NASA TECHNICAL MEMORANDUM

Report No. 53971

STRESS CORROSION CRACKING OF Ti-6Al-4V TITANIUM ALLOY IN VARIOUS FLUIDS

By James G. Williamson
Astronautics Laboratory

November 19, 1969

NASA

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

MSFC - Form 3190 (September 1968)

TECHNICAL REPORT STANDARD TITLE PAGE

1. REPORT NO. NASA TM X-53971	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
4. TITLE AND SUBTITLE STRESS CORROSION CRACKING OF Ti-6Al-4V TITANIUM ALLOY IN VARIOUS FLUIDS		5. REPORT DATE November 19, 1969 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) James G. Williamson		8. PERFORMING ORGANIZATION REPORT #
9. PERFORMING ORGANIZATION NAME AND ADDRESS NASA-George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812		10. WORK UNIT NO. 11. CONTRACT OR GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

This report was prepared by Astronautics Laboratory

16. ABSTRACT

An investigation of the stress corrosion susceptibility of Ti-6Al-4V alloy in various fluids was initiated because of the recent unexpected failures of this alloy in both nitrogen tetraoxide and absolute methanol. This study has indicated that Ti-6Al-4V alloy is susceptible to stress corrosion cracking in absolute methanol in both the annealed and solution treated and aged (STA) conditions. The threshold value for annealed material appears to be near 50 percent of the yield strength or approximately 70,000 psi, while the value of STA material is somewhat less. Long term exposure tests (two years) indicated that the Ti-6Al-4V alloy is not susceptible to stress corrosion cracking in acetone, Aerozine 50, distilled water, absolute ethanol, Freon PCA, Freon MF, hydraulic oil (MIL-H-5606), absolute isoproponal, monoethyl hydrazine, RP-1 fuel and trichloroethylene.

17. KEY WORDS	18. DISTRIBUTION STATEMENT STAR Announcement

19. SECURITY CLASSIF. (of this report)	20. SECURITY CLASSIF. (of this page)	21. NO. OF PAGES	22. PRICE
U	U	18	3.00

MSFC - Form 3292 (May 1969)

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SUMMARY

An investigation of the stress corrosion susceptibility of Ti-6Al-4V alloy in various fluids was initiated because of the recent unexpected failures of this alloy in both nitrogen tetraoxide and absolute methanol. This study has indicated that Ti-6Al-4V alloy is susceptible to stress corrosion cracking in absolute methanol in both the annealed and solution treated and aged (STA) conditions. The threshold value for annealed material appears to be near 50 percent of the yield strength or approximately 70,000 psi, while the value of STA material is somewhat less. There did not appear to be any significant difference in the susceptibility in relation to grain direction.

Long term exposure tests (two years) indicated that the Ti-6Al-4V alloy is not susceptible to stress corrosion cracking in acetone, Aerozine 50, distilled water, absolute ethanol, Freon PCA, Freon MF, hydraulic oil (MIL-H-5606), absolute isopropanol, monomethyl hydrazine, RP-1 fuel and trichloroethylene.

Absolute methanol should not be allowed to come in contact with Ti-6Al-4V alloy under any conditions. As noted above, several other suitable cleaning solvents are available for cleaning this material. However, these fluids should not be used for pressurizing titanium tanks until studies using precracked type specimens and using fracture mechanics techniques are employed.

INTRODUCTION

Until a few years ago, all textbooks and handbooks stated that titanium and titanium alloys were immune to stress corrosion cracking. Later there were a few exceptions to this rule, such as the possibility of cracking in red fuming nitric acid, but these were regarded simply as curiosities. The first incident to shake this firm confidence in titanium's immunity to stress corrosion cracking arose in 1955. G. W. Bauer, while making a 700°F creep test of Ti-6Al-4V alloy, found a crack. This was traced back to a salty fingerprint and was determined to be stress corrosion cracking. Other researchers soon confirmed these conclusions. Later when it was determined that titanium would be the most efficient material for a large part of the Supersonic Transport, the work on the hot salt cracking of this alloy increased many-fold.

In 1964, B. F. Brown (ref. 1) was measuring fracture mechanics parameters (K_{Ic}) of various metals including titanium alloys. He found that stress, salt water, time, and a pre-existing crack could lead to stress corrosion failure of many titanium alloys even at room temperature.

In January 1965, a small Ti-6Al-4V alloy RCS tank fabricated by Bell Aerosystems Company for North American Rockwell failed after being filled with nitrogen tetraoxide (N_2O_4) and pressurized to about 100 ksi wall stress (ref. 2). Failure analysis concluded that the failure mode was stress corrosion and the probable cause was contamination (possibly chlorides) prior to heat treatment. In order to study the problem, ten additional tanks were put into test to represent a sampling of production runs to ensure that the contamination problem was an isolated one, or associated with a particular production period. Thirty-four hours after the tanks had reached test temperature and pressure, the first failure had occurred. Three other tanks burst in the next nine hours of test. When the failed tanks were examined metallurgically, thousands of stress corrosion cracks per tank were found.

In October 1966, the failure of a Ti-6Al-4V alloy tank occurred during a pressure test in which absolute methanol, procured to Federal Specification O-M-232d, was being used. Subsequent tests established that exposure of this alloy to moderately high stresses in the presence of absolute methanol could lead to a form of stress corrosion cracking failure.

The purpose of this study was to determine the stress corrosion susceptibility of Ti-6Al-4V alloy in absolute methanol and other fluids commonly used with pressure vessels made from this material.

EXPERIMENTAL PROCEDURE AND RESULTS

This study was divided into three separate phases. The objective of the first phase was to determine the stress corrosion susceptibility of Ti-6Al-4V titanium alloy in several alcohols and Freon solvents using notch-type tensile specimens. The objective of the second phase was to determine the stress corrosion susceptibility of Ti-6Al-4V alloy both when exposed to the various fluids contained by the many Ti-6Al-4V pressure vessels used in the Saturn V vehicle and when exposed to processing. The third phase objective was to determine the approximate threshold stress level of Ti-6Al-4V alloy in absolute methanol and to study the effect of water in inhibiting the stress corrosion cracking of titanium in absolute methanol.

The chemical analyses and mechanical properties of the sheet and plate Ti-6Al-4V alloy used in this study are given in Table I. To determine the stress corrosion susceptibility of Ti-6Al-4V alloy in various alcohols and Freons the double notch-type specimen (Figure 1) was used. This type of specimen was stressed in a standard creep machine to a load of 120 ksi as shown in Figures 2 and 3. The specimens were made from sheet (0.063 inch) material in the solution treated and aged (STA) condition. Absolute alcohols meeting military specifications were used. The Freons were purchased from E. I. du Pont de Numours and Company.

The results of exposing the double-notch tensile specimens to absolute methyl, ethyl and isopropyl alcohols, trichloromonofluoromethane (Freon MF) and trichlorotrifluoroethane (Freon TF) are shown in Table II. This table indicates the load to which the specimens were stressed and the time required for failure of the individual specimens. The last column indicates the failure time of the specimens when exposed to methanol after being previously exposed to the other fluids for the time shown in column three. For example, a specimen was exposed to ethanol for 3036 minutes (50 1/2 hours) and did not fail. This specimen was then removed from the ethanol and exposed to methanol at the same stress level and it failed in 96 minutes. As can be seen from this table, the Ti-6Al-4V alloy is very susceptible to stress corrosion cracking in absolute methanol. There did not appear to be any significant difference between stress corrosion susceptibility and grain direction. Some specimens were tested with the mill scale intact while others were pickled. The scale was removed from the specimens by vapor blasting. The specimens were cleaned in a hot alkaline solution and dipped in a 20 percent nitric acid solution for 30 seconds. The two types of scale removal used did not appear to influence the time to failure. There were no failures in the other fluids tested in this phase of the study.

In order to determine the effect of using absolute methanol as a cleaning agent for Ti-6Al-4V alloy, notched specimens were exposed to this fluid in the unstressed condition from one to two weeks and then stressed to 120 ksi in trichloromonofluoromethane and in trichlorotrifluoroethane. There were no failures and metallographic examination did not reveal any cracks in the specimens.

In the second phase of this study the stress corrosion susceptibility of Ti-6Al-4V alloy in various fluids was studied The fluids used were as follows:

a. Kerosene base fuel (RP-1)

b. Acetone

c. Hydraulic fluid (MIL-H-5606)

d. Trichloroethylene

e. Isopropanol, absolute

f. Trichlorotrifluoroethane (Freon PCA)

g. Ethyl alcohol, absolute

h. Monomethyl hydrazine

i. Aerozine 50

j. Methylene chloride

k. Methyl ethyl ketone

l. Methanol, absolute

Annealed and STA titanium alloy Ti-6Al-4V sheet material (Table I) was used for this phase of the study. The sheet (0.063 inch) material was fabricated into U-bend type specimens (Figure 4). This type of specimen stresses the material to a very high level. The legs of the 3/4 inch width specimen were held with a nut and bolt. The specimens (three each) were totally immersed in the various fluids in glass containers. They were exposed to the various fluids for approximately two years.

The results of this long term exposure of the U-bend type specimens are shown in Table III. This table shows that only specimens exposed to absolute methanol failed after two years exposure. All specimens exposed to the absolute methanol failed in from three to five days. The fluids selected were those with which various Ti-6Al-4V alloy pressure vessels used in Saturn stages come in contact for an extended period of time or those used during the cleaning process.

Since trichloromonofluoromethane and trichlorotrifluoroethane solvents are used almost exclusively in the cleaning of Ti-6Al-4V alloy pressure vessels, welded specimens were tested to determine if the solvents would affect the weld or heat affected zone of this alloy. The rectangular type specimens (4 inch x 5/8 inch x 1/4 inch) were taken from a Bell Auxiliary Propulsion System tank. The weld bead was in the center of the specimen. The specimens were stressed by constant deflection using a fixed span snap-in frame (Figure 5). With this method the length of the specimen is calculated to give the desired stress at the maximum point of deflection (ref. 3). All of the specimens were stressed to approximately 115 ksi and exposed to these two solvents for two years. No failures occurred during this exposure period.

The objective of the third phase of this program was to determine the approximate threshold stress level of Ti-6Al-4V alloy in absolute methanol and to study the effectiveness of water in inhibiting this cracking phenomenom. The threshold stress level is defined as the lowest sustained tensile stress at which stress corrosion cracking can occur. Rectangular type specimens, as discussed above and are shown in Figure 5, were also used for this study. The specimens were stressed to various levels as shown in Table IV. Both annealed and STA Ti-6Al-4V alloy were used in this study.

The results of this study are shown in Table IV. From these data it can be seen that the solution treated and aged material is more susceptible to stress corrosion cracking than annealed material in absolute methanol. It appears that the threshold value for annealed material is near 50 percent of the yield strength, or approximately 70 ksi. The threshold value of the STA material is somewhat less than the annealed material but was not determined more accurately in this study.

The studies to determine the effectiveness of water in inhibiting the stress corrosion cracking of Ti-6Al-4V alloy in methanol were conducted using the U-bend type specimen. This type of specimen was discussed previously and shown in Figure 4. The specification grade absolute methanol used in these studies contained 0.02 to 0.03 percent water. Sufficient distilled water was added to make up solutions containing 0.25 percent, 0.50 percent, 1.00 percent and 3.00 percent total water content. The U-bend specimens were immersed in these solutions in sealed containers to prevent any further moisture build-up from the atmosphere.

None of the specimens failed after being exposed to solutions containing 0.25, 0.50, 1.00 and 3.00 percent water for six months. These same type specimens failed in absolute methanol in 3 to 5 days. However, when 10 ppm Cl^- in the form of sodium chloride (16.5 ppm) was added to the solutions containing 0.50 and 1.00 percent water, the specimens failed within two days. Four times this amount of chlorides was added to the solution containing 3.0 percent water but the specimens did not fail.

CONCLUSIONS AND RECOMMENDATIONS

This study has indicated that Ti-6Al-4V titanium alloy is susceptible to stress corrosion cracking in absolute methanol in both the annealed and solution treated and aged conditions. The threshold value for annealed material in the un-notched condition is near 50 percent of the yield strength or approximately 70 ksi while the threshold value of the STA material is somewhat less. There did not appear to be any significant difference in cracking susceptibility in relation to grain direction.

Long term tests (two years) indicated that the Ti-6Al-4V alloy is not susceptible to stress corrosion cracking in acetone, Aerozine 50, distilled water, absolute ethanol, Freon PCA, Freon MF, hydraulic oil (MIL-H-5606), absolute isopropanol, monomethyl hydrazine, RP-1 fuel and trichloroethylene.

Absolute methanol should not be allowed to come in contact with Ti-6Al-4V alloy under any circumstance. Several other fluids are available for cleaning this alloy. However, before these fluids can be used for pressurizing, studies using precracked type specimens and fracture mechanics techniques must be made. This type of study was beyond the scope of this work.

As little as 0.25 percent water added to absolute methanol appears to inhibit the stress corrosion cracking phenomena. However, the danger of contamination with chlorides would make it necessary to use at least 3 percent water to assure complete inhibition, and this is not considered to be practical under many test conditions.

The use of notched specimens appears to be an excellent accelerated test method for studying stress corrosion cracking of titanium alloy. Highly loaded specimens failed within minutes in absolute methanol and did not fail after as long as four days in the other fluid tested.

REFERENCES

1. Brown, B. F. ASTM Annual Meeting, Lafayette, Indiana, June 13-18, 1965.

2. Johnson, Robert E.; Kappett, George F. and Korb, L. J., A Case History of Titanium Stress Corrosion in Nitrogen Tetroxide, Presented at the 1966 National Metal Congress October 31 - November 3, 1966, Chicago, Illinois.

3 Humphries, T. S., Procedures for Externally Loading and Corrosion Testing Stress Corrosion Specimens. George C. Marshall Space Flight Center, Technical Memorandum X-53483, 1966.

TABLE I. CHEMICAL ANALYSIS AND PROPERTIES OF Ti-6Al-4V ALLOY SHEET AND PLATE

Chemical Analysis

Sample	Al	V	C	N_2	H_2	O_2
Sheet, Annealed	5.9	4.15	0.013	0.011	0.007	0.09
Sheet, STA*	5.9	4.15	0.013	0.011	0.008	0.11
Plate, Annealed	6.2	4.05	0.018	0.008	0.012	0.11
Plate, STA*	6.2	4.05	0.018	0.008	0.009	0.09

Mechanical Properties

Sample	T.S. (ksi)	Y.S. (ksi)	El. (% in 0.5")	Grain Direction
Sheet, Annealed	143	136	13.0	Longitudinal
	145	136	12.5	L. Transverse
Sheet, STA*	165	158	4.0	Longitudinal
	161	151	4.5	L. Transverse
Plate, Annealed	129	115	12.9	Short Transverse
Plate, STA*	149	130	11.0	Short Transverse

*Solution Treated and Aged

TABLE II. STRESS CORROSION OF Ti-6Al-4V ALLOY* IN VARIOUS ALCOHOLS AND FREONS USING NOTCHED SPECIMENS

Fluid	No. Spec.	Stress Level ksi	Exposure Time Min (days)	Failure Time Min (days)	Failure Time in** Methanol, Min (days)
Methanol	1	120	17 (0.012)	17 (0.012)	---
	2	120	27 (0.019)	27 (0.019)	---
	3	120	38 (0.026)	38 (0.026)	---
	4	120	65 (0.045)	65 (0.045)	---
	5	120	114 (0.079)	114 (0.079)	---
Ethanol	1	120	3036 (2.11)	---	96 (0.067)
Isopropanol	1	120	6360 (4.42)	---	48 (0.033)
Freon MF	1	120	2520 (1.75)	---	47 (0.033)
	2	120	4320 (3.00)	---	
Freon TF	1	120	2880 (2.00)	---	305 (0.21)
Air	1	120	5760 (4.00)	---	---
	1	120	6360 (4.42)	---	---

*Material in STA Condition, stressed in transverse grain direction

**When some specimens did not fail in a fluid it was then exposed to methanol, last column gives time to failure.

TABLE III. STRESS CORROSION OF Ti-6Al-4V ALLOY IN VARIOUS FLUIDS USING U-BEND TYPE SPECIMENS

Fluid	(2 Years Exposure) No. Specimens	Days to Failure
Methanol	3	3 to 5
RP-1 Fuel	3	NF*
Acetone	3	NF
Freon PCA (113)	3	NF
Trichloroethylene	3	NF
Isopropyl Alcohol	3	NF
Distilled Water	3	NF
Ethyl Alcohol	3	NF
Monomethyl Hydrazine (MMH)	3	NF
Hydraulic Oil (MIL-H-5606)	3	NF
Methylene Chloride	3	NF
Methyl Ethyl Ketone	3	NF
Methanol (2 days exposure) + MMH	3	NF
Methanol (2 days exposure)+ Aerozine 50	3	NF
Aerozine 50	3	NF

* No Failures

TABLE IV. THRESHOLD STRESS LEVEL OF Ti-6Al-4V ALLOY* IN ABSOLUTE METHANOL USING BEND TYPE SPECIMENS

Stress Level % of Y.S.	No. Specimens	Average Days to Failure	
		Annealed	STA
100	4	6	2
90	4	20	7
80	4	48	14
70	4	32	7
60	4	54	15
50	4	NF**	38

* Alloy in the STA Condition

** Specimens did not fail

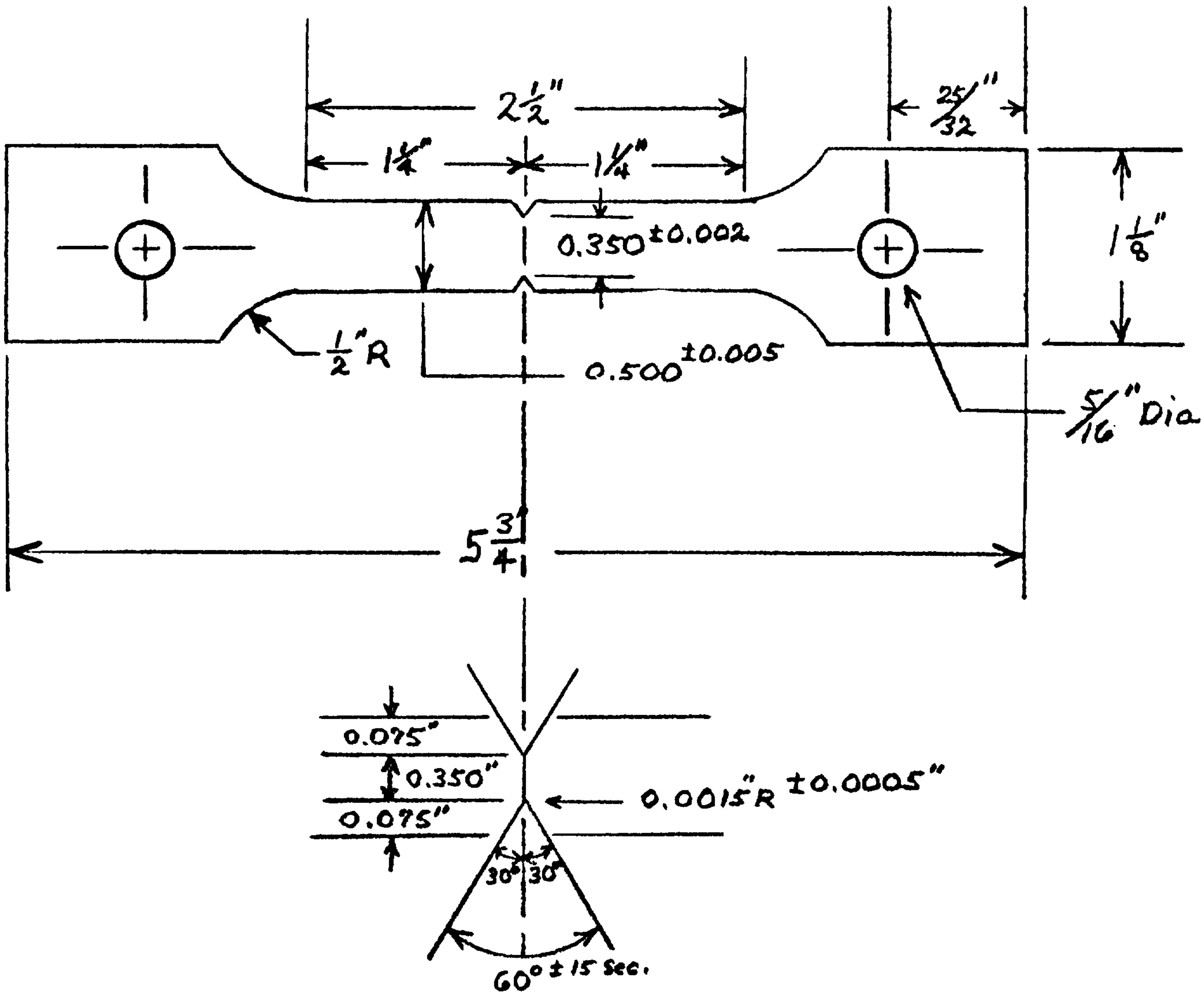

Figure 1 - Notch Tensile Specimen

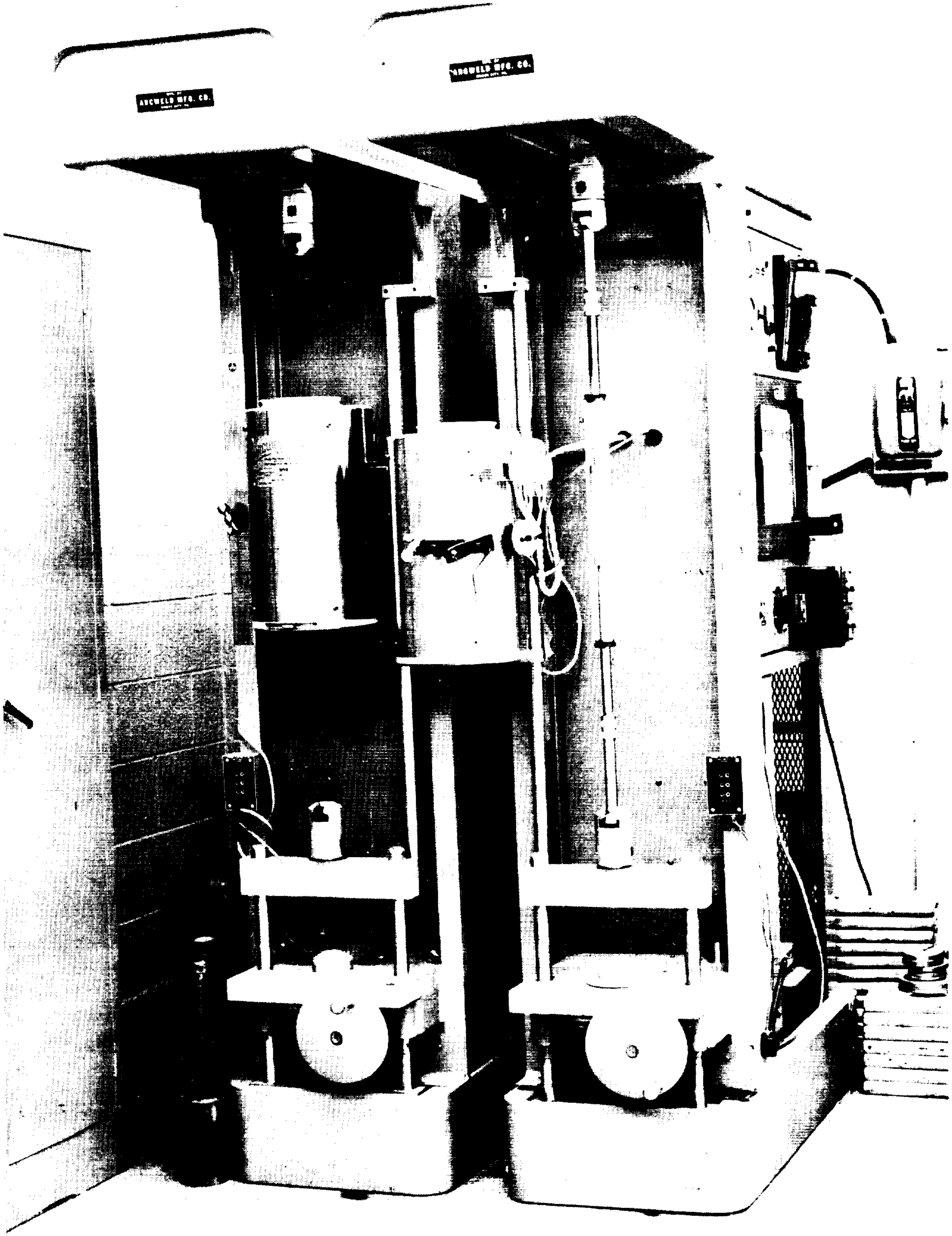

Figure 2 - Creep Machines for Stressing Notched Specimens

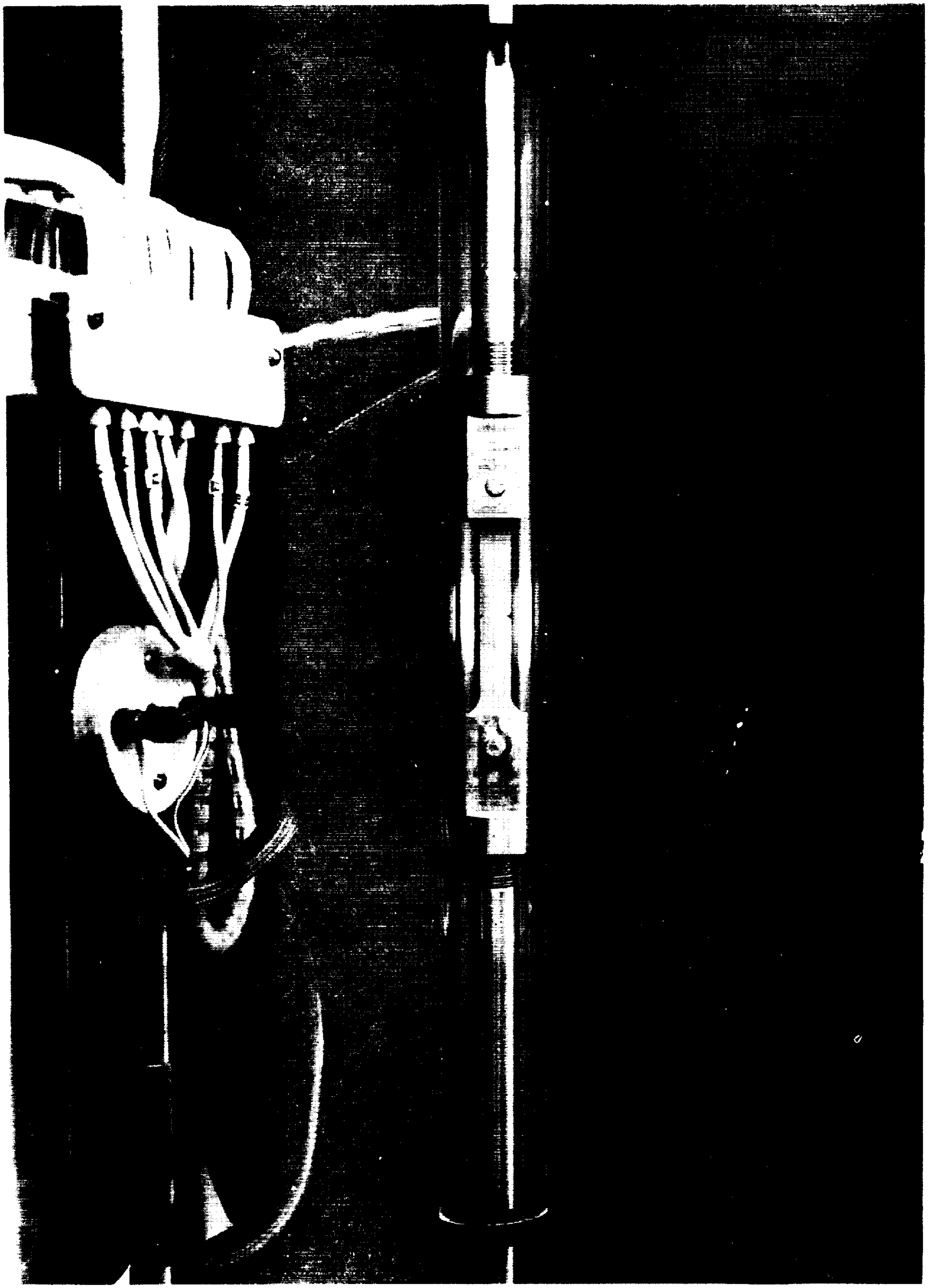

Figure 3 - Stressed Notched Specimen

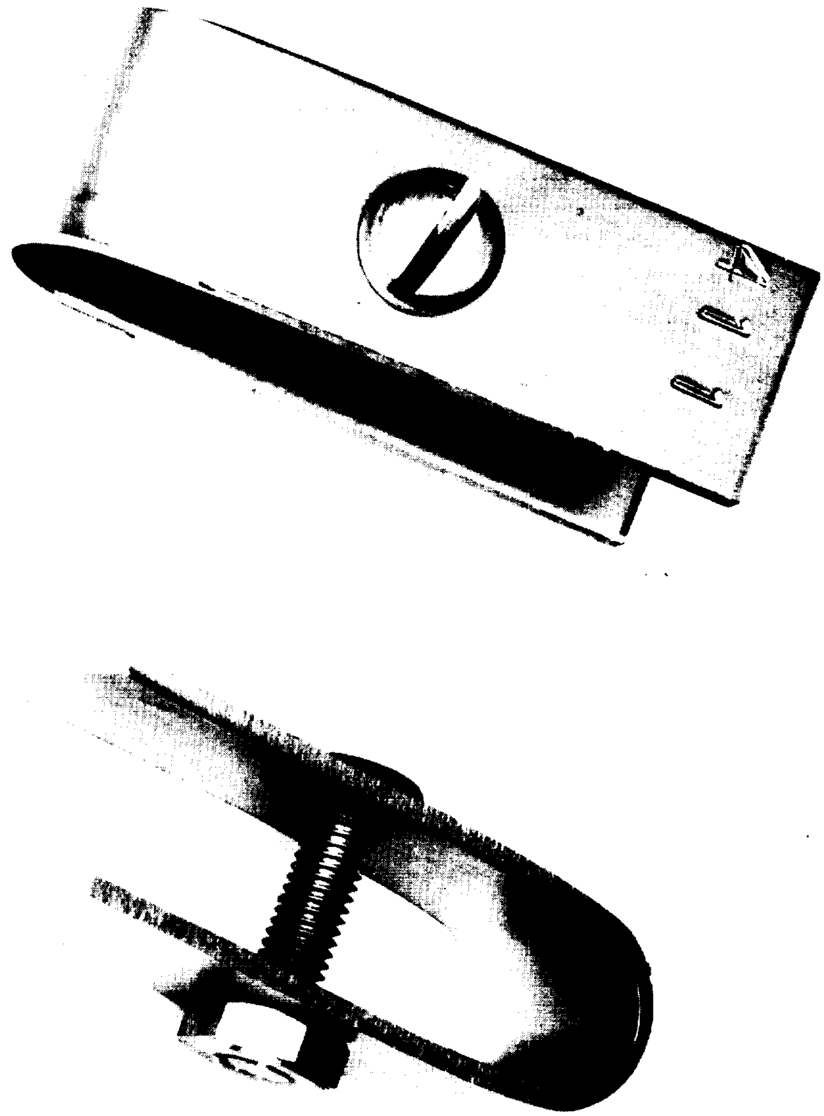

Figure 4 - Stressed U-Bend Specimens

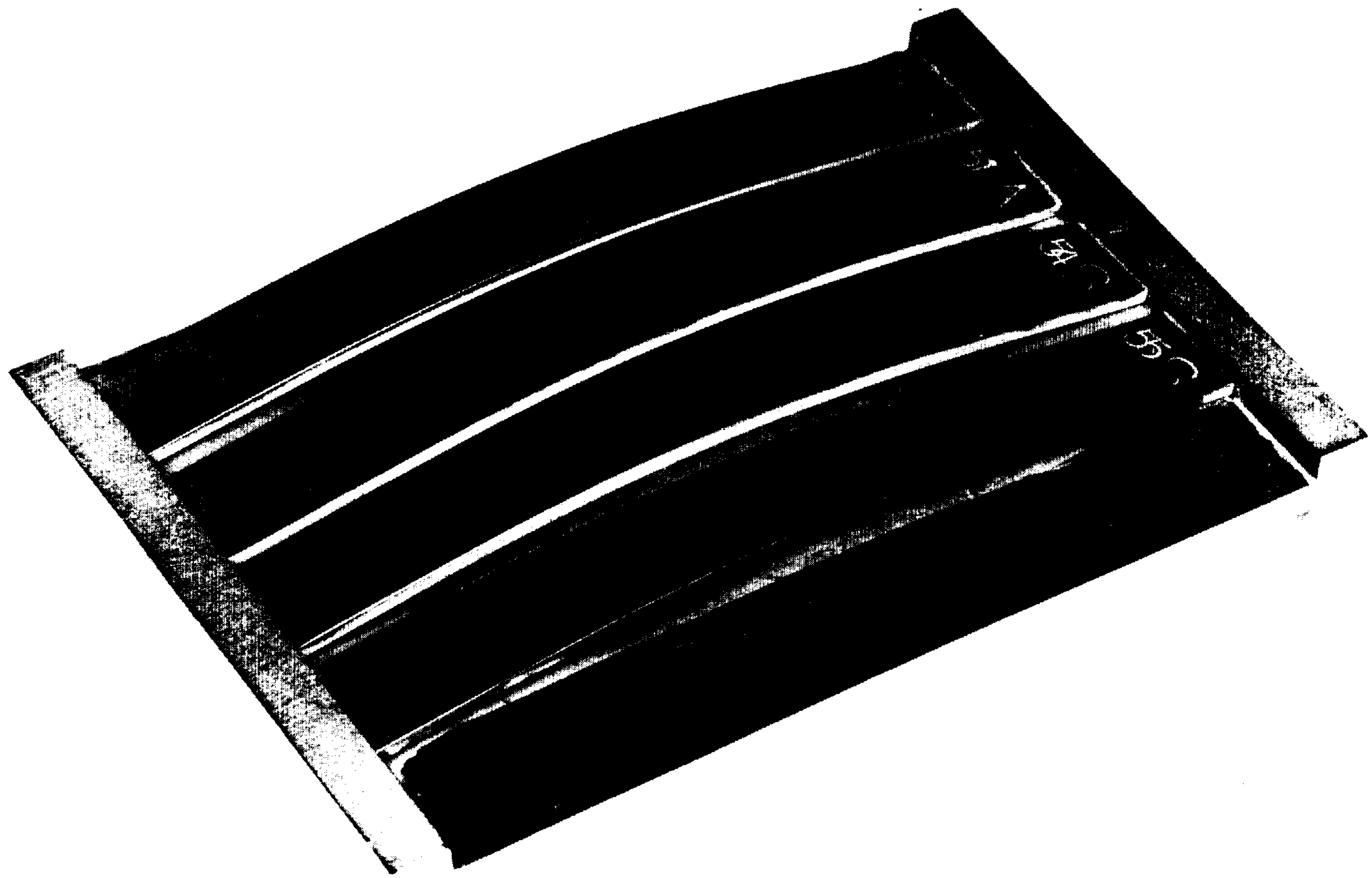

Figure 5 - Stressed Bend Beam Specimens

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By

James G. Williamson

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This document has also been reviewed and approved for technical accuracy.

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