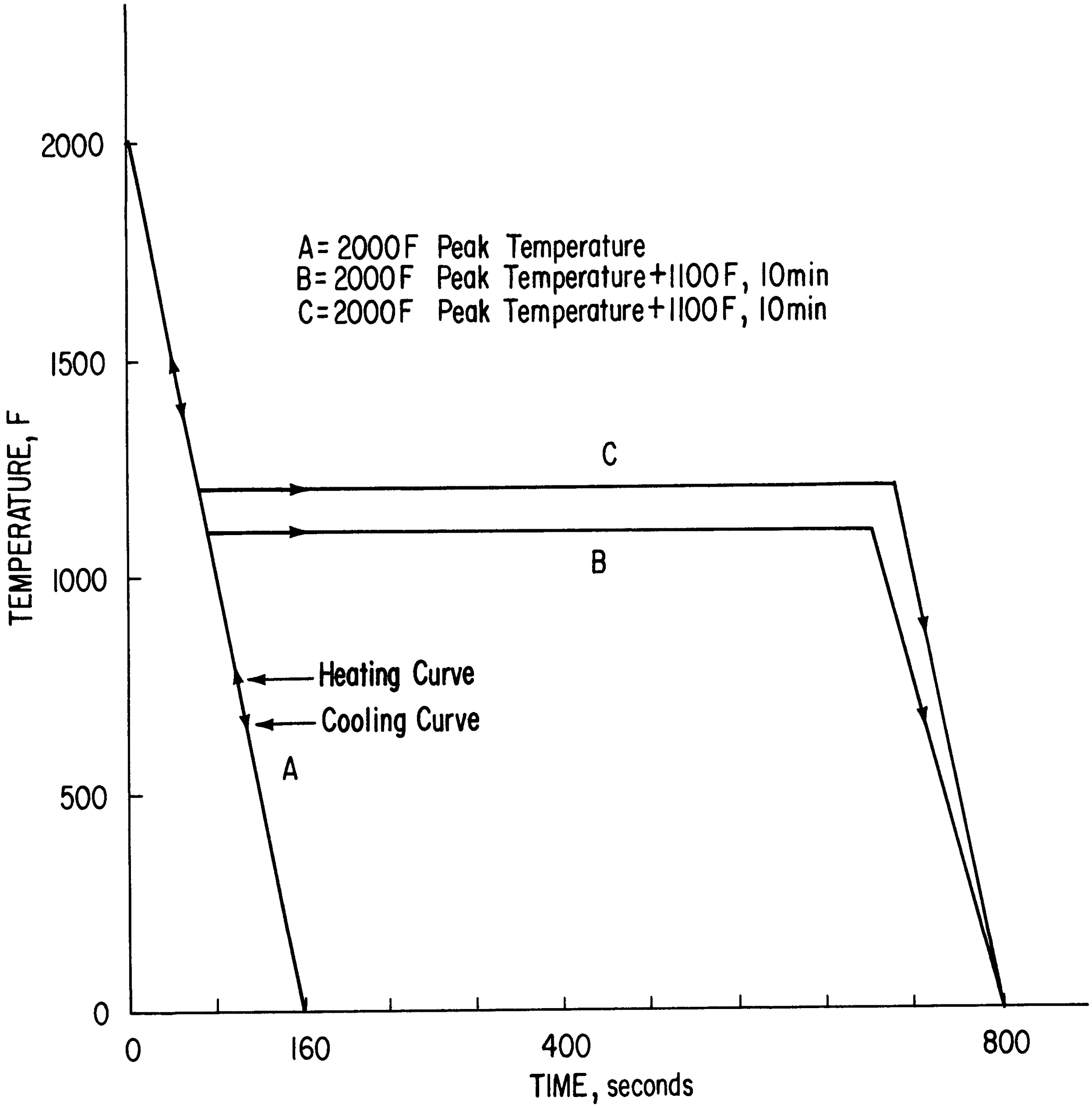


Figure 13
Effect of 0.09 wt percent Palladium Addition on the Sea-Water Embrittlement of Ti-7Al-2Cb-1Ta Alloy



Temperature Range	Cooling Rate
2000 F — RT	14 F/sec
2000 F — 1200 or 1100 F	10 F/sec
1200 or 1100 F — RT	15 F/sec

Figure 14
Gleeble Produced Thermal Cycles

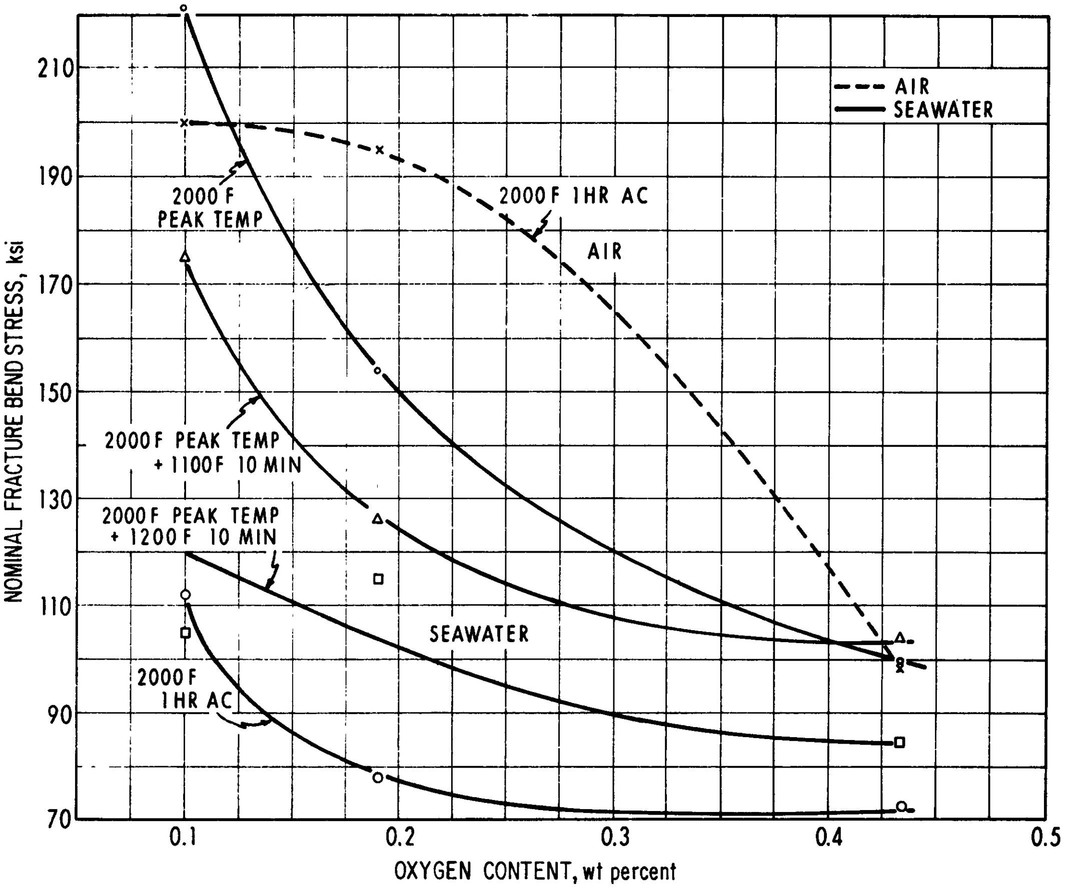


Figure 15
Effect of Oxygen & Thermal Treatment on the Sea-Water Embrittlement of Ti-7Al-2Sn-1Mo-1V Alloy

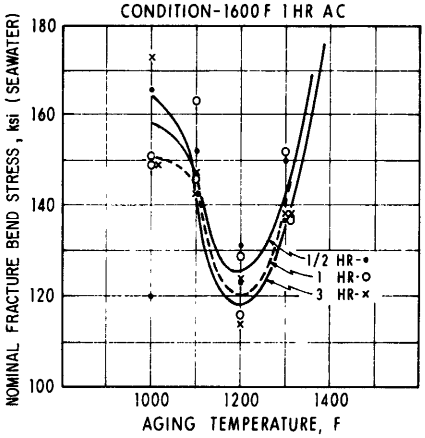


Figure 16
Effect of Aging on the Sea-Water Embrittlement of Ti-6Al-4V (0.16 wt percent oxygen) Alloy

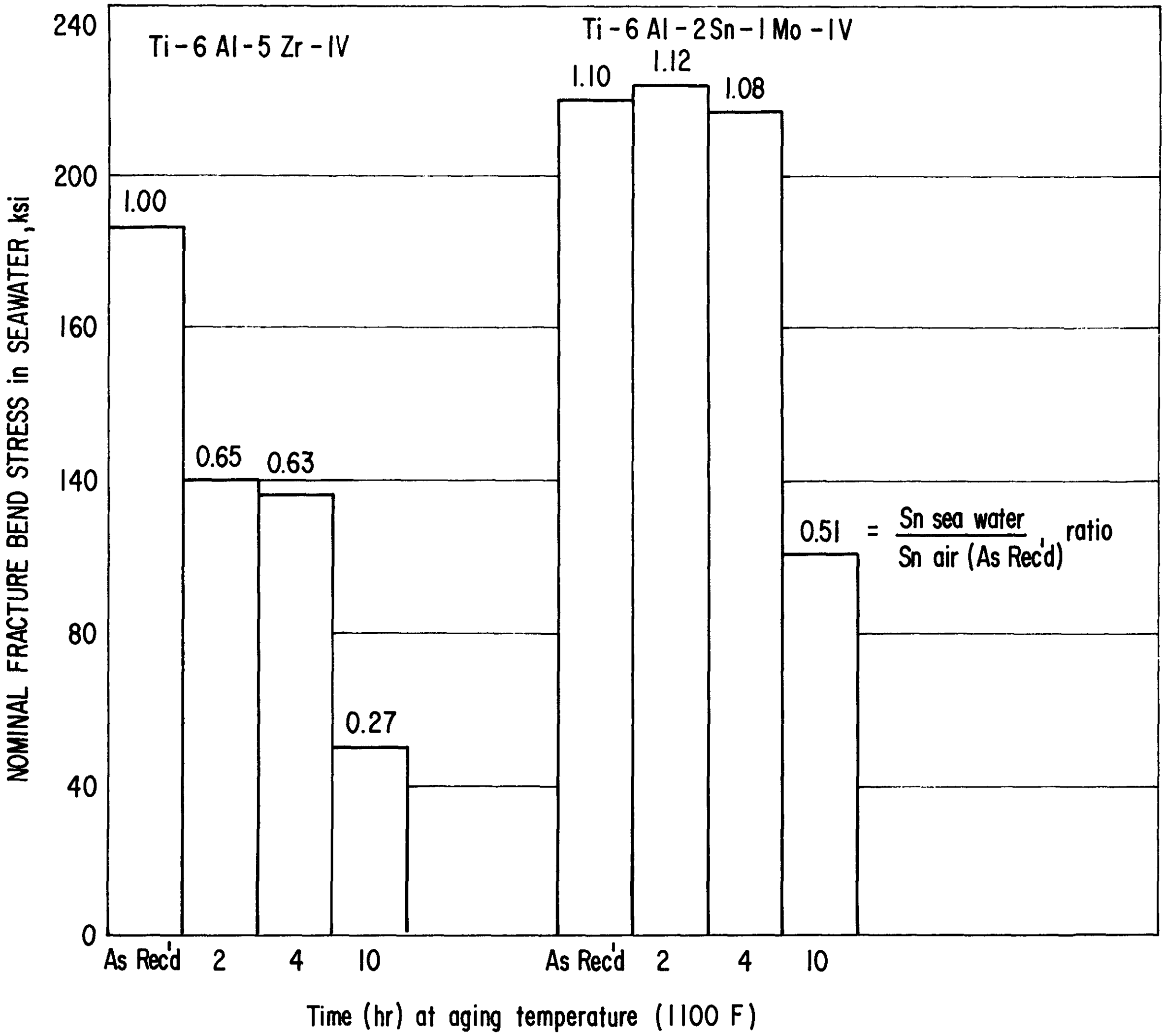
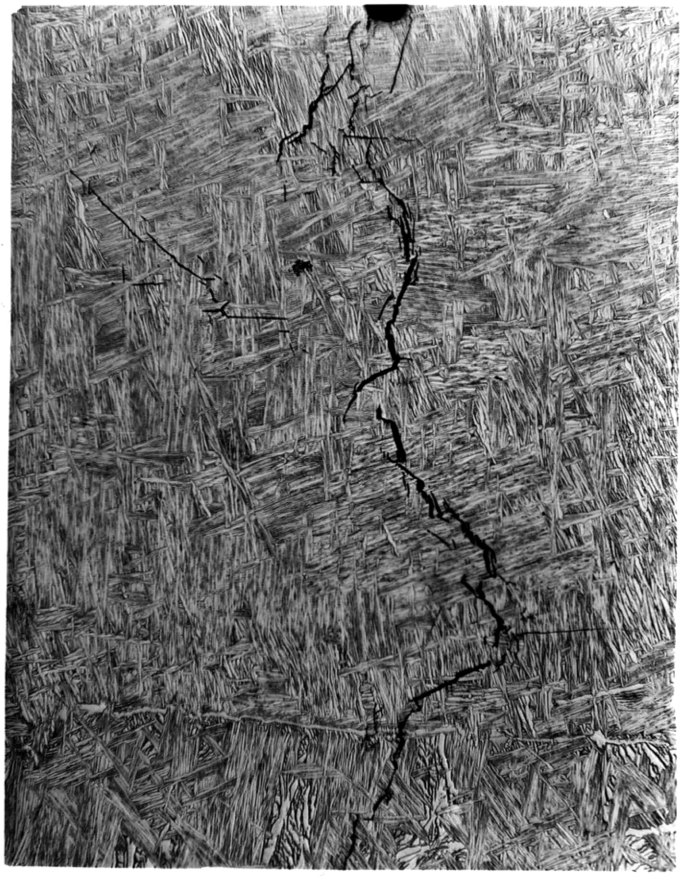


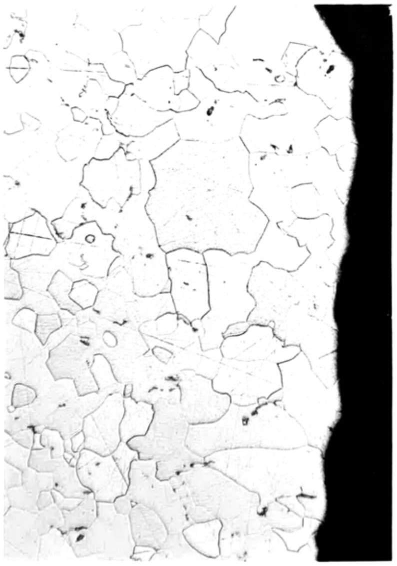
Figure 17
Effect of Aging on the Sea-Water Embrittlement of Ti-6Al-5Zr-1V
and Ti-6Al-2Sn-1Mo-1V Alloys



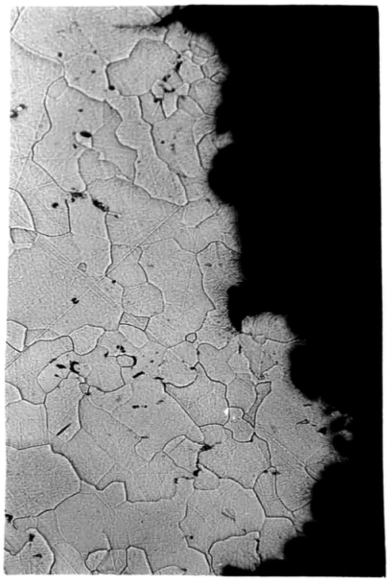
Item (a)
75X

Item (b)
250X

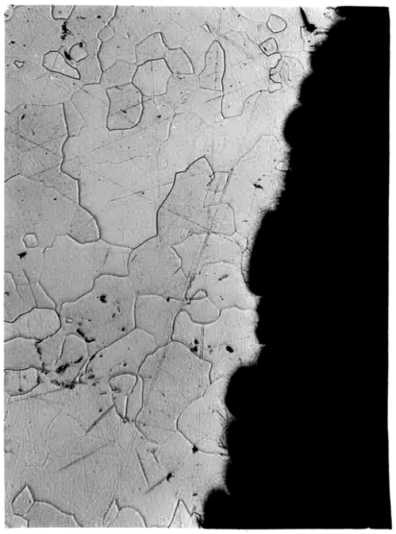
Figure 18 - Crack Network in a Partially Failed Ti-7Al-2Cb-1Ta Specimen in the Beta-Rolled and Beta-Annealed Condition



Item (a)
Fatigue Cracked
Zone



Item (b)
Sea-Water
Embrittlement Zone



Item (c)
Fast Fracture
Zone

Figure 19 - Fractured Specimen of Titanium RS-70 Showing the Fracture Path Through the Test Sample (75X)

250X

Figure 20
Partially Failed Alloy Ti-5Al-2.5Sn
(As-Received Condition)

Appendix A

Technical References

1. Brown, B. F., "Progress in the Development of Test Concepts for Stress Corrosion Cracking," NRL Tech Memo 6320 - 44, Dec 1964
2. Brown, B. F., "A New Stress-Corrosion Cracking Test for High-Strength Alloys," Materials Research and Standards, Vol. 6, No. 3, Mar 1966, pp. 129-133
3. Lane, I. R. Jr., J. L. Cavallaro, and A. G. S. Morton, "Fracture Behavior of Titanium in the Marine Environment," MEL R&D Phase Rept 231/65, Jul 1965
4. Lane, I. R., Jr., J. L. Cavallaro, and A. G. S. Morton, "Sea-Water Embrittlement of Titanium," Stress-Corrosion Cracking of Titanium, ASTM STP 397, ASTM, 1966, p. 246
5. Cavallaro, J. L., "Ti-6Al-2Cb-1 Ta-0.8Mo Titanium Alloy as a Structural Material for Marine Applications," MEL R&D Phase Rept 506/66, Jan 1967
6. Wolff, A. K., L. R. Aronin, and S. Abkowitz, "Development of Titanium Alloys for Deep-Diving Vehicles," Nuclear Metals, Inc., Final Rept to MEL for the period 25 Feb 1963 through 25 Apr 1964, on Contr N600(615 33)59922
7. Wood, R. A., D. N. Williams, and H. R. Ogden, "The Melting and Fabricating of Palladium-Modified Ti-7Al-2Cb-1Ta Alloys" Battelle Memorial Institute, Final Rept to MEL on Contr N161-26241, Jan 1966
8. Wood, R. A., D. N. Williams, and H. R. Ogden, "The Melting and Fabricating of Nickel-Modified Ti-7Al-2Cb-1Ta Alloys," Battelle Memorial Institute, Final Rept to MEL on Contr N161-26241, Jan 1966
9. Crossley, F. A., "Titanium-Aluminum Equilibrium Diagram," MEL Sponsored Rept 431/65, Final Rept on Contr N161-25952, IIT Research Institute, Oct 1965
10. Crossley, F. A., "Titanium-Rich End of the Titanium-Aluminum Equilibrium Diagram," Trans AIME, Vol. 236, Aug 1966, p. 1174
11. Goode, R. J., et al, "Metallurgical Characteristics of High Strength Structural Materials," Tenth Quarterly Rept, NRL Rept 6454, Apr 1966
12. Puzak, P. P., et al, "Metallurgical Characteristics of High Strength Structural Materials," Eleventh Quarterly Rept, NRL Rept 6513, Aug 1966
13. Nippes, E. F., "The Weld Heat-Affected Zone," Welding Journal Research Supplement, Vol. 38, 1959, pp. 1s - 18s
14. Logan, H. L., Research National Bureau Standard, Vol. 48, 1952, pp. 99-105
15. Wald, G. G., "Effect of Heat Treatment on Salt Water Delayed Fracture of Titanium Alloys," paper presented at annual meeting of AIME, Los Angeles, Calif., 1967
16. Feige, N. G., and T. Murphy, "Fracture Behavior of Titanium Alloys in Aqueous Environment," paper presented at WESTEC Conference, Los Angeles, Calif., 1966
17. Crossley, F. A., "Research and Development of Physical Metallurgy of Titanium, "MEL Sponsored Rept 114/67, Final Rept on Contr Nonr-4766(00), IIT Research Institute, Apr 1967

18. Seagle, S.R., G.S. Hall, and O. Bertea, "Aqueous Stress-Corrosion Cracking Behavior of High-Aluminum Titanium-Base Alloys," paper presented at annual meeting AIME, Los Angeles, Calif., 1967
19. Williams, J., "Beta Phase Decomposition in Binary Titanium Alloys," paper presented at Modern Metallurgical Microscopy Seminar Series, NRL, Washington, D.C., 3 May 1967
20. Rosenberg, H.W., and D.B. Hunter, "The Titanium-Rich Portion of the Ti-Pd Phase Diagram," *Trans AIME*, Vol. 233, Apr 1965, p. 682
21. Lane, I.R., Jr., and J.L. Cavallaro, "Metallurgical and Mechanical Aspects of the Seawater Stress Corrosion of Titanium," ASTM STP on Applications-Related Phenomena in Titanium (in preparation)
22. Brown, B.F., *et al*, "Marine Corrosion Studies, Third Interim Rept of Progress," NRL Memo Rept 1634, Jul 1965
23. Judy, R.W., *et al*, "Fractographic Analysis of Ti-7Al-2Cb-1Ta and Ti-6Al-4V Fractures Developed in "Wet" Fatigue," NRL Rept 6330, Jul 1965
24. Brauer, F.E., "Formation of Ti_3Al and its Embrittling Effects on Titanium-Aluminum Alloys," thesis submitted to Virginia Polytechnic Institute in partial fulfillment of M.S. degree, Spring 1967
25. Sutton, H., *et al*, *J. Inst Metals*, Vol. 71, 1945, p. xvii
26. Uhlig, H.H., "New Perspectives in the Stress Corrosion Problem," *Physical Metallurgy of Stress-Corrosion Fracture*, Interscience, 1959
27. Lennox, T.J., Jr., *et al*, "Marine Corrosion Studies: Stress-Corrosion Cracking, Deep Ocean Technology, Cathodic Protection, Corrosion Fatigue," NRL Memo Rept 1711, May 1966
28. Meyn, D.A., "Stress Corrosion Cracking of Ti-7Al-2Cb-1Ta Alloy," paper presented at 1965 Fall Meeting of AIME, Detroit, Mich., 18 Oct 1965
29. Beck, T.R., "Stress-Corrosion Cracking of Titanium Alloys Heat Treatment Effects, SCC Velocity in Various Solvents and Electrochemical Kinetics with Ti: 8-1-1 Alloy," Boeing Scientific Research Labs, Quarterly Progress Rept No. 2 on Contr NAS 7-489, Dec 1966
30. Sanderson, G., and J.C. Scully, "Some Observations on the Stress-Corrosion Cracking of Titanium Alloys," Proc. Conf. on Environment-Sensitive Mechanical Behavior, Baltimore, Md., 1965 (in preparation)
31. Ogden, H.R., *et al*, "Studies of the Mechanism of Crack Propagation in Salt Water Environments of Candidate Supersonic Transport Titanium Alloy Materials," Battelle Memorial Ins, Final Rept to FAA on Contr Fa-SS-66-1, Jan 1966
32. Gerberich, W.W., "Acoustic Emission and Stress-Corrosion Cracking in Titanium," Aerojet-General Corp. Tenth Monthly Progress Rept, on Contract N600(61533)65927, 4 May 1967.
33. Scully, J.C., "Kinetic Features of Stress-Corrosion Cracking," paper to be published in *Corrosion Science*

34. Pugh, E. N., "Current Understanding of the Mechanisms of Stress-Corrosion Cracking," paper presented at 96th AIME Annual Meeting, Los Angeles, Calif., 20 Feb 1967
35. Pugh, E. N., "On the Mechanism(s) of Stress-Corrosion Cracking," RIAS (Martin Co.), First Technical Rept to A. R. O. (D) on Project DA-31-124-AROD-258, Aug 1965
36. Nielsen, N. A., "The Role of Corrosion Products in Crack Propagation in Austenitic Stainless Steel: Electron Microscopic Studies," *Physical Metallurgy of Stress-Corrosion Fracture*, Interscience, N. Y. 1959, p. 121
37. Westwood, A. R. C., "Effects of Environment on Fracture Behavior," *Fracture of Solids*, Interscience, N. Y., 1963, p. 553
38. Westwood, A. R. C., and M. H. Kamdar, *Phil. Mag.*, Vol. 9, 1963, p. 787
39. Westwood, A. R. C., *et al*, *Phil. Mag.*, Vol. 10, 1964, p. 345
40. Westwood, A. R. C., *et al*, *Acta Met.*, Vol. 13, 1965, p. 695
41. Westwood, A. R. C., and H. Rubin, *J. Appl. Phys.*, Vol. 33, 1962, p. 2001

Appendix B
Chemical Composition, Weight Percent

Nominal Composition	MEL Code	Heat No.	Al	Sn	Zr	Mo	V	Cb	Ta	Ni	Pd	Fe	Mn	Si	C	N	H (PPM)	O
Ti-7Al-2Cb-1Ta	EDV	30935	6.9					2.4	1.1			0.13			0.02	0.01	40	0.068
Ti-6Al-2Cb-1Ta, -0.8Mo	EJO	292555	6.1			0.73		2.3	1.0			0.06			0.02	0.007	60	0.073
Ti-6Al-2Sn-1Mo-1V	DYV	V-2576	5.86	2.0		1.13	1.02					0.064			0.023	0.008	60	0.070
	EBD	V-2632	6.0	2.1		1.0	1.0					0.067			0.026	0.012	44	0.084
	EBE	V-2638	6.2	2.2		1.1	1.0					0.065			0.022	0.010	36	0.199
	EBF	V-2644	6.1	2.0		1.1	1.1					0.10			0.027	0.0156	36	0.417
Ti-6Al-2Sn-1Mo-2V	EBJ	V-2634	5.9	2.1		1.0	1.8					0.035			0.023	0.0102	47	0.082
	EBK	V-2640	6.0	2.0		1.0	2.0					0.074			0.024	0.0115	54	0.189
	EBL	V-2646	6.2	2.1		1.0	2.1					0.098			0.025	0.0131	44	0.402
Ti-7Al-2Sn-1Mo-1V	EBG	V-2633	7.0	2.0		1.0	1.0					0.057			0.027	0.0110	40	0.099
	EBH	V-2639	7.1	2.1		1.0	1.0					0.060			0.022	0.0096	44	0.189
	EBI	V-2645	7.3	2.1		1.0	1.0					0.098			0.020	0.0104	25	0.434
Ti-6Al-5Zr-1V	DYU	V-2575	6.3		4.8		1.0					0.06			0.023	0.006	80	0.06
Ti-6Al-4Zr-1V	EAT	V-2629	6.0		3.9		1.0					0.065			0.023	0.0108	44	0.072
	EAU	V-2635	6.2		4.0		1.0					0.097			0.023	0.0167	33	0.236
	EAV	V-2641	6.0		4.0		1.1					0.018			0.021	0.0138	41	0.403
Ti-6Al-4Zr-2V	EAZ	V-2631	6.0		3.8		1.8					0.043			0.027	0.0106	27	0.080
	EBA	V-2637	6.0		3.9		2.0					0.113			0.022	0.0138	29	0.227
	EBC	V-2643	6.0		4.0		2.0					0.10			0.025	0.0114	42	0.424
Ti-7Al-2Cb-1Ta	EIS	2(1)	6.45					1.94	1.15			0.05	0.001	0.005	0.0087	0.008	11	0.084
Ti-7Al-2Cb-1Ta-Pd	EIT	3(1)	6.40					1.93	1.14		0.09	0.05	0.001	0.005	0.008	0.0069	7.5	0.081
Ti-7Al-2Cb-1Ta-.075Ni	EIV	6(1)	6.40					2.03	1.00	0.10		0.04	0.001	0.005	0.0052	0.0128	10	0.080
Ti-7Al-2Cb-1Ta-.2Ni	EIX	8(1)	6.30					1.87	1.06	0.21		0.007	0.001	0.004	0.0053	0.0097	9	0.073
Ti-7Al-2Cb-1Ta-X	EIR	1(1)	6.37					1.98	1.12			0.19	0.32	0.007	0.0154	0.008	15	0.0925
Ti-7Al-2Cb-1Ta-Y-Pd	EIU	4(1)	6.39					2.18	1.11		0.09	0.19	0.29	0.03	0.0114	0.0104		0.0865
Ti-7Al-2Cb-1Ta-X-07Ni	EIW	5(1)	6.42					2.10	1.07	0.09		0.20	0.32	0.007	0.0089	0.0134	12	0.1190
Ti-7Al-2Cb-1Ta-X-Ni	EIY	7(1)	6.36					2.03	1.08	0.22		0.20	0.33	0.007	0.0083	0.01	9	0.0695
Ti-7Al-1Cb	EIZ	J(2)	6.8					1.0				0.07			0.04	0.01	29	0.072
	EJD	N(2)	6.8					1.0				0.07			0.04	0.01	29	0.141
Ti-7Al-3Cb	EEG	V-2975	6.95					2.92				0.082	0.002		0.023	0.008	23	0.103
Ti-7Al-3Cb	EJA	K(2)	6.8					3.0				0.08			0.04	0.01	29	0.062
	EJE	P(2)	6.9					3.1				0.08			0.03	0.01	25	0.116
Ti-7Al-5Cb	EJB	L(2)	7.0					5.0				0.09			0.04	0.01	26	0.071
	EJF	Q(2)	6.9					5.1				0.09			0.05	0.01	25	0.132
Ti-7Al-7Cb	EJC	M(2)	6.8					6.5				0.10			0.04	0.01	23	0.058
	EJG	S(2)	6.9					6.7				0.10			0.06	0.01	28	0.139
Ti-8Al-1Cb	EJH	E(2)	8.0					1.0				0.07			0.03	0.01	23	0.056
Ti-8Al-3Cb	EJI	G(2)	7.8					3.1				0.08			0.03	0.01	32	0.073
Ti-8Al-5Cb	EJJ	H(2)	7.7					5.0				0.09			0.04	0.01	32	0.081
Ti-8Al-7Cb	EJK	I(2)	8.1					7.1				0.10			0.05	0.01	28	0.080
Ti-7Al-3Cb-2.5Sn	EEF	V-2974	6.94	2.62				3.10				0.086	0.001		0.025	0.007	24	0.042

(1) Heat designation used by Battelle Memorial Institute. See references 7 and 8.

(2) Heat designation used by Nuclear Metals, Incorporated. See reference 6.

Appendix B
Chemical Composition, Weight Percent (Continued)

Nominal Composition	MEL Code	Heat No.	Al	Sn	Zr	Mo	V	Cb	Ta	Ni	Pd	Fe	Mn	Si	C	N	H (PPM)	O
Ti-3Al	EJR	V-3266	2.91									0.073				0.006		0.075
Ti-5Al	EJS	V-3267	5.08									0.042				0.006		0.085
Ti-6Al	EJT	V-3268	6.08									0.038				0.006		0.097
Ti-7Sl	EJU	V-3269	7.16									0.031				0.012		0.076
Ti-8Al	EJV	V-3270	8.12									0.031				0.010		0.062
Ti-2Mo	EJW	V-3271				2.06						0.053				0.006		0.083
Ti-8Mo	EJX	V-3272				8.15						0.061				0.007		0.082
Ti-4V	EJY	V-3273					4.12					0.040				0.010		0.099
Ti-12V	EJZ	V-3274					12.3					0.047				0.013		0.116
Ti-2Ni	EKA	V-3275								2.02		0.014				0.010		0.086
Ti-7Ni	EKB	V-3276								6.96		0.002				0.014		0.066
Ti-5Fe	EKC	V-3277										05.72				0.010		0.069
Ti-6Cb	EKD	V-3279						6.02				0.032				0.010		0.077
Ti-17Cb	EKE	V-3280						17.02				0.014				0.010		0.072
Ti-6Al-2.5Sn	EET	V-3028	6.12	2.51								0.014	0.001		0.022	0.010	47	0.062
Ti-5Al-2.5Sn	DUO		5.38	2.43								0.12			0.07	0.018	27	0.154
Ti-35A	EIN	D-9313										0.06			0.027	0.011	40	0.08
Ti-55A	EIO	G-135										0.12			0.022	0.011	40	0.11
Ti-75A	EIP	D-6144										0.17			0.021	0.015	40	0.22
Ti-RS70	DZO											0.09			0.030	0.007	70	0.317

DISTRIBUTION LIST

NAVSEC (SEC 6101D) (6)
NAVSEC (SEC 6132)
NAVSHIPS (SHIPS 2021) (2)
NAVSHIPS (SHIPS 031)
NAVSHIPS (SHIPS 0342)
NAVSHIPS (SHIPS 03422)
DSSPO-DSSPO (PM 1122 and PM 11221) (2)
NASL (Code 934) (2)
NRL (Codes 6300, 6320, 6382, 6383) (4)
NAVSECPHILADIV
NSRDC (Codes 735 and 042) (2)
DDC (20)
CO ONR, London (2)

New York University
School of Engineering & Science
University Heights
Bronx, N.Y. 10453
(Attn: Dr. Harold Margolin)

Commanding Officer
Frankford Arsenal
Philadelphia, Pa. 19124
(Attn: R.E. Edelman)

Commanding General
U.S. Army Missile Command
Redstone Arsenal, Ala. 35808
(Attn: AMSMI-RBL)

Wright-Patterson AFB
Aeronautical Systems Div.
Dayton, Ohio 45433
(Attn: ASRCTB, T.S. Felker)

Commanding Officer
U.S. Army Materials Research Agency
Watertown Arsenal
Watertown, Mass. 02172
(Attn: OPT)

U.S. Army Materials Research Agency
Bldg. 131
Watertown, Mass. 02172
(Attn: P.R. Smoot)

Commanding Officer
U.S. Army Research Office
Box CM, Duke Station
Durham, North Carolina 27701
(Attn: Chief, Information Processing Office)

Titanium Metals Corp. of America
P.O. Box 309
Toronto, Ohio 43964
(Attn: D. L. Day)

Titanium Metals Corp. of America
195 Clinton Rd.
West Caldwell, N.Y. 07006
(Attn: Norman Feige)

Titanium Metals Corp. of America
223 Broadway
New York, N.Y. 10007
(Attn: W.W. Minkler)

Titanium Metals Corp. of America
Henderson, Nevada 89015
(Attn: A. Hatch)

Battelle Memorial Institute (2)
505 King Ave.
Columbus, Ohio 43201
(Attn: H.R. Ogden and W.K. Boyd)

Battelle Memorail Institute
Defense Metals Information Center
505 King Ave.
Columbus, Ohio 43201

Crucible Steel Corp. of America
P.O. Box 7257
Pittsburgh, Pa. 15213
(Attn: V.C. Peterson)

Westinghouse Electric Corp.
Missile Launching & Handling Project
Hendy Ave.
Sunnyvale, Calif. 94086
(Attn: J.J. Austin)

Westinghouse Electric Corp.
Research and Development
Pittsburgh, Pa. 15146
(Attn: E.T. Wessel)

DISTRIBUTION LIST (Continued)

Westinghouse Electric Corp. (2)
ORE, Bay Bridge
Annapolis, Md. 21404
(Attn: Michael Kaschak & John Symonds)

Captain W.E. Heronemus, USN
Asst. Naval Attache
Office of the Naval Attache
London, England

Lockheed California Co.
Dept. 77/11, Bldg. 170
Factory B-1
Burbank, Calif. 91503
(Attn: George Wald)

North American Aviation, Inc.
Los Angeles Div.
International Airport
Los Angeles, Calif. 90009
(Attn: George Martin)

North American Aviation, Inc. (2)
Autonetics Div., Dept. 020
3370 Mira Loma Ave.
Anaheim, Calif. 92805
(Attn: Jack Hadley & D.H. Pickrell, Jr.)

General Dynamics Corp.
Electric Boat Div.
Dept. 413
Groton, Conn. 06340
(Attn: E.R. Jerome)

General Dynamics Corp.
Electric Boat Div.
Marine Technology Center
P.O. Box 911
San Diego, Calif. 92112
(Attn: M. Husain)

Lockheed Missiles and Space Co.
Research Lab.
3521 Hanover St.
Palo Alto, Calif. 94304
(Attn: Leo Schapiro)

Mitron Research & Development Corp.
Waltham, Mass. 02154
(Attn: S. Abkowitz)

IIT Research Institute
Technology Center
10 West 35th St.
Chicago, Ill. 60616
(Attn: Irwin Broverman)

Martin Co.
Research Inst. for Advanced Studies
1450 S. Rolling Rd.
Baltimore, Md. 21227
(Attn: A.J. Sedricks)

Boeing Scientific Research Lab (2)
P.O. Box 3981
Seattle, Wash. 98124
(Attn: M.J. Blackburn & T.R. Beck)

Reactive Metals, Inc. (3)
Niles, Ohio 44446
(Attn: R.E. Seagle, H. Kessler & W. Love)

Whittaker Corp.
Nuclear Metals Div.
West Concord, Mass. 01781
(Attn: Saul Isserow)

NASA (Code RRM)
Materials - 5th floor
600 Independence Ave., S.W.
Washington, D.C. 20546
(Attn: R.H. Raring)

Metcut Research Associates, Inc.
3980 Rosslyn Dr.
Cincinnati, Ohio 45209
(Attn: W.E. Jamison)

Northrup Corp.
Northrup Norair Div.
3901 W. Broadway
Hawthorne, Calif. 90250
(Attn: M. Katcher)

DISTRIBUTION LIST (Continued)

Lehigh University
Dept. of Metallurgy & Materials Science
Bethlehem, Pa. 18015
(Attn: John Wood)

E.I. Dupont de Nemours & Co.
Bldg. 304, Experimental Station
Wilmington, Del. 19801
(Attn: Donald Warren)

Massachusetts Institute of Technology
Room 8-409
Dept. of Metallurgy
Cambridge, Mass. 02139
(Attn: R. Ricketts)

General Electric Co.
Flight Propulsion Div.
Advanced Alloy Evaluation
Cincinnati, Ohio 45215
(Attn: V.J. Erdeman)

Arizona Chemicopper Co.
Technical Director
Bagdad, Ariz. 86321
(Attn: W.J. Yurko)

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)* Naval Ship Research & Development Center Annapolis Division Annapolis, Maryland	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3 REPORT TITLE

Embrittlement of Titanium in Seawater

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Research and Development Report

5 AUTHOR(S) *(First name, middle initial, last name)*

Cavallaro, J. L.

6 REPORT DATE October 1967	7a. TOTAL NO OF PAGES 44	7b. NO OF REFS 42

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) 2483
b. PROJECT NO S-F020 01 01 c. S-4607 Task 1189 and 0721 d.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* Assigt 87 115 AD661 463

10 DISTRIBUTION STATEMENT

This document has been approved for public release and sale; it's distribution is unlimited.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY NAVSEC

13 ABSTRACT

Sea-water stress- corrosion tests on notched cantilever-beam specimens of Alloy Ti-7Al-2Cb-1Ta (Ti-721) demonstrated that it has a transition in behavior with increasing notch sharpness. Sea-water tests on Alloy Ti-721 indicate that a threshold stress level exists below which stress corrosion does not occur. Sea-water stress corrosion is dependent on the presence of embrittling constituents in the alloy. Alloy chemistry and heat treatment are the most significant factors which control sensitivity. The results of tests made on a series of Ti-Al binary alloys indicate that aluminum in solid solution does not cause stress corrosion, but that it is caused by a finite amount of a coherent Ti_3Al. A decrease in aluminum and oxygen contents and the addition of isomorphous beta stabilizers improve the resistance of Ti-Al alloys to sea-water stress corrosion by suppressing the formation of Ti_3Al. A stress-sorption cracking mechanism is suggested as a general model for the embrittlement of titanium and titanium alloys in seawater.

(Author)

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Unclassified

Security Classification

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Embrittlement						
Titanium						
Hull structure						
Marine environment						
Physical metallurgy						
Stress corrosion						
Alloys						
Microstructures						
Fracture paths						
Mechanical rupture						
Cantilever beam test						
Plane strain						

DD FORM 1 NOV 65 **1473** (BACK)
(PAGE 2)

Unclassified
Security Classification