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STRUCTURAL FASTENERS FOR EXTREME ELEVATED TEMPERATURES

T. A. ROACH and E. F. GOWEN, JR.

STANDARD PRESSED STEEL CO.

M. H. ORTNER and S. J. KLACH

VITRO LABORATORIES

TECHNICAL REPORT AFFDL-TR-66-107

SEPTEMBER 1966

AIR FORCE FLIGHT DYNAMICS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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300 - December 1966 - C0192-14-265

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FOREWORD

This report covers work performed under Contract AF33(657)-11684 from June 1963 to June 1966. This contract was initiated under Project No. 1368, Task No. 136807, "Structural Fastening Technology." Work was administered under the direction of the Air Force Flight Dynamics Laboratory, Research and Technology Division with SM/Sgt. J. C. Ingram as Project Engineer.

The report was prepared by T. A. Roach and E. F. Gowen, Jr. of Standard Pressed Steel Laboratories and M. H. Ortner and S. J. Klach of Vitro Laboratories.

Vitro Laboratories was a major subcontractor to SPS Laboratories for the oxidation protective coatings application and evaluation efforts required during this program.

The manuscript was released by the authors August 10, 1966 for publication as an RTD technical report.

This technical report has been reviewed and is approved.

Robert L. Cavanagh

ROBERT L. CAVANAGH
Chief, Applied Mechanics Branch
Structures Division

ABSTRACT

Fasteners of several materials and configurations were developed, manufactured, coated and tested in various modes of oxidation and mechanical properties were characterized by extensive testing. The materials utilized were molybdenum alloy TZM, columbium alloys Cb752 and C129Y, tantalum alloys T-222 and 90Ta-10W, and several dispersion strengthened metals. Protective coatings were adapted to fasteners, the columbium coating being an electrophoretically applied adaption of the Tapco Cr-Ti-Si coating and the tantalum coating being an electrophoretically applied WSi_2 coating. A facility for dynamic oxidation testing was developed capable of exposing small parts to 3200°F in air moving at 250 ft./second. The deformability limits of the coating-substrate "systems" were established. Deformability of the systems was found to be insufficient to permit the development of a deformable blind fastener. Threaded fasteners were manufactured from a limited number of dispersion strengthened nickel base metals and were tested. Results indicate the feasibility of fastener manufacture from these materials and show considerable promise for their use in the 1800°F to 2200°F temperature range.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

ILLUSTRATIONS

ILLUSTRATIONS (continued)

ILLUSTRATIONS (continued)

ILLUSTRATIONS (continued)

ILLUSTRATION (continued)

ILLUSTRATIONS (continued)

ILLUSTRATIONS (continued)

ILLUSTRATIONS (continued)

TABLES

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TABLES (continued)

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GLOSSARY OF TERMS

Alumina	-	Aluminum oxide
Al_2O_3	-	Aluminum oxide
Barrier	-	A layer of material placed between coating and the substrate to minimize diffusion between them.
Cb	-	Columbium, a refractory metal having a melting temperature of 4380 F and a density of .31 pounds per cubic inch.
Cb752	-	A columbium base refractory alloy developed by Union Carbide containing 10% tungsten and 2.5% Zirconium.
C129Y	-	A columbium base refractory alloy developed by Boeing and Wah Chang containing 10% tungsten and 10% hafnium.
Cr-Ti-Si	-	A protective coating for columbium base alloys consisting of chromium, titanium, and silicon.
Diffusion Zone	-	That zone of substrate into which some coating material has diffused during elevated temperature cycling.
Fansteel 85	-	A columbium base refractory alloy developed by Fansteel containing 28% tantalum, 10.5% tungsten, and 0.9% zirconium.
Flush Head	-	Head designed to fit 100 countersunk hole with the top of head flush with the outer surface.
HF	-	Hydrofluoric acid.
HNO_3	-	Nitric acid
Interface	-	The surface where two members meet, i.e. the coating - substrate interface.
Ksi	-	Thousand pounds per square inch.
Magnesia	-	Magnesium oxide.
MgO	-	Magnesium oxide.

Mo	-	Molybdenum, a refractory metal having a melting temperature of 4720 ^{0}F and a density of .368 pounds per cubic inch.
$MoSi_2$	-	Molybdenum disilicide, a material widely used as a protective coating on molybdenum and its alloys.
Newton	-	The basic unit of force in the International System of Units defined as the force that gives to a mass of one kilogram, an acceleration of one meter per second per second.
Partial pressure	-	Any pressure less than atmospheric pressure; that is, less than 760 torr.
Refractory metal	-	Any metallic element or alloy having a melting temperature above 4000 ^{o}F.
Setter	-	A device used to support parts during furnace exposures.
Si	-	Silicon.
Silica	-	Silicon dioxide
SiO_2	-	Silicon dioxide
Substrate	-	The base material on which a coating is deposited.
Ta	-	Tantalum, a refractory metal having a melting temperature of 5425 °F and a density of .600 pounds per cubic inch.
TAPCO	-	A group within Thompson Ramo Wooldridge which applies coatings to refractory metals.
Ta-10W	-	A tantalum base refractory alloy containing 10% tungsten.
ThO_2	-	Thorium dioxide
Thoria	-	Thorium dioxide
Torr	-	A unit of pressure equal to 1 mm of mercury; one atmosphere equalling 760 torr or 760 mm of mercury.

TRW	-	Thompson Ramo Wooldridge
tsi	-	Tons per square inch
TZM	-	A molybdenum base refractory alloy developed by Climax Molybdenum containing .5% titanium and .08% zirconium.
T-111	-	A tantalum base refractory alloy developed by Westinghouse containing 10% tungsten and 2.5% hafnium.
T-222	-	A tantalum base refractory alloy developed by Westinghouse containing 9.6% tungsten, 2.4% hafnium, and .01 carbon.
W	-	Tungsten, a refractory metal having a melting temperature of 6170° F and a density of .697 pounds per cubic inch.
1/4-20	-	Quarter inch diameter with 20 threads for each inch of length.
1/4-28	-	Quarter inch diameter with 28 threads for each inch of length.

SECTION I

INTRODUCTION

This program was initiated by the Air Force Flight Dynamics Laboratory of the Research and Technology Division to investigate, study, and experimentally evaluate the problem areas associated with the use of structural fasteners at extreme elevated temperatures. Mechanical fasteners are required in coated refractory alloy structures because joining techniques such as welding, brazing, and bonding are not yet feasible in terms of structural soundness and reproducibility. In retrospect, all flight structures, regardless of metal employed or operational temperature, will require significant numbers of mechanical fasteners.

Work covered during the performance of this program included:

1. Survey
2. Refractory Thread Form Study
3. Adaptation of Tantalum Alloys to Fasteners
4. Adaptation of Electrophoretically Applied Coatings to Fasteners of Molybdenum, Columbium, and Tantalum Based Alloys
5. Development of Semi Blind Bolts of Columbium and Tantalum Based Alloys
6. Study of Deformable Fasteners
7. Development of Mechanical Properties Data of Various Configurations of Columbium and Tantalum Based Alloy Bolts
8. Study of Refractory Alloy Fastener Applications
9. Initial Study of Available Dispersion Strengthened Metals for Adaptability to Fasteners
10. Develop Extensive Oxidation Information on Fasteners and Joints

The survey was required to solidify the thinking of prospective fastener users, material suppliers, coating vendors, and fastener manufacturers all of whom had some definite ideas on coated refractory fasteners. The survey was used to help establish the goals and objectives of the program.

Study of refractory alloy fasteners started in 1957, but almost all the work was accomplished on molybdenum. The utilization of molybdenum is limited with current coatings because of the oxidation and embrittlement characteristics. For this reason the majority of the work of this program was on columbium and on tantalum, about which little was known as fasteners.

Many processes for applying coatings and many coating chemistries were semi-commercially available at the start of the program. All had problems.

A coating technique unproven at the initiation of this program but with great potential for conversion to fastener requirements was the electrophoretic coating technique. Prior history had indicated that electrophoresis could hold the very close tolerances required by the complex, small shapes of fasteners. In addition, the process was adaptable to the various coating chemistries of other deposition techniques.

To fully utilize refractory alloys in flight structures, all types of fasteners should be available. These include nuts, bolts, rivets, semi-blind and blind types. Standard threaded fasteners and rivets had been fabricated from various molybdenum and columbium alloys, but no exploratory development had been initiated to truly exploit their potential for efficient structural utilization. Nothing had been accomplished in tantalum or dispersion strengthened alloys. This program was oriented toward filling these voids and developing useful design allowables applicable to high performance flight vehicle structures.

Oxidation characteristics of refractory fasteners are almost a completely overriding consideration. For this reason, static, dynamic and partial pressure oxidation tests were standard requirements throughout the program.

To actually determine the utility of the fastener, studies of stress-relaxation were conducted to develop user information.

To present a reasonable spectrum of the elevated temperature field, the dispersion strengthened metals group was included. A complete state-of-the-art study along with certain data are presented in this report.

SECTION II

SUMMARY OF RESULTS

A summary of typical mechanical and oxidation test results on columbium and tantalum alloy fasteners is contained in Tables I, II, and III. These tables represent typical results which are an average of the several configurations evaluated during the course of the program.

Oxidation testing was conducted after various partial pressure exposures, however, because of the complexity and variation of the results they did not lend themselves to summarization.

Detailed data on both the summarized results as well as fatigue, relaxation, application, and oxidation can be found in the tables in Sections VIII and IX.

TABLE I

SUMMARY OF PROPERTIES OF Cb 752 THREADED FASTENERS
WITH VITRO Cr-Ti-Si COATING

Temperature		Tensile Strength		Shear Strength		Static Oxidation Life - Hours	Dynamic Oxidation Life - Hours
°F	°C	KSI	KN/cm^2	KSI	KN/cm^2		
-320	-196	36.5	25.2	92.0	63.4	---	---
80	28	80.5	55.5	64.0	44.1	---	---
600	316	59.6	41.1	39.1	27.0	---	---
2000	1093	44.3	30.5	29.6	20.4	---	---
2200	1204	36.4	25.1	25.8	17.8	60 - 79	2.7
2400	1316	30.5	21.0	19.8	13.7	28 - 38	1.2 - 2.3
2600	1427	21.2	14.6	---	---	6 - 12	0.53 - 0.96
2800	1538	---	---	---	---	.50 - .75	0.03 - 0.3

TABLE II

SUMMARY OF PROPERTIES OF C129Y THREADED FASTENERS
WITH VITRO Cr-Ti-Si COATING

Temperature		Tensile Strength		Shear Strength		Static Oxidation Life-Hours	Dynamic Oxidation Life - Hours
°F	°C	KSI	KN/cm^2	KSI	KN/cm^2		
-320	-196	37.2	25.6	75.0	51.7	---	---
80	28	92.0	63.4	70.0	48.2	---	---
600	316	68.1	47.0	42.3	29.2	---	---
2000	1093	47.6	32.8	33.2	22.9	---	---
2200	1204	37.6	25.9	27.0	18.6	50 - 76	3.9
2400	1316	31.9	22.0	22.3	15.4	30 - 35	1.2 - 1.8
2600	1427	23.4	16.1	---	---	6 - 12	0.7 - 1
2800	1538	---	---	---	---	.33 - 1	0.05 - 0.18

TABLE III

SUMMARY OF PROPERTIES OF T-222 THREADED FASTENERS
WITH VITRO Si/WSi COATING

Temperature		Tensile Strength		Shear Strength		Static Oxidation Life - Hours	Dynamic Oxidation Life - Hours
°F	°C	KSI	KN/cm^2	KSI	KN/cm^2		
-320	-196	185	127	125	86.1	---	---
80	28	130	89.5	92	63.4	---	---
600	316	100	68.9	56.9	39.3	---	---
2000	1093	87.7	60.5	53.1	36.6	---	---
2200	1204	77	53.1	---	---	---	---
2400	1316	59.2	40.8	35.4	24.4	134	0.9 - 2.1
2600	1427	49.0	33.8	---	---	---	---
2800	1482	---	---	---	---	4.5 - 71	0.6 - 1.2
3000	1649	---	---	---	---	1.5 - 6	0.3 - 0.8
3200	1760	---	---	---	---	0.5 - 3.5	---

SECTION III

SURVEY

The first major activity under this contract consisted of a comprehensive survey of present and potential user of refractory fasteners, coating sources and material suppliers. The objective of this survey was to determine:

1. The requirements and preferences of ultimate fastener users as to materials, coatings, fastener configurations, environmental conditions and other special requirements.

2. Coating state of the art to select coating systems which might be included in the program.

3. Base metal availability, prices and specifications.

This survey was conducted primarily during Fall 1963, but was continued throughout the program in areas in which the materials or coatings were not sufficiently developed to warrant an early decision. This was primarily true in the tantalum alloy and tantalum alloy coating areas.

The decisions made as a result of the original survey included the following:

1. Use Cb752 as one of the columbium base alloys.

2. Adapt the TRW Cr-Ti-Si coating chemistry to the electrophoretic coating technique for columbium base alloys.

3. Investigate threaded, semi-blind and blind fasteners throughout the program.

4. Study the characteristics of all coatings selected at partial pressures.

5. Recrystallized materials were to be purchased throughout the program to provide data readily applicable to design in view of the recrystallizing effect produced by most coating processes.

6. TZM with $MoSi_2$ coating was selected for use in the thread form requirement study.

The continuing survey resulted in the following decisions:

7. C129Y was selected as the second columbium alloy.

8. T-222 was selected as the tantalum base alloy.

9. Electrophoretically applied WSi_2 was chosen as the coating for the T-222 fasteners.

The detailed information gathered during the survey is contained in Appendix I.

SECTION IV

THREAD FORM REQUIREMENT STUDY

A. BACKGROUND AND TEST PROGRAM

The thread form requirement study had as its main objective the investigation of the effect of thread form on the oxidation characteristics of electrophoretically coated fasteners. Previous work in the coating of fasteners by other techniques indicated a high degree of sensitivity to coating failure on sharp corners. Accordingly, most hardware was prepared for coating with liberal radii.

Since few fasteners had been coated by the electrophoretic technique, it was deemed advisable to investigate the susceptibility of this technique to premature failures due to sharp corners. A program was therefore established to compare the 65% refractory thread form with a truncated refractory thread form. These thread forms are illustrated in Figure 1.

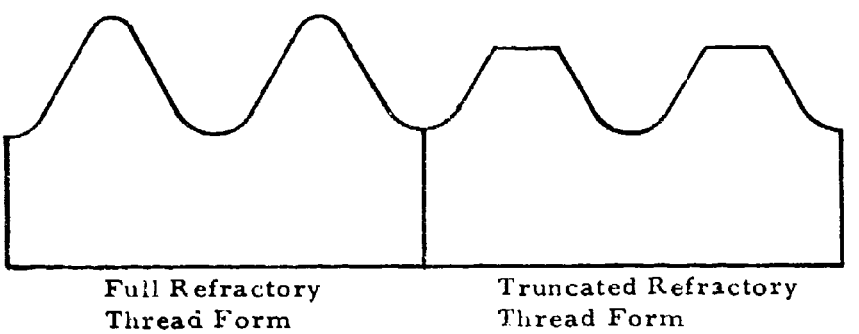


Figure 1. Fastener Thread Forms

The production of the full refractory thread form in the internal threads (nuts) represents a considerable expense compared to the truncated refractory thread form. However, the production of the refractory thread form on the external thread (bolt) does not involve increased expense except for procurement of special thread roll dies. For this reason it was decided that the requirement study would utilize bolts with refractory thread form tested in conjunction with nuts with either the refractory thread form or the truncated refractory thread form. The bolts and nuts were tested both as separate parts and in joints by tightening them into cylinders.

The TZM - $MoSi_2$ system was chosen for these tests for several reasons. First, this system had been extensively tested and had proven reliability substantiated by much test data. Second, the coating technology was in an advanced state and could be applied by existing techniques in a short period of time.

The oxidation tests were conducted in static air and in air moving at 200 ft./sec. The test temperature was 2600°F for the static tests and 2800°F for the dynamic tests.

A detailed description of the test procedures is contained in Section VIII.

The results of the tests are summarized in Table IV. Representative specimens are shown in Figures 2 through 5.

B. DISCUSSION OF RESULTS

Examination of the test results in Table I indicates the following:

The similar lives of the full refractory and truncated refractory thread forms in joints as well as in detail parts, indicate that the survival potential of the two thread forms is essentially the same.

The failures are in no way associated with the nut threads. This is evidenced by the fact that in several specimens failure of the coating on the outside surface of a nut led to complete substrate failure in to the coating on the nut thread.

Specimen life in the dynamic air tests was considerably less than that in the static air tests. The principal contributing factor to this failure acceleration appears to be the flow of silica from the air stream impingement side of the specimen. The silica builds up on the back side of the specimen, thus leaving the upstream side without the protection of the silica layer. This phenomenon is shown in Figure 6.

C. ESTABLISHMENT OF THREAD FORM

In view of the similar survival potential exhibited by the full 65% refractory thread form and the truncated refractory thread form in internal threads, it was decided that:

1. All internal threads produced on parts for this program would have the truncated refractory thread form.

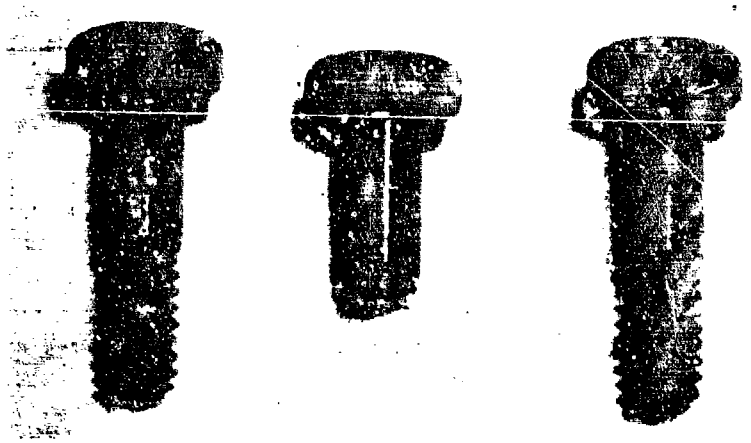
2. All external threads produced would have the full 65% refractory thread form.

TABLE IV

SUMMARY OF OXIDATION TEST RESULTS ON $MoSi_2$ COATED TZM FASTENERS

	Static Oxidation Tests at Vitro (a)		Static Oxidation Tests at SPS (b)		Dynamic Oxidation Tests at SPS	
Specimen Configuration	Life (Hrs) at 2600°F (1427°C)	Failure Location	Life (Hrs) at 2600°F (1427°C)	Failure Location	Life (Hrs) at 2800°F (1538°C)	Failure Location
Bolt with full refractory thread form	79-103 79-103 56	Thread (c) Thread Thread (c)		---	.40 .90 .88	Body and head Body and head Body and head
Nut with full refractory thread form	108 160 81	Hex corner (c) Hex corner (c) Hex corner (c)	28-33	Hex corner	.53 .50 .30	Hex corners Hex corners Hex corners
Nut with truncated refractory thread form	56 81 77	Hex corner (c) Hex corner (c) Hex corner (c)	28-33	Hex corner	.54 .32 .56	Hex corners Hex corners Hex corners
Joint with refractory thread form bolt and refractory thread form nut	21 7-22 7-22	Nut-cylinder interface Nut face Interface of nut & bolt with cyl.	13-18 21-25	Bolt-cylinder interface Nut-cylinder interface	.30 .40 .45	Hex corners Hex corners Hex corners
Joint with refractory thread form bolt and truncated refractory thread form nut	7-22 24-39 24-39	Nut face Bolt-cylinder interface Nut-cylinder interface	10-13 7-12 9-13	Nut-cylinder interface Nut-cylinder interface End of bolt	.30 .45 .60	Hex corners Hex corners Hex corners

(a) Continuous exposure
(b) 5-6 hour cycles
(c) At point of contact with Al_2O_3 support



Bolts With Full Refractory Thread Form

Nuts With Full Refractory Thread Form

Nuts With Truncated Refractory Thread Form

Figure 2. Static Oxidation Test Specimens - $MoSi_2$ Coated TZM Tested at 2600°F (1427°C)

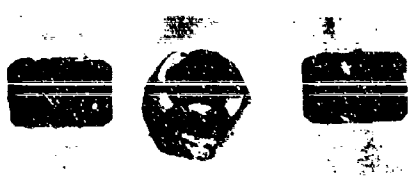
Joint Specimens With Full Refractory Thread Form Bolts and Full Refractory Thread Form Nuts

Joint Specimens With Full Refractory Thread Form Bolts and Truncated Refractory Thread Form Nuts

Figure 3. Static Oxidation Test Specimens - $MoSi_2$ Coated TZM Tested at 2600°F (1427°C)

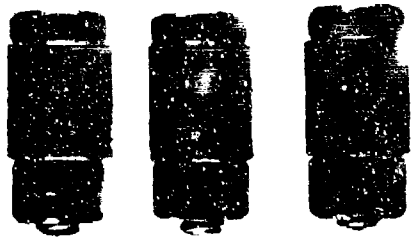
Bolts With Full Refractory Thread Form

Nuts With Full Refractory Thread Form

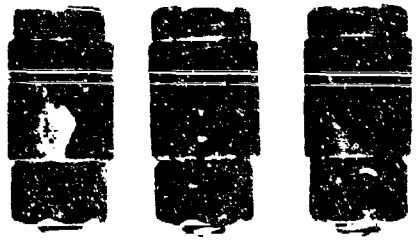


Nuts With Truncated Refractory Thread Form

Figure 4. Dynamic Oxidation Test Specimens - $MoSi_2$ Coated TZM Tested at 2800°F (1538°C)



Joint Specimens With Full Refractory Thread Form Bolts
and Full Refractory Thread Form Nuts



Joint Specimens With Full Refractory Thread Form Bolts
and Truncated Refractory Thread Form Nuts

Figure 5. Dynamic Oxidation Test Specimens - $MoSi_2$ Coated TZM Tested at 2800°F (1538°C)

Air Flow

Same specimen viewed
from down stream side

Figure 6. Joint Specimen After Dynamic Oxidation Test Showing Flow of Silica in the Direction of Air Stream

SECTION V

MANUFACTURING

A. MATERIAL PROCUREMENT

The materials selected for the manufacture of threaded fasteners were as described in the survey conclusions:

TZM (thread form requirement study only)
Cb752
C129Y
T-222

These were all purchased in the fully recrystallized condition (see Section XII, Metallography) in rods of suitable diameters for the manufacture of 1/4-20 hex head and flush head bolts and 1/4-20 hex nuts, .270 inches and .400 inches respectively. The suppliers of these materials were as follows:

TZM - Climax Molybdenum
Cb752 - Union Carbide Corporation
C129Y - Wah Chang
T-222 - Fansteel Metallurgical Corporation

In addition, a quantity of FS-85 for fixtures was purchased from Union Carbide and Fansteel Metallurgical Corporation. T-222 for the early coating studies was purchased from Wah Chang. The tantalum alloy manufacturing study program material, 90Ta-10W, was purchased from National Research Corporation.

B. MANUFACTURING TECHNIQUES

The manufacturing techniques utilized were generally identical with those established in the program "Research, Development and Test of Refractory Metal Alloy Fastener," AF33(616)-8104 conducted by Republic Aviation. (1) These techniques were well established for molybdenum and columbium alloys prior to the start of this program. Methods for the manufacture of tantalum alloy fasteners, however, were not established. A study was therefore initiated for the purpose of determining the degree to which molybdenum and columbium manufacturing procedures would need to be modified in the manufacture of tantalum alloy fasteners.

Since this study was begun prior to the selection of T-222 for the test program, 90Ta-10W was chosen for the study alloy as it was readily available. The study consisted of the manufacture of sufficient 90Ta-10W, 1/4-20 hex head bolts and companion nuts to establish manufacturing techniques.

The previously established procedures were generally applicable to the manufacture of 90Ta-10W fasteners and to the subsequent manufacture of all configurations in the T-222 fasteners.

All bolts were fabricated by hot forging the heads and rolling the threads. The finished surfaces on the parts were produced by centerless grinding. Hex sockets in the point-drive bolts were produced by drilling and broaching while the hex sockets in the other flush head configuration were produced during the hot forging operation.

Nuts were produced by hot forging, drilling and tapping.

As mentioned in the survey conclusions, all bolts were produced with the 65% refractory thread form and all nuts were produced with the truncated refractory thread form.

Drawings of the chosen configurations are shown in Figures 7 through 10.

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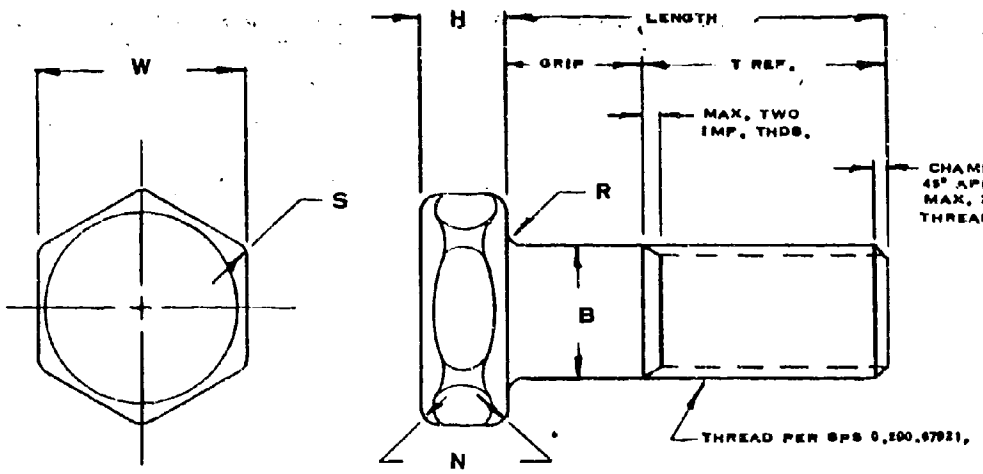
SHEET 1 OF 1

DRAWING NUMBER SD.300.67538

REVISION



THREAD	B DIA.	H	N RAD.	R RAD.	S RAD.	T REF.	W	X	Y
1/4-20 NS	.2490 .2460	.167 .137	.035 .020	.020 .010	.040 .025	.503	.435 .425	.008	.0045

NOTES:

1. MATERIAL: TANTALUM ALLOY - MOLYBDENUM ALLOY, OR COLUMBIUM ALLOY.
2. FINISH: OXIDATION RESISTANT COATING .0021-.0029 THICK.
3. CONCENTRICITY: HEAD AND BODY WITHIN "X" T.I.R.
   BODY AND THREAD P.D. WITHIN "Y" T.I.R.
4. PART NUMBERS: THE BASIC PART NUMBER IS 67538
   FIRST DASH NUMBER DESIGNATES DIAMETER IN SIXTEENTHS.
   SECOND DASH NUMBER DESIGNATES GRIP LENGTH IN SIXTEENTHS.
   EXAMPLE: 67538-4-8 1/4-20 BOLT, .500 GRIP, 1.003 LONG.
5. GRIP LENGTHS AVAILABLE IN 1/16TH INCH INCREMENTS, LENGTH NOMINAL GRIP + T.
6. DIMENSIONS ARE BEFORE COATING.
7. SURFACE ROUGHNESS PRIOR TO COATING: BODY, BEARING SURFACE OF HEAD, THREAD ROOT, AND SIDES OF THREADS, 32 MICRO INCHES - OTHER SURFACES, 125 M.I. PER MIL-STD-10.

TOLERANCES ± AND UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS

CUSTODIAN: JENKINTOWN, PA.

TITLE

BOLT, HEXAGON HEAD, REFRACTORY MATERIAL

DRAWN BY G.W.N DATE 5-2-66

APPROVED R.T.S DATE 5-2-66

PART NUMBER

67538

339 REV. 968

Figure 7

STANDARD PRESSED STEEL CO.
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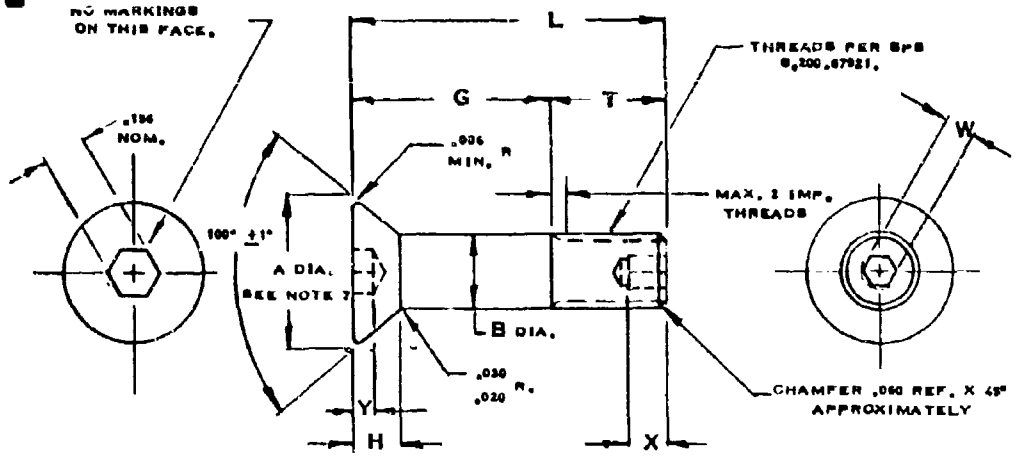
SHEET 1 OF 1

SPS 300.67536 REVISION



PART NO.	THREAD	A DIA.	B DIA.	G ±.010	H REF.	L +.031 −.016	T REF.	W	X MIN.	Y MIN.
67536-4-009	1/4-20 NS	.402 .322	.2490 .2460	.282	.068	.709	.447	.095 .094	.196	.111

NOTES:

1. MATERIAL: TANTALUM ALLOY – MOLYBDENUM ALLOY, OR COLUMBIUM ALLOY.
2. FINISH: OXIDATION RESISTANT COATING .0021–.0029 THICK.
3. SURFACE ROUGHNESS PRIOR TO COATING: FLAT AND CONICAL SURFACES OF HEAD, ROOT, AND SIDES OF THREADS AND BODY, 32 M.I., OTHER SURFACES 125 M.I.
4. CONCENTRICITY: CONICAL SURFACE OF HEAD AND BODY DIAMETER WITHIN .002 T.I.R. THREAD P.D. WITH BODY DIAMETER WITHIN .0045 T.I.R.
5. ROUND ALL SHARP EDGES .010 R. MINIMUM.
6. PART NUMBER CONSISTS OF BASIC PART NUMBER WHICH IS 67536 AND TWO DASH NUMBERS.
   FIRST DASH NUMBER DESIGNATES DIAMETER IN SIXTEENTHS.
   SECOND DASH NUMBER DESIGNATES GRIP LENGTH, IN 1/32NDS CLOSEST TO NOMINAL GRIP.

   EXAMPLE: 67536-4-009 1/4-20 NS BOLT, .282 GRIP, .709 LONG.
7. A MAXIMUM EQUALS THEORETICAL MAXIMUM SHARP CORNER, MINIMUM IS ABSOLUTE MINIMUM WITH RADIUS.

TOLERANCES ± .010 AND 2° UNLESS OTHERWISE NOTED

STANDARDS AND SPECIFICATIONS	TITLE	DRAWN BY G.W.N. DATE 5-2-66
	BOLT, SPECIAL FLUSH HEAD	APPROVED R.T.S. DATE 5-2-66
CUSTODIAN: JENKINTOWN, PA.		PART NUMBER 67536

SSC REV. 668

Figure 8

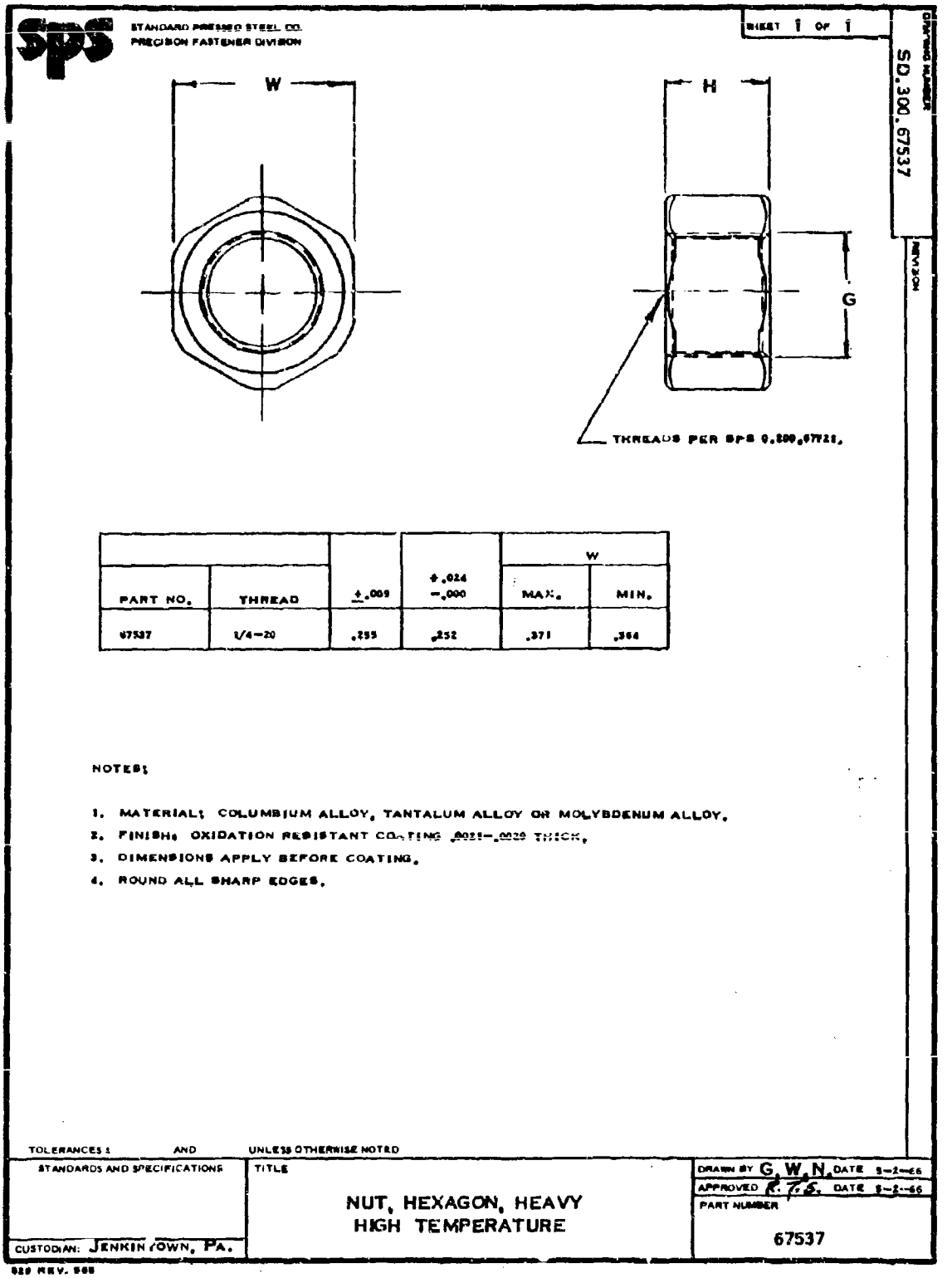
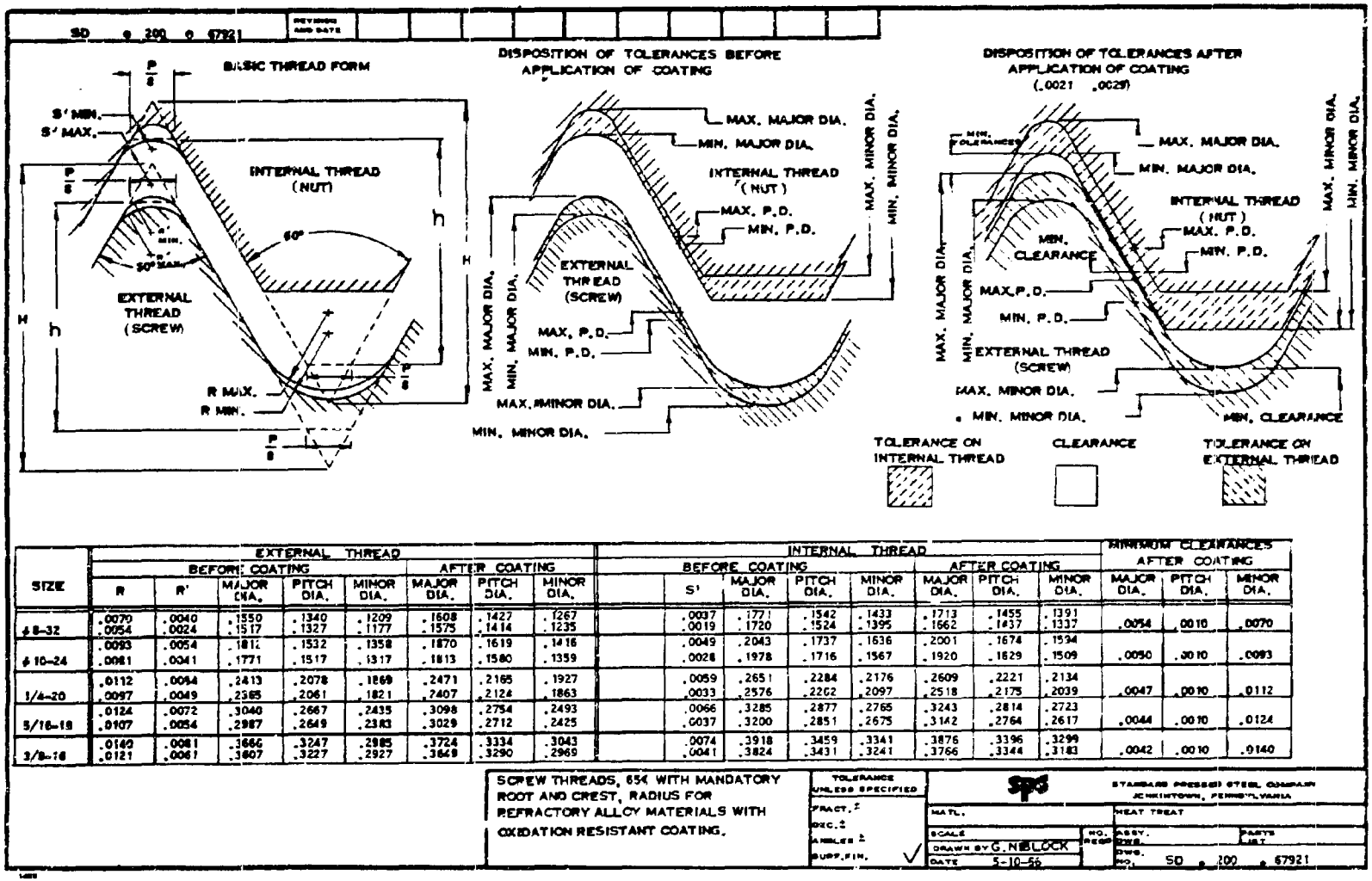

STANDARD PRESSED STEEL CO.
PRECISION FASTENER DIVISION
SHEET 1 OF 1
DRAWING NUMBER
SD.300.67537
REVISION
W
H
G
THREADS PER SPS 0.500.67721.
PART NO.
THREAD
±.009
+.024 −.000
W
MAX.
MIN.
67537
1/4-20
.255
.252
.371
.364
NOTES:
1. MATERIAL: COLUMBIUM ALLOY, TANTALUM ALLOY OR MOLYBDENUM ALLOY.
2. FINISH: OXIDATION RESISTANT COATING .0021-.0029 THICK.
3. DIMENSIONS APPLY BEFORE COATING.
4. ROUND ALL SHARP EDGES.
TOLERANCES ± AND UNLESS OTHERWISE NOTED
STANDARDS AND SPECIFICATIONS
TITLE
NUT, HEXAGON, HEAVY
HIGH TEMPERATURE
DRAWN BY G. W. N. DATE 8-2-66
APPROVED R. T. S. DATE 8-2-66
PART NUMBER
67537
CUSTODIAN: JENKINTOWN, PA.
SPS REV. 5/65

Figure 9



SIZE	EXTERNAL THREAD								INTERNAL THREAD							MINIMUM CLEARANCES AFTER COATING		
	BEFORE COATING					AFTER COATING			BEFORE COATING				AFTER COATING					
	R	R'	MAJOR DIA.	PITCH DIA.	MINOR DIA.	MAJOR DIA.	PITCH DIA.	MINOR DIA.	S'	MAJOR DIA.	PITCH DIA.	MINOR DIA.	MAJOR DIA.	PITCH DIA.	MINOR DIA.	MAJOR DIA.	PITCH DIA.	MINOR DIA.
#8-32	.0070 .0054	.0040 .0024	.1550 .1517	.1340 .1327	.1209 .1177	.1608 .1575	.1427 .1414	.1267 .1235	.0037 .0019	.1771 .1720	.1542 .1524	.1433 .1395	.1713 .1662	.1455 .1437	.1391 .1337	.0054	.0010	.0070
#10-24	.0093 .0081	.0054 .0041	.1812 .1771	.1532 .1517	.1358 .1317	.1870 .1813	.1619 .1580	.1416 .1359	.0049 .0028	.2043 .1978	.1737 .1716	.1636 .1567	.2001 .1920	.1674 .1629	.1594 .1509	.0050	.0010	.0093
1/4-20	.0112 .0097	.0064 .0049	.2413 .2365	.2078 .2061	.1869 .1821	.2471 .2407	.2165 .2124	.1927 .1863	.0059 .0033	.2651 .2576	.2284 .2202	.2176 .2097	.2609 .2518	.2221 .2175	.2134 .2039	.0047	.0010	.0112
5/16-18	.0124 .0107	.0072 .0054	.3040 .2987	.2667 .2649	.2435 .2383	.3098 .3029	.2754 .2712	.2493 .2425	.0066 .0037	.3285 .3200	.2877 .2851	.2765 .2675	.3243 .3142	.2814 .2764	.2723 .2617	.0044	.0010	.0124
3/8-16	.0140 .0121	.0081 .0061	.3666 .3607	.3247 .3227	.2985 .2927	.3724 .3648	.3334 .3290	.3043 .2965	.0074 .0041	.3918 .3824	.3459 .3431	.3341 .3241	.3876 .3766	.3396 .3344	.3299 .3183	.0042	.0010	.0140

SCREW THREADS, 65% WITH MANDATORY ROOT AND CREST, RADIUS FOR REFRACTORY ALLOY MATERIALS WITH OXIDATION RESISTANT COATING.

TOLERANCE UNLESS SPECIFIED
FRACT. ±
DEC. ±
ANGLES ±
SURF. FIN. √

SPS STANDARD PRESSED STEEL COMPANY JENKINTOWN, PENNSYLVANIA

MATL. HEAT TREAT
SCALE NO. RECD
DRAWN BY G. NEBLOCK
DATE 5-10-56
ASSY. PARTS LIST
DWG. NO. SD • 200 • 67921

Figure 10

SECTION VI

COATING DEVELOPMENT

A. DESCRIPTION OF THE ELECTROPHORETIC PROCESS

Electrophoresis is defined as the movement of charged particles through a liquid medium under the influence of an applied electric field. The phenomenon was first observed as early as 1809 and received much theoretical attention during the years 1920 - 1940 (2-5).

With the exception of recently developed electrophoretic painting and enameling processes, however, commercial applications were confined mainly to the electron tube industry (6, 7). Excellent review articles covering the theory (8) and a variety of applications of this technique (9, 10) are available in the literature.

Electrophoretic dispersions used by Vitro for coating would be classified as lyophobic sols by the colloid chemist; that is, they are dilute suspensions of fine particles in a fluid medium and the stability of the suspensions against flocculation is governed primarily by the concentration of electrolyte or polar additive (i.e. zein) which is present in the bath. The major difference between the coating baths used by Vitro and the more familiar aqueous suspensions is that the coating materials are dispersed in a non-aqueous medium (usually isopropanol-nitromethane) instead of in water. The dielectric constant of the alcoholic medium is reduced to approximately 20 as compared to 80 in water. The non-aqueous medium is preferred for electrophoretic deposition since high coating rates are attained at moderate voltages without the formation of gas bubbles at the specimen surface as would be observed in water.

In common with aqueous sols, electrophoretic suspensions are stabilized by coulombic repulsion between the suspended particles arising from the presence of a charged double layer at the surface of each particle. The charge arises from adsorption of the cations (produced by the added electrolyte) upon the dispersed particles, and the double layer is formed by alignment of the electronegative end of the "solvent" molecules and/or the ions in solution with the fixed, adsorbed, ionic charges. The double layer is therefore similar to a capacitor with the fluid medium acting as the dielectric. The reduced dielectric constant of the alcoholic medium with respect to water will therefore lower the charge density at the particle surfaces, and, in media of extremely low dielectric constant (such as benzene), stabilization of the dispersion may be impossible. An additional refinement which must be added to this model is that one plate of the microscopic capacitor, namely the counterions formed by the dissolved ions and/or solvent molecules, is mobile rather than fixed, due to diffusional effects arising from thermal agitation of the liquid molecules. The double layer is therefore somewhat diffuse and the potential within the double layer decreases gradually with increasing distance from the surface of the particles. The potential which

exists between the fixed adsorbed surface charges on the particles and the shear plane of the diffuse double layer is termed the zeta potential (Z).

A widely accepted theory due to Stern (14) gives the mobility (U) of a dispersed particle as a function of the applied field (E), zeta potential (Z), and dielectric constant (D) and viscosity (n) of the fluid medium as follows:

$$U = \frac{ZED}{4\pi n}$$

In a medium of specified n and D, therefore, the mobility (coating rate) is directly proportional to the applied field and to the zeta potential and essentially independent of particle shape, size, and composition. The principal advantages of the electrophoretic coating technique are:

1. Flexibility with respect to coating materials to be deposited.

2. Efficient utilization of coating materials and rapid deposition rates.

3. Excellent dimensional uniformity and coverage of irregular surfaces.

To form an electrophoretic deposit, the coating materials are prepared in the form of a fine powder and, if more than one component is desired in the coating, the individual powders are weighed in the required proportion and blended. For most common coating materials the powders are commercially available. If a finer particle size is desired, the powders are ball-milled in alundum, steel, or silicon carbide-lined jars. The powder mixture is then added to a mixture of isopropanol and nitromethane. The powders generally acquire a static surface charge during ball-milling and a charge may also be induced on the particle surfaces by the addition of certain protein-like proprietary additives. The resulting dispersion is therefore stabilized by electrostatic repulsion of the charged particles. The dispersion concentration is generally maintained between 2 and 10 wt. %, depending upon the coating rate which is required. The coating equipment consists of a stainless steel tank with an overflow at the top and an opening at the bottom. The dispersion is agitated by a recirculating pump whose exhaust is connected to the bottom of the coating tank. The tank serves as an inert electrode and the article to be coated is the second electrode. The electrodes are connected to a D.C. rated power supply and an external timer which cuts off the power after a set interval. Coating is accomplished at 20-200 V.D.C. and about 5-20 ma for 0.25-5 minutes depending upon the coating thickness which is desired. After coating, the article is dried in air or under an infra-red lamp and, if the point of electrode contact must also be coated, this area is manually "patched" by applying some of the powdered material of the dispersion with a rounded tool. The coating, at

this point, is about 40% dense and has considerable green strength, however, it is not yet bonded to the substrate or fully densified. To increase the density and strength of the green coating, the article may then be hydrostatically pressed at 10,000 - 100,000 psi. The coating is then sintered or hot-pressed to increase its density and to bond it to the substrate. It is here that the most variability is encountered in the process. The sintering time, temperature, and atmosphere must be adjusted to the properties of the coating-substrate system. Following sintering, the coating is evaluated by microscopic inspection of the surface and of sections through the specimen, and physical and chemical measurements such as density, porosity, mechanical properties, chemical uniformity, and oxidation or abrasion resistance are made.

B. PREPARATION OF THE Cr-Ti-Si COATING BY ELECTROPHORETIC DEPOSITION

On the basis of the survey (Section III), the TAPCO Cr-Ti-Si coating was chosen for application to columbium-base alloy structural fasteners by means of the electrophoretic technique. This coating, which is applied by TAPCO by a two-step vacuum pack cementation process, consists of a diffusion barrier (approximately 0.5 mil thick) of $(TiCb)Cr_2$ plus a second layer which contains a complex mixture of the silicides of chromium, columbium and titanium. The major phases present in the silicide layer and their relative concentrations are not known with certainty but are believed to be mixed phases of the M_3Si and M_5Si_3 type (11).

1. Preliminary Experiments

In this study two approaches were examined to adapt the TRW Cr-Ti-Si vacuum pack cementation coating to the electrophoretic coating process. In the first approach, based upon discussions with TAPCO, chromium was electrophoretically deposited upon a columbium alloy and heat treated to form a 0.5 mil thick diffusion barrier of $CbCr_2$ which was then overcoated with a 2 mil-thick outer layer of 75% $CrSi_2$-25% $TiSi_2$. The second approach was a 2-step procedure involving the deposition and sintering of prealloyed chromium titanium powder, followed by siliconization of the diffused Cr-Ti layer.

The $CrSi_2$ and $TiSi_2$ powders used for the first approach were purchased from Shieldalloy Corporation, and the chromium powder from M & R Refractory Metals, Inc.

Two $75CrSi_2$-$25TiSi_2$ coating dispersions were prepared by mechanical blending of the individual powders and by presintering weighed portions of the two powders at 2550°F to form a single phase solid solution which was then reground.

Then 0.0025 inch thick coatings were deposited from each of the dispersions on chromized Cb-752 panels. The coated panels were hydrostatically pressed at 30 tsi and sintered in purified argon for 15 minutes and one hour at 2500°F. All of the coatings interacted with the chromized substrates to form rough, uneven deposits. This interaction was particularly severe with the mechanically blended powders and was less serious when the presintered materials were used. Three specimens prepared from the prealloyed powders yielded lives of 16, 17, and 24 hours at 2500°F in static oxidation. This approach to the preparation of the Cr-Ti-Si coating was then abandoned in favor of a 2-step procedure involving the codeposition and sintering of chromium and titanium metal powders followed by siliconizing of the diffused Cr-Ti layer.

The Cr-Ti layer was formed by electrophoretic deposition from a dispersion containing 43% chromium and 57% titanium. The metal powders were either mixed directly or were prealloyed at 2550°F for one hour in pure argon prior to deposition. The as-deposited coatings were initially isostatically pressed at 20 tsi and then sintered in argon for one hour at 2460° - 2550°F (prealloyed powders) or 2370° - 2505°F (mixed powders). The prealloyed powders fired at 2460°F were well sintered and bonded to the substrate, while the same coatings fired above 2460°F blistered and flowed. The coatings prepared from the mixed Cr-Ti powders exhibited erratic sintering characteristics and these experiments were discontinued. Siliconization was accomplished by either setting the coated sample in a bed of silicon powder plus various activators, or by electrophoretically depositing silicon upon the sintered Cr-Ti layer and sintering in an activated bed or in a moderate vacuum with no activator present. A summary of many of the experimental conditions and results is listed in Table V. The C-129Y alloy was used for these tests.

In a series of experiments of this type an optimum procedure was developed utilizing the prealloyed 43Cr-57Ti powder. The prealloyed material was deposited and sintered without pressing for one hour at 2550°F in argon. Then an electrophoretic silicon coating was deposited and heat treated for 2 hours at 2450°F at a pressure of 0.1 torr. The characteristics of the Tapco pack Cr-Ti-Si coating, the electrophoretic Cr-Ti-Si coating, and the electrophoretic Cr-$MoSi_2$ coating are compared in Table VI.

The electrophoretic and pack methods for producing the Cr-Ti-Si coating differ mainly in the technique of application and in the fact that the electrophoretic coating is heat treated at a higher temperature, higher pressure, and for a shorter time than the pack coating.

Metallographs of the Vitro Cr-Ti-Si coating on D-36 sheet and of the Tapco coating on D-43 sheet are shown in Figures 11 and 12. The similarity of the structure of the two coatings and of the microhardness of the outer silicide layers is readily apparent. The major difference between the two coatings is that the substrate coated by electrophoresis is recrystallized while the sample coated by pack cementation is not. This difference occurs due to the higher temperature used to sinter the electrophoretic coating.

A series of Cb-752 and C-129Y samples were coated with a nominal 2.5 mil thick Cr-Ti-Si coating according to the procedure described in Table VI and the specimens were tested for oxidation resistance at 2500°F in one atmosphere of convective air. Fairly consistent oxidation lives in excess of 30 hours were achieved on panel and on bolt specimens as shown in Table VII, but the life of the coated nuts was greatly reduced. A study was then made of the effect of siliconization time upon the reliability of the coating.

TABLE V

SILICONIZING OF Cr-Ti COATINGS ON COLUMBIUM C-129Y ALLOY

Cr-Ti Coating Type	Siliconizing Method	Bed Composition	Temperature °F	Temperature °C	Time (hr.)	Atmosphere	Remarks
Prealloyed	Bed	Al_2O_3-25Si	2552	1400	1	Argon	Rough coating
Prealloyed	Bed	Al_2O_3-25Si	2462	1350	1	Argon	Rough coating
Prealloyed	Bed	Al_2O_3-25Si	2372	1300	1	Argon	No reaction
Prealloyed	Bed	Si-5NaCl	2372	1300	1	Argon	Coating rough and blistered
Prealloyed	Bed	Si-5NaCl	2192	1200	1	Argon	Coating rough and blistered
Prealloyed	Bed	Si-5NaCl	2012	1100	1	Argon	Coating rough and blistered
Prealloyed	Bed	50BN-48Si-2NaCl	2372	1300	1	Argon	Coating rough and blistered
Prealloyed	Bed	50BN-48Si-2NaCl	2192	1200	1	Argon	Coating rough and blistered
Prealloyed	Bed	50BN-48Si-2NaCl	2012	1100	1	Argon	Coating rough and blistered
Prealloyed	Electrophoretic coating	Al_2O_3-5NaCl	2372	1300	1	Argon	Surface smooth, edges rough
Prealloyed	Electrophoretic coating	None	2372	1300	1	0.1 mm vac.	Rough edges

TABLE VI

COMPARISON OF PACK AND ELECTROPHORETIC COATINGS FOR COLUMBIUM BASE ALLOYS

	Tapco "D"	Vitro Cr-$MoSi_2$	Vitro Cr-Ti-Si
Coating constituents	Cr-Ti, Si	Cr-$MoSi_2$	Cr-Ti, Si
Coating method	Pack cementation	Electrophoresis	Electrophoresis
Procedure			
1) Clean	Degrease and sandblast	Degrease and sandblast	Degrease and sandblast
2) Cycle 1 materials	Prealloyed 60 Cr-40 Ti + 0.4% KF	67 Al_2O_3-33 Cr	Prealloyed 43 Cr-57 Ti
3) Cycle 1 conditions	8 hours, 2250°F (1232°C) 0.01 - 0.05 Torr	3 hours, 2500°F(1371°C) in argon at 1 atm.	1 hour, 2450°F (1343°C) in argon at 1 atm.
4) Cycle 2 materials	Si + 4% KF	$MoSi_2$	Si
5) Cycle 2 conditions	4 hours, 2050°F (1121°C) 0.01 - 0.05 Torr	Press 30 tsi Sinter 1 hour, 2550°F (1399°C) in argon at 1 atm.	6 hours 2370°F (1299°C) 0.1 Torr

2. Effect of Siliconizing Time on the Oxidation Resistance of the Electrophoretic Cr-Ti-Si Coating

In the siliconizing experiments, C-129Y panels were coated with the 43Cr-57Ti composition as before, and then siliconized for 4, 6, and 8 hours. The completed panels were then oxidation tested in convective air at 2600°F. The results are summarized in Table VIII. Although no increase in life was noted when the siliconization time was increased from 4 to 6 or 4 to 8 hours, there was much less scatter in the results, and the minimum life of 25 hours at 2600°F for the 6 hour siliconization was felt to be a considerable improvement over the 30 hours at 2500°F for the 2 hour siliconization time.

Photomicrographs of the Cr-Ti-Si coating on C-129Y panels were made after siliconization times of 2, 4, 6, and 8 hours. The photographs, indicating the relative coating depth and microhardness of the various specimens, are shown in Figure 13. When the siliconization time was increased from 2 hours to 4 hours, both the depth of the coating layer and its microhardness increased significantly. Further increase in siliconization time resulted in only minor changes in the hardness and thickness of the coating. The results indicated that only partial siliconization was achieved in two hours. In subsequent experiments to investigate the effect of variation in the composition of the Cr-Ti layer, the siliconization time was therefore held constant at 6 hours.

3. Effect of Composition of the Cr-Ti Layer on the Oxidation Resistance of the Electrophoretic Cr-Ti-Si Coating

The effect of the Cr-Ti coating composition on the oxidation life of the Cr-Ti-Si coating system was investigated briefly, with emphasis on a composition having a higher chromium content. On the basis of analytical data reported by Tapco for its Cr-Ti-Si coating, it was decided to examine a 65 Cr-35 Ti composition.

Six C-129Y specimens (1-1/2" x 1/2" x 0.020") were tumbled, sandblasted, and electrophoretically coated with prealloyed 65 Cr-35 Ti. The coated specimens were densified at 10 tsi and sintered in argon at 2550°F for 1 hour. The Cr-Ti coated specimens were then electrophoretically coated with silicon and heat treated at 2370°F for 6 hours under reduced pressure (<0.1 mm). The overall coating thickness on all specimens was 2.75 mils.

Table IX lists the oxidation resistance of the six coated specimens at 2600°F in convective air. No increase in protective life was noted over the previously used 43 Cr-57 Ti composition, and all coatings exhibited edge failure.

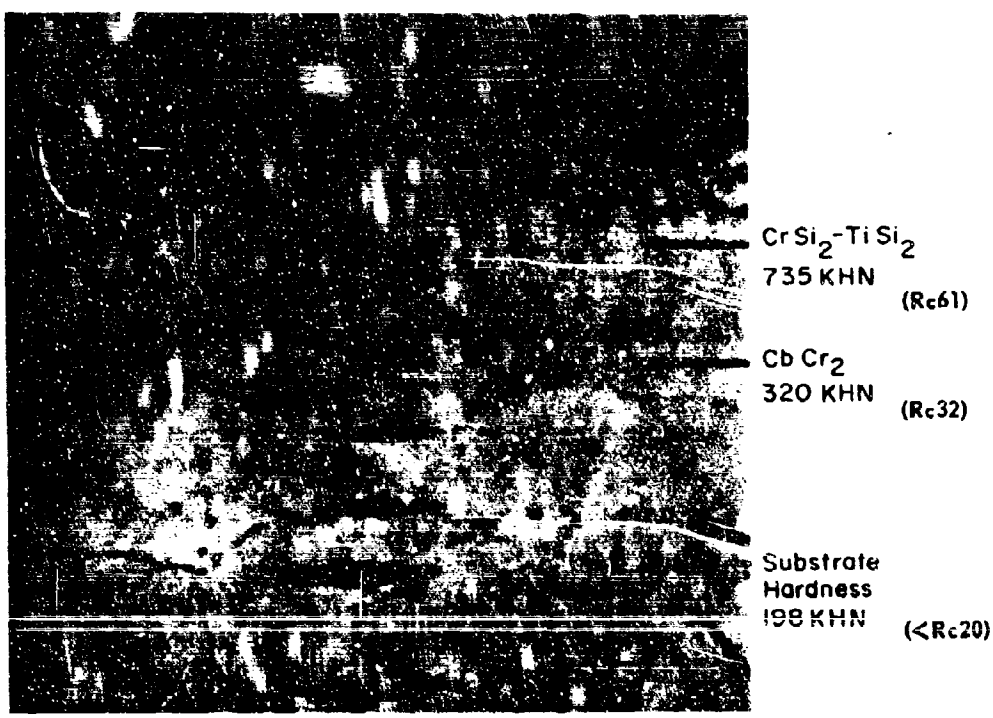


Figure 11. Vitro Cr-Ti-Si Coating on D-36 Sheet (unetched)

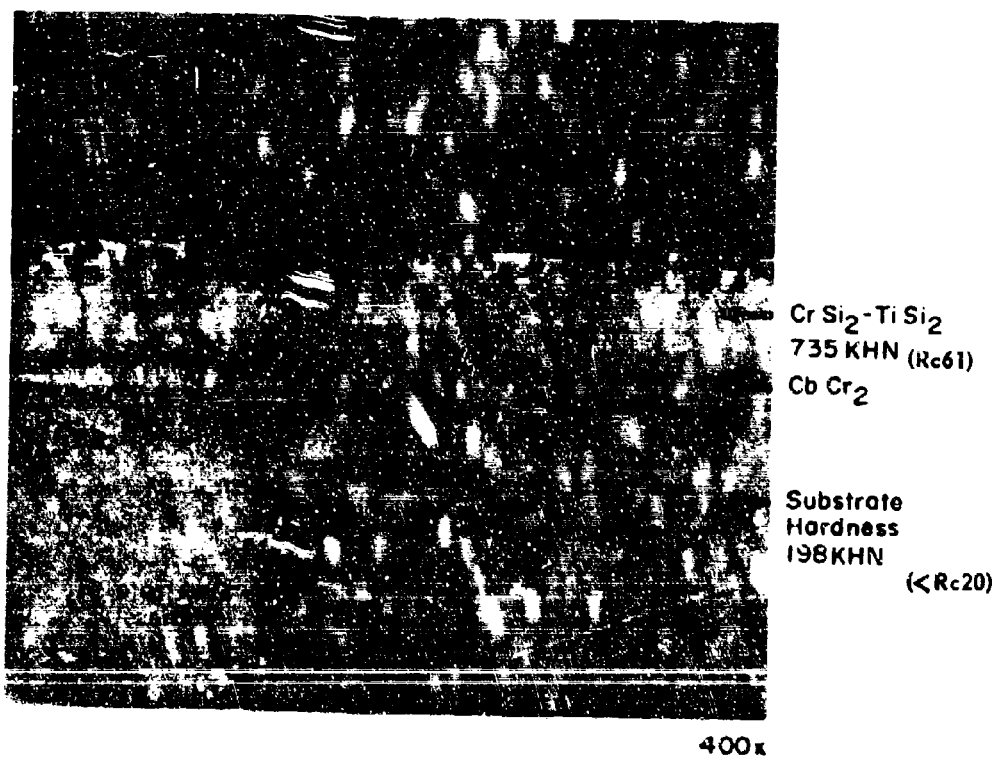


Figure 12. TRW-Coated D-43 Sheet (unetched)

TABLE VII

OXIDATION LIFE AT 2500°F (1371°C) OF VITRO Cr-Ti-Si COATED Cb-752 AND C-129Y SAMPLES (2 HOUR SILICONIZATION)

Type of Specimen	Oxidation Life (hrs.)*	Type of Failure
Cb-752 Panel	49-113 53-116	Completely oxidized Completely oxidized
C-129Y Panel	49-113 96	Completely oxidized Edge failure
Cb-752 1/4-20 Bolt	30-45 30-45	Completely oxidized Completely oxidized
Cb-752 1/4-20 Nut	17	Surface failure at edge of hex

*Where a range is given, the specimen failed overnight or during the weekend.

TABLE VIII

SILICONIZING TIME vs. OXIDATION LIFE OF VITRO Cr-Ti-Si COATED C-129Y AT 2600°F (1427°C) IN AIR

Spec. No.	Siliconizing Time (hrs.)	Oxidation Life (hrs.)	Remarks
1	4	23.5	Failed at edges
2	4	25-32	Failed at edges
3	4	25-32	Failed at edges
4	6	31.5	Failed at corner
5	6	25-32	Failed at edges
6	6	25-32	Failed at edges
7	8	32.5	Failed at edges
8	8	25-32	Failed at edges
9	8	25-32	Failed at flat surface

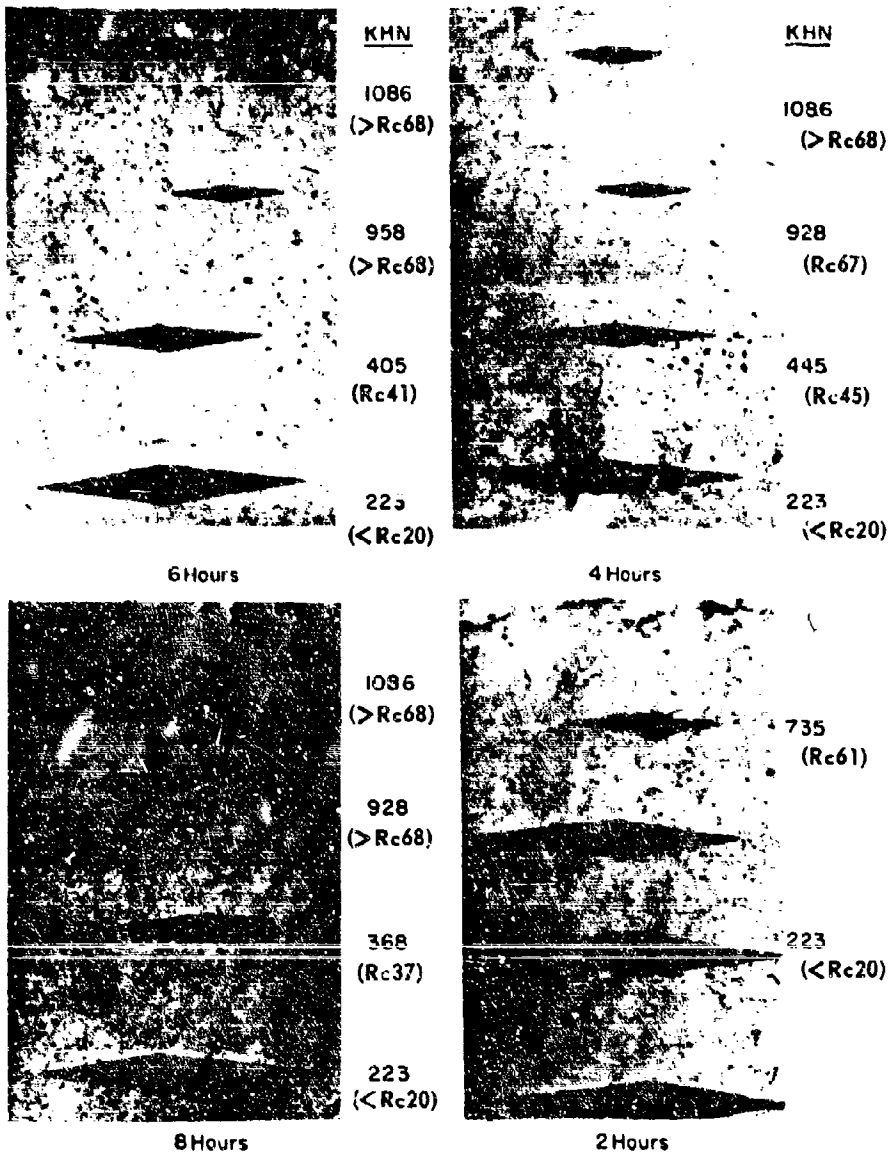


Figure 13. Effect of Time of Siliconization on Structure of Cr-Ti-Si Coating on C-129Y Alloy

(Magnification 800X, Knoop Hardness Values at 50 Gram Load Siliconization Conditions 2372°F (1300°C) at <0.1 Torr Pressure)

TABLE IX

OXIDATION LIFE OF 65 Cr-35 Ti-Si COATINGS ON C-129Y AT 2600°F (1427°C) IN AIR

Spec. No.	Oxidation Life (hrs.)	Remarks
1	27	Coating failed at edges
2	27	Coating failed at edges
3	27	Coating failed at edges
4	27	Coating failed at edges

4. Bend and Impact Tests of Cr-Ti-Si Coated Cb-752 Specimens

Following initial processing studies on the Cr-Ti-Si coating, a set of eight Cb-752 bend test specimens (2" x 1/2" x 0.030") were coated with Cr-Ti-Si to a thickness of 2.5 ± 0.4 mil as follows:

a. Tumble bend test specimens in porcelain mill for 24 hours in water to round off corners and edges. The Charpy specimens were not tumbled.

b. Sandblast all specimens with No. 60 grit alumina.

c. Wash with water and degrease with acetone.

d. Electrophoretically deposit prealloyed 43 Cr-57 Ti powder.

e. Sinter Cr-Ti coating at 2500°F for one hour in certified argon.

f. Electrophoretically deposit silicon coating.

g. Heat treat at 2370°F for two hours under reduced pressure (<0.1 torr).

h. Brush off excess silicon.

The results of the bend tests on the electrophoretically coated specimens and on a set of specimens pack-coated by Tapco indicated no difference in ductility due to the method of application of the Cr-Ti-Si coating. This comparison is described in Section X.

C. DEVELOPMENT OF AN ELECTROPHORETIC Si-WSi_2 COATING FOR TANTALUM ALLOY THREADED FASTENERS

It was concluded from the survey (Section III) that the W-Si coating system represented the best state-of-the-art prospect as a useful coating for tantalum alloy fasteners for use to temperatures of 3200°F. This coating system was therefore recommended to and approved by the Air Force Project Engineer.

Two basic approaches were decided upon for application of the W-Si coating to tantalum alloy substrates, namely: (a) a two-cycle W-Si system comprising sintering of an electrophoretically deposited tungsten coating followed by a siliconization treatment, and (b) a single-cycle WSi_2 coating consisting of depositing and sintering WSi_2 powders. The following section describes the experimental effort in these areas.

1. Two-Cycle W-Si Coating on Ta-10W and T-222 Alloy

For this investigation Ta-10W and T-222 alloy sheet was purchased from the National Research Corporation and the Wah Chang Corporation, respectively. The Ta-10W was obtained as annealed sheet, 0.020 inch thick, and the T-222 as 0.040 inch sheet. Tungsten metal powder was purchased from Sylvania with an average particle size of 0.8-1.1 microns.

In preliminary coating experiments, it was found that good adherence to Ta-10W could not be obtained when a densified (5 tsi) or undensified tungsten coating was simultaneously siliconized and sintered at 2370°F for times up to 16 hours in vacuum. After 16 hours, however, the coating was hard and dense and the substrate remained ductile.

To improve adherence, the procedure was modified so that the tungsten deposit was first dipped in a saturated solution of $Ni(NO_3)_2$ in isopropanol, then densified at 10 tsi and sintered in argon for one hour at 2370°F. The resultant coating, which was adherent, was then siliconized for three hours at 2370°F in vacuum. Under these conditions the WSi_2 coating adhered to the Ta-10W, but the substrate became embrittled. The experiment was then repeated, using half the concentration of the saturated nickel solution, and increasing the tungsten sintering temperature to 2550°F (1400°C) and the siliconizing time to 16 hours. A photomicrograph of this sample is shown in Figure 14. The photomicrograph indicates almost complete siliconization of the tungsten coating (based upon the microhardness traverse) and a slight increase in the hardness of the substrate from 235 kg/mm^2 (as-received) to 326 kg/mm^2 (heat treated and coated). Photomicrographs of a Ta-10W coupon after coating with tungsten and molybdenum by the nickel-dip procedure, pressing at 10 tsi, and sintering for 1 hour at 2550°F in argon are shown in Figure 15 together with uncoated Ta-10W coupons which underwent the same heat treatment. The uncoated coupons increased in hardness to 323

kg/mm^2 after heat treatment and, after coating with molybdenum and tungsten, evidenced an additional increase to 351 and 388 kg/mm^2, respectively.

In order to maintain ductility in the Ta-10W substrate, the nickel content of the coating was reduced by dipping the as-deposited coatings in $Ni(NO_3)_2 \cdot 6H_2O$-isopropanol solutions ranging in concentrations from 5% to 25%. In all cases the substrate became embrittled when fired at 2550°F for 2 hours in argon. Moreover, at the lower nickel concentration (5%) the tungsten coatings exhibited decreased adherence.

In another approach to the adherence problem, sandblasted Ta-10W specimens were chemically cleaned in a 3:1:1 volume ratio of Lactic acid-HNO_3-HF solution for 5 minutes, rinsed, dried, and subsequently coated electrophoretically with tungsten or with molybdenum without nickel-activation. The as deposited coatings were densified at 10 tsi and fired at 2550°F for 2 hours in argon. The resultant coatings were adherent, and the substrate remained ductile yielding a hardness value of 322 kg/mm^2 which is identical to the value obtained on an uncoated Ta-10W substrate that was heat treated in the same manner. Photomicrographs of typical samples are shown in Figure 16.

On the basis of these results a series of experiments were then conducted in order to optimize the tungsten coating procedure with respect to sintering time and densification pressure. Densification pressures of 10 tsi and 20 tsi, and sintering times of 2 hours, 4 hours, and 6 hours were investigated. The results indicated that a densification pressure of 20 tsi and a sintering time of 2 hours are optimum. As shown in Figure 17, the porosity of the tungsten coating decreased considerably when the densification pressure was increased from 10 to 20 tsi. After densification at 20 tsi, no further decrease in porosity was noted when the sintering time at 2550°F was increased from 2 hours to 6 hours. Photomicrographs of samples prepared under these conditions are shown in Figure 18.

Coatings of W-Si were then applied to 40 mil T-222 coupons according to the following procedure:

a. Substrate Preparation. Prior to coating, the T-222 specimens were tumbled in an alumina mill containing Burundum cylinders and water. This operation rounded off all sharp edges and corners. The panels were then sandblasted using #60 grit aluminum and finally chemically cleaned in a 3:1:1 volume ratio of Lactic acid-HNO_3-HF for 5 minutes, rinsed, and dried.

b. Tungsten Coating on T-222. Tungsten coatings were electrophoretically applied to T-222 specimens to a green thickness of 4.5 mils.

Microhardness 235kg/mm^2
(50g Load) (<Rc20)

To-10W (As Received)

Silicon-Rich Phase

Silicided Tungsten Coating
Hardness 1011kg/mm^2 (>Rc68)
(50g Load)

To-10W Substrate
Hardness 326kg/mm^2 (Rc33)
(50g Load)

Unetched 520x

Figure 14. Ta-10W (As Received) and After Coating with Ni-Activated Tungsten and Siliconizing 16 Hours at 2370°F (1300°C)

(W Sintering Conditions, Press at 10 tsi, Sinter 1 Hour at 2550°F, 1400°C, in Argon)

Heat-Treated, But Uncoated
Ta-10W Substrate

Hardness = 323 kg/mm^2 (50g-Load)
(Rc33)

Unetched 250x

Molybdenum Coating

Ta-10W Substrate
Hardness = 351 kg/mm^2 (50g Load)
(Rc35)

Unetched 250x

Sintered Tungsten Coating

Ta-10W Substrate
Hardness = 388 kg/mm^2 (50g-Load)
(Rc40)

Unetched 250x

Figure 15. Nickel-Activated Molybdenum Coated and Tungsten Coated Ta-10W

(Sintering Conditions, Press at 10 tsi, Sinter 1 Hour at 2550°F, 1400°C, in Argon)

322 kg/mm^2 (Rc33)
(50 gm Load)

W Coating on Ta-10W Unetched, 250x

322 kg/mm^2 (Rc33)
(50gm Load)

Mo Coating on Ta-10W 250x

Figure 16. Tungsten and Molybdenum Coatings on Sandblasted and Chemically Cleaned Ta-10W

Densification
Pressure 10 t si

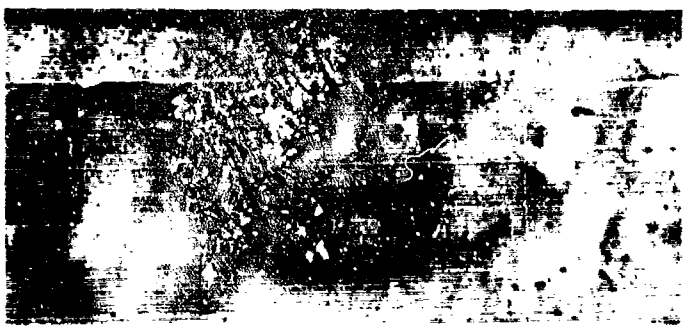
Unetched, 250x

Densification
Pressure 20 t si

Unetched, 250x

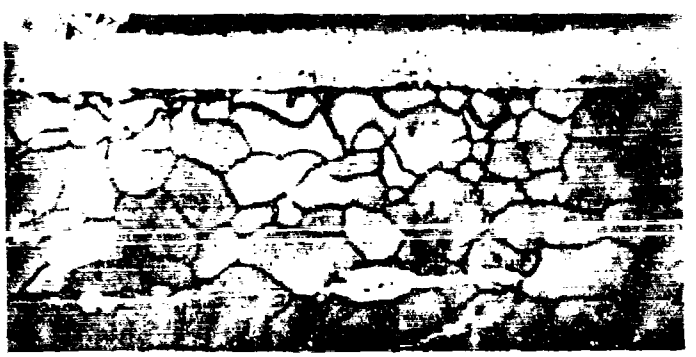
Figure 17. Effect of Densification Pressure on Porosity of W-Coated Ta-10W

(Samples Sintered 2 Hours at 2550°F, 1400°C, in Argon)



1400°C
2 Hrs-Argon

Unetched, 250x



1400°C
6 Hrs-Argon

250x

Figure 18. Effect of Sintering Time on W-Coated Ta-10W, Densified at 20 TSI

(This as-deposited thickness yielded a 3.0 mil siliconized coating.) The as-deposited coatings were densified at 20 tsi and fired in argon for 3 hours. This treatment produced a sintered coating that was adherent but somewhat porous. The substrate retained its ductility, yielding a Knoop microhardness value of 351 kg/mm^2 for the as-received T-222.

c. Siliconization of W Coated T-222. Siliconization of the W coating was carried out by electrophoretically depositing approximately 10 mil thick (green) silicon coatings, followed by heat treatment at 2370°F for 16 hours under reduced pressure (<0.1torr). The coated specimens were ductile and completely siliconized. Some porosity was also noted in the coating. Hardness values of 1011 kg/mm^2 and 351 kg/mm^2 were obtained on the coating and substrate respectively, near the coating-substrate interface. Photomicrographs of the specimen at various stages of coating preparation are shown in Figure 19.

2. Oxidation Tests of the W-Si Coating on Ta-10W and T-222 Alloy

Several specimens of the W-Si coating system on 20 mil thick Ta-10W and 40 mil thick T-222 alloy substrates were tested for oxidation resistance at 2700° and 3000°F under static conditions. The results of these tests are listed in Table X. Oxidation lives ranging from 0.2 to 6.5 hours were realized. All of the specimens except one exhibited corner or edge failure. A typical corner failure is shown in Figure 20.

The results of this experiment also indicated that utilization of the thicker T-222 substrates did not improve the edge or corner performance of the W-Si coating at 2700°F over that obtained with 20 mil coupons.

In examining the corner failures in these early experiments, it seemed likely that the failures were, to some extent, attributable to the absence of glass formation and self-healing at 2700°F. Visual examination showed very little glass formation even after long exposure at 2700°F.

In subsequent oxidation tests performed at 3000°F, a considerable amount of glass formation was noted, however, the glass was quite fluid at 3000°F and this led to premature deterioration of the coating.

According to TRW this might be expected, since direct siliciding of tungsten yields a silicon-rich WSi_2 phase which forms the low melting (3100°F-3200°F) SiO_2 upon oxidation. On the other hand, TRW found that by using a W-Si pack as a siliciding medium a coating is obtained that is deficient in silicon and which forms a higher melting oxide (perhaps $W_2Si_2O_7$)upon oxidation. Therefore, in an attempt to decrease

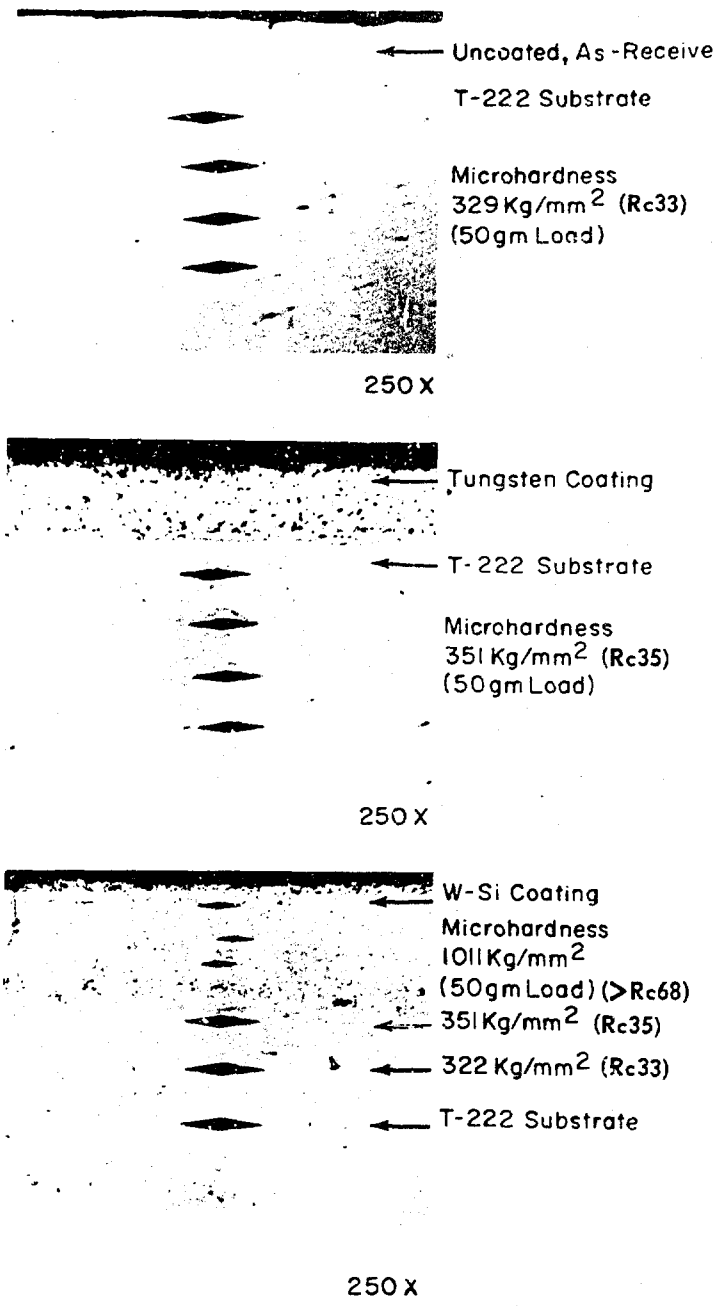
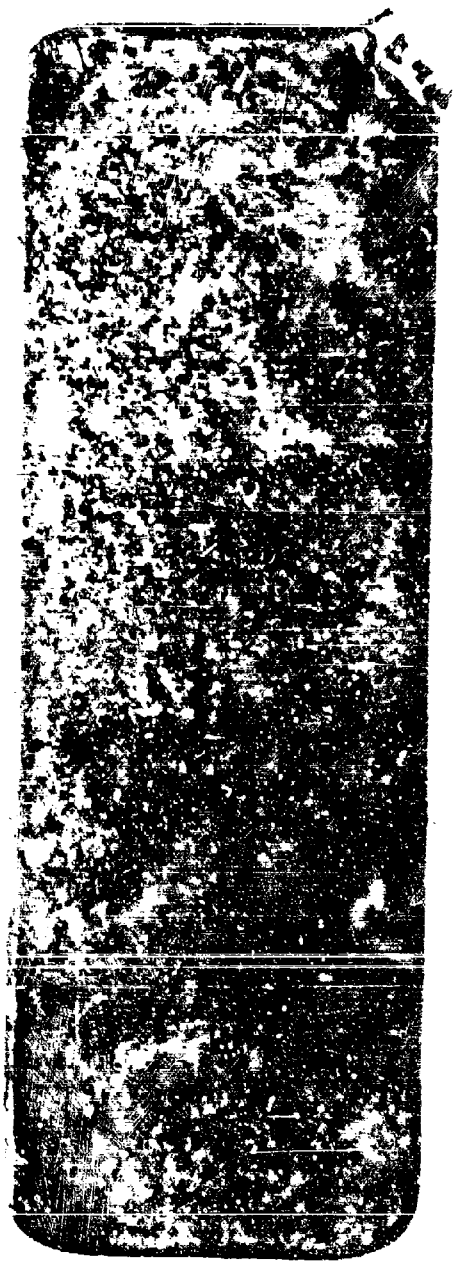


Figure 19. Tungsten Coated and Tungsten-Silicon Coated T-222 Alloy



Magnification 5 x

Figure 20. Typical Edge Failure of 0.020 Ta-10W, Coated with 2.5 Mils of W-Si (Exposed 130 Minutes at 2700°F, 1482°C, in Static Air)

the fluidity of the glass formed during oxidation at 3000°F, several coatings were prepared on Ta-10W which were expected to be deficient in silicon. These partially silicided W-Si coatings were prepared as described previously, however, the time of siliconization at 2370°F was reduced from 10 hours to 6 hours. Partial siliconization was obtained by this procedure as indicated by the microhardness of this coating (shown in Figure 21) as compared to the fully-siliconized tungsten coating shown in Figure 19. Unfortunately, however, the partially silicided coatings had considerably less oxidation resistance than the fully silicided specimens, and failed at the edges and on the surface in 1-2 minutes at 3000°F in air.

Since little promise was evidenced by the oxidation test data of the electrophoretic W-Si coating, this system was abandoned in favor of the direct electrophoretic deposition of WSi_2. Work on this system is described in the next section.

3. Si-WSi_2 Coatings on Ta-10W and T-222 Alloy

Previous experience with $MoSi_2$ coatings on TZM alloy and with coatings such as Cr-$MoSi_2$ for columbium alloys indicated that direct electrophoretic deposition of an intermetallic compound such as WSi_2, or $MoSi_2$ usually provides a coating with better oxidation resistance than a coating of mixed composition formed by siliconization of molybdenum or tungsten metal. For this reason experiments were conducted on the direct coating of Ta-10W with the compound WSi_2.

The raw material used was a commercial-325 mesh powder obtained from Shieldalloy. The relatively coarse powder was ball-milled for 48 hours to reduce its average particle size, and the milled product was then acid leached, washed with distilled water, and dried.

Initially, approximately 3 mil coatings were formed on Ta-10W by isostatically densifying the green deposit at 30 tsi and sintering in argon for 2 hours at 2550°F. Considerable fuming was noted when these specimens were inserted in an air furnace at 3000°F, and failure occurred in 10-15 minutes, thus indicating the presence of uncombined tungsten in the coating. The next coating, which was 1 mil thick after processing, was therefore embedded in silicon and fired for an additional hour at 2460°F in order to silicide the free tungsten. This coating survived 30 minutes at 3000°F and then failed at the surface. Two specimens were then coated to a thickness of 2.7-3.0 mils and sintered for a total of 3 hours (1 hour in silicon). This procedure resulted in only slight improvement in oxidation life. These samples survived 95 minutes and 150 minutes at 3000°F before surface failure was noted. Photomicrographs of these specimens after oxidation are shown in Figures 22 and 23 and Table XI summarizes the test results.

Figure 21. W-Si Coating on Ta-10W After Partial Siliconization for 6 Hours at 2370°F, (1300°C)

296 kg/mm^2 (50gm Load
(Rc29)

296 kg/mm^2 (50gm Load)
(Rc29)

400 x

Figure 22. WSi_2 Coating on Ta-10W Exposed 30 Minutes at 3000°F (1650°C) in Static Air

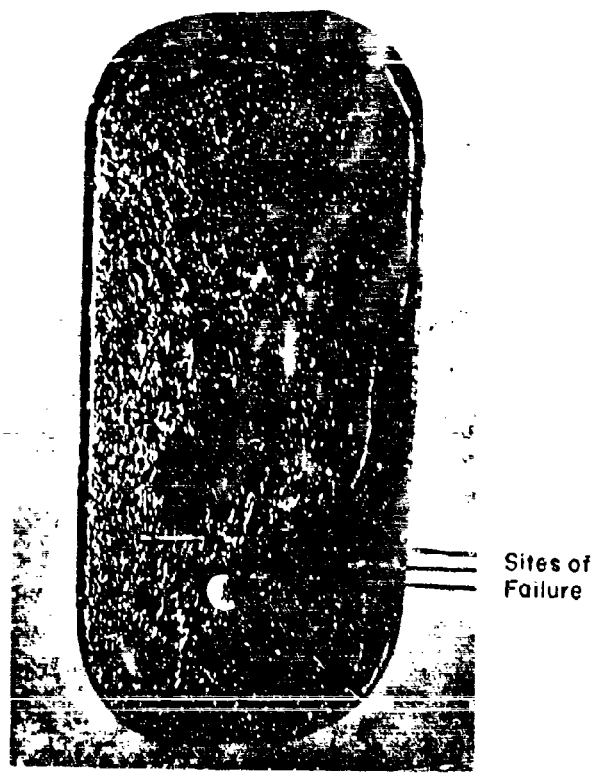


Figure 23. WSi_2 Coated Ta-10W Exposed 30 Minutes at 3000°F (1650°C) in Air

TABLE X

STATIC OXIDATION LIFE OF W-Si COATING ON Ta-10W AND T-222 AT 2700°F (1482°C) AND 3000°F (1650°C)

Spec. No.	Coating System	Substrate	Oxidation Life at 2700°F (1482°C)(hrs.)	Oxidation Life at 3000°F (1650°C)(hrs.)	Area of Failure
1(1)	W-Si	Ta-10W	1.0	-	Corner
2(1)	W-Si	Ta-10W	0.5	-	Corner
3(1)	W-Si	Ta-10W	1.3	-	Flat Surface
4(1)	W-Si	Ta-10W	0.8	-	Corner
5	W-Si	Ta-10W	2.1	-	Corner
6	W-Si	T-222	0.4	-	Corner
7	W-Si	T-222	0.8	-	Corner
8	W-Si	T-222	0.3	-	Corner
9	W-Si	T-222	0.2	-	Corne
10(2)	W-Si	T-222	6.5	-	Corner
11	W-Si	T-222	-	0.3	Edge
12	W-Si	T-222	-	0.8	Corner
13	W-Si	T-222	-	0.3	Edge
14	W-Si	T-222	-	0.2	Edge
15	W-Si	T-222	-	0.2	Edge

(1) Nickel-activated W coating.

(2) Specimen cycled after the 6th hour.

TABLE XI

STATIC OXIDATION TESTS AT 3000°F (1650°C)
OF WSi_2 COATING ON Ta-10W

Spec. No.	Coating Thickness (mils)	Life at 3000°F (mins)	Area of Failure	Silicon Embedding
1	3.0	10	Edge	No
2	3.0	15	Edge	No
3	1.0	30	Surface	Yes
4	2.7	95	Surface	Yes
5	3.0	150	Surface	Yes

In the next series of experiments, the sintering temperature of the WSi_2 was increased from 2550°F to 2910°F. A comparison of the coatings sintered at these temperatures is shown in Figure 24. Increasing the sintering temperature to 2910°F resulted in some improvement in the density of the WSi_2 coating and in the formation of a dense diffusion zone. The diffusion zone, however, appeared to be formed at the expense of depletion of silicon from the coating. In the bottom photograph of Figure 24 a new phase can be seen in the WSi_2 coating adjacent to the diffusion zone, as well as an increase in porosity in this region. Embedment of the 2910°F WSi_2 coating is silicon and sintering for 1 hour at 2400°F in argon had little effect upon this depleted zone as careful examination of the upper photograph of Figure 25 indicates. This coating was oxidation tested at 3000°F and yielded erratic and short lives ranging from 20-95 minutes in six tests. Finally, the 2910°F sintered WSi_2 was vacuum siliconized by coating with silicon and heating at 2370°F for 16 hours at a pressure less than 0.1 torr. The microphotograph of this coating, shown in the lower half of Figure 25, indicates that the silicon-depleted region adjacent to the diffusion zone was repaired, porosity in this region was reduced, and the hardness of the diffusion zone reached a maximum (1470 kg/mm^2) in comparison with previous siliconization treatments.

Oxidation tests at 3000° and 3200°F of the vacuum-siliconized WSi_2 coating on Ta-10W and T-222 were very promising as shown in the data of Table XII. Lifetimes of 3 1/4 - 7 hours were obtained for the coating

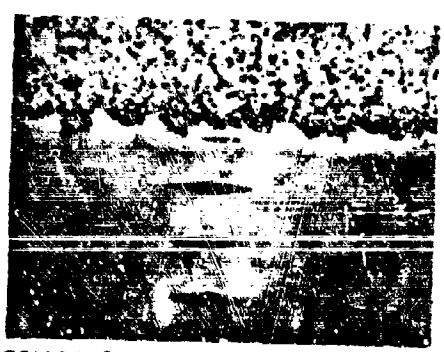
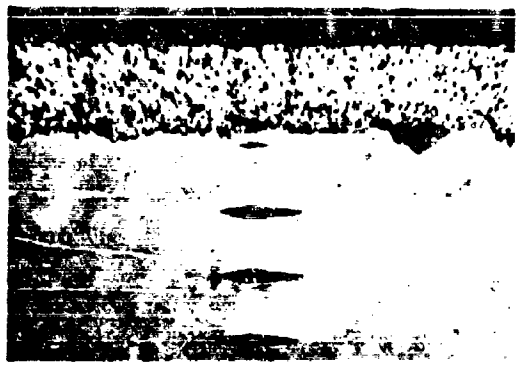


Figure 24. WSi_2 Coating on Ta-10W Sintered at 2550°F (1400°C) and 2910°F (1600°C)

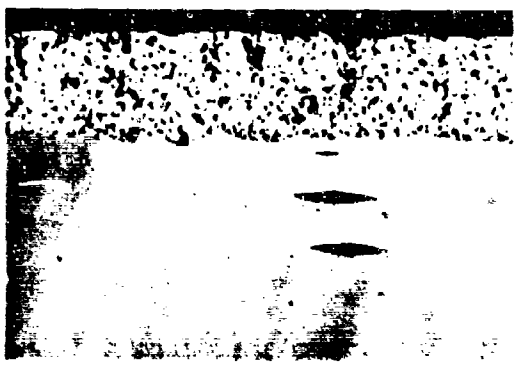


WSi_2

Diffusion Zone 1140 kg/mm^2 (>Rc68)

Ta-10W 245kg/mm^2 (Rc21)

Siliconized 1 hr 1350°C in Argon — 250x, Unetched



WSi_2

Diffusion Zone 1470 kg/mm^2 (>Rc68)

Ta-10W, 320 kg/mm^2 (Rc32)

16hr Siliconization 1300°C, < 0.1 Torr — 250x, Unetched

Figure 25. Effect of Siliconization Procedure on WSi_2 Coating on Ta-10W, Sintered at 2910°F (1600°C)

on both alloys at 3000°F and the coating survived 3 3/4-5 hours at 3200°F on Ta-10W. Several of the coatings were unfailed after 5-7 hours exposure as indicated in Table XII. Poorer results were obtained on T-222 at 3200°F, but this set of specimens was discolored and the samples were believed to be contaminated. Four new T-222 specimens were coated and rerun at 3200°F and these yielded the expected oxidation lives of 3.0, 4.5, 3.75 and 2.8 hours.

An important characteristic noted for the vacuum-siliconized WSi_2 coating on both Ta-10W and T-222 was its excellent thermal shock resistance. On several occasions specimens were removed rapidly from a 3000°F air furnace and then reinserted with no damage to the coating.

All oxidation tests at 3000°F were performed, up to this point, using a WSi_2 pellet on an alumina plate as a setter. The transparent glass formed upon the coating and upon the pellet fused together during oxidation testing, and in several tests failure was observed at the point of contact of the setter and of the specimen. For this reason a new three-layer setter consisting of a base of Al_2O_3, a middle layer of MgO, and an upper layer of ThO_2 was developed. This particular sequence yields the highest liquidus temperatures for the various binary oxides which can be formed from SiO_2, Al_2O_3, ThO_2, and MgO as the following table indicates.

Liquidus Temperatures for Various Oxide Combinations (12)

	Al_2O_3		MgO		SiO_2		ThO_2	
	°F	°C	°F	°C	°F	°C	°F	°C
Al_2O_3	3722	2050	3506	1930	2813	1545	3182	1750
MgO	3506	1930	5072	2800	2804	1540	3812	2100
SiO_2	2813	1545	2804	1540	3110	1710	3092	1700
ThO_2	3182	1750	3812	2100	3092	1700	5522	3050

At the first test using this setter, vacuum-siliconized WSi_2 on T-222 was tested at 3000°F and yielded a 14-hour oxidation life without failure (with one cycle to room temperature) as compared to the 3-5 hours obtained in previous tests with a WSi_2 setter. The sample was easily removed from the upper ThO_2 layer during testing and no interactions could be observed at the ThO_2-MgO or Mgo Al_2O_3 interface.

TABLE XII

OXIDATION TEST RESULTS OF WSi_2 COATINGS IN Ta-10W AND T-222
(16 HOUR SILICONIZATION POST-TREATMENT)

Spec. No.	Coating System	Oxidation Life @3000°F, 1650°C; hrs.	Oxidation Life @3200°F, 1760°C; hrs.	Remarks
1	WSi_2 on Ta-10W	3.5	---	Failed where coating was in contact with WSi_2 setter
2	WSi_2 on Ta-10W	6.0	---	Still O.K.
3	WSi_2 on Ta-10W	7.0	---	Still O.K.
4	WSi_2 on Ta-10W	4.0	---	Failed at corner & edge
5	WSi_2 on Ta-10W	---	3.0	Failed at corner
6	WSi_2 on Ta-10W	---	3.75	Failed at corner
7	WSi_2 on Ta-10W	---	5.5	Failed where coating was in contact with setter
8	WSi_2 on Ta-10W	---	5.5	Catastrophic failure
9	WSi_2 on Ta-10W	---	3.0	Failed at edge
10	WSi_2 on Ta-10W	---	5.5	Catastrophic failure
11	WSi_2 on T-222	4.5	---	Failed at corner
12	WSi_2 on T-222	3.25	---	Failed at corner
13	WSi_2 on T-222	3.0	---	Failed at edge
14	WSi_2 on T-222	7.0	---	Still O.K.
15	WSi_2 on T-222	5.0	---	Failed at flat surface
16	WSi_2 on T-222	---	0.50*	Failed at edge & corner
17	WSi_2 on T-222	---	0.50*	Failed at edge & corner
18	WSi_2 on T-222	---	0.25*	Failed at edge & corner
19	WSi_2 on T-222	---	0.17*	Failed at edge
20	WSi_2 on T-222	---	0.50*	Failed at corner
21	WSi_2 on T-222	---	3.0	Failed at edge
22	WSi_2 on T-222	---	4.5	Failed at setter contact
23	WSi_2 on T-222	---	3.75	Failed at edge
24	WSi_2 on T-222		2.8	Failed at edge & corner

*These specimens were discolored and are believed to have been contaminated.

To further investigate the effect of siliconization time, several WSi_2 coated T-222 specimens were electrophoretically coated and siliconized for time intervals of 24, 32, and 48 hours at 2370° F under reduced pressure (<0.1 mm). Photomicrographs showing coating structure, depth of diffusion, and substrate and diffusion zone hardness values are shown in Figure 26. Coating density appears unaffected by time in this range. Silicon diffusion into the substrate increased with time as would be expected, but the substrate retained its ductility for siliconization time up to 48 hours as evidenced by the hardness values.

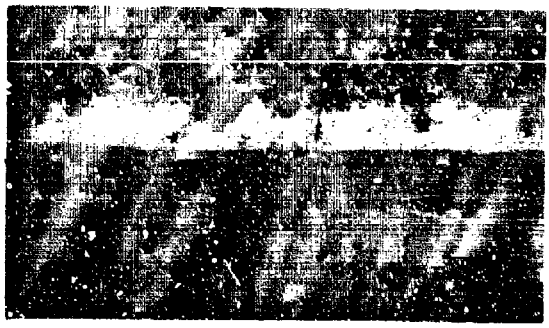
No difference was observed in the oxidation resistance of the three coating systems at 3000°F. All coatings were 2.5 mils thick and failed at random intervals ranging from 1 to 4.5 hours. The oxidation test results are summarized in Table XIII.

The average life of the 14 specimens siliconized for times longer than 16 hours was 2.5 hours at 3000°F, compared to 4.8 hours for previous specimens siliconized for 16 hours. Since no improvement in life was gained by increasing the time of siliconization, the 16-hour siliconization period was established as the standard siliconizing cycle for the WSi_2 coating, and all tantalum alloy hardware subsequently prepared in this program was coated with WSi_2, sintered in argon at 2910°F for 2 hours, and then post-siliconized for 16 hours at reduced pressure.

4. Barrier Layer Coatings For WSi_2-Coated Ta-10W Alloy

An attempt was made to extend the useful life of the Si/WSi_2 coating system by means of a diffusion-type barrier interposed between the coating and the substrate. The barrier coatings investigated are listed in Table XIV. The coatings were electrophoretically deposited on Ta-10W, heat-treated as indicated in the table, and screened for oxidation resistance at 3000°F in an induction-heated tube furnace, using a WSi_2 pellet setter. The barrier layers ranged from 1.0 to 1.5 mils in thickness and the overall coating thickness on all specimens was 2.5-3.1 mils.

Metallographic comparison of the tungsten and molybdenum barrier layers on Ta-10W sintered at 2550°F and at 2910°F (see Figures 27 and 28) indicated that the density of the molybdenum was improved while that of the tungsten was not affected by increasing the temperature. Some porosity was evident at the interface between the tungsten coating sintered at 2910°F and the tantalum substrate.



WSi_2 Coating

Diffusion Zone-1140 kg/mm^2 (>Rc68)
(50 gm Load

T222 Substrate-285 kg/mm^2 (Rc28)
(50 gm Load)

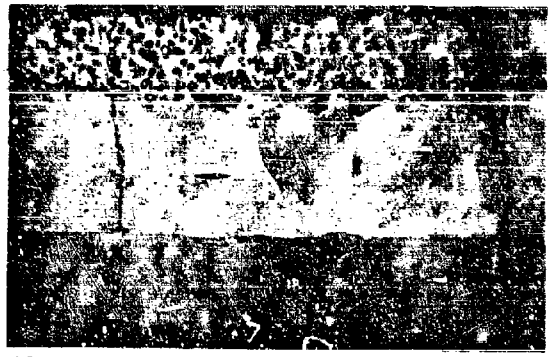
24 Hr. Siliconization 250x

WSi_2 Coating

Diffusion Zone-1140 kg/mm^2 (>Rc68)
(50 gm Load)

T222 Substrate-265 kg/mm^2 (Rc25)
(50 gm Load)

32 Hr. Siliconization 250x



WSi_2 Coating

Diffusion Zone-1140 kg/mm^2 (>Rc68)
(50 gm Load)

T222 Substrate-275 kg/mm^2 (Rc26)
(50 gm Load)

48 Hr Siliconization 250x

Figure 26. WSi_2-Coated T-222 Alloy Siliconized at Various Time Intervals at 2370°F (1300°C) Under Reduced Pressure

TABLE XIII

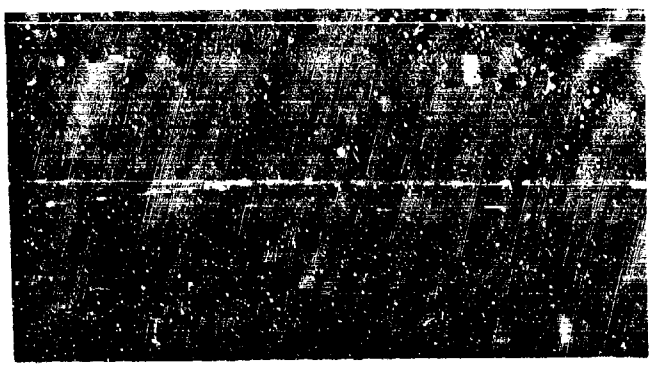
EFFECT OF VACUUM-SILICONIZATION TIME ON THE OXIDATION BEHAVIOR OF WSi_2 COATED T-222 ALLOY SPECIMENS AT 3000°F (1650°C)

Test No.	Siliconization Time (hrs.)	Oxidation Life @ 3000°F (1650°C)	Region of Failure
1	24	2.0 hrs.	Edge
2	24	1.5	Flat surface
3	24	3.0	Corner
4	24	3.0	Edge
5	24	3.5	Contact with setter
6	32	1.0	Flat surface
7	32	1.5	Edge
8	32	3.0	Corner
9	32	4.2	Corner
10	32	2.5	Contact with setter
11	48	1.8	Edge
12	48	2.2	Corner
13	48	2.5	Edge
14	48	3.0	Edge

TABLE XIV

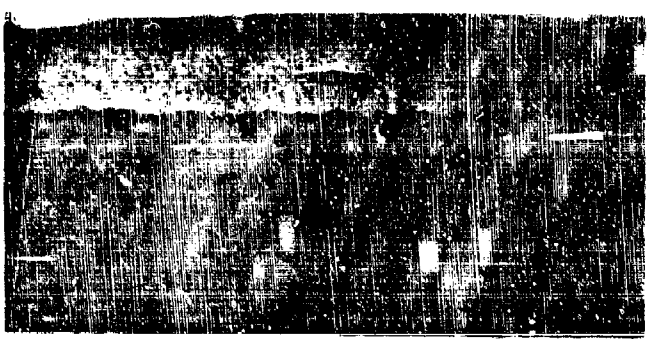
BARRIER LAYER COATINGS ON Ta-10W

System	Description	Barrier Layer Sintering in Argon (Time and Temperature)	Siliconization Time and Temperature	Reference Figure No.
a-1	W-Si	2 hrs. 2550°F(1400°C)	24, 40, 48 hrs. 2370°F (1300°C), 0.1 torr	27, 31
a-2	W-Si	2 hrs. 2910°F(1600°C)	16 hrs., 2370°F(1300°C) 0.1 torr	27
b-1	W-Mo-Si	(W & Mo) 2 hrs. 2550°F(1400°C)	24, 40, 48 hrs. 0.1 torr	28, 30
b-2	W-Mo-Si	(W & Mo) 2 hrs. 2910°F(1600°C)	16 hrs., 2370°F(1300°C) 0.1 torr	29
c	WSi_2-W	(W & WSi_2) 2 hrs. 2910°F(1600°C)	1 hr., 2460°F(1350°C)Argon	32
d	WSi_2-Mo	(Mo & WSi_2) 2 hrs. 2910°F(1600°C)	1 hr., 2460°F(1350°C)Argon	32
e	WSi_2-Cr	Cr- 3 hrs. 2460°F(1350°C) WSi_2 2 hrs. 2910°F(1600°C)	1 hr., 2460°F(1350°C)Argon	33
f	WSi_2-Cr-W	Cr - 3 hrs. 2460°F(1350°C) W - 2 hrs. 2550°F(1400°C) WSi_2 2 hrs. 2910°F(1600°C)	- - 1 hr., 2460°F(1350°C)Argon	33
g	WSi_2-Cr-Mo	Cr - 3 hrs. 2460°F(1350°C) Mo - 2 hrs. 2550°F(1400°C) WSi_2 - 2 hrs. 2910°F(1600°C)	- - 1 hr., 2460°F(1350°C)Argon	-
h	WSi_2-Cr-Cb	Cr - 3 hrs. 2460°F(1350°C) Cb - 2 hrs. 2910°F(1600°C)		-
i	WSi_2-$CbCr_2$	2 hrs. 2910°F(1600°C)	1 hr., 2460°F(1350°C)Argon	34
j	WSi_2-43Cr/57Ti	WSi_2- 2 hrs. 2910°F(1600°C) Cr/Ti 1 hr. 2550°F(1400°C)	1 hr., 2460°F(1350°C)Argon	34
k	$MoSi_2$-Cr	Cr - 3 hrs. 2460°F(1350°C) $MoSi_2$ 2 hrs. 2910°F(1600°C)	1 hr. 2460°F(1350°C) Argon	35



Densification
Pressure 20 tsi

2 hrs. 2550°F Unetched, 250x



W Coating
218kg/mm^2 (<Rc20)

Ta-10W
493kg/mm^2 (Rc48)

2 hrs. 2910°F Unetched, 250x

Figure 27. Tungsten Coatings on Ta-10W, Pressed at 20 t.s.i. and Sintered in Argon

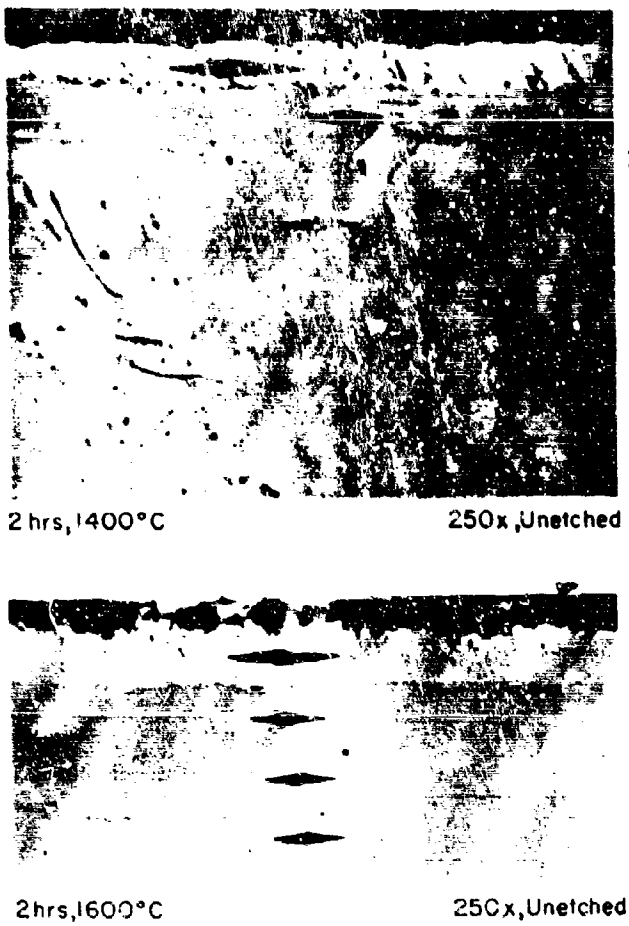


Figure 28. Molybdenum Coatings on Ta-10W, Pressed at 10 t.s.i. and Sintered in Argon

A photomicrograph of the W-Mo dual barrier sintered at 2910°F is shown in Figure 29. Application of the 2910°F W-Mo coating to Ta-10W resulted in hardening and embrittlement of the substrate. However, both the molybdenum barrier alone and the W-Mo dual barrier appeared quite dense after this heat treatment cycle. The effect of various siliconization times upon the 2550° and 2910°F tungsten and W-Mo barriers is shown in Figures 29-32. After 24 hours vacuum-siliconization of the 2550°F W-Mo barrier (Figure 30) no diffusion of silicon into the substrate is evident. After 40, however, the complex silicide coating appears to be single phase and more dense, diffusion and reaction of silicon with the substrate has begun, and scattered porosity appears at the interface between the silicided substrate and the original coating. The depth of diffusion into the substrate and the interface porosity continues to increase when the siliconization time is extended to 48 hours and evidence appears of two silicide phases in the outer coating.

Approximately the same behavior is seen (Figure 31) when the time of vacuum siliconization of the 2550°F tungsten barrier coating is increased from 24 to 48 hours. It is evident, however, that diffusion of silicon through the tungsten coating is much more rapid than through the W-Mo coating. This is undoubtedly due to the higher density of the sintered W-Mo coating (compare Figures 27 and 29 top) before siliconization. After 48 hours siliconization of the tungsten coating, an extremely dense and deep diffusion zone is formed in the substrate with a microhardness close to that of WSi_2. The approximate hardnesses of the various refractory metal silicides are tabulated below for reference.

Approximate Vickers Microhardness (50g Load) of Refractory Metal Silicides (13)

Compound	Microhardness (kg/mm^2)
$MoSi_2$	1300
$TiSi_2$	820 - 890
Ta_5Si_3, Ta_2Si, $TaSi_2$	1200 - 1500
Cr_3Si, Cr_3Si_2, $CrSi$, $CrSi_2$	900 - 1200
WSi_2	1100

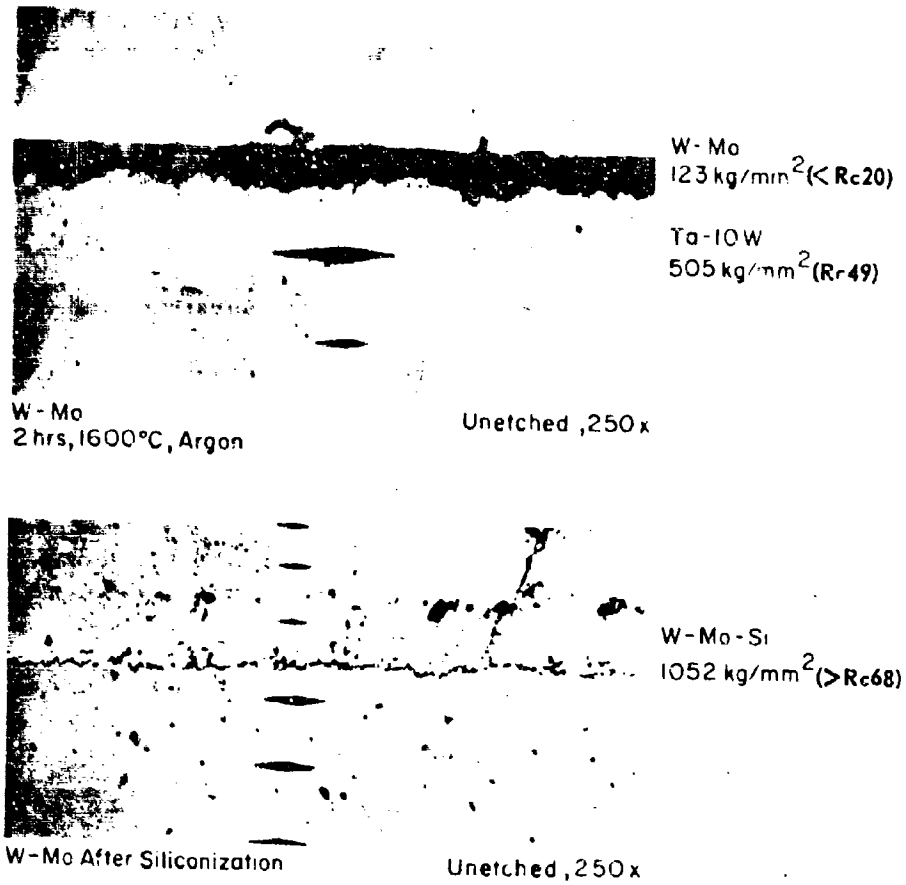


Figure 29. W-Mo-Si Coating (System b-2) on Ta-10W

W - Mo - Si

Ta - 10W
493 kg/mm^2
(Rc48)

24 hr. Siliconization 250x, Unetched

W - Mo - Si

Diffusion Zone
1138 kg/mm^2 (>Rc68)

Ta - 10W
368 kg/mm^2 (Rc37)

40 hr. Siliconization 250x, Unetched

W - Mo - Si

Diffusion Zone
1138 kg/mm^2 (>Rc68)

Ta - 10W
400 kg/mm^2 (Rc41)

48 hr. Siliconization 250x, Unetched

Figure 30. W - Mo - Si Coating (System b-1) on Ta - 10W (W and Mo Sintered 2 Hours 2900°F, 1593°C, in Argon. Vacuum Siliconized 2370°F, 1300°C, Various Times, <0.1 Torr)

W-Si
900 kg/mm^2 (Rc67)

Ta-10W
320 kg/mm^2 (Rc32)

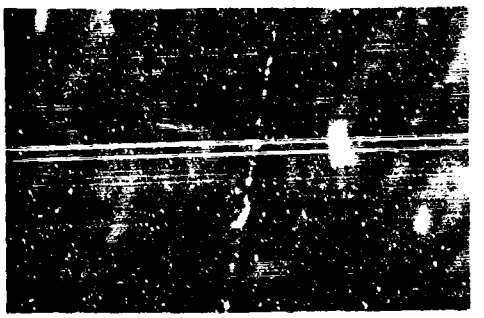
24 hr. Siliconization 250x, Unetched

W-Si
1138 kg/mm^2 (>Rc68)

Diffusion Zone
1235 kg/mm^2 (>Rc68)

Ta-10W
250 kg/mm^2 (Rc22)

40 hr. Siliconization 250x, Unetched



W-Si
900 kg/mm^2 (Rc67)

Diffusion Zone
1140 kg/mm^2 (>Rc68)

Ta-10W
260 kg/mm^2 (Rc24)

48 hr. Siliconization 250x, Unetched

Figure 31. W-Si Coating (System a-1) on Ta-10 W After Various Siliconization Times

Figure 32. WSi_2-Mo (System d) and WSi_2-W (System c) Coatings on Ta-10W (W, Mo, WSi_2 Sintered 2 Hours in Argon Siliconized 1 Hour 2460°F, 1350°C, in Argon)

Photomicrographs of the WSi_2 coating over the molybdenum barrier (system d), tungsten barrier (system c), and various chromium-containing barriers (system e, f, i, and j) on Ta-10W are shown in Figures 32 through 34 System k of Table XI ($MoSi_2$ over chromized Ta-10W) is shown in Figure 35. Deposition of the compounds WSi_2 over the various barriers, followed by siliconization in argon yielded a more porous outer coating than those obtained by vacuum siliconization of tungsten (compare Figures 31 and 32, for example). Each of the chromium-containing coatings on Ta-10W (systems e through k) caused embrittlement of the substrate. Chromizing of Ta-10W, however, yielded a dense diffusion zone which, judging from its microhardness (see Figures 33 and 35), was probably predominantly $TaCr_2$.

The effect of siliconization time on the oxidation resistance of the tungsten and tungsten-molybdenum barrier layer coatings on Ta-10W sintered at 2550°F (systems a-1 and b-1) is summarized in Table XV. In general, the oxidation life at 3000°F increased with increasing siliconization time, however, with one exception no sample survived more than one hour's exposure to air. The oxidation life of the chromium-containing barrier layer coatings was generally poor as shown in Table XVI. Increasing the sintering temperature of the tungsten or molybdenum-tungsten barrier layers from 2550°F to 2910°F did not improve the oxidation resistance of these vacuum siliconized coatings (systems a-2 and b-2) or coatings formed by depositions of WSi_2 over the 2910°F sintered barriers, followed by siliconization of the WSi_2-W and WSi_2-Mo at 1350°C for 1 hour in argon (systems c and d). The results of 3000°F oxidation tests on these coatings are summarized in Table XVII.

Since none of the barrier layer systems yielded oxidation lives equivalent to that of the Si/WSi_2 coating, (compare Table XII with Tables XV-XVII), work on the barrier layer coatings was discontinued and Si/WSi_2 coatings were prepared on T-222 threaded fasteners for further oxidation and mechanical property testing.

5. Preparation And Oxidation Tests of Si/WSi_2-Coated T-222 Alloy Threaded Fasteners

A problem was encountered in early coating trials of the Si/WSi_2 system on tantalum alloy threaded fasteners. There was a marked tendency toward crack development in the roots of the threads after sintering, probably caused by excessive shrinkage of the as-deposited coating during drying. Attempts to resolve the cracking problem by utilizing coarse particles or by adjusting the solvent ratio or zein and electrolyte concentration were not successful. Since time did not

WSi_2

Cr-W 900 kg/mm^2 (Rc67)

Ta-10W 400 kg/mm^2 (Rc41

WSi_2-Cr-W 250x, Unetched

WSi_2

Cr Diffusion Zone

Ta-10W 400 kg/mm^2 (Rc41

WSi_2-Cr 250x, Unetched

Figure 33. WSi_2-Cr (System e) and WSi_2-Cr-W (System f) Coatings on Ta-10W

WSi_2
$CbCr_2$

Ta-10W 445 kg/mm^2 (Rc48)

WSi_2-$CbCr_2$ 250x, Unetched

WSi_2
43 Cr/57 Ti

Ta-10W

WSi_2-43Cr/57Ti 250x, Unetched

Figure 34. WSi_2-$CbCr_2$ (System i) and WSi_2-43 Cr/57 Ti (System j) Coatings on Ta-10W

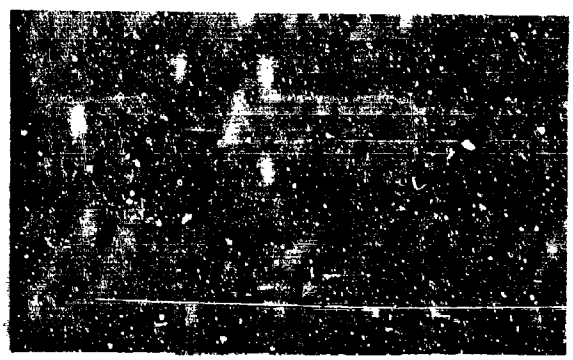


Figure 35. $MoSi_2$-Cr (System k) Coating on Ta-10W

TABLE XV

OXIDATION TEST RESULTS OF W-Si (System a-1)
W-Mo-Si (System b-1) COATINGS ON Ta-10W

Coating System	Siliconizing Time (hrs)	Oxidation Life @3000°F (1650°C)(Min)	Remarks
W-Si	24	3	Failed at edge and corner
W-Si	24	30	Failed at edge and corner
W-Si	40	20	Failed at corner
W-Si	40	20	Failed at corner
W-Si	48	50	Failed at corner & flat surface
W-Si	48	60	Failed at edge
W-Mo-Si	24	20	Failed at corner
W-Mo-Si	24	15	Failed at corner & patch
W-Mo-Si	24	15	Failed at edge & patch
W-Mo-Si	40	35	Failed at patch
W-Mo-Si	40	25	Failed at edge
W-Mo-Si	40	40	Failed at edge & patch
W-Mo-Si	48	50	Failed at edge & patch
W-Mo-Si	48	30	Failed at edge
W-Mo-Si	48	288*	Failed where coating contacted WSi_2 setter

* Specimen cycled after 168 minutes

TABLE XVI

OXIDATION TEST RESULTS OF WSi_2-CHROMIUM CONTAINING BARRIER LAYER COATING ON Ta-10W

Description	Oxidation Life @3000°F (1650°C)(Min)	Remarks
WSi_2-Cr	60	Failed at corner
WSi_2-Cr	15	Failed at corner
WSi_2Cr	18	Failed at corner & edge
WSi_2-Cr	28	Failed at corner
WSi_2-Cr	25	Failed at corner
WSi_2-Cr	10	Failed at corner
WSi_2-Cr-W	15	Failed at corner
WSi_2-Cr-W	15	Failed at corner
WSi_2-Cr-W	25	Failed at corner
WSi_2-Cr-Mo	30	Failed at corner
WSi_2-Cr-Mo	15	Failed at edge
WSi_2-Cr-Mo	50	Failed at corner
WSi_2-Cr-Mo	30	Failed at flat surface
WSi_2-Cr-Cb	5	Failed at edge & corner
WSi_2-Cr-Cb	10	Failed at edge
WSi_2-Cr-Cb	10	Failed at edge
WSi_2-Cr-Cb	25	Failed at edge & corner
WSi_2-Cr-Cb	10	Failed at edge & corner
WSi_2-Cb-Cr_2	55	Failed at edge & corner
WSi_2-Cb-Cr_2	65	Failed at corner
WSi_2-43Cr-57Ti	7	Failed at edge & corner
WSi_2-43Cr-57 Ti	5	Failed at corner
$MoSi_2$-Cr	5	Failed at corner
$MoSi_2$-Cr	20	Failed at corner & edge
$MoSi_2$-Cr	5	Failed at edge
$MoSi_2$-Cr	144	Still O.K.

TABLE XVII

OXIDATION TESTS OF W-Si, W-Mo-Si, WSi_2-Mo, AND WSi_2-W COATINGS ON Ta-10W

Coating System (See Table XIV)	Description	Oxidation Life @3000°F(1650°C)(Min)	Area of Failure
a-2	W-Si	15	Corner and surface
	W-Si	30	Surface
	W-Si	20	Corner and surface
	W-Si	15	Corner
	W-Si	18	Corner
b-2	W-Mo-Si	30	Corner
	W-Mo-Si	75	Edge
	W-Mo-Si	50	Edge and Corner
	W-Mo-Si	45	Corner
	W-Mo-Si	45	Surface
d	WSi_2-Mo	30	Surface
	WSi_2-Mo	65	Surface
	WSi_2-Mo	35	Surface
	WSi_2-Mo	10	Surface
	WSi_2-Mo	20	Surface
f	WSi_2-W	10	Corner
	WSi_2-W	25	Corner
	WSi_2-W	15	Corner and surface
	WSi_2-W	10	Corner and edge
	WSi_2-W	10	Corner

permit a more systematic approach in which all of the variables affecting the stability of the electrophoretic dispersion could be examined quantitatively, it was decided to utilize increased densification pressure (30 tsi to 50 tsi) on the as-deposited coating in order to close the crack seams. This technique was found to be quite effective. Although small crack seams could be detected microscopically after the sintering and siliconization cycle, the microcracks had no effect on the oxidation life of the coated fastener at 3000°F, due to the formation of a self-healing glass. Results comparable to previously tested coupon specimens were obtained on Si/WSi_2-coated 1/4-20, T-222 studs as shown in Table XVIII. The specimens tested at 2400°F and 2700°F were preoxidized in air for 15 minutes at 3000°F in order to promote glass formation and prevent pest failures at the low test temperatures. Without this preoxidation treatment, the coating survived only 2.8 hours at 2400°F and 0.5 hour at 2700°F. After preoxidation, however, an oxidation life of 576 hours at 2400°F (including 15 cycles to room temperature) was obtained on a Si/WSi_2-coated Ta-10W coupon, and a life in excess of 104 hours at 2400°F was achieved on a coated T-222 stud as shown in Table XVIII. Preoxidation also increased the test performance of the studs at 2700°F from about 0.5 hour to 12 hours.

TABLE XVIII

OXIDATION BEHAVIOR OF WSi_2-COATED T-222 ALLOY STUDS AT VARIOUS TEMPERATURES

Test No.	Oxidation Life in Hours 2400°F (1316°C)	2700°F (1482°C)	3000°F (1650°C)	3200°F (1760°C)	Region of Failure
1(1)	576	—	--	--	Still intact
2(2)	38	--	--	--	Corner
3(3)	44	—	--	--	Corner
4	104-120	--	--	--	Thread
5	104-120	--	--	--	Thread
6	--	12-27	--	--	Completely oxidized
7	--	11	--	--	Thread
8	--	--	2.2	--	Shank
9	--	--	6.0	--	Still intact
10	--	--	5.3	--	Shank in contact with setter
11	--	--	--	1.0	Thread
12	--	--	--	1.8	Shank in contact with setter
13	--	--	--	0.8	Thread and Shank

(1) WSi_2 coating on Ta-10W preoxidized at 3000°F for 5 minutes and cycled every 20 hours after 96 hours of static testing.

(2) Same as (1) except cycled 5 times at 2 hour intervals during work day and tested continuously overnight.

(3) Same as (2) but cycled 8 times.

NOTE: Where range in hours is given, specimen failed during the night.

SECTION VII

COATING OF FASTENERS

A. APPLICATION OF COATING

Following completion of the coating development work the appropriate coatings were applied to the various fasteners and miscellaneous parts.

A description of the coating apparatus used for the point-drive fasteners involves all of the details considered in the coating of the less difficult configurations and is therefore presented.

A preliminary method was tried for coating the sockets of the point-drive fasteners by filling the socket with a dilute slurry of Cr/Ti, and then drying and sintering the fastener. This method did not yield tolerances equivalent to an electrophoretic coating, and several of the slurry coatings contained microcracks. Several fasteners were coated by this procedure while a concurrent study was made of an electrode configuration which would permit electrophoretic coating of the socket. A satisfactory coating jig was developed which is shown in Figure 36. The jig consists of two point contacts which hold the fastener in an inverted position within the coating bath. Electrical contact is maintained between the point cathode and the head of the fastener. The auxiliary point anode is positioned in the center of the socket of the point-drive fastener and is insulated from the fastener by a glass bead. One sample coated in this jig was oxidation tested at 2500°F for 31 hours before failure occurred at a defect on the surface of the lead thread. No failure was noted in the socket. In view of this result all point drive fasteners were electrophoretically processed in this equipment.

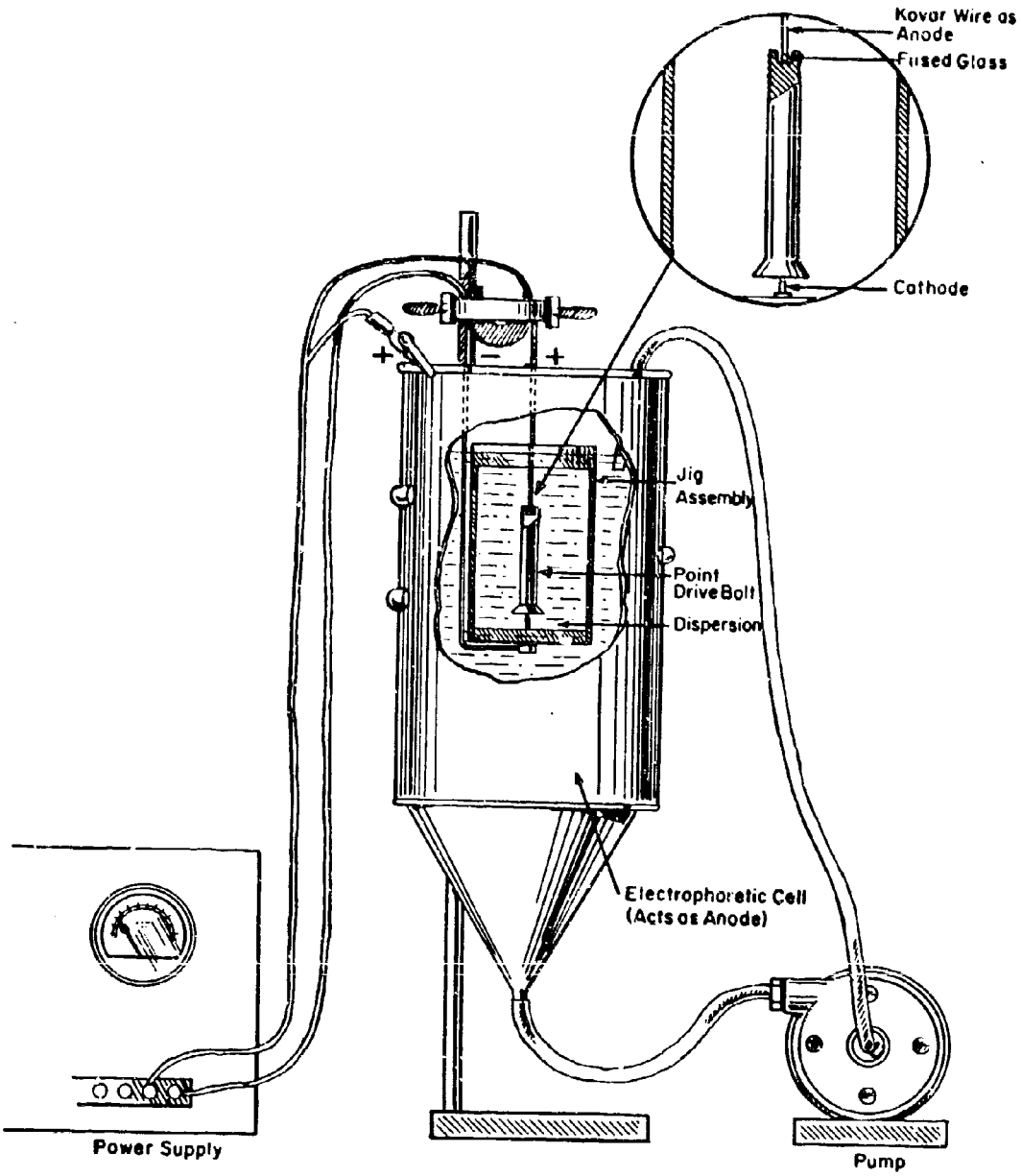


Figure 36. Coating Jig for Point Drive Fasteners

B. TOLERANCE CONTROL

In order to verify the narrow tolerance range previously attained by Vitro's electrophoretically applied coatings, a series of measurements was made on each of the representative coating systems throughout the program.

Since dimensional measurements were performed at both the S. P. S. Metrology Laboratory and at Vitro during the course of the program, the objective of the first experiment was to cross-check results at the two laboratories by measuring the same coated parts, in order to determine if a systematic error was incurred due to the use of different measuring instruments. For this purpose, a series of $MoSi_2$-coated, TZM 1/4-20 studs were prepared. The studs were approximately two inches long with a one-half inch length of thread at each end. Each stud was stamped at one end with an identifying letter which also served as an index mark for the angular position of the thread. The pitch diameter of each uncoated sample was measured at four indexed points on the second and sixth threads at each end. Body diameter measurements were made at two points on the shank. The pitch diameter was measured at SPS with a Pratt and Whitney No. 35 TRI Roll Thread Comparator equipped with Type 5 rolls, and the body diameter was determined with a Brown and Sharpe No. 245 Indicating Bench Micrometer. The studs were then sent to Vitro where the measurements were repeated with a duplicate set of instruments, after first calibrating Vitro's TRI Roll Gage against a master setting plug whose pitch was accurately determined at the SPS Metrology Laboratory. The studs were then coated under identical conditions at Vitro to a nominal thickness of 2.5 mils, and the pitch diameter and body diameter measurements were repeated at both Vitro and SPS.

All of the measurements are listed in Tables XIX and XX. It will be noted from the data of Table XIX that uncoated sample numbers A, B, C, and R, Q, S, and K represent two groups whose pitch diameters differ by 0.003-0.004 inch. The body diameters of all seven samples shown in Table XX however, represent a single statistical population. The arithmetic means ($\bar{x}$), variances (s^2), standard deviations (s), and number of measurements (n) from which these statistics were derived are summarized in Table XXI.

To test the hypothesis that the means of the measurements made at SPS and Vitro are equal, the "t-test" was used (14). Although the equality of the measurements is almost self-evident from the data of Table XXI, a sample calculation will be made for the measurements of the pitch diameter of samples R, Q, S, and K, after coating, taken at SPS($\bar{x}_1$) and at Vitro ($\bar{x}_2$).

$$t = \left[\bar{x}_1 - \bar{x}_2\right] \Big/ Sp\,(n_1 + n_2/n_1\,n_2)\;1/2, \text{ where}$$

$$Sp^2 = s_1^2\,(n_1 - 1) + s_2^2\,(n_2 - 1) \Big/ n_1 + n_2 - 2$$

For the special case $n_1 = n_2$, the formulae reduce to:

$$t = \left[\bar{x}_1 - \bar{x}_2\right] \Big/ Sp\,(2/n_1)\;1/2 \text{ and } Sp^2 = (s_1^2 + s_2^2) \Big/ 2$$

From Table XXI

$$S_p^2 = 1/2\,(17.74 + 13.84)\,10^{-8} = 15.79 \times 10^{-8}$$

$$S_p = 3.97 \times 10^{-4}$$

$$t = 1 \times 10^{-4}/3.97 \times 10^{-4}\,(1/4) = 1.01$$

Since the calculated value of t does not exceed critical value of $t_c = 2.66$, the hypothesis that the means of the measurements made at the two laboratories are equal may be accepted at the 99% confidence level. Finally, since there is no difference between the measurements made at each laboratory, all values obtained for the increase in pitch diameter and for the coating thickness may be considered a single statistical population. The 99% confidence ($M_{99\%}$) intervals about the mean of these values can then be derived from Table XXI as follows:

$$M_{99\%} = \bar{x}_i \pm 2.58\, s_i/n_i^{1/2}, \text{ or}$$

$$\Delta \text{ Pitch Diameter} = 0.0057 \pm 2.58\,(3.3 \times 10^{-4})/7.48 = 0.0057 \pm 0.00011 \text{ in.}$$

$$\text{Coating Thickness} = 0.00248 \pm 2.58\,(2.2 \times 10^{-4})/3.74 = 0.00248 \pm 0.00015 \text{ in.}$$

The tolerance intervals shown below for a determination, at either laboratory, of the coating thickness or of the increase in pitch diameter due to the coating will include 95% of the measurements at a confidence level of 0.95.

Tolerance limits for Δpitch diameter = $0.0057 \pm (2.35)(3.303)\,10^{-4} =$
0.0057 ± 0.00077.

Tolerance limits for coating thickness = $0.00248 \pm (3.012)(2.234)\,10^{-4} =$
0.00248 ± 0.00067.

The significance of these calculations was that thread measurements made at either S. P. S. or at Vitro could be accepted with confidence by the other facility. Furthermore, the variances in body diameter and in pitch diameter of the as-fabricated fastener do not significantly increase in magnitude as a result of application of the molybdenum disilicide coating. In all cases, the uniformity of the coating was within the limits of accuracy of the instruments exployed and the variability which is inherent in the rolled thread.

This excellent dimensional control on the coated studs was further verified in subsequent measurement taken by Vitro and S. P. S. on three coated 1/4-20 TZM bolts, the result of which are shown in Table XXII. For these samples, all coated pitch diameter measurements were within the blueprint tolerance of 0.212-0.2165 inch, and all body diameter measurements were within the blueprint tolerance of 0.2471-0.2492 inch (0.2439-0.2444 uncoated plus 0.0016-0.0024 coating thickness).

In later phases of the program, dimensional tolerances were confirmed for Cr/Ti-Si coated Cb-752 and WSi_2-coated T-222 threaded fasteners. The measurements are listed in Tables XXIII and XXIV. The mean pitch diameters and the tolerance limits which will contain 95% of the tested population at a confidence level of 95% were found to be:

Cr-Ti-Si Coating System on Cb-752

P. D. = 0.2161 ± 0.0017 in. before coating

R. D. = 0.2227 ± 0.0010 in. after coating

WSi_2 Coating System on T-222

P. D. = 0.2070 ± 0.0005 in. before coating

P. D. = 0.2160 ± 0.0016 in. after coating

The average increases in pitch diameter and body diameter for the WSi_2 coating were 0.0086 inch and 0.0048 inch, respectively, which is in excellent agreement with the ratio of 4:1 (coating buildup on one side) expected for a 60° thread.

TABLE XIX

ELECTROPHORETIC COATING OF 1/4-20 TZM STUDS COMPARISON OF PITCH DIAMETER MEASUREMENTS AT SPS AND VITRO

		Letter End P. D.				Plain End P. D.			
		Letter Up		Lowest Reading		Letter Up		Lowest Reading	
Sample	Measurement*	2nd Th'd	6th Th'd	2nd Th'd	6th Th'd	2nd Th'd	6th Th'd	2nd Th'd	6th Th'd
A	SB	.2082	.2083	.2082	.2083	.2081	.2082	.2081	.2082
	VB	.2078	.2084	.2075	.2083	.2077	.2086	.2075	.2081
	VC	.2139	.2139	.2136	.2136	.2139	.2142	.2133	.2137
	SC	.2146	.2141	.2145	.2138	.2142	.2143	.2140	.2140
	ΔPD(SPS)	.0064	.0058	.0063	.0055	.0061	.0061	.0059	.0058
B	SB	.2081	.2080	.2080	.2080	.2080	.2082	.2080	.2081
	VB	.2079	.2082	.2075	.2079	.2080	.2080	.2079	.2079
	VC	.2142	.2139	.2136	.2135	.2136	.2134	.2131	.2131
	SC	.2139	.2136	.2136	.2133	.2132	.2137	.2130	.2135
	ΔPD(SPS)	.0058	.0056	.0056	.0053	.0052	.0055	.0050	.0054
C	SB	.2077	.2076	.2076	.2075	.2077	.2077	.2076	.2077
	VB	.2068	.2076	.2066	.2074	.2076	.2077	.2074	.2076
	VC	.2134	.2135	.2130	.2132	.2136	.2134	.2135	.2132
	SC	.2137	.2131	.2136	.2130	.2137	.2133	.2135	.2131
	ΔPD(SPS)	.0060	.0055	.0060	.0055	.0060	.0056	.0059	.0054
	SB	.2118	.2118	.2115	.2113	.2119	.2118	.2116	.2115
	VB	.2121	.2118	.2112	.2113	.2119	.2118	.2118	.2116
	VC	.2180	.2176	.2174	.2171	.2175	.2168	.2173	.2167
	SC	.2178	.2174	.2172	.2169	.2175	.2168	.2172	.2165
	ΔPD(SPS)	.0060	.0056	.0057	.0056	.0056	.0050	.0056	.0050
Q	SB	.2118	.2118	.2115	.2115	.2119	.2115	.2113	.2111
	VB	.2120	.2117	.2116	.2115	.2117	.2118	.2105	.2111
	VC	.2178	.2175	.2173	.2169	.2170	.2169	.2167	.2167
	SC	.2180	.2174	.2174	.2170	.2176	.2170	.2171	.2165
	ΔPD(SPS)	.0062	.0056	.0059	.0055	.0057	.0055	.0056	.0054
S	SB	.2117	.2113	.2115	.2112	.2120	.2118	.2114	.2112
	VB	.2115	.2113	.2110	.2112	.2116	.2114	.2114	.2112
	VC	.2176	.2173	.2171	.2170	.2178	.2173	.2173	.2168
	SC	.2172	.2173	.2169	.2168	.2178	.2177	.2171	.2167
	ΔPD(SPS)	.0055	.0060	.0054	.0056	.0058	.0059	.0057	.0055
K	SB	.2111	.2111	.2108	.2110	.2111	.2113	.2108	.2109
	VB	.2113	.2112	.2109	.2110	.2114	.2112	.2109	.2109
	VC	.2179	.2170	.2176	.2169	.2175	.2174	.2170	.2170
	SC	.2174	.2165	.2173	.2164	.2170	.2169	.2167	.2166
	ΔPD(SPS)	.0063	.0054	.0065	.0054	.0059	.0056	.0059	.0057

* Legend: S = SPS C = After Coating
V = Vitro B = Before Coating

TABLE XX

ELECTROPHORETIC COATING OF 1/4-20 TZM STUDS COMPARISON OF BODY DIAMETER MEASUREMENTS AT SPS AND VITRO

Sample	Measurement	Letter End O. D.	Plain End O. D.	Coating Thickness Letter End	Coating Thickness Plain End
A	SB	.24673	.24732		
	VB	.24651	.24750	.00232	.00228
	VC	.25115	.25205		
	SC	.25115	.25197		
B	SB	.24723	.24652		
	VB	.24731	.24640	.00261	.00225
	VC	.25253	.25090		
	SC	.25241	.25160		
C	SB	.24650	.24723		
	VB	.24651	.24731	.00276	.00297
	VC	.25203	.25324		
	SC	.25168	.25290		
R	SB	.24729	.24714		
	VB	.24740	.24718	.00230	.00236
	VC	.25200	.25190		
	SC	.25209	.25188		
Q	SB	.24714	.24728		
	VB	.24729	.24743	.00240	.00218
	VC	.25208	.25179		
	SC	.25223	.25215		
S	SB	.24719	.24735		
	VB	.24722	.24742	.00266	.00256
	VC	.25254	.25255		
	SC	.25243	.25263		
K	SB	.24717	.24725		
	VB	.24718	.24721	.00252	.00259
	VC	.25221	.25239		
	SC	.26245	.25223		

S = SPS B = Before Coating
V = Vitro C = After Coating

TABLE XXI

ANALYSIS OF DIMENSIONAL MEASUREMENTS
AT SPS AND VITRO ON 1/4-20 TZM STUDS

	$\bar{x}$	$s^2 \times 10^8$	$s \times 10^4$	n
SPS Measurements Before Coating (in.)				
P. D. (Samples A, B, C)	0.2080	6.57	2.5625	24
P. D. (Samples R, Q, S, K)	0.2114	11.68	3.217	32
O. D.	0.24709	8.34	2.89	14
SPS Measurements After Coating (in.)				
P. D. (Samples A, B, C)	0.2137	21.00	4.582	24
P. D. (Samples R, Q, S, K)	0.2171	17.74	4.212	32
Δ P. D.	0.0057	10.91	3.303	56
O. D.	0.25213	20.92	4.574	14
Vitro Measurements Before Coating (in.)				
P. D. (Samples A, B, C)	0.2077	20.74	4.554	24
P. D. (Samples R, Q, S, K)	0.2114	13.74	3.707	32
O. D.	0.24713	13.85	3.720	14
Vitro Measurements After Coating (in.)				
P. D. (Samples A, B, C)	0.2136	10.91	3.303	24
P. D. (Samples R, Q, S, K)	0.2172	13.84	3.720	32
P. D.	0.25210	34.41	5.866	14
Coating Thickness = $\frac{\Delta \text{ O. D.}}{2}$	0.00248	4.99	2.234	14

TABLE XXII
DIMENSIONS OF THREE 1/4-20 TZM
BOLTS BEFORE AND AFTER COATING

Specimen*	O.D.	At Point	Center	Near Runout
A1	.24345-.24350	.2067	.2069	.2068
A2	.24344-.24349	.20683	.20684	.20685
A3	.24355-.24340	.2059	.2066	.2059
A4	.24792-.24872	.21379	.21373	.21392
A5	.24760-.24819	.2132	.2137	.2134
B1	.24345-.24350	.2068	.2068	.2069
B2	.24344-.24348	.20679	.20692	.20704
B3	.24340-.24338	.2060	.2062	.2064
B4	.24753-.24812	.21401	.21429	.21441
B5	.24770-.24805	.2134	.2138	.2140
C1	.24320-.24328	.2066	.2067	.2069
C2	.24319-.24325	.20680	.20685	.20708
C3	.24315-.24320	.2059	.2064	.2060
C4	.24763-.24837	.21435	.21437	.21435
C5	.24770-.24800	.2136	.2141	.2137

*Specimen code:

1. Before coating, measured at Vitro
2. Before coating, measured at SPS
3. After sandblasting, measured at Vitro
4. After coating, measured at Vitro
5. After coating, measured at SPS

TABLE XXIII

DIMENSIONAL MEASUREMENTS ON Cb-752
1/4-20 HEX HEAD BOLTS BEFORE AND AFTER COATING

Before Coating

Spec No	P.D. 2nd Thd.	Low P.D. 2nd Thd.	High P.D. 2nd Thd.	P.D. 6th Thd.	Low P.D. 6th Thd.	High P.D. 6th Thd.	Body Diam.
1	.2156	.2153	.2158	.2159	.2158	.2161	.2433
2	.2158	.2157	.2158	.2160	.2158	.2161	.2432
3	.2168	.2166	.2168	.2170	.2168	.2170	.2433
			After Prealloyed 43Cr-57Ti Coating				
1	.2206	.2205	.2208	.2202	.2200	.2205	.2461
2	.2212	.2210	.2214	.2211	.2208	.2212	.2465
3	.2223	.2222	.2223	.2221	.2218	.2221	.2466
			After 2 Hour Siliconization				
1	.2219	.2217	2220	.2217	.2213	.2219	.2466
2	.2232	.2231	2233	.2228	.2227	.2231	.2471
3	.2237	.2235	2240	.2228	.2226	.2231	.2471

TABLE XXIV

PITCH DIAMETER MEASUREMENT
ON WSi_2 COATED AND UNCOATED
T-222 1/4-20 STUDS

Specimen* No.	"T" End		Numbered End		
	P.D 2nd Th'd	P. D. 7th Th'd	P. D. 2nd Th'd	P. D. 7th Th'd	Body Diameter
2	.2175	.2173	.2172	.2169	.2523.0
2a*	.2077	.2074	.2075	.2072	.2465.0
3	.2161	.2158	.2162	.2162	.2522.0
3a	.2079	.2075	.2077	.2077	.2473.8
6	.2167	.2163	.2163	.2160	.2519.0
6a	.2073	.2071	.2070	.2072	.2470.0
7	.2156	.2155	.2154	.2157	.2522.1
7a	.2075	.2074	.2071	.2072	.2477.0
8	.2152	.2151	.2145	.2140	.2511.0
8a	.2073	.2074	.2074	.2074	.2469.9

* a = before coating

SECTION VIII

OXIDATION TEST PROGRAM

A. PROGRAM OUTLINE

The test conducted in this portion of the test program consisted of:

1. Static oxidation tests in still air at: 2000-2800°F for columbium alloys

   2400-3200°F for the tantalum alloy

2. Dynamic oxidation test in air moving at:
   200 Ft/sec at: 2200-2800°F for columbium alloys

   2400-3000°F for the tantalum alloy

3. Partial pressure tests at 10^{-2} torr and 1 torr at:
   2000-2600°F for columbium and tantalum alloys

These tests were conducted, when appropriate, on all fastener configurations. All tests described in this section were conducted at Standard Pressed Steel except the static oxidation tests on T-222 which were conducted at Vitro Laboratories.

Detailed descriptions of the procedures and results follow.

B. PROCEDURES AND EQUIPMENT

1. Static Oxidation - These tests were conducted in a tubular globar furnace with 3" diameter mullite muffle using high purity, alumina boats to support the parts. This furnace is shown in Figure 37. It is controlled by means of Platinum-Platinum + 10% Rhodium thermocouples used in conjunction with a Leeds and Northrup current adjusting type controller and a saturable core reactor. The correlation between part temperature and furnace temperature was constantly checked by inserting a Pt-Pt+10% Rh thermocouple with the junction directly beneath the alumina boat.

   Because of the difficulty involved in the observation of all surfaces of a fastener during test, a program of cyclic oxidation was established. This consisted of exposing the parts to three, 4-6 hour cycles (with inspection between cycles), followed by cycles

from 16-20 hours until failure was observed. Time to heat from room temperature to test temperature or cool from test temperature was about 20 minutes.

The static oxidation tests on T-222, which were conducted at Vitro, were performed in an induction heated tube furnace with an alumina muffle. The parts were supported on three-layer setters as described in Section VI, C. Exposure was continuous.

2. Dynamic Oxidation - These tests were conducted in an apparatus built specifically for this purpose. The apparatus has a capability of subjecting parts to air velocities of up to 250 ft/sec and temperatures of up to 3000°F.

The test apparatus consisted of an A.C. arc device which was controlled by a variable reactance coil. This arc device was so constructed as to permit passage of metered air through the arc gap thereby heating the air to near arc temperatures. The specimen being tested was placed on the downstream side of the arc in the air stream. A refractory chamber was provided at this location for support of the specimen. After a few minutes of operation the chamber and specimen were close to equilibrium conditions, thus minimizing the heat lost by the specimen through radiation. Specimens in the chamber were supported by alumina fingers except in the case of T-222 where the parts were inserted through a hole in the chamber and were externally supported. Photographs of the apparatus are shown in Figures 38 through 41.

a. Control of Parameters

(1) Temperature - Control was accomplished by means of the coarse adjustments of the choke coil in the 440 V.A.C. line and by the fine adjustment of the current in the D.C. field coil surrounding the arc device. Temperature was measured by means of a Pyro optical pyrometer after the correlation between downstream-optical temperature and upstream actual temperature had been established using emissivity determined in the tube furnace and optical temperature readings taken on the upstream side of the specimen. Temperatures reported in the results are optical readings corrected for emissivity and position.

(2) Air Velocity - Air volume and pressure were varied and metered prior to entering the arc. The hot air stream velocity was then calculated on the basis of ambient and specimen temperature, initial and discharge pressure, initial flow rate, and the throat area around the specimen.

3. Partial Pressure Oxidation - These tests were conducted in two different facilities dependent upon the partial pressure level desired. The procedures differed somewhat and are therefore discussed separately.

   a Partial Pressure Level - 10^{-2} torr - These tests were conducted in the cold wall vacuum furnace shown in Figure 42. This furnace is capable of operation up to 3000°F and is equipped to operate at any preset pressure level down to 10^{-4} torr. Tests at the 10^{-2} torr level were conducted as follows: Insert parts into chamber on suitable support and seal furnace. Pump down to 10^{-2} torr and heat to temperature (heating begins at 5×10^{-2} torr). Hold at temperature for the desired length of time. Cool to room temperature. Raise pressure to 1 atmosphere and remove parts from furnace.

   b Partial Pressure Level-1mm - These tests were conducted in the tube furnace shown in Figure 37. It is a tubular globar furnace with a mullite muffle adapted for vacuum operation through the use of vacuum tight seals and a mechanical vacuum pump capable of maintaining a pressure of 5×10^{-2} torr in the tube. Desired pressure levels are maintained by a controlled leak at the end of the tube opposite the pumping system. The tests were conducted as follows:

   With furnace at 2000°F and dry argon flowing through the muffle, slowly insert part into the center of the furnace. Shut off argon, seal tube end and evacuate to 1 torr. Raise temperature to test level. Hold the desired length of time. Reduce temperature to 2000°F. Shut vacuum system off and raise pressure to 1 atmosphere by admitting argon.

   Open tube end, continue argon flow, and withdraw part to end of tube. Remove part when it cools to room temperature.

C. TEST PROGRAM AND RESULTS

1. Static Oxidation - The tests of static oxidation were performed on columbium alloys at 2200°F, 2400°F, 2600°F, and (in a few cases) 2800°F. All pieces were tested to failure except for two pieces which were exposed for 116 hours with no failure, the test being discontinued at that time. The results of these tests are shown in Table XXV and Table XXVI and are graphically presented in Figure 43. Photographs of tested parts are shown in Figures 44, 45, and 46.

The tests of T-222 were conducted at 2400°F, 2700°F, 3000°F, and 3200°F. All pieces were tested to failure except those pieces which had not failed in 134 hours. The results of these tests are shown in Table XXIV. Photographs of some tested parts are shown in Figure 47.

2. Dynamic Oxidation - These tests were performed at 2200°F, 2400°F, and 2600°F on columbium alloys and at 2400°F, 2700°F, and 3000°F on T-222. All tests were continued to failure.

   Orientation of the columbium hex head bolts and nuts was with the bolt centerline vertical, and therefore perpendicular to the hot air stream which is horizontal. Some parts were tested with the bolt head up while others were tested with the bolt head down.

   Testing of the flush head bolts in the same position as the hex head bolts would have exposed the thin edge of the head to conditions which they would not encounter in service since they would be installed in countersunk holes and would not protrude.

   The flush heads were therefore oriented as shown in Figure 48. The temperature of the threaded end was used as the controlling temperature.

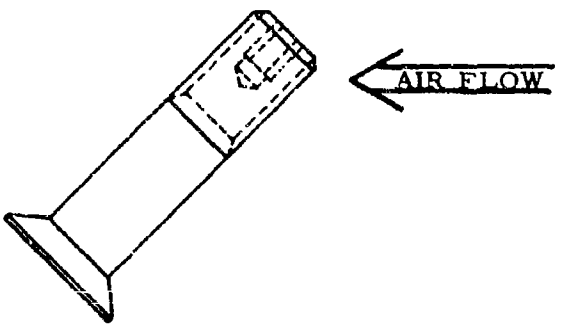


Figure 48. Columbium Alloy Flush Head Bolt DynamicOxidation Specimen Orientation

The T-222 bolts were tested as shown in Figure 49 to avoid the high temperature reaction between the WSi_2 coating and the Al_2O_3 test specimen supports.

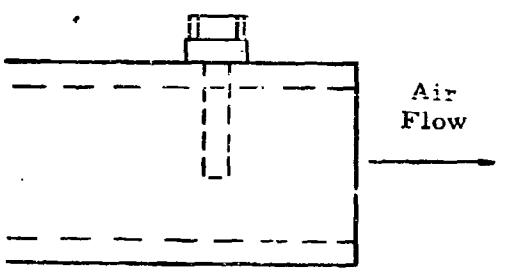


Figure 49. T-222 Oxidation Test Specimen Orientation

The results of the dynamic oxidation tests are shown in Tables XXVIII, XXIX, and XXX. The columbium alloy test results are shown graphically in Figure 50 and photographs of columbium and tantalum test pieces are shown in Figures 51 through 55.

3. Partial Pressure - These tests were devised to simulate the effects of elevated temperatures and low pressures encountered during high velocity flight at altitudes of 30-50 miles above the earth. These environments were investigated in terms of their effects on the base metal-coating system directly and on their effects on the ability of the coating system to withstand subsequent atmospheric pressure elevated temperature exposure. Since prior oxidation was believed to have an influence on the partial pressure effects, a preoxidation treatment of 2000°F for 15 minutes was adopted. This was considered the maximum exposure which the materials would experience prior to encountering low pressure. The importance of this preoxidation was evaluated by testing several parts without this treatment.

   a. Columbium Alloys with Cr-Ti-Si Coating - The first tests were conducted at 3000°F to observe the mode of failure under extreme conditions. Two Cb752 and C129Y bolts were preoxidized at 2000°F in air for 15 minutes then heated to 3000°F at 10^{-2} torr of air. After 12 minutes at temperature, severe outgassing from the specimens caused the chamber pressure to increase to above .05 torr at which pressure the furnace heating control automatically shuts off. The parts were cooled to room temperature as described above. Examination of the specimens showed severe blistering of the coating over the entire surface (Figure 56a). These specimens were then tested in air and failed after 2 minutes between 2000°F and 2200°F (while being heated toward 2400°F). Failure occurred by base metal oxidation over the entire surface (Figure 56b).

   The next tests were run at 2600°F, 10^{-2} torr of air using Cb752 and C129Y hex head bolts. After 6 hours, severe flaking of the coating had occurred. Two pieces (one of each material) were then tested in air in the following sequence:

   1 hour - 2400°F - (Figure 57a)
   +1 hour - 2600°F - (Figure 57b)
   +1 hour - 2600°F - Failure (Figure 57c)

   The remaining pieces were exposed at 2600°F and 10^{-2} torr up to a total of 23 hours (Figures 58a and 58b). They were then heated in air and failed before reaching 2200°F (Figure 58c).

   The effect of the lack of preoxidation on the partial pressure failures was assessed by exposing Cb752 and C129Y bolts to the

2600°F - 10^{-2} torr environment without previous oxidation. After 13 hours the coating had flaked severely (Figure 59a). Exposure of these specimens to 2400°F air resulted in failure of the Cb752 specimen in 3 hours and the C129Y specimen in 7 hours (Figure 59b). These lives are considerably less than would be expected without the partial pressure treatment.

An uncoated Cb752 bolt was processed through all 2600°F - 10^{-2} torr cycles as a control. It remained completely free of oxidation throughout the tests.

The nuts were free spinning on all specimens after partial pressure cycles.

A summary of these tests is shown in Table XXVIII.

Following the above described preliminary tests, an orderly program was established to perform the following:

Preoxidize Cb752 and C129Y bolts and nuts at 2000°F for 15 minutes. Expose these bolts and nuts to 2000°F and 2400°F at 10^{-2} torr and 1 torr for 4 hours then subject the pieces thus exposed to static air at 2400°F to failure. The results of this program are contained in Table XXXII and the tested parts are shown in Figures 60 and 61.

b. Tantalum Alloy with Si-WSi_2 Coating - The initial tests were conducted at 10^{-2} torr and 2600°F to determine the rate of coating volatilization under these conditions. Preoxidized parts exposed for 10 minutes lost an average of 4 mg/cm^2 and parts exposed 1 hour lost an average of 6.5 mg/cm^2. The effect of preoxidation on this behavior was determined by exposing a few as coated studs to 10^{-2} torr and 2600°F for 10 minutes. The pieces lost an average of 6.5 mg/cm^2. Additional parts were exposed to .01 torr and 2600°F for 1 hour with a resulting average loss of 4.2 mg/cm^2. These were then exposed in air at 2400°F and they failed in three hours. This compares to the 2400°F life of unpreoxidized Si-WSi_2 coated T-222 reported in Section VI. Exposure to parts to 10^{-2} torr and 2400°F produced weight losses averaging 4.1 mg/cm^2 and subsequent failure at 2400°F in air in two hours. T-222 hex head and flush head bolts exposed at .01 torr and 2200°F lost an average of $<$.1 mg/cm^2 and failed in subsequent 2400°F air exposure in two and six hours respectively.

Exposure at 1 torr and 2400°F for 7 hours produced less than .01 mg/cm^2 weight loss and exposure at 1 torr and 2200°F for 7 hours produced no weight loss. The 2400°F bolts failed in three hours in air at 2400°F and the 2200°F bolts failed in 5 and 12 hours.

The results of these tests are shown in Table XXXIII and typical tested parts are shown in Figures 62 and 63.

D. DISCUSSION OF RESULTS

Results of the static oxidation tests of the columbium alloys indicate that the oxidation lives of the two alloys in both configurations are essentially equal and the areas of failure are distributed over several locations.

The dynamic oxidation test results show a significant reduction in life compared to the static oxidation results. The dynamic results were generally only 4-8% of the static results.

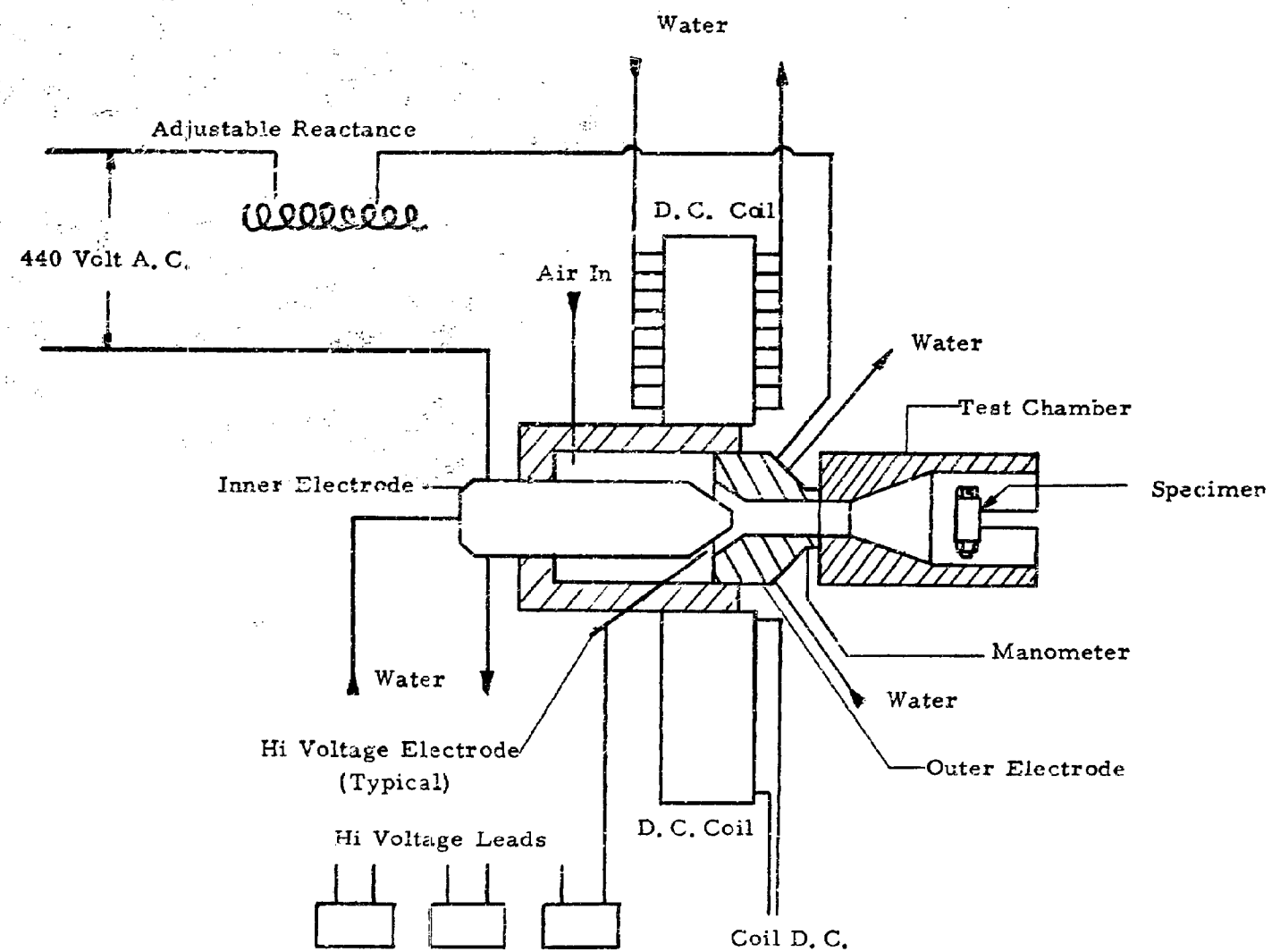
At the 2400°F test temperature which was common to the columbium and tantalum alloys, the dynamic oxidation lives were essentially equal for all three alloys.

In the partial pressure tests on columbium alloys the results indicate that C129Y is unaffected by exposure to 2000°F or 2400°F at 10^{-2} torr or 1 torr for up to 4 hours. The Cb752, on the other hand, exhibits a degrading effect which is most significant at 1 torr for both temperatures.

The Si-WSi_2 coated T-222 exhibits considerable degradation of coating at both 1 torr and 10^{-2} torr at temperatures as low as 2200°F. This degradation occurs despite the absence of any significant weight loss at the lower temperatures. The degradation appears to remove the benefit of the preoxidation and results in 2400°F oxidation lives similar to those reported in Section VI for unpreoxidized Si/WSi_2 coated T-222, 2.8 hours.

Figure 37 - Static Oxidation and 1 Torr Partial Pressure Oxidation Test Equipment.

(Shown set up for partial pressure tests)



Schematic of Dynamic Air Oxidation Test Apparatus Gun and Test Chamber

Figure 38

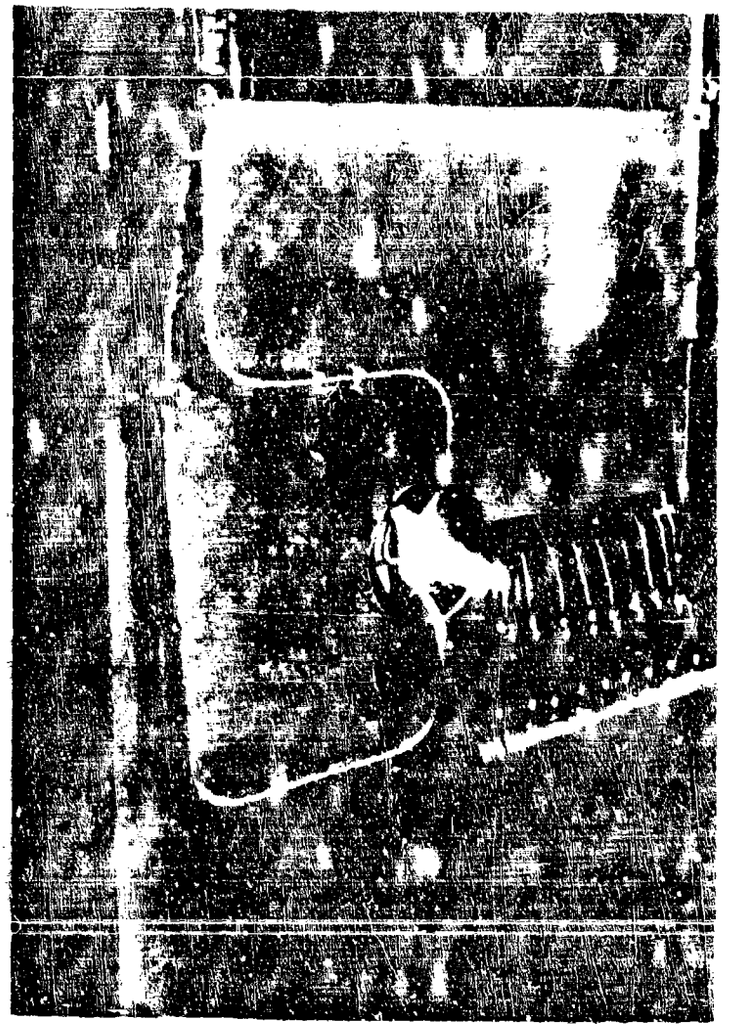


Figure 39. Dynamic Oxidation Test Apparatus Showing Hot Air Stream Without Test Chamber

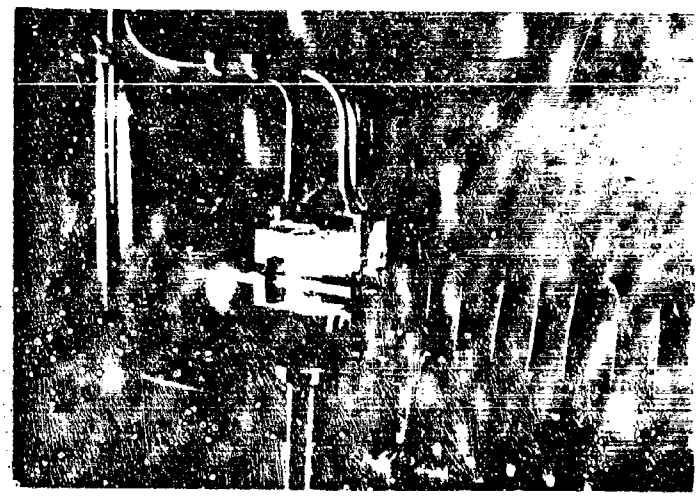


Figure 40 Specimen Holder and Test Chamber With Specimen Outside Chamber.

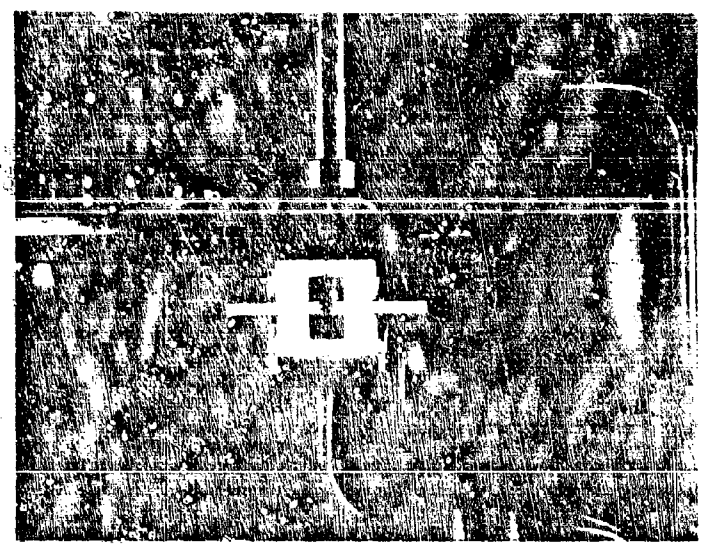


Figure 41 Specimen Holder and Test Chamber With Specimen in Chamber.

Figure 42 Partial Pressure Oxidation Test Equipment for 10^{-2} torr Tests

TABLE XXV

STATIC OXIDATION LIFE OF VITRO Cr-Ti-Si COATED COLUMBIUM ALLOY

1/4-20 HEX HEAD BOLTS AND NUTS

Test Temperature		Cb 752		C129Y	
		Life (hours)	Location of Failure	Life (hours)	Location of Failure
°F	°C				
2200	1204	73-79 60-76	Head Nut Bearing Face & Head	60-76 50-53	Th'd Crest-Nut Corners Th'd Crest-Nut Corners
2400	1316	34-38 28-32	Th'd Crest & Fillet * Nut Corner	30-35 30-35	Th'd Crest Fillet *
2600	1427	6-12 6-12 6-12	Nut Face & Fillet * Nut Face, Fillet* & Head Th'd Crests	6-12 12-18 6-12	Fillet* - Body Th'd Crest & Fillet* Fillet*
2800	1538	3/4 1/2	Thread Thread	1/3 1	Thread Thread

* Under Head Fillet

TABLE XXVI

STATIC OXIDATION LIFE OF VITRO Cr-Ti-Si COATED COLUMBIUM ALLOY
1/4-20 POINT-DRIVE BOLTS AND NUTS

Test Temperature		Cb752		C129Y	
		Life (hours)	Location of Failure	Life (hours)	Location of Failure
°F	°C				
2200 F	1204 C	32-48 72-88	Thread Head and Thread	116 116	No Failure No Failure
2400 F	1316 C	14-21 14-21	Thread Head and Thread	14-21 28-32	Head and Thread Nut
2600 F	1427 C	9-12 8-11	Head and Nut Head	9-12 8-11	Head Thread and Nut

TABLE XXVII

STATIC OXIDATION LIFE OF Si/WSi_2 COATED

1/4-20 T-222 BOLTS *

Test Temperature		Hex Head Bolts		Flush Head (Point-Drive) Bolts	
°F	°C	Life (hours)	Location of Failure	Life (hours)	Location of Failure
2400	1316	150 150 150	No Failure No Failure No Failure	134 134 134	No Failure No Failure No Failure
2700	1482	10.5 20-35 71.5	Head and Threads Totally Oxidized Shank	4.5 7.5-23 31-47	Hex Recess Totally Oxidized Totally Oxidized
3000	1650	1.5 2.5 2.8	Shank and Head Head Shank and Head	2.2 5.8 3.3	Hex Recess Threads Threads
3200	1760	3.5 2.5 3.5	Shank No Failure Head	0.5 0.5 0.7	Head Shank and Head Threads

* 2400°F and 2700°F specimens were preoxidized at 2910°F for 15 minutes prior to testing.

TABLE XXVIII

DYNAMIC OXIDATION LIFE OF VITRO Cr-Ti-Si COATED COLUMBIUM ALLOY
1/4-20 HEX HEAD BOLTS AND NUTS (AIR VELOCITY 200 FT. /SEC.)
61 meters/sec.

Test Temperature		Cb 752 Alloy			C129Y Alloy	
		Position	Life (hours)	Failure Location	Life (hours)	Failure Location
°F	°C					
2200	1204	U	2.7	All Upstream Surfaces	3.9	All Upstream Surfaces
2400	1316	U	2.3	All Upstream Surfaces	1.35	All Upstream Surfaces
		D	1.2	All Upstream Surfaces	1.20	Thread and Nut
		U	2.1	Nut, Thread and Head	1.80	Thread and Nut
2600	1427	U	.53	All Surfaces	.9	Thread and Nut
		U	.960	Nut and Thread	.69	Complete Surface
		D	.60	Nut, Thread and Head	1.04	Complete Surface
2800	1538	U	.3	Head and Body	.3	Thread and Nut
		D	.025	Head and Body	.18	Thread and Nut
		U	.07	Head and Body	.05	Thread and Nut

H- Head up during test
D- Head down during test

TABLE XXIX

DYNAMIC OXIDATION LIFE OF VITRO Cr-Ti-Si COATED COLUMBIUM ALLOY 1/4-20 POINT-DRIVE BOLTS (AIR VELOCITY 200 Ft/sec- 61 meters/sec)

Test Temperature		Cb752		C129Y	
°F	°C	Life (hours)*	Failure Location	Life (hours)*	Failure Location
2200	1204	2.40	Hex-Recess and Threads	3.3	Hex-Recess and Threads
		2.10	Hex-Recess and Threads	3.6	Hex-Recess and Threads
		2.40	Hex-Recess and Threads		
2400	1316	0.90	Hex-Recess and Threads	1.8	Hex-Recess and Threads
		1.20	Hex-Recess and Threads	2.1	Hex-Recess and Threads
		1.30	Hex-Recess and Threads		
2600	1427	.41	Hex-Recess and Threads	.39	Hex-Recess and Threads
		.16	Hex-Recess and Threads	.39	Hex-Recess and Threads
		.48	Hex-Recess and Threads		

* Parts check at 0.3 hour intervals except when failure became obvious during a cycle.

TABLE XXX

DYNAMIC OXIDATION LIFE Si/WSi_2 COATED T-222 1/4-20 HEX HEAD BOLTS - THREADS EXPOSED (VELOCITY 200 FT/SEC-61 METERS/SEC)

Test Temperature		Life (Hours)*	Failure Location
°F	°C		
2400	1316	3.1 2.2 0.9	Thread Thread Thread
2700	1482	0.6 0.9 1.2	Thread Thread Thread
3000	1649	0.3 0.3 0.8	Thread Thread Thread

* Parts check at .3 hour intervals except when failure became obvious during a cycle

TABLE XXXI

SUMMARY OF 10^{-2} TORR PARTIAL PRESSURE TEST ON 1/4-20 COLUMBIUM ALLOY BOLTS AND NUTS

	TEST SEQUENCE →				
Specimen	Preox 2000°F (1093°C)	2600°F - 10^{-2} torr (1427°C)	2400°F Air (1316 C)	2600°F Air (1427°C)	Figure No.
Cb752 hex head	15 min.	6 hrs. (Flaking)	1 hr.	2 hrs. - Failure	57
C129Y hex head	15 min.	6 hrs. (Flaking)	1 hr.	2 hrs. - Failure	
Cb752 hex head	15 min.	23 hrs. (Flaking after 6 hrs.)	2 min. Failure (Below 2200°F)	---	
C129Y hex head	15 min.	23 hrs. (Flaking after 6 hrs.)	2 min Failure (Below 2200°F)		58
Cb752 hex head	----	13 hrs.	3 hrs. - Failure	----	59
C129Y hex head	----	13 hrs.	7 hrs. - Failure		
Cb752 hex head	15 min.	12 min.	2 min. (bet. 2200°F & 2400°F)	----	56
C129Y hex head	15 min.	12 min.	2 min. (bet. 2200°F & 2400°F)		

TABLE XXXII

OXIDATION LIFE OF VITRO Cr-Ti-Si COATED 1/4-20 POINT-DRIVE FASTENERS AT 2400°F (1316°C) IN STATIC AIR AFTER FOUR HOURS OF PARTIAL PRESSURE EXPOSURE. ALL PARTS PREOXIDIZED AT 2000°F (1093°C) FOR 15 MINUTES PRIOR TO PARTIAL PRESSURE EXPOSURE

Partial Pressure History			Material	Exposure at 2400°F (1316°C) in Static Air		
				Life-hrs	Location of Failure	Average Life
Temp.	Pressure	Time				
2000°F (1093°C)	10^{-2} torr	4 hrs.	Cb752	14-18 6-12	Nut Corner Thread Crest	13
			C129Y	26-30 32-34	Nut Faces Nut Faces	32
2400°F (1316°C)	10^{-2} torr	4 hrs.	Cb752	2-6 12-16	Thread Crest Thread Crest	10
			C129Y	20-24 22-24	Thread Root Nut Faces	23
2000°F (1093°C)	1 torr	4 hrs.	Cb752	0-4 2-6	Thread Thread	3
			C129Y	24-30 20-22	Nut Faces Thread Crest	24
2400°F (1316°C)	1 torr	4 hrs.	Cb752	0-4 2-6	Thread Crest Thread Crest	3
			C129Y	36-40 18-24	Nut Faces & Thread Nut Faces	30

Static Oxidation Life of Vitro Cr-Ti-Si Coated Point Drive Bolts at 2400°F without Partial Pressure Exposure - Cb752 14-21 hours; C129Y 14-32 hours.

TABLE XXXIII

SUMMARY OF PARTIAL PRESSURE TEST RESULTS ON Si/WSi_2 COATED 1/4-20 T-222 BOLTS

→ TEST SEQUENCE →

Specimen	Pre-ox - 2912°F (1500°C) - 15 minutes	Partial Pressure Exposure	Average Wt. Loss mg/cm^2	2400°F in Air	Fig. No.
T-222 Flush Head	Yes	10^{-2} torr 2600°F 10 min.	4	---	62a
T-222 Studs	No	10^{-2} torr 2600°F 10 min.	6.5	---	62b
T-222 Flush Head	Yes	10^{-2} torr 2600°F 1 hour	6.5	---	62c
T-222 Hex Heads	Yes	10^{-2} torr 2600°F 1 hour	4.1	---	62d
T-222 Hex Heads	Yes	10^{-2} torr 2600°F 1 hour	4.2	Failed in 3 hrs.	62e
T-222 Hex Heads	Yes	10^{-2} torr 2400°F 1 hour	4.1	Failed in 2 hrs.	62f
T-222 Flush Heads	Yes	10^{-2} torr 2200°F 1 hour	< .1	Failed in 2 hrs.	63a
T-222 Hex Heads	Yes	10^{-2} torr 2200°F 7 hours	< .1	Failed in 6 hrs.	63b
T-222 Flush Heads	Yes	1 torr 2400°F 7 hours	< .1	Failed in 3 hrs.	63c
T-222 Flush Heads	Yes	1 torr 2200°F 7 hours	0	Failed in 5 and 12 hrs.	63d

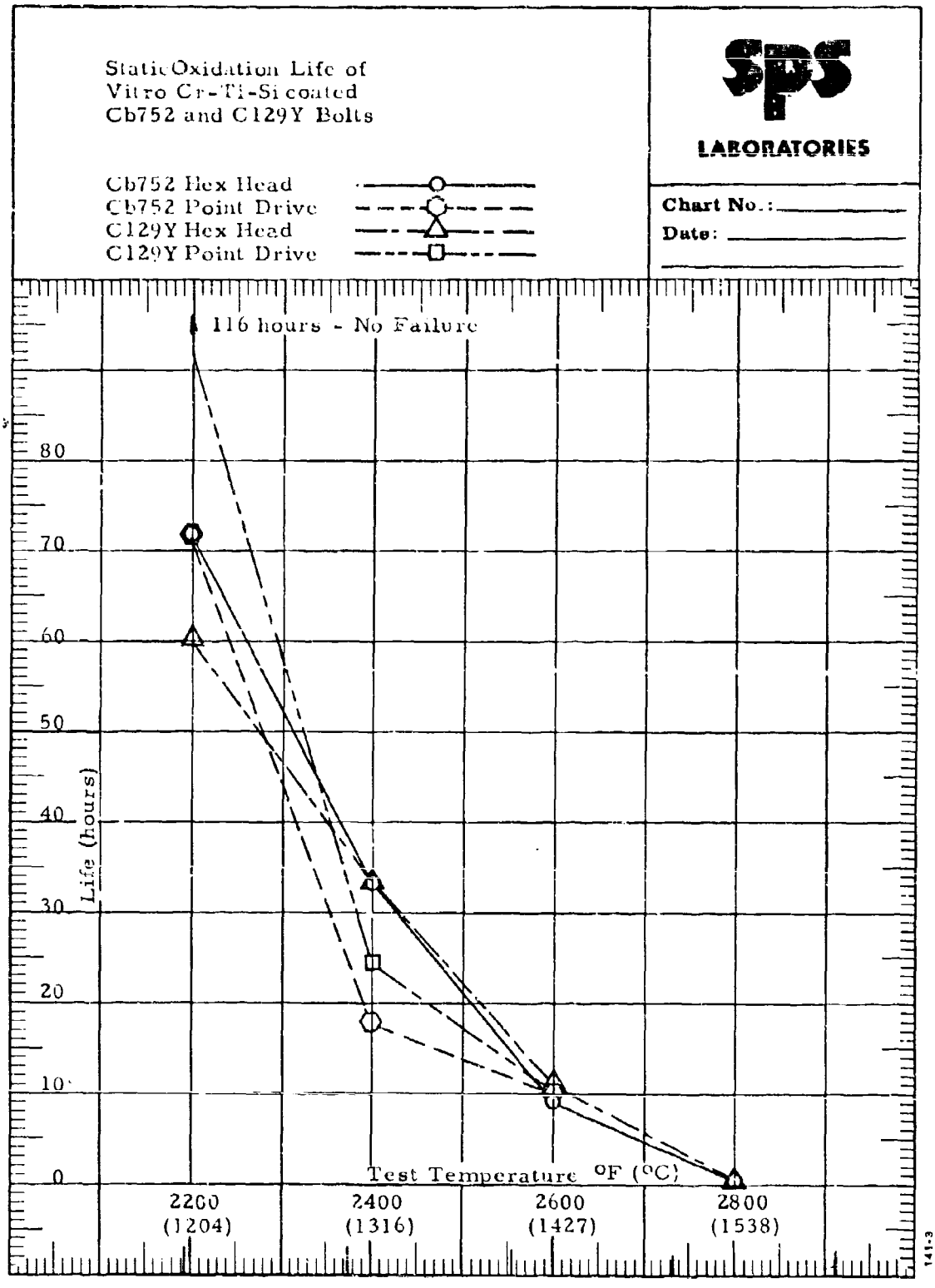
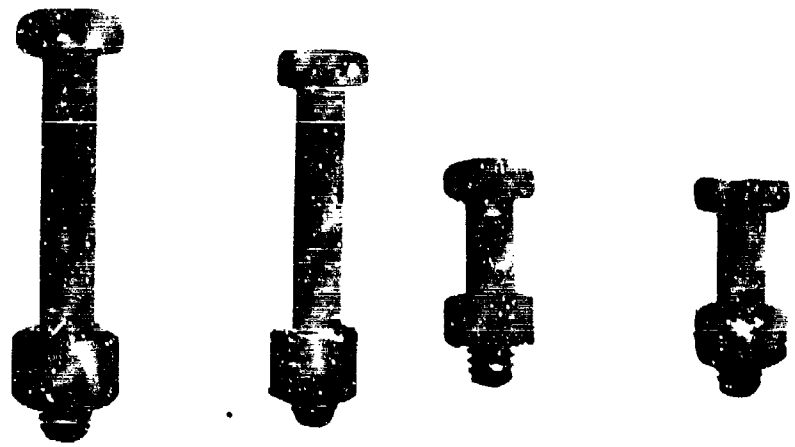
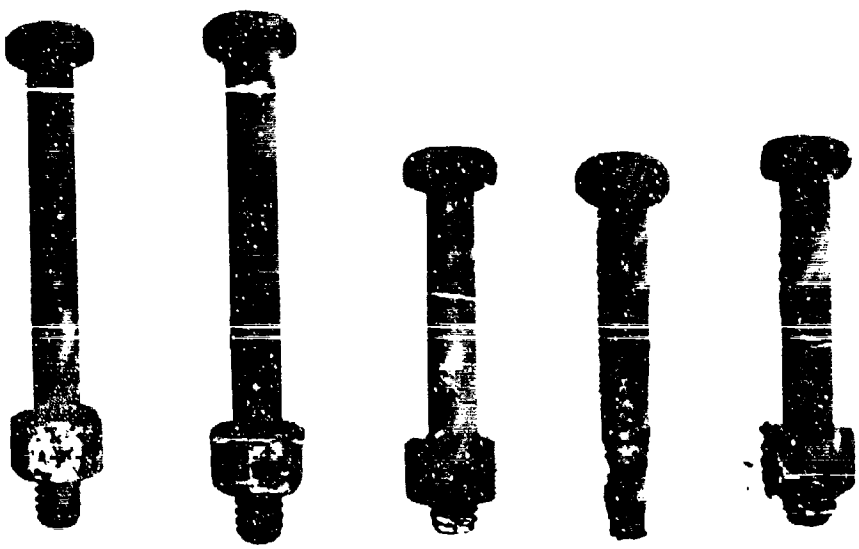

Static Oxidation Life of
Vitro Cr-Ti-Si coated
Cb752 and C129Y Bolts
Cb752 Hex Head
Cb752 Point Drive
C129Y Hex Head
C129Y Point Drive
SPS
LABORATORIES
Chart No.:
Date:
116 hours - No Failure
80
70
60
50
40
30
20
10
0
Life (hours)
Test Temperature °F (°C)
2200
(1204)
2400
(1316)
2600
(1427)
2800
(1538)
141-3

Figure 43



2200°F
(1204°C)

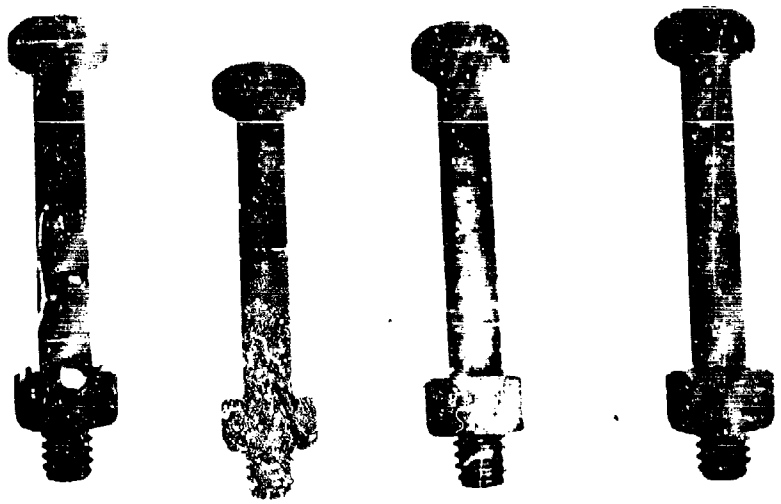
2400°F
(1316°C)



2600°F
(1427°C)

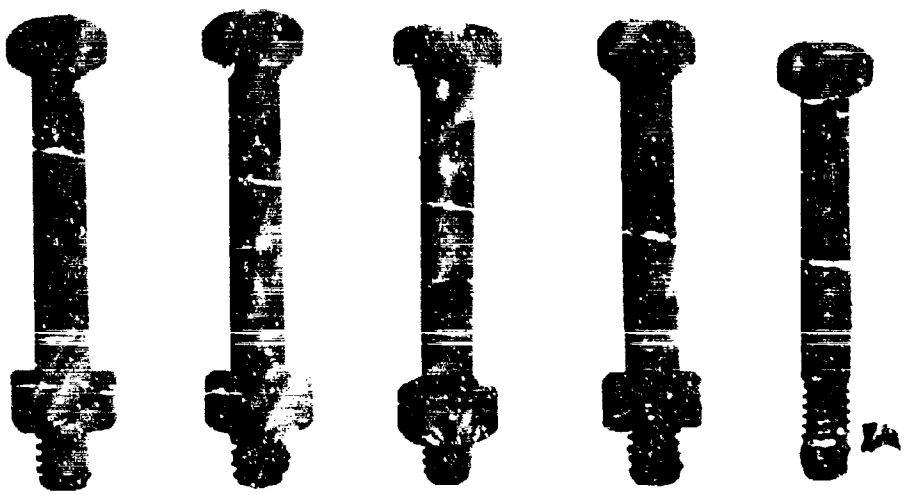
2800°F
(1538°C)

Figure 44 Cb 752 Static Oxidation Specimens
Vitro Cr-Ti-Si Coated



2200°F
(1204°C)

2400°F
(1316°C)



2600°F
(1427°C)

2800°F
(1538°C)

Figure 45. C129Y Static Oxidation Specimens, Vitro Cr-Ti-Si Coated

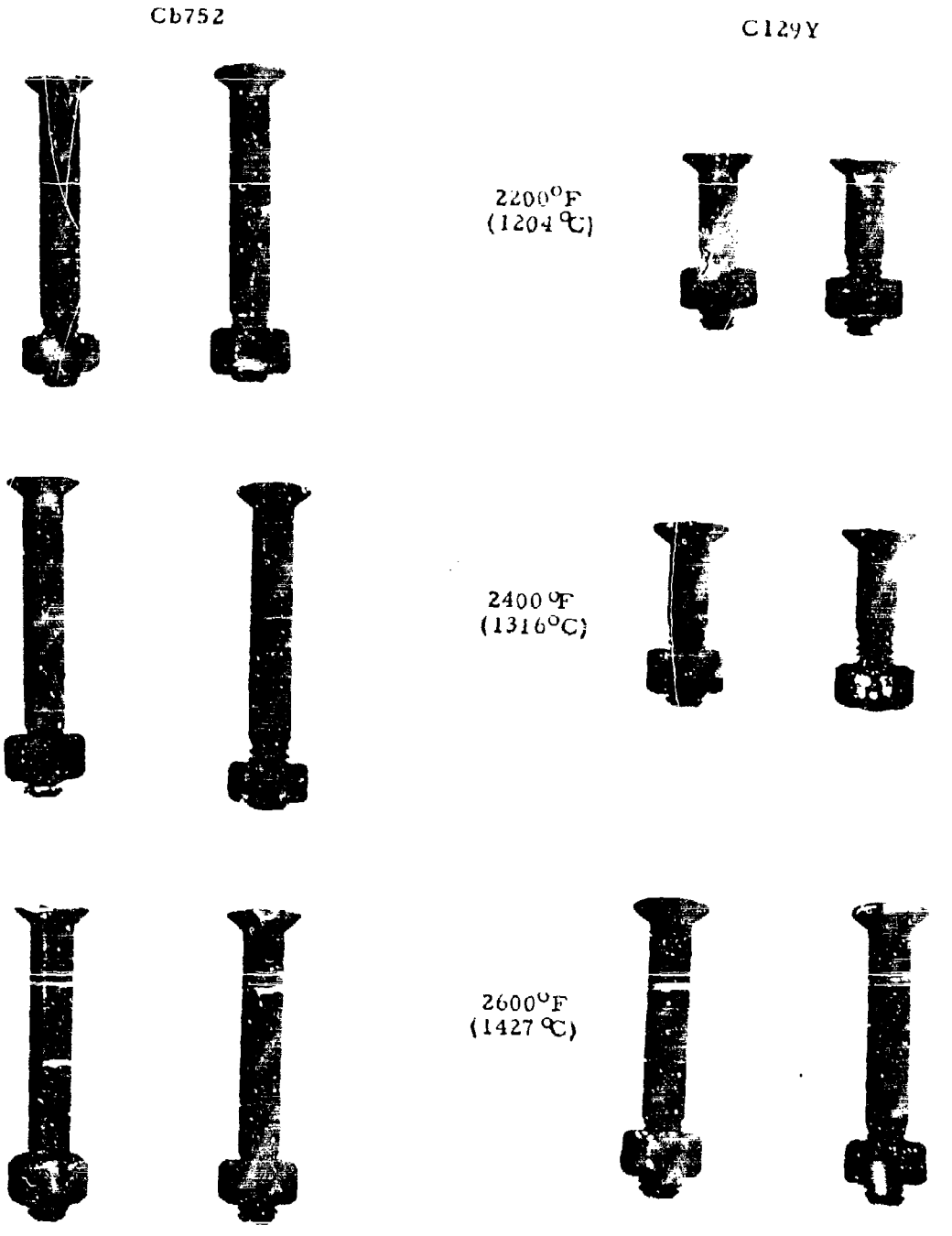


Figure 46 Static Oxidation Specimens - Columbium Alloy Vitro Cr-Ti-Si Coated Point-Drive Bolt

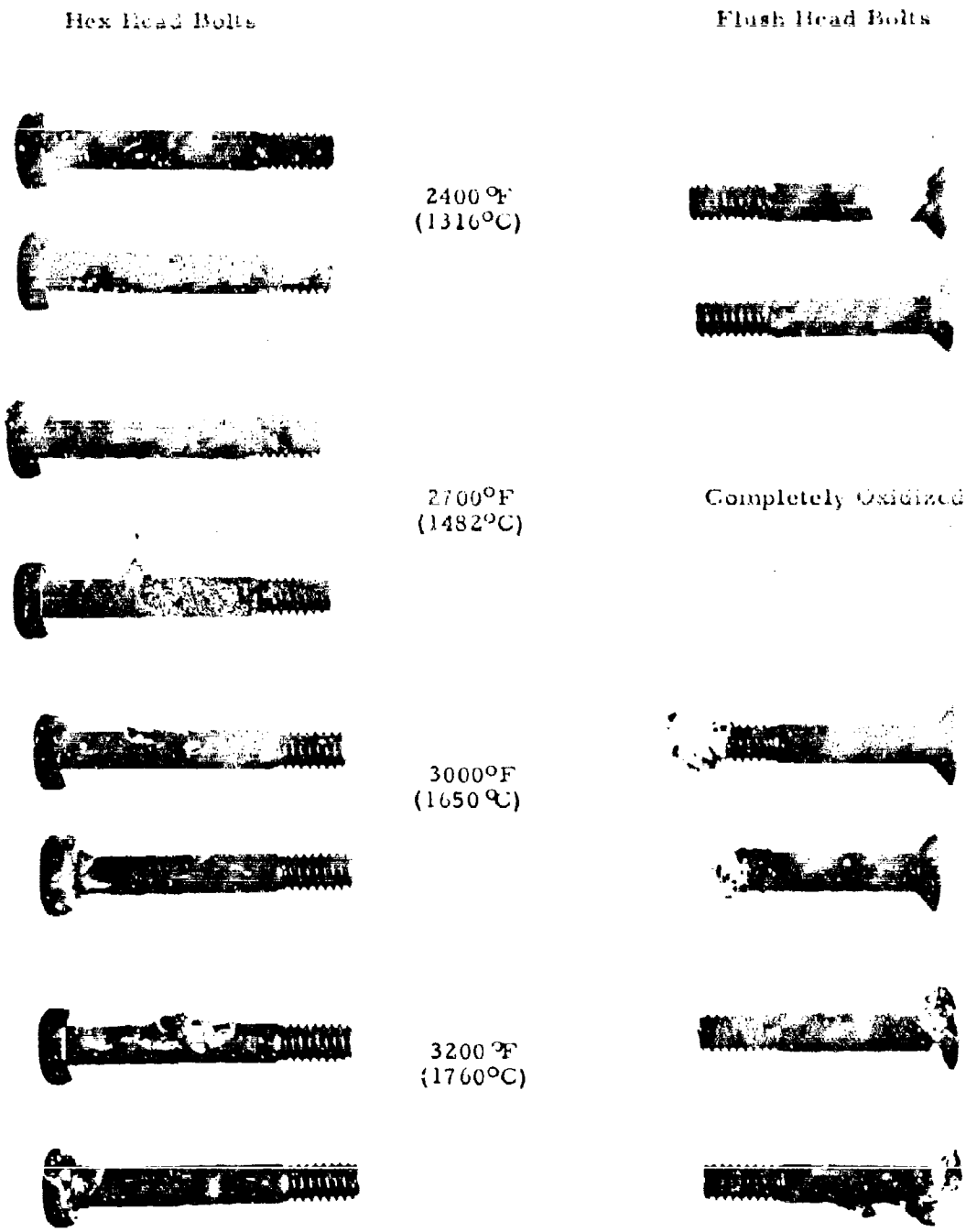


Figure 47 Static Oxidation Specimens - Si/WSi_2 Coated T-222

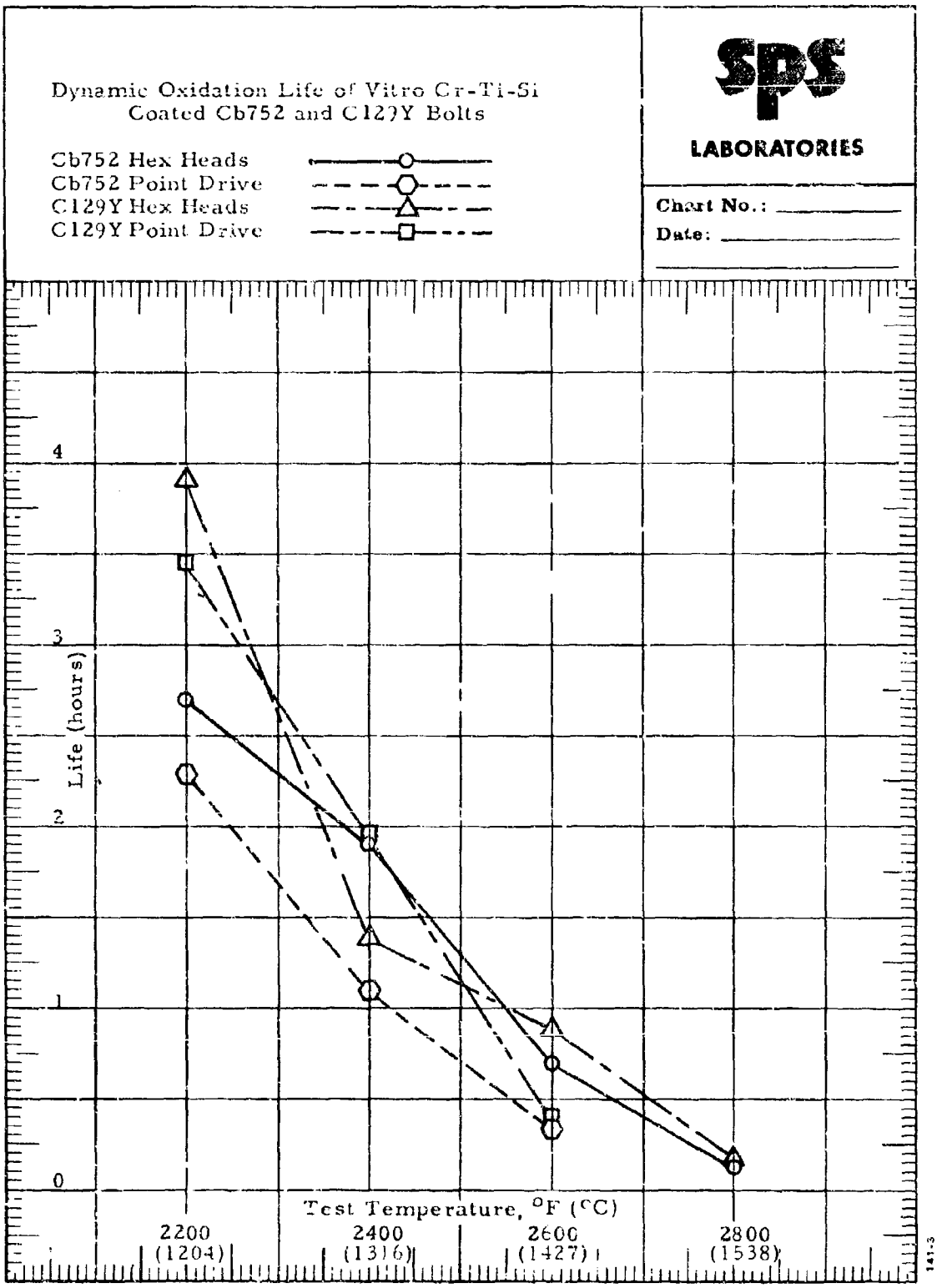
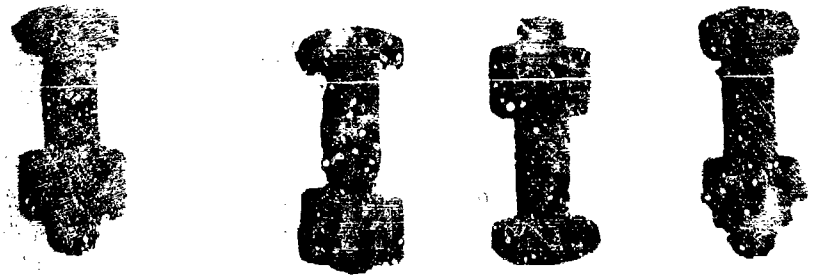
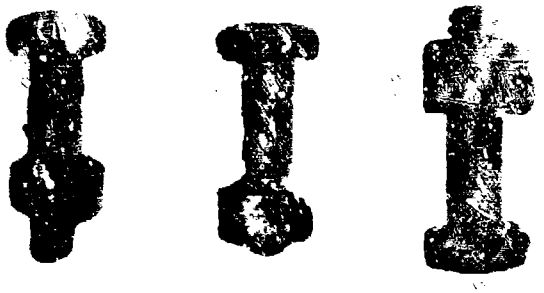

Dynamic Oxidation Life of Vitro Cr-Ti-Si Coated Cb752 and C129Y Bolts
Cb752 Hex Heads
Cb752 Point Drive
C129Y Hex Heads
C129Y Point Drive
SPS
LABORATORIES
Chart No.:
Date:
Life (hours)
0
1
2
3
4
Test Temperature, °F (°C)
2200 (1204)
2400 (1316)
2600 (1427)
2800 (1538)
141-3

Figure 50



2200°F
(1204°C)

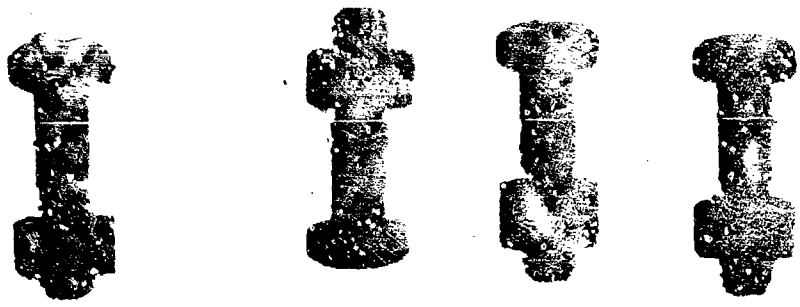
2400°F
(1316°C)



2600°F
(1427°C)

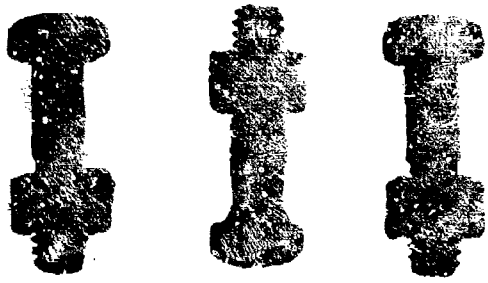
2800°F
(1538°C)

Figure 51 Cb 752 Hex Head Dynamic Oxidation Specimens, Vitro Cr-Ti-Si Coated (Tested in position shown)



2200°F
(1204°C)

2400°F
(1316°C)



2600°F
(1427°C)

2800°F
(1538°C)

Figure 52 C129Y Hex Head Dynamic Oxidation Specimens, Vitro Cr-Ti-Si coated (Tested in position shown)

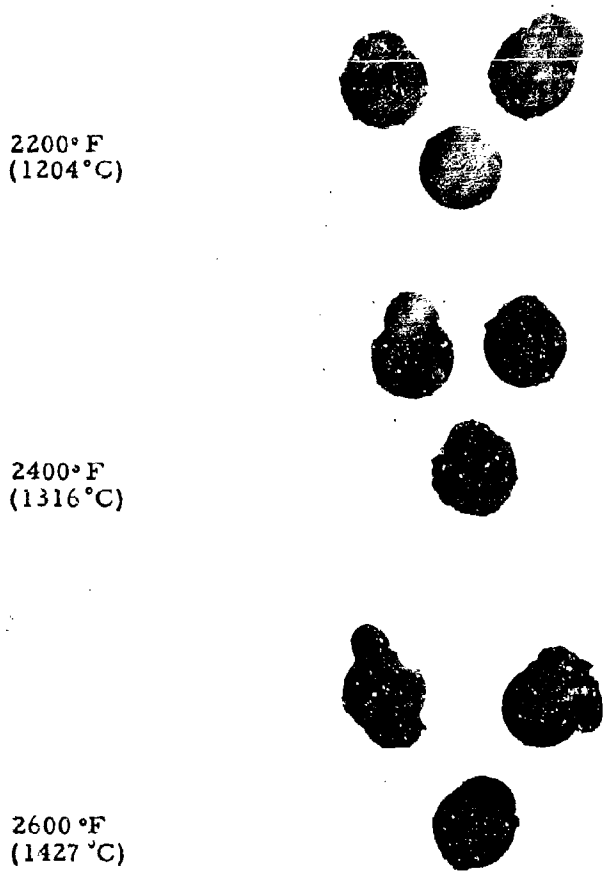


Figure 53 Cb752 Point Drive Dynamic Oxidation Specimens, Vitro Cr-Ti-Si Coated

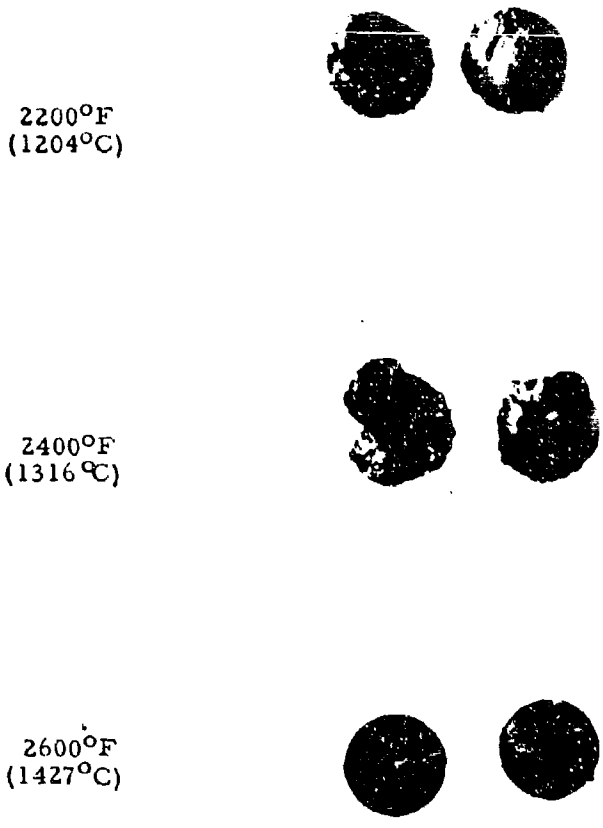


Figure 54 C129Y Point-Drive Dynamic Oxidation Specimens, Vitro Cr-Ti-Si Coated

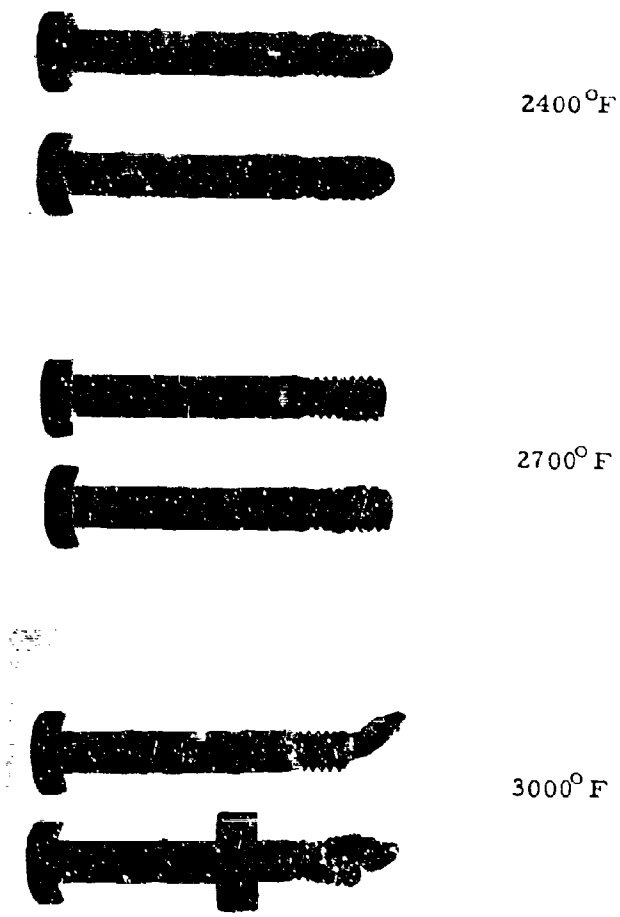
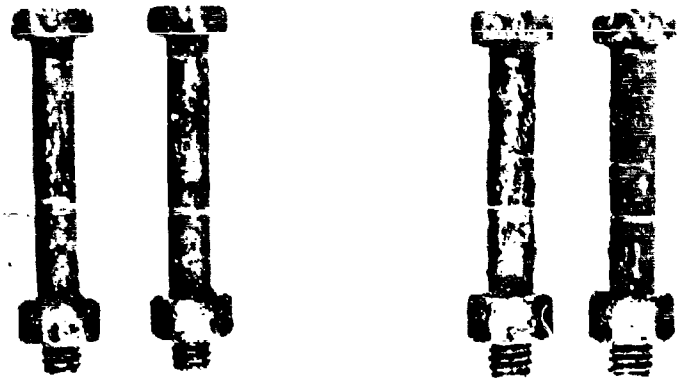
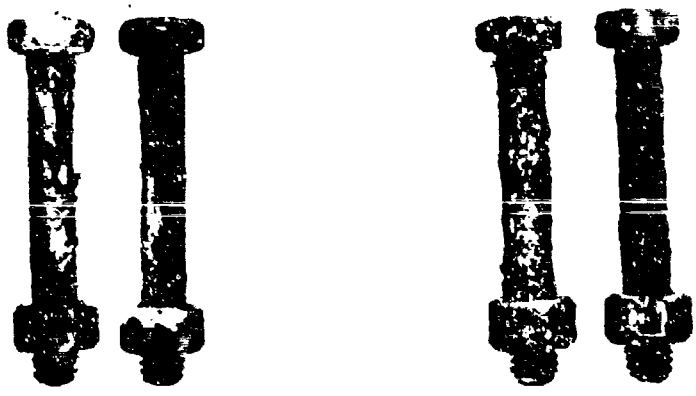


Figure 55 T-222 Dynamic Oxidation Specimens, Si/WSi_2 Coated



Cb 752 C129Y

a. Preoxidized - 2000°F (1093°C) - 15 minutes in air, Exposed at 10^{-2} torr - 12 minutes 3000°F (1650°C)



Cb 752 C129Y

b. Exposed as in a, plus 2000°F (1093°C) in air - 2 minutes

Figure 56 Vitro Cr-Ti-Si Coated Columbium Alloy Fasteners Oxidation Tested as shown.

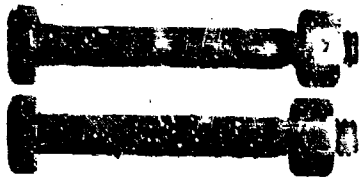
Cb 752

C129Y

a. Preoxidized - 2000°F (1093°C) - 15 minutes in air, Exposed at 10^{-2} torr - 2600°F (1427°C) - 6 hours 2400°F (1316°C) in air - 1 hour

Cb 752

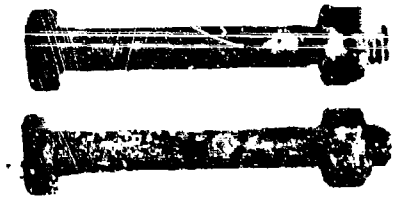
C129Y



b. Exposed as in a, plus 2600°F (1427°C) - 2600°F in air 1 hour

Cb 752

C129Y

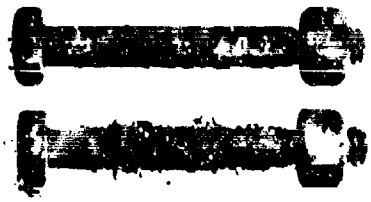


c. Exposed as in b, plus 2600°F (1427°C) in air - 1 hour.

Figure 57. Vitro Cr-Ti-Si Coated Columbium Alloy Fasteners Oxidation Tested as shown.

Cb752

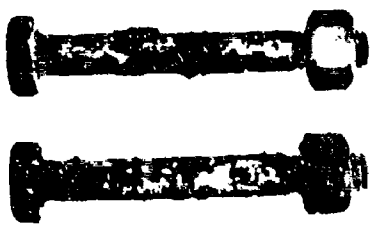
C129Y



a. Preoxidized - 2000°F (1093°C) - 15 minutes in air, Exposed at 10^{-2} torr - 2600°F (1427°C) - 10 hours

Cb752

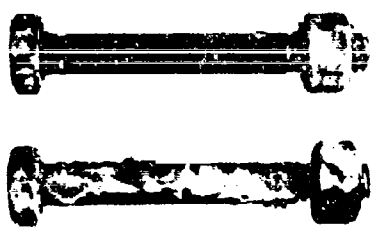
C129Y



b. Exposed as in a, plus 10^{-2} torr - 2600°F (1427°C) - 13 hours (Total 23 hours.)

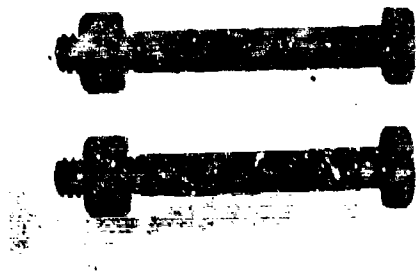
C129Y

Cb752

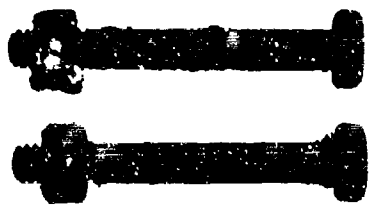


c. Exposed as in b, plus 2000-2200°F (1093-1204°C) in air - 5 minutes

Figure 58 Vitro Cr-Ti-Si Coated Columbium Alloy Fasteners Oxidation Tested as Shown

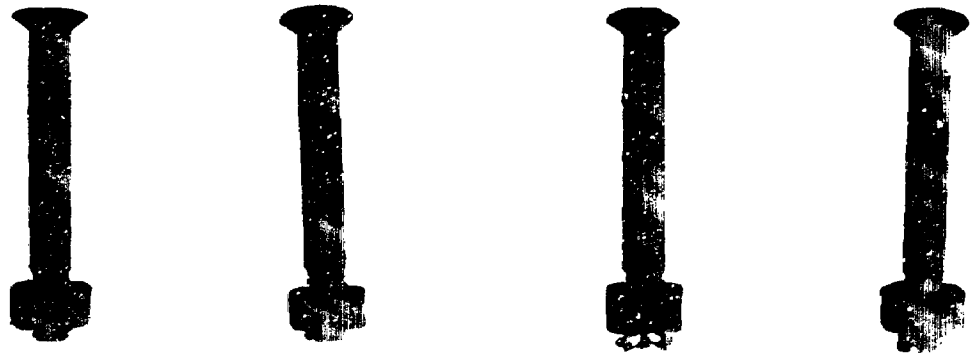


a. Exposed at 10^{-4} torr - 2600°F (1427°C) - 13 hours. (Not preoxidized).



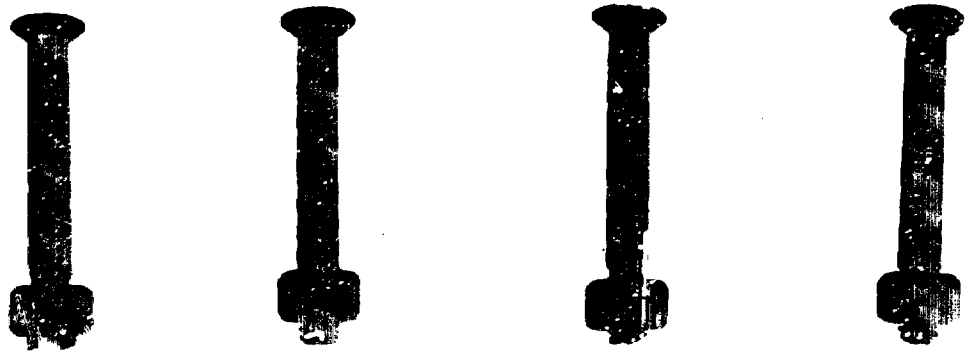
b. Exposed as shown in a, plus 2400°F (1316°C)in air 3 hours - Cb 752, 7 hours C129Y

Figure 59. Vitro Cr-Ti Si Coated Columbium Alloy Fasteners Oxidation Tested as shown.



a. 2000°F - 10^{-2} torr - 4 hours (1093° C)

b. 2000 F - 1 torr - 4 hours (1093° C)



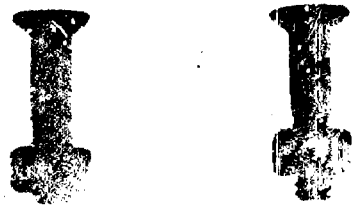
c. 2400°F - 10^{-2} torr - 4 hours (1316°C)

d. 2400°F - 1 torr - 4 hours (1316°C)

Figure 60 Partial Pressure Oxidation Specimens - Cb752 Vitro Cr-Ti-Si Coated - Exposed to partial pressures and temperatures as shown prior to 2400°F (1316°C) static air exposure to failure. See Table XXXII.

a. 2000°F - 10^{-2} torr - 4 hours (1093°C)

b. 2000°F - 1 torr - 4 hours (1093°C)

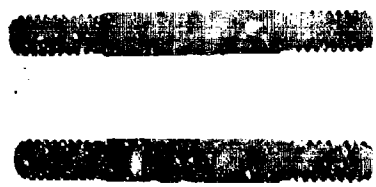


c. 2400°F - 10^{-2} torr - 4 hours (1316°C)

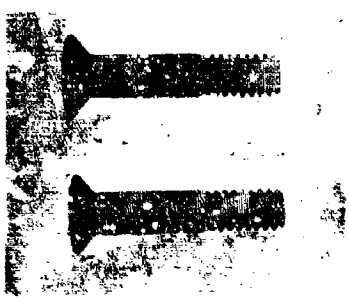
d. 2400°F - 1 torr - 4 hours (1316°C)

Figure 61 Partial Pressure Oxidation Specimens - C129Y Vitro Cr-Ti-Si Coated - Exposed to partial pressures and temperatures as shown prior to 2400° F (1316° C) static air exposure to failure. See Table XXXII.

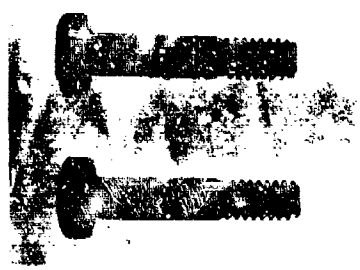
a. 10^{-2} torr - 2600°F
10 minutes



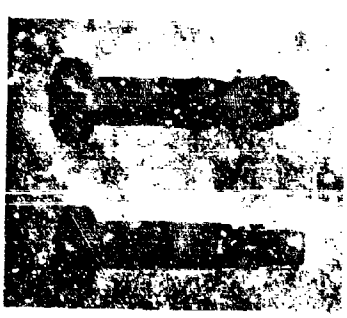
b. 10^{-2} torr - 2600°F
10 minutes



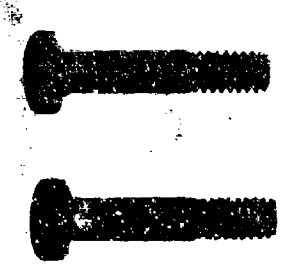
c. 10^{-2} torr - 2600°F
1 hour



d. 10^{-2} torr - 2600°F
1 hour

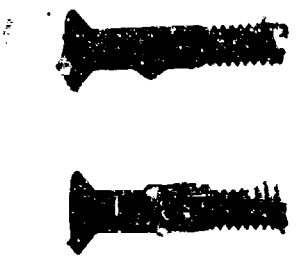


e. 10^{-2} torr -2600°F
1 hour plus 2400 F
in air - 3 hrs.

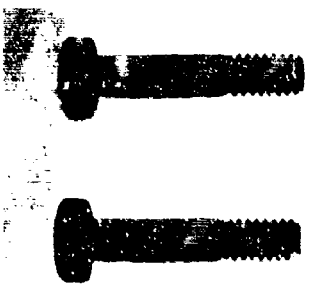


f. 10^{-2} torr - 2600°F
1 hour plus 2400 F
in air - 2 hrs.

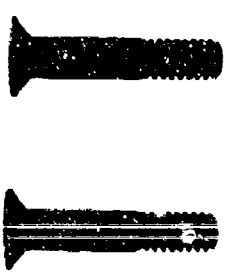
Figure 62 Partial Pressure Test Specimens
Si/WSi_2 Coated - All preoxidized except b.



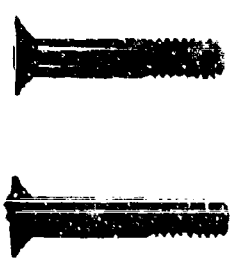
a. 10^{-2} torr - 2200°F - 1 hour
plus 2400°F in air - 2 hours



b. 10^{-2} torr - 2200°F - 7 hours
plus 2400°F in air - 6 hours



c. 1 torr - 2400°F - 7 hours
plus 2400°F in air - 3 hours



d. 1 torr - 2200°F - 7 hours
plus 2400°F in air - 5-12 hours

Figure 63 - Partial Pressure Test Specimens
Si/WSi_2 Coated - All Preoxidized

SECTION IX

MECHANICAL TESTING

A. PROGRAM OUTLINE

The mechanical testing portion of this program required the testing of all material-configuration combinations as follows:

Ultimate Tensile Strength
Ultimate Shear Strength
Fatigue Life at 50% of Ultimate Tensile Strength
Relaxation in a Tightened Joint

The tests were conducted at temperatures of from -320° F to 2600° F.

B. PROCEDURES AND EQUIPMENT

1. Ultimate Tensile Strength and Ultimate Shear Strength Tests

All tensile and shear tests were conducted in a Tinius Olsen 30,000 pound tensile testing machine.

Heating for tests at 600° F and above was accomplished by means of a Satec platinum-rhodium wound resistance furnace, capable of attaining 2800° F. The furnace was controlled by a Leeds & Northrup current adjusting control and a saturable core reactor.

Primary temperature measurement was by means of a platinum, platinum - 10% rhodium thermocouple positioned within one inch of the part being tested. Temperature accuracy was determined periodically by means of a Pyro optical pyrometer sighting through a viewing port directly in line with the test piece. The furnace was sufficiently well sealed at the ends to approximate "black body" conditions thereby permitting use of direct readings from the optical pyrometer. These readings consistently agreed with the thermocouple readings within $\pm$10° F. The furnace was altered to provide a protective atmosphere during the heating and cooling cycles to prolong the life of the fixtures. A photograph of the setup is shown in Figure 64.

The fixtures used for these tests are shown in Figures 65 through 70. They were all made of Fansteel 85 and were coated by TRW with Cr-Ti-Si coating to a thickness of .003".

The life of the fixtures was prolonged by the application of a coating of the $MoSi_2$ - Colloidal SiO_2 slurry in areas in which the coating had failed and in areas of possible mechanical damage. A few sets of coated fixtures were painted with this slurry prior to any elevated temperature exposure. These fixtures performed exceptionally well insofar as general oxidation is concerned.

The tests were performed according to the following procedure:

a. Assemble test fixtures and test piece into furnace and attach to machine.
b. Align furnace with test assembly and position test piece opposite viewing window.
c. Seal ends of furnace by packing with Fiberfrax and clamping with transite plates.
d. Insert thermocouple.
e. Turn on furnace - set controller to test temperature.
f. When temperature reaches 1000° F, turn on dry nitrogen at 15 cubic feet per hour.
g. When part temperature reaches 40° below set temperature, turn gas off (temperature rises 20 - 40° due to removal of cooling effect of the gas)
h. Allow part to remain at test temperature for sufficient time to assure temperature uniformity throughout test system. (10 minutes for 2000° F tests to no hold time at 2600° F due to slow approach to test temperature)
i. Pull test. Strain rate is 0.025 inches/inch/minutes up to yield and approximately 0.05 inches/inch/minute to failure. (for shear tests, continue cross head movement until fixtures separate as indicated by drop of load to 0)
j. Turn gas on, 15 cubic feet per hour.
k. Allow furnace to cool to 1000° F slowly
l. Shut off gas
m. When furnace reaches 400° F, remove test links and broken test piece.

2. Fatigue Tests

All tests were conducted on a Baldwin-Lima-Hamilton Ivy Fatigue Machine which maintains a constant load despite yielding or other elongation of the test system. The fixtures used for elevated temperatures are shown in Figures 65 through 70. Heating was accomplished by means of the platinum-rhodium wound furnaces that were used for the tensile and shear tests. Heating and cooling cycles were as described for tensile and shear tests. The fatigue test setups are shown in Figures 71, 72 and 73.

The fatigue tests were conducted utilizing two different methods of load application. These were as follows:

a. Axial Fatigue

These tests were conducted by applying the test loads in the axial direction. The maximum load was 50 percent of the ultimate tensile strength at the respective temperature. The minimum load was 10 percent of the maximum load.

b. Joint Shear Fatigue

These tests were conducted by applying the test load in the transverse shear direction. To accomplish this the parts were assembled into the double shear fixtures shown in Figures 67 and 68. The bolts and companion nuts were then tightened to 50 inch-pounds to simulate a typical preload condition in a tightened joint. Clearance was maintained at all times between fixture elements to minimize the effect of friction between the fixtures on the results of the test. Thus all applied load was carried by the bolt being tested. The maximum applied load was 50 percent of the ultimate shear strength at the respective temperature. The minimum load was 10 percent of the maximum load.

All tests were run at 1200 cycles per minute and were stopped at approximately 140,000 cycles if failure had not occurred.

3. Relaxation Tests

a. Preparation of Test Assemblies

The test assemblies consisted of coated hex head bolts and companion nut, tightened into simulated joints consisting of cylinders of Cb 752. The cylinders were uncoated. A typical assembly is shown in Figure 74.

The bolt and nut were tighened to the maximum torque which could be applied without danger of cracking the coating. This had been previously determined to be 50 in. -lb., on parts which had been pre-oxidized at 2000° F for 15 minutes in still air. Fifty inch-pounds produced a typical bolt elongation of 0.0012 inches for Cb alloys and .0007" for T-222. Based on a room temperature modulus of elasticity of 16×10^6 psi for Cb alloys and 28×10^6 psi for T-222 and an effective bolt length of 1.75 inches, the room temperature preload was 11,000 psi. In order to provide a smooth measuring area, it was necessary to spot drill the ends of the bolts thereby removing a small area of coating. The presence of the bare refractory alloy precluded the possibility of running the tests in air. In addition the results of partial pressure exposure tests indicated that exposure of these assemblies to vacuum at 2000° F and above would result in loss of the preload by loss of coating thickness in the bearing areas. It was therefore decided that the tests would be run in dry Argon. This provided an additional benefit since it permitted the use of uncoated cylinders thereby greatly reducing the amount of apparent relaxation which would take place as a result of plastic flow of the coating under the compressive stresses

Length measurements were taken on a Pratt-Whitney Super Micrometer. Measurements were taken as follows:

(1) Original length of the bolt
(2) Length of the bolt after application of 50 in. -lbs.
(3) Length of the bolt after high temperature soak.
(4) Length of the bolt after disassembly

b. Heating Equipment

The high temperature cycles were performed in the Harper tubular globar furnace described in the Oxidation Test Section. A protective atmosphere of dry Argon was provided throughout the cycles.

c. Test Procedure

The tests were performed as follows:

(1) Pre-oxidize bolts and nuts at 2000° F for 15 minutes in still air. This applies to Cb alloys only, since the T-222 parts had been previously preoxidized at 2912° F (1500° C).
(2) Center drill center of thread and head end of bolt.
(3) Measure length of bolt to nearest .0001 inch. Assembly bolt and nut into cylinder and tighten to 50 in. -lbs.
(4) Measure length of bolt.
(5) Place assembly on an alumina boat and insert into cold end of furnace (furnace temperature 2000° F).
(6) Assemble end plate of furnace and purge furnace with dry Argon.
(7) Continue Argon flow and push assembly slowly into hot zone of furnace (time from room temperature to 2000° F, 10 minutes).
(8) Raise furnace temperature to desired level.
(9) Hold at temperature for desired length of time.
(10) Remove assembly slowly from hot zone, allow to cool, remove from furnace.
(11) Measure length of bolt in assembly.
(12) Disassemble nut and bolt.
(13) Measure length of bolt.

Figure 74. Relaxation test Assembly Coated Cb 752 Bolt and Nut on an Uncoated Cb 752 Cylinder.

C. TEST PROGRAM AND RESULTS

1. Columbium Alloys

The mechanical tests on columbium alloy fasteners consisted of the following:

a. Ultimate tensile strength at -320°F, room temperature, 600°F, 2000°F, 2200°F, 2400°F and 2600°F.
b. Shear strength at -320°F, room temperature, 600°F, 2000°F, 2200°F and 2400°F.
c. Fatigue life at -320°F, room temperature, 600°F, 2000°F and 2400°F.
d. Relaxation at 2000°F, 2200°F and 2400°F.

All the above tests were conducted on Cr-Ti-Si coated parts in the as coated condition. Additional tests were conducted on bare parts whenever practical.

The effect of a preoxidation treatment on the tensile strength of coated parts was evaluated by exposing several C129Y flush head bolts to 2600°F in air for 15 minutes then performing room temperature tensile tests. The resulting strengths averaged 3007 pounds compared to an as coated strength of 3010 pounds.

The effect of one hour exposure at various elevated temperatures was evaluated by exposing Cb752 and C129Y flush head bolts to 2000°F, 2200°F, 2400°F and 2600°F in air followed by tensile testing at room temperature.

2. Tantalum Alloy

The mechanical tests on T-222 consisted of the following:

a. Ultimate tensile strength at -320°F, room temperature, 600°F, 2000°F, 2200°F and 2600°F.
b. Shear strength at -320°F, room temperature, 600°F, 2000°F, and 2400°F.
c. Fatigue life at -320°F, room temperature, 600°F, 2000°F, and 2400°F.
d. Relaxation at 2000°F, 2200°F and 2400°F.

Some of the above tests were conducted on fasteners in the as Si/WSi_2 coated condition. However, during the final Ta coating work at Vitro it was discovered that preoxidation of Si/WSi_2 parts at 2912° F for 15 minutes produced a marked improvement in the subsequent oxidation life at 2400° F and 2700° F. With this benefit in mind a few mechanical tests were performed on preoxidized parts. The results were remarkable. Strength was increased over the entire range from room temperature to 2600° F. In view of the dual benefit thus afforded by the preoxidation treatment, all parts were subsequently preoxidized prior to tests.

The results of the mechanical property tests are contained in Tables XXXIV to XLVI and Figures 80 to 88.

D. REUSABILITY

Throughout the program, data was collected on the factors involved in the re-use of refractory metal fasteners. The disassembly of tested parts was carefully observed to determine ease of removal, coating damage and any other significant items.

The following results were obtained based on the disassembly of Cb 752 and C129Y fasteners.

1. Seventy-five percent of the parts exposed to 2000° F or 2200° F for up to two hours were able to be disassembled without damage to the coating. The remaining 25 percent were able to be disassembled easily, but minor damage occurred to the coating, generally in the thread area.

2. Parts exposed to 2400° F for up to 2 hours were able to be disassembled in 50 percent of the cases with some coating damage occurring, generally in the thread area. Attempts to disassemble the balance met with bolt failure or severe damage to the coating both in the threads and on the wrenching surfaces.

3. Parts exposed to 2600° F for as little as 15 minutes all suffered either bolt failure by shearing or severe coating damage.

E. DISCUSSION OF RESULTS

While the mechanical property test results are generally self explanatory; there are a few items which should be discussed. These include :

1. Coating of columbium alloy fasteners has the effect of reducing the room temperature tensile and shear strengths 7% and 4% respectively.

2. Coating of T-222 fasteners has the effect of reducing the room temperature tensile strength 35% in the as coated condition. This loss is partly recovered during the preoxidation treatment, the resulting tensile strength being only 20% below the bare tensile strength. Room temperature shear however is increased about 8% by the coating whether or not the coating has been preoxidized. The 600° F shear strength is reduced nearly 20% by the coating.

3. Relaxation resistance of the coated parts tested appears to be strongly dependent on the tendency of the coating to flow under stress. This is most clearly evident in the T-222 results where all preload was lost in one hour at 2000° F. This result is not suprising in view of the large amount of glass formed on the surface of the coating during preoxidized The glass evidently flows under pressure thereby reducing the preload to zero.

TABLE XXXIVA

ULTIMATE TENSILE STRENGTH OF 1/4-20 Cb 752 AND C129Y BOLTS - VITRO Cr-Ti-Si COATED
(English System Units)

Test Temperature °F	Cb 752				C129Y			
	Hex Head		Point Drive (Flush Head)		Hex Head		Point Drive (Flush Head)	
	Pounds	PSI(Av.)	Pounds	PSI(Av.)	Pounds	PSI(Av.)	Pounds	PSI(Av.)
-320	1075		1150		980		1350	
	1060	33 500	1360	39 500	1350	36 600	1060	37 800
80	2670		2500		2790		3000	
	2560	82 100	2530	78 800	2900	89 500	3020	94 500
600	1875		1875		2200		2150	
	1900	59 200	1950	60 000	2150	68 300	2175	68 000
2000	1325		1475		1560		1570	
	1375		1450		1450		1515	
	1400	42 800	1455	45 900	1500	47 200	1490	47 900
2200	1125		1180		1280		1140	
	1150		1110		1165		1150	
	1165	36 000	1230	36 700	1245	38 600	1200	36 500
2400	903		1072		1022		1055	
	940		984		985		1005	
	975	29 500	950	31 400	1000	31 400	1025	32 400
2600	695		685		725		725	
	730		665		795		711	
	630	21 500	640	20 800	750	23 800	754	22 900
Uncoated								
-320	5240				---	---		
	5440	168 000						
80	3400				3240			
	3430	107 000			3460	105 000		
600	2310				2380			
	2340	73 000			2370	74 700		

(All tensile stresses based on Tensile Stress Area of 0.03182 square inches)

TABLE XXXIVB

ULTIMATE TENSILE STRENGTH OF 1/4-20 Cb 752 AND C129Y BOLTS - VITRO Cr-Ti-Si COATED
(International System Units)

Test Temperature °C	Cb 752				C129Y			
	Hex Head		Point Drive (Flush Head)		Hex Head		Point Drive (Flush Head)	
	Newtons	Newtons/cm²	Newtons	Newtons/cm²	Newtons	Newtons/cm²	Newtons	Newtons/cm²
-196	4 780		5 110		4 360		6 000	
	4 720	23 100	6 050	27 200	6 900	25 200	4 720	26 100
27	11 700		10 100		12 400		13 350	
	11 400	56 500	11 250	54 300	12 900	61 700	13 500	65 200
316	8 340		8 330		9 780		9 550	
	8 450	40 800	8 670	41 300	9 550	47 000	9 660	46 800
1093	5 890		6 560		6 940		6 970	
	6 110		6 450		6 450		6 740	
	6 220	29 500	6 460	31 600	6 670	32 500	6 620	33 000
1204	5 000		5 250		5 700		5 070	
	5 110		4 940		5 180		5 110	
	5 180	24 800	5 470	25 300	5 530	26 600	5 340	25 100
1316	4 020		4 770		4 550		4 690	
	4 180		4 380		4 380		4 450	
	4 340	20 300	4 220	21 600	4 450	21 600	4 550	22 300
1427	3 090		3 050		3 220		3 230	
	3 250		2 960		3 540		3 160	
	2 300	14 800	2 850	14 350	3 340	16 400	3 350	15 700
Uncoated -								
-320	23 300				---	---		
	24 200	116 000						
80	15 100				14 400			
	15 250	73 700			15 400	72 300		
600	10 300				10 600			
	10 400	50 300			10 500	51 500		

(All tensile stresses based on Tensile Stress Area of 0.205 square centimeters)

TABLE XXXVA

TENSILE STRENGTH OF T-222 HEX HEAD BOLTS
BARE AND VITRO Si/WSi_2 COATED
(English System Units)

Temperature °F	Si/WSi_2 Coated				Bare	
	Preoxidized at 3000°F 15 Minutes		As coated			
	Pounds	PSI (Av.)	Pounds	PSI (Av.)	Pounds	PSI (Av.)
-320	---	---	5425 5360 5335	169 000	6800 6950 6625	213 000
80	4060 4170	129 000	3440 3535 3520	109 000	4560 4900 4835	150 000
600	3070 3080 2925	95 000	2600 2505 2650	81 500	3630 3700 3700	115 000
2000	2830 2825 2825	89 000	2490 2520	78 800		
2200	2440 2425 2480	77 000	---	---		
2400	1925 1935 1865	60 500	1690 1675 1810	54 100		
2600	1525 1545 1610	49 000	---	---		

(All tensile stresses based on Tensile Stress Area of 0.03182 square inches)

TABLE XXXVB

TENSILE STRENGTH OF T-222 HEX HEAD BOLTS
BARE AND VITRO Si/WSi_2 COATED
(International System Units)

Temperature °C	Si /WSi_2 Coated				Bare	
	Preoxidized at 3000°F 15 Minutes		As Coated			
	Newtons	Newtons /cm^2	Newtons	Newtons/cm^2	Newtons	Newtons /cm^2
-196	---	---	2420 2380 2370	 11,600	30 300 30 900 29 500	 147 000
27	18 100 18 600	 88 800	15 300 15 750 15 700	 75 000	20 300 21 800 21 500	 103 000
316	13 700 13 700 13 000	 65 500	11 600 11 500 11 800	 56 100	16 150 16 500 16 500	 79 200
1093	12 600 12 600 12 600	 61 300	11 100 11 200	 54 300		
1204	10 850 10 800 11 050	 53 100	---	---		
1316	8 550 8 600 8 300	 41 700	7 520 7 450 8 050	 37 300		
1427	6 780 6 860 7 150	 33 800	---	---		

(All tensile stresses based on Tensile Stress Area of 0.205 square centimeters)

TABLE XXXVIA

TENSILE STRENGTH OF T-222 FLUSH HEAD BOLTS
BARE AND VITRO Si/WSi2 COATED AND PREOXIDIZED

(English System Units)

Test Temperature °F	Point Drive				Hex Recess in Head (All Coated)	
	Coated					
	Pounds	PSI (Av.)	Pounds	PSI (Av.)	Pounds	PSI (Av.)
-320	6475 6975 6875	213 000	6850 6900 6975	217 000	6350 6400	200 000
80	4160 4240 4400	134 000	4930 4860 4820	150 000	4000 4300	130 000
600	3290 3410 3425	106 000	3780 3850 3740	119 000	---	---
2000	2760 2750 2730	86 500	---	---	---	---
2200	---	---	---	---	2475 2440 2460	77 200
2400	---	---	---	---	1765 1825 1935	57 800
2600	---	---	---	---	1600 1580 1480	48 700

(All tensile stresses based on Tensile Stress Area of 0.03182 square inches)

TABLE XXXVIB

TENSILE STRENGTH OF T-222 FLUSH HEAD BOLTS
BARE AND VITRO Si/WSi2 COATED AND PREOXIDIZED
(International System Units)

Test Temperature °C	Point Drive				Hex Recess in Head (All Coated)	
	Coated		Bare			
	Newtons	Newtons/cm^2	Newtons	Newtons/cm^2	Newtons	Newtons/cm^2
-196	28 800 31 000 30 600	147 000	30 500 30 700 31 100	149 500	28 300 28 500	137 800
27	18 500 18 400 19 600	92 200	21 900 21 600 21 400	103 000	17 800 19 150	89 500
316	14 650 15 200 15 200	73 000	16 850 17 150 16 650	82 000	---	---
1093	12 300 12 250 12 150	59 600	---	---	---	---
1204	---	---	---	---	11 000 10 850 10 950	53 100
1316	---	---	---	---	7 850 8 110 8 600	39 800
1427	---	---	---	---	7 110 7 030 6 580	33 500

(All tensile stresses based on Tensile Stress Area of 0.205 square centimeters)

TABLE XXXVII

EFFECT OF ELEVATED TEMPERATURE EXPOSURE IN AIR ON THE ROOM TEMPERATURE TENSILE STRENGTH OF 1/4-20 COLUMBIUM ALLOY FLUSH-HEAD BOLTS WITH VITRO Cr-Ti-Si COATING

Room Temperature Tensile Strength

Prior Exposure	Cb 752				C129Y			
	Pounds	PSI	Newtons	N/cm^2	Pounds	PSI	Newtons	N/cm^2
As Coated	2515	79 000	11 200	54 500	3010	94 500	13 400	65 200
2000°F(1093°C) 1 hour	2470 2350	75 700	11 000 10 500	52 200	2980 2960	93 300	13 300 13 200	64 300
2200°F(1204°C) 1 hour	2240 2350	72 000	9 950 10 450	49 600	3000 2940	93 300	13 400 13 100	64 300
2400°F(1316°C) 1 hour	2250 2350	72 300	10 000 10 500	49 800	3000 2960	93 600	13 350 13 200	64 600
2600°F (1427°C) 1 hour	2220 2240	70 000	9 860 9 950	43 300	2950 2980	93 100	13 150 13 300	64 200

TABLE XXXVIIIA

SHEAR STRENGTH OF
1/4-20 Cb 752 AND C129Y BOLTS
VITRO Cr-Ti-Si COATED
(English System Units)

Test Temperature °F	Cb 752		C129Y	
	Pounds	PSI (Av.)	Pounds	PSI (Av.)
-320	9000 9100 8900	92 000	7500 8000 6550	75 000
80	6200 6350 6420	64 500	6840 6850 6890	70 000
600	4100 3750 3650	39 100	4125 4070 4225	42 300
2000	2810 3025 2875	29 600	3200 3300 3250	33 200
2200	2500 2500 2575	25 800	2625 2655 2665	27 000
2400	1945 2000 1885	19 800	2175 2240 2130	22 300
Uncoated - -320	12 700 12 750	130 000	12 000 11 800	121 500
80	6 070 6 140	62 300	6 720 6 660	68 300
600	4 390 4 270	44 300	3 850 4 150	40 800

TABLE XXXVIIIB

SHEAR STRENGTH OF
1/4-20 Cb 752 AND C129Y BOLTS
VITRO Cr-Ti-Si COATED
(International System Units)

Test Temperature °C	Cb 752		C129Y	
	Newtons	Newtons/cm^2	Newtons	Newtons/cm^2
-196	40 000 40 500 39 600	63 400	33 400 35 600 29 100	51 600
27	27 600 28 200 28 500	44 400	30 400 30 500 30 700	48 200
316	18 250 16 700 16 250	26 900	18 350 18 100 18 900	29 200
1093	12 500 13 500 12 800	20 400	14 250 14 700 14 450	22 900
1204	11 100 11 100 11 500	17 800	11 700 11 800 11 850	18 600
1316	8 650 8 900 8 375	13 650	9 660 9 950 9 460	15 400
Uncoated - -196	56 500 56 700	89 500	53 300 52 500	83 600
27	27 000 27 300	43 000	29 900 29 700	47 100
600	19 500 19 000	30 600	17 150 18 500	28 200

TABLE XXXIXA

SHEAR STRENGTH OF 1/4-20 T-222 BOLTS
BARE AND VITRO WSi_2 COATED
(English System Units)

Shear Strength

Test Temperature °F	Coated Vitro WSi_2		Bare	
	Pounds	PSI (Av.)	Pounds	PSI (Av.)
-320	12 100* 12 250* 12 350*	125 000	12 400 12 875 12 500	129 000
80	8 900* 9 000* 9 100*	92 000	8 000 8 450 8 500	85 000
	9 200* * 9 000* * 9 000* *	92 500		
600	5 420** 5 580** 5 720**	56 900	6 640 6 980 6 900	69 800
2000	5 200**	53 100	---	---
2400	3 485**	35 400	---	---

* As coated
**Coated and preoxidized at 2912°F for 15 minutes

TABLE XXXIXB

SHEAR STRENGTH OF 1/4-20 T-222 BOLTS
BARE AND VITRO WSi_2 COATED
(International System Units)
Shear Strength

Temperature °C	Coated Vitro WSi_2		Bare	
	Newtons	Newtons/cm^2	Newtons	Newtons/cm^2
-196	53 800* 54 500* 55 000*	86 000	55 200 57 200 55 600	88 800
27	39 600* 40 100* 40 500*	63 400	35 600 37 600 37 800	58 500
	40 900** 40 100** 40 100**	63 700		
316	24 100** 24 800** 25 500**	39 200	29 500 31 100 30 700	48 200
1093	23 100**	36 600	---	---
1316	15 500**	24 400	---	---

* As coated

**Coated and preoxidized at 1500°C for 15 minutes

TABLE XL

AXIAL FATIGUE LIFE OF COLUMBIUM ALLOY 1/4-20 FASTENERS

Maximum Load - 50% of Ultimate Tensile Strength
Minimum Load - 5% of Ultimate Tensile Strength except where noted

Test Temperature °F	Test Temperature °C	Material	Head Configuration	Maximum Stress PSI	Maximum Stress N/cm²	Minimum Stress PSI	Minimum Stress N/cm²	Life, Cycles	Failure Location
-320	-196	Cb 752	Hex	28 000	19 300	2800	1930	40 000	Thread
								20 000	Thread
			Flush	19 600	13 500	1960	1350	150 000	No Failure
				29 200*	20 200	2920	2020	12 500	Thread
				29 200*	20 200	2920	2020	21 000	Head
		C129Y	Hex	28 000	19 300	2800	1930	40 000	Thread
								20 000	Thread
			Flush	17 300	11 900	1730	1190	150 000	No Failure
				25 900*	17 800	2590	1780	---	Broke Loading
80	27	Cb 752	Hex	44 800	30 900	4480	3090	15 000	Thread
								13 500	Thread
								5 000	Thread
			Flush	39 200	27 000	3920	2700	13 000	Head
								13 000	Head
								9 000	Head
		C129Y	Hex	49 000	33 800	4900	3380	5 500	Thread
								11 000	Thread
								15 000	Thread
			Flush	47 000	32 400	4700	3240	8 500	Head
								7 000	Thread
								6 000	Thread
600	316	Cb 752	Hex	31 100	21 400	3110	2140	74 000	Thread
								315 000	Thread
								36 000	Thread
			Flush	29 200	20 200	2920	2020	19 000	Thread
								40 000	Thread
								43 000	Thread
		C129Y	Hex	33 800	23 300	3380	2330	64 000	Thread
								65 000	Thread
								115 000	Thread
			Flush	33 000	22 700	3300	2270	27 000	Thread
								36 000	Thread
								12 000	Thread
2000	1093	Cb 752	Hex	21 200	14 600	2120	1460	140 000	No Failure
								140 000	No Failure
								7 000	Thread
			Flush	22 800	15 700	2280	1570	11 000	Thread
								5 000	Thread
								4 500	Thread
		C129Y	Hex	23 200	16 000	2320	1600	6 500	Thread
								26 000	Thread
								4 000	Thread
			Flush	23 200	16 000	2320	1600	141 000	No Failure
								157 000	No Failure
								160 000	No Failure
2400	1316	Cb 752	Hex	14 500	10 000	1450	1000	64,000	Thread
								150 000	No Failure
								140 000	No Failure
			Flush	15 700	10 800	1570	1080	145 000	No Failure
								153 000	No Failure
								123 000	Thread
		C129Y	Hex	15 700	10 800	1570	1080	110 000	Thread
								71 000	Thread
								4 000	Thread
			Flush	16 100	11 100	1610	1110	132 000	Thread
								138 000	Thread
								108 000	Thread

* 75% Ultimate Tensile Strength

TABLE XLI

SHEAR FATIGUE TESTS RESULTS ON Cb 752 AND C129Y
1/4-20 FLUSH HEAD BOLTS WITH VITRO Cr-Ti-Si COATING
(TESTED AT 1200 CYCLES/MIN.)

Temperature		Material	Max. Shear Stress		Min. Shear Stress		Life Cycles	Failure Location and Remarks
°F	°C		PSI	N/cm2	PSI	N/cm2		
2000	1093	Cb 752	14 800	10 200	1480	1020	140 000	No Failure
							150 000	No Failure
		C129Y	16 600	11 400	1660	1140	270 000	No Failure
							170 000	No Failure
2400	1316	Cb 752	10 000	6 890	1000	689	140 000	No Failure
							152 000	No Failure
		C129Y	11 200	7 710	1120	771	140 000	No Failure
							140 000	No Failure

TABLE XLII

AXIAL FATIGUE TEST RESULTS ON T-222
BOLTS WITH VITRO Si/WSi_2 COATING

Temperature		Maximum Stress (50% of UTS),		Minimum Stress (5% of UTS),		Life, Cycles and Location of Failure*		
°F	°C	PSI	N/cm^2	PSI	N/cm^2	Hex Head	Flush Head Point Drive	Flush Head Hex Recess in Head
-320	-196	104 000	71 600	1040	716	14 000 TRO 16 000 TRO 12 000 Thread	19 000 Thread	14 000 Thread 19 000 Thread
80	27	65 000	44 800	6500	4480	28 000 Thread 36 000 TRO 37 000 TRO	24 000 Thread 28 000 Thread	16 000 Thread 19 000 Thread 15 000 Thread
600	316	47 500	32 700	4750	3270	58 000 Thread 100 000 TRO 120 000 Thread	---	96 000 Thread 97 000 Thread 85 000 Thread
2000	1093	44 500	30 700	4450	3070	150 000 NF 150 000 NF	---	85 000 Thread 60 000 Head
2400	1316	30 000	20 700	3000	2070	150 000 NF 171 000 NF	---	200 000 NF 200 000 NF

TRO - Thread Runout
NF - No Failure

TABLE XLIII

RELAXATION TEST DATA ON Cb 752 1/4-20 HEX HEAD BOLTS PRELOADED TO 11,000 PSI (7570 N/cm^2) AND EXPOSED TO ELEVATED TEMPERATURE AS SHOWN

Temperature		Time	Length After Soak	Length After Soak	Change in	Residual Load	
°F	°C	(Hrs.)	(Seated)	(Unseated)	Length	psi	N/cm^2
2400	1316	2	2.1178	2.1177	0.0001	915	631
2200	1204	2	2.1126	2.1124	0.0002	1830	1260
2000	1093	1	2.1179	2.1174	0.0005	4570	3150
2000	1093	1	2.1156	2.1151	0.0005	4570	3150
2000	1093	2	2.1044	2.1040	0.0004	3660	2520
2000	1093	5	1.8829	1.8826	0.0003	3200	2200
2000	1093	5	1.8684	1.8681	0.0003	3200	2200
2000	1093	5	1.8843	1.8840	0.0003	3200	2200
2000	1093	5	1.8880	1.8875	0.0005	5300	3650

$$\text{Residual Load} = \frac{\text{Change in Length}}{\text{Cylinder Length} + 1/3 \text{ Nut Height}} \times E$$

TABLE XLIV

RELAXATION TEST DATA ON C129Y 1/4-20 HEX HEAD BOLTS PRELOADED TO 11,000 PSI (7570 N/cm^2) AND EXPOSED TO ELEVATED TEMPERATURES AS SHOWN

Temperature		Time	Length After Soak	Length After Soak	Change in	Residual Load	
°F	°C	(Hrs.)	(Seated)	(Unseated)	Length	psi	N/cm^2
2400	1316	2	2.1095	2.1095	0.0000	0	0
2200	1204	2	2.1138	2.1137	0.0001	930	641
2000	1093	1	2.1114	2.1110	0.0004	3660	2520
2000	1093	1	2.1146	2.1144	0.0002	1830	1260
2000	1093	2	2.1112	2.1109	0.0003	2790	1920
2000	1093	5	2.1154	2.1150	0.0004	3660	2520
2000	1093	5	2.1178	2.1175	0.0003	2790	1920
2000	1093	5	2.1219	2.1215	0.0004	3660	2520
2000	1093	5	2.1258	2.1255	0.0003	2790	1920

$$\text{Residual Load} = \frac{\text{Change in Length (upon unseating)}}{\text{Cylinder Length} + 1/3 \text{ Nut Height}} \times E$$

TABLE XLV

PERCENTAGE OF 11,000 PSI (7570 N/cm^2) PRELOAD REMAINING IN TIGHTENED 1/4-20 COLUMBIUM BOLTS AFTER HIGH TEMPERATURE EXPOSURE

Temperature		Time	Cb 752	C129Y
°F	°C			
2400	1316	2 hours	8%	0
2200	1204	2 hours	17%	8%
2000	1093	5 hours	31%	27%
2000	1093	2 hours	31%	23%
2000	1093	1 hour	42%	24%

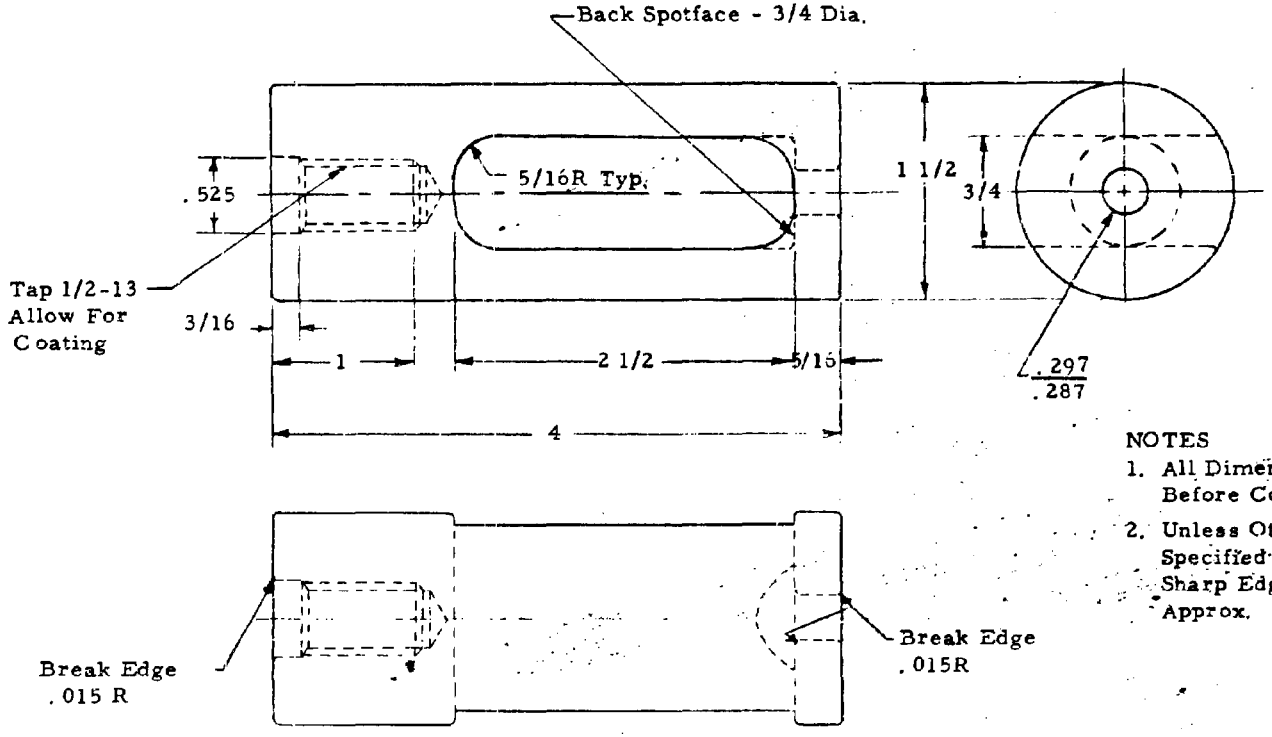
TABLE XLVI

PERCENTAGE OF 11,000 PSI (7570 N/cm^2) PRELOAD REMAINING IN TIGHTENED 1/4-20 T-222 BOLTS AFTER HIGH TEMPERATURE EXPOSURE

Temperature		Time	% Preload Remaining
°F	°C		
2400	1316	2 hours	0
2200	1204	2 hours	0
2000	1093	2 hours	0
2000	1093	1 hour	0
2000	1093	30 minutes	0

Figure 64. Test Facility for 600° - 2600°F Tensile and Shear Testing.

PI • 300 • 61048	REVISION AND DATE	Rdrwn 2-26-65



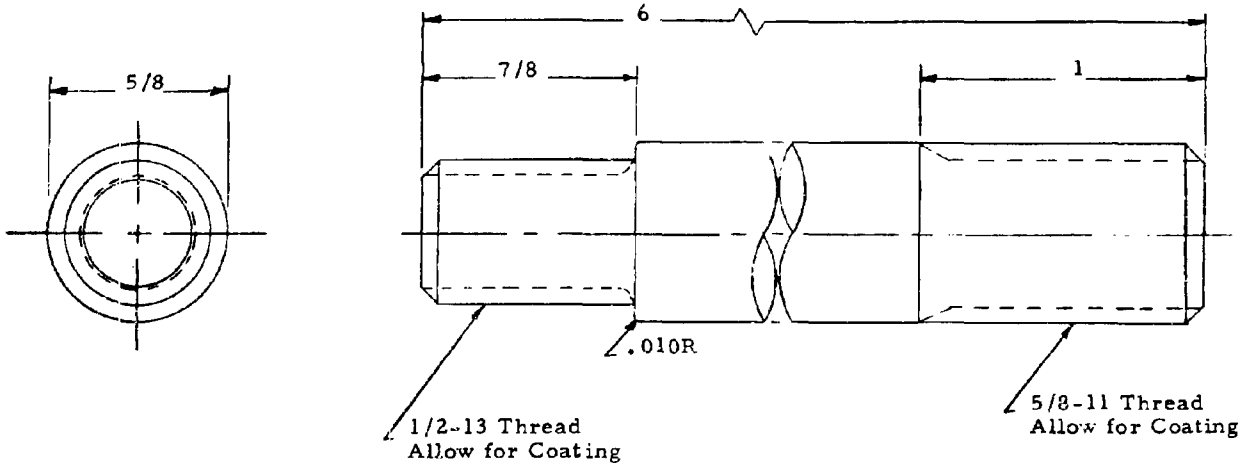
NOTES
1. All Dimensions Before Coating
2. Unless Otherwise Specified Break Sharp Edges 1/32R Approx.

Figure 65

Elevated Temp Tensile Test Fixture	TOLERANCE UNLESS SPECIFIED FRACTIONS ± 1/64 DECIMALS ± .005 ANGLES ± SURFACE FINISH	STANDARD PRESSED STEEL COMPANY JENKINTOWN, PENNSYLVANIA DRAWN BY R. Waeltz DATE 2-26-65	MATERIAL AND HEAT TREAT Columbium Alloy FS 85 with Cr-Ti-Si Coating

1071-1 REV. 661

PD 302	61047	REVISION AND DATE



Notes

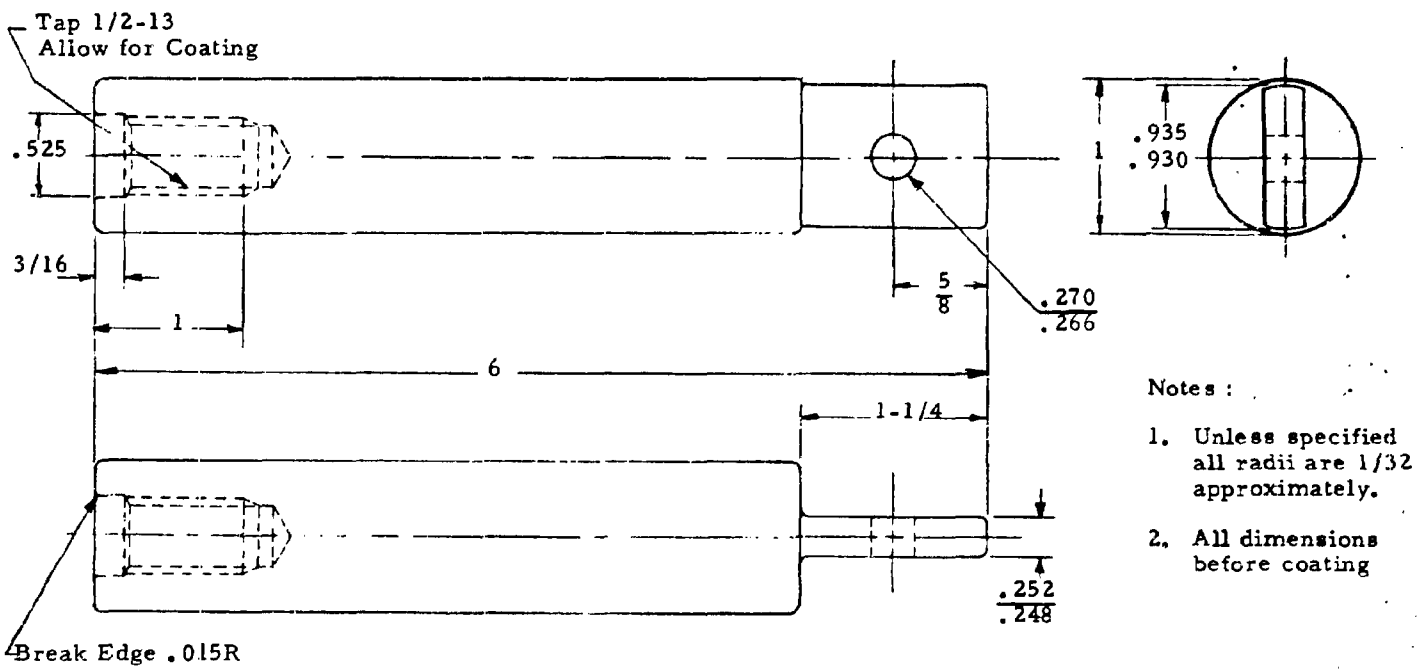
1. All Dimensions before coating.

Figure 66

Stud for Elevated Temp Shear & Tensile Test Fixtures	TOLERANCE UNLESS SPECIFIED FRACTIONS ± 1/64 DECIMALS ± .005 ANGLES ± SURFACE FINISH	STANDARD PRESSED STEEL COMPANY JENKINTOWN, PENNSYLVANIA	
		DRAWN BY R. Waeltz	MATERIAL AND HEAT TREAT Columbium Alloy FS85 with Cr-Ti-Si Coating
		DATE 2-26-65	

1071-1 REV. 861

PD #300 & 61047 | REVISION AND DATE: Rdrwr 2-26-65



Notes :

1. Unless specified all radii are 1/32 approximately.
2. All dimensions before coating

Elevated Temp. Shear Test Fixture

TOLERANCE UNLESS SPECIFIED
FRACTIONS ± 1/64
DECIMALS .005
ANGLES ±
SURFACE FINISH

STANDARD PRESSED STEEL COMPANY
JENKINTOWN, PENNSYLVANIA

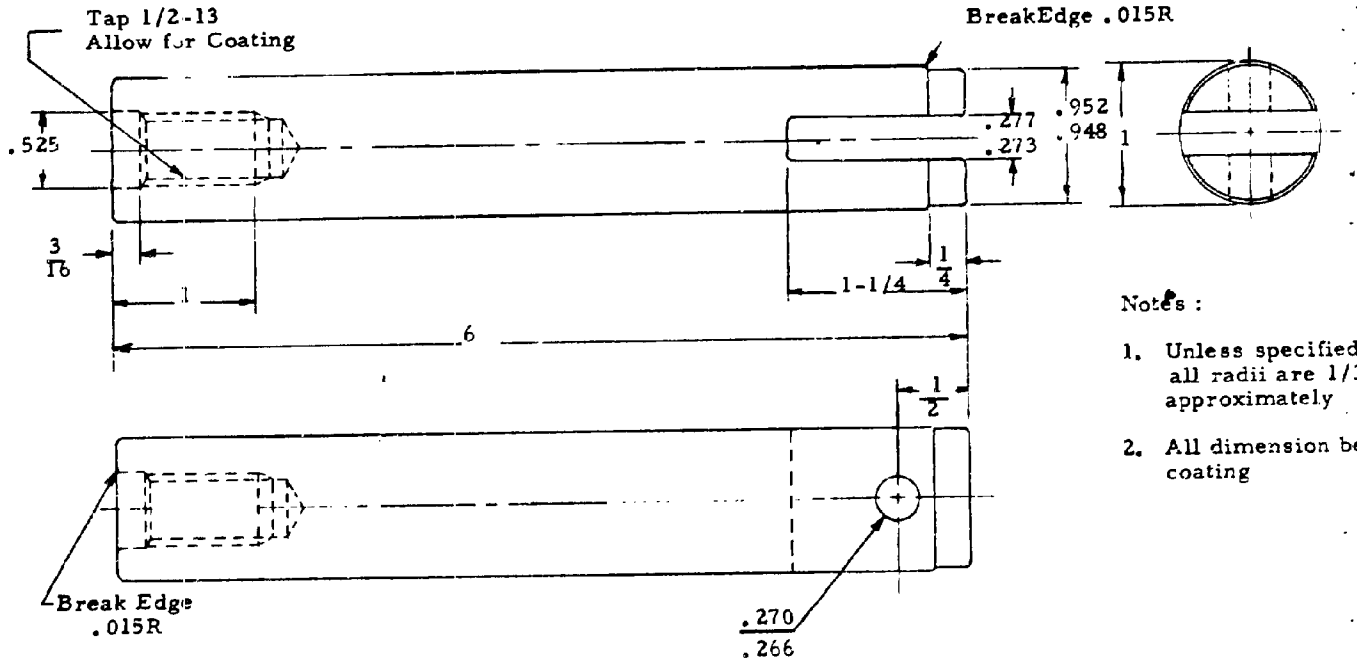
DRAWN BY R. Waeltz
DATE 2-26-65

MATERIAL AND HEAT TREAT
Columbium Alloy FS85 with Cr-Ti-Si Coating

1071-1 REV. 861

Figure 67

PD • 301 • 61047	REVISION AND DATE



Notes :

1. Unless specified all radii are 1/32 approximately
2. All dimension before coating

Elevated Temp Shear Test Fixture	TOLERANCE UNLESS SPECIFIED FRACTIONS ± 1/64 DECIMALS ± .005 ANGLES ± SURFACE FINISH	SPS STANDARD PRESSED STEEL COMPANY JENKINTOWN, PENNSYLVANIA DRAWN BY R. Waeltz DATE 2-26-65	MATERIAL AND HEAT TREAT Columbium Allloy FS 85 with Cr-Ti-Si Coating

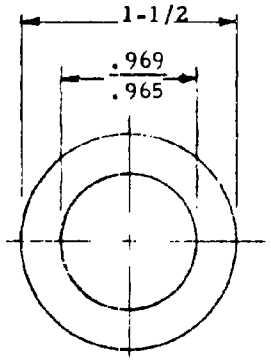
1071-1 REV. 661

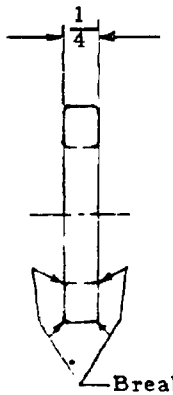
Figure 68

PD • 303 • 61047	REVISION AND DATE										

Notes :

1. All dimensions before coating





Break Edges .010 R

Figure 69

Ring for Elevated Temp. Shear Test Fixture	TOLERANCE UNLESS SPECIFIED FRACTIONS ±1/64 DECIMALS ± .005 ANGLES ± SURFACE FINISH	SPS STANDARD PRESSED STEEL COMPANY JENKINTOWN, PENNSYLVANIA DRAWN BY R. Waeltz DATE 2-26-65	MATERIAL AND HEAT TREAT Columbium Alloy FS85 with Cr-Ti-Si Coating

1071-1 REV. 881

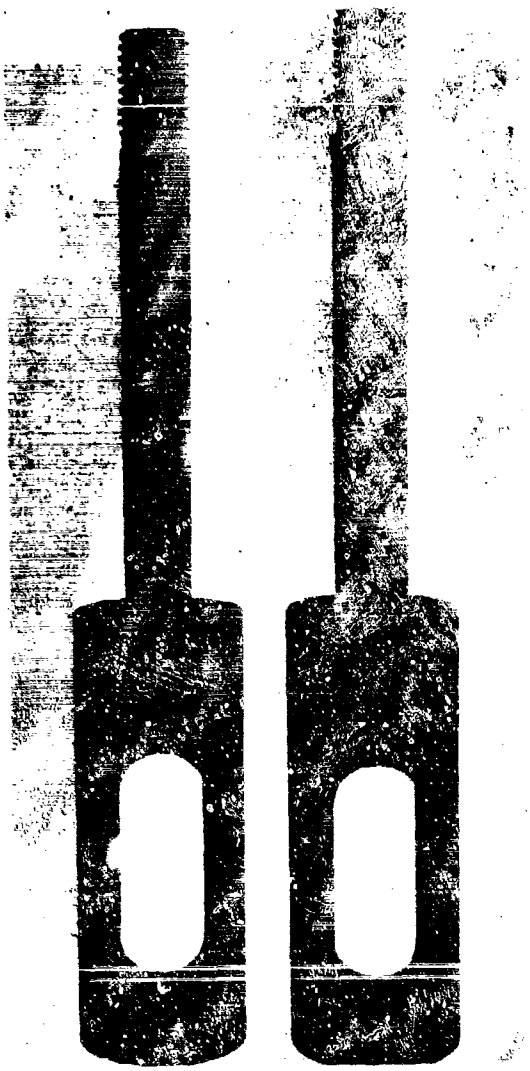


Figure 70. Tensile Test Links After Eight Tests at 2400° F. (Material FS-85-TRW Cr-Ti-Si Coated)

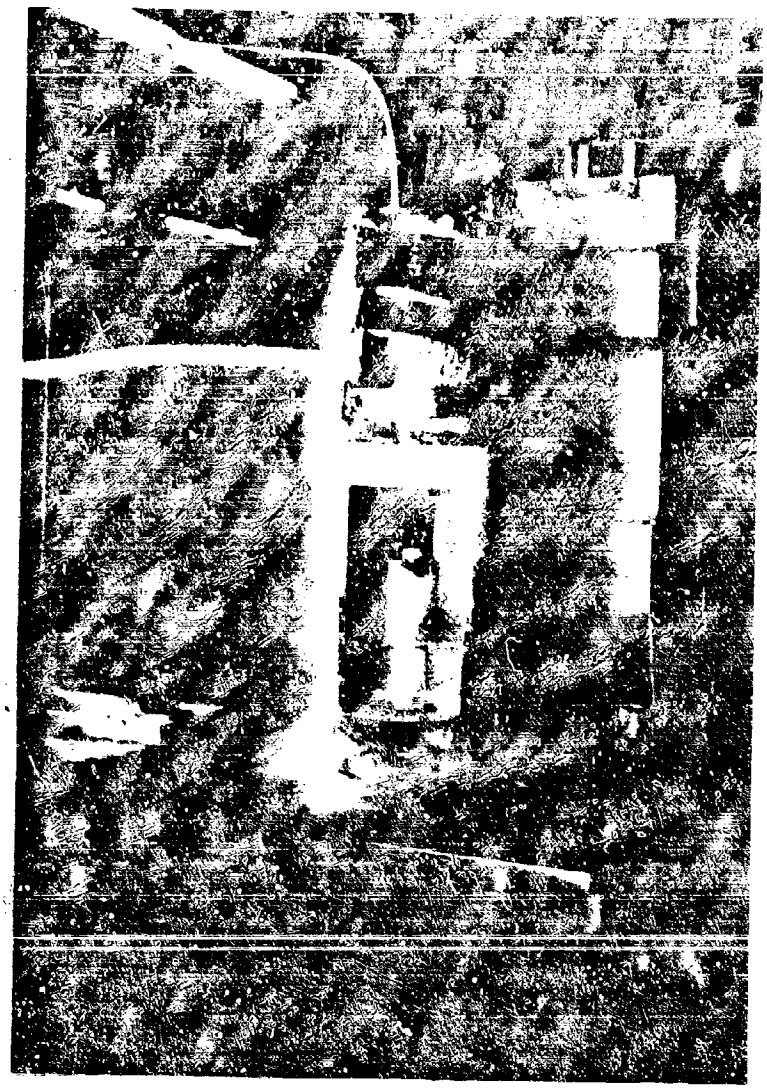


Figure 71. Set-up for -320°F Fatigue Tests.

Figure 72. Set-up for Room Temperature Fatigue Tests.

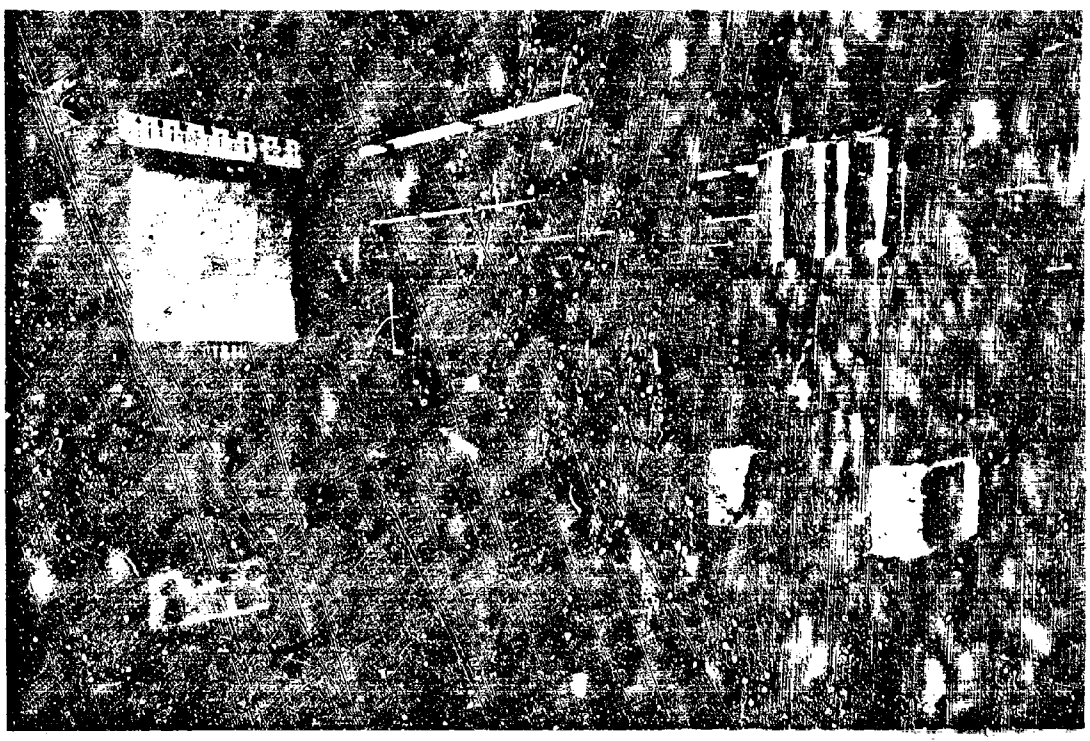


Figure 73. Set-up For Elevated Temperature Fatigue Testing.

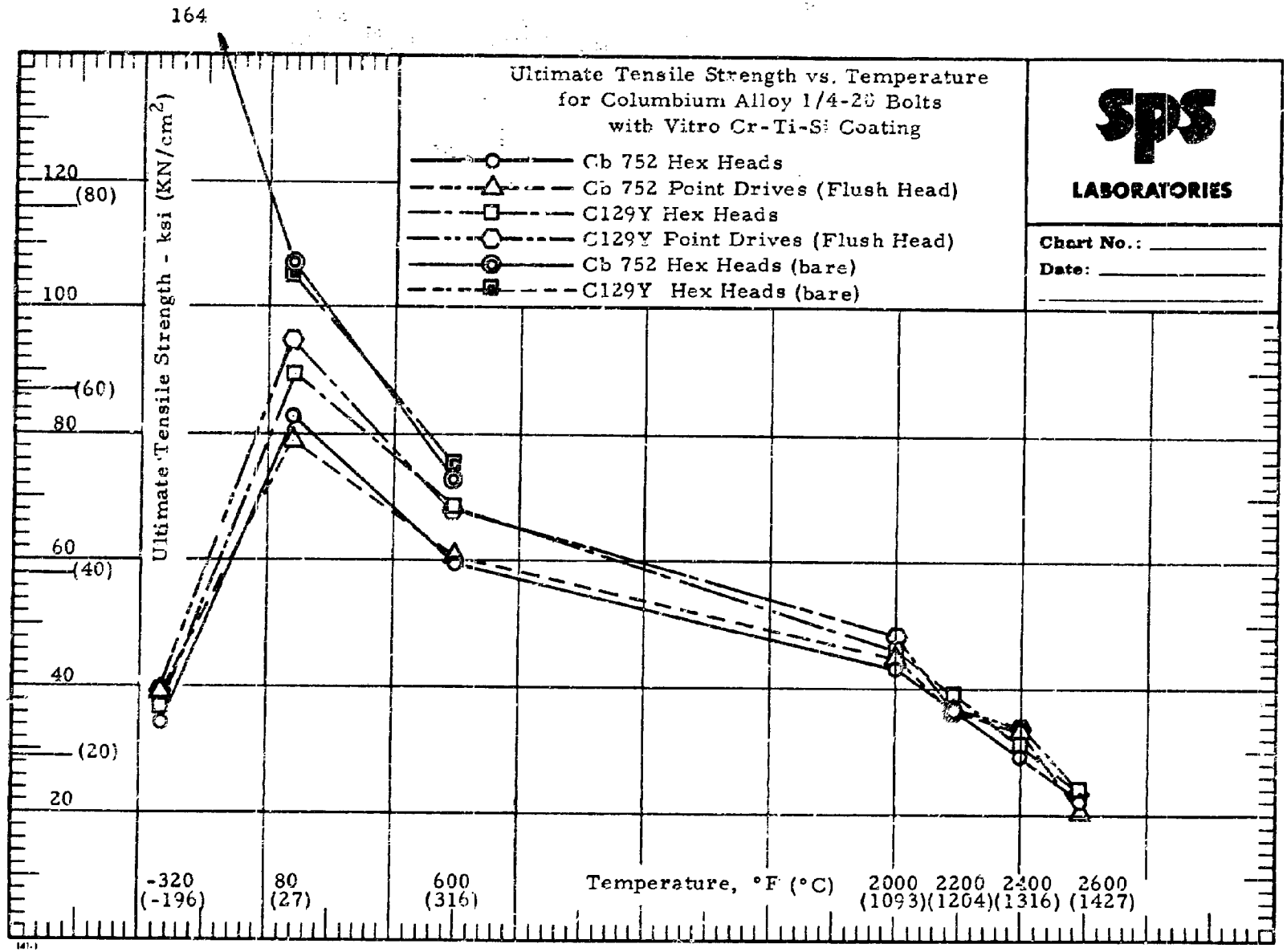

Ultimate Tensile Strength vs. Temperature
for Columbium Alloy 1/4-20 Bolts
with Vitro Cr-Ti-Si Coating
Cb 752 Hex Heads
Cb 752 Point Drives (Flush Head)
C129Y Hex Heads
C129Y Point Drives (Flush Head)
Cb 752 Hex Heads (bare)
C129Y Hex Heads (bare)
SPS
LABORATORIES
Chart No.:
Date:
Ultimate Tensile Strength - ksi (KN/cm²)
164
120
(80)
100
(60)
80
60
(40)
40
(20)
20
-320
(-196)
80
(27)
600
(316)
Temperature, °F (°C)
2000
(1093)
2200
(1204)
2400
(1316)
2600
(1427)

Figure 75

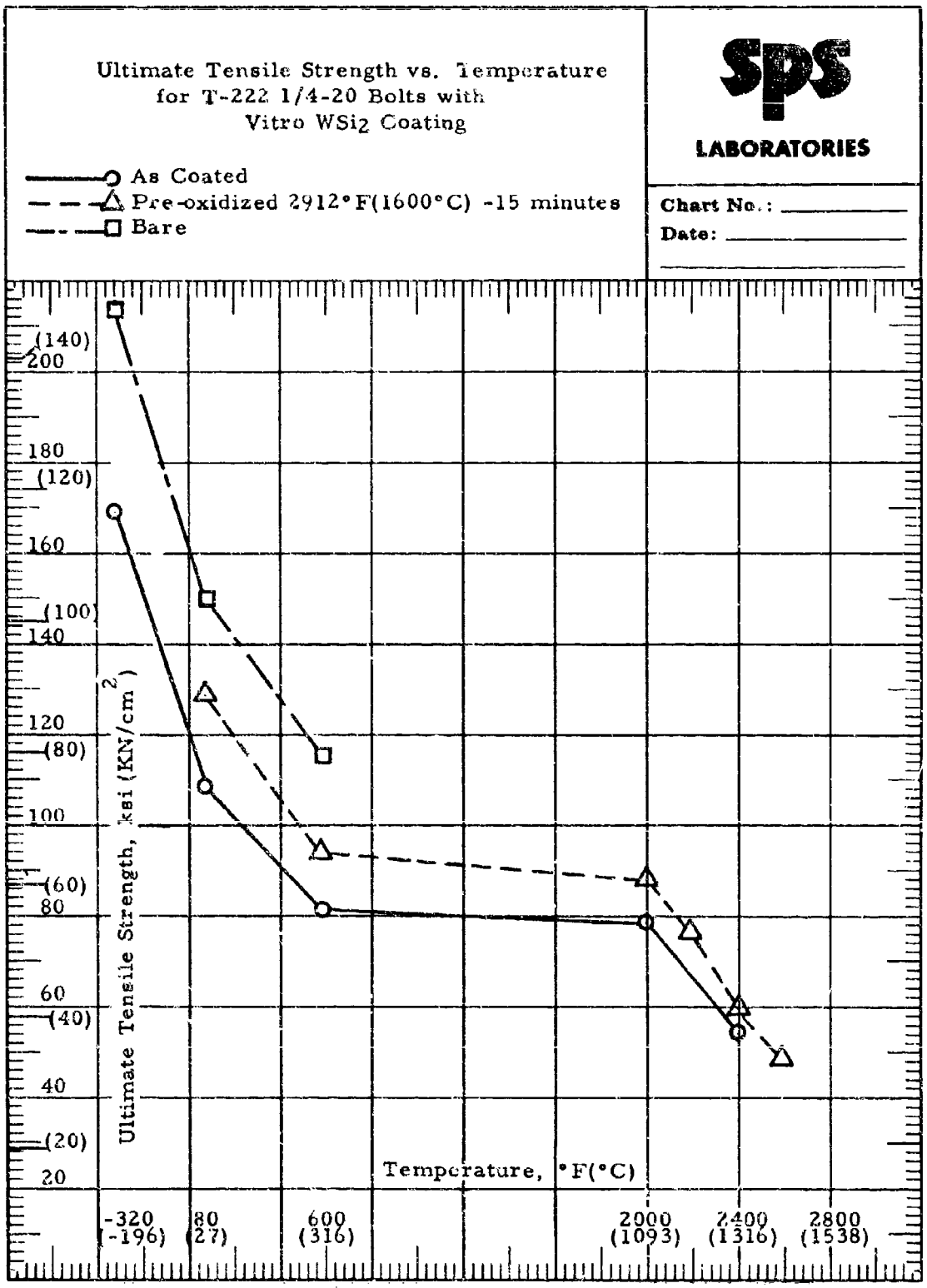

Ultimate Tensile Strength vs. Temperature
for T-222 1/4-20 Bolts with
Vitro WSi2 Coating
As Coated
Pre-oxidized 2912°F(1600°C) -15 minutes
Bare
SPS
LABORATORIES
Chart No.:
Date:
Ultimate Tensile Strength, ksi (KN/cm2)
(140)
200
180
(120)
160
(100)
140
120
(80)
100
(60)
80
60
(40)
40
(20)
20
Temperature, °F(°C)
-320 (-196)
80 (27)
600 (316)
2000 (1093)
2400 (1316)
2800 (1538)

Figure 76

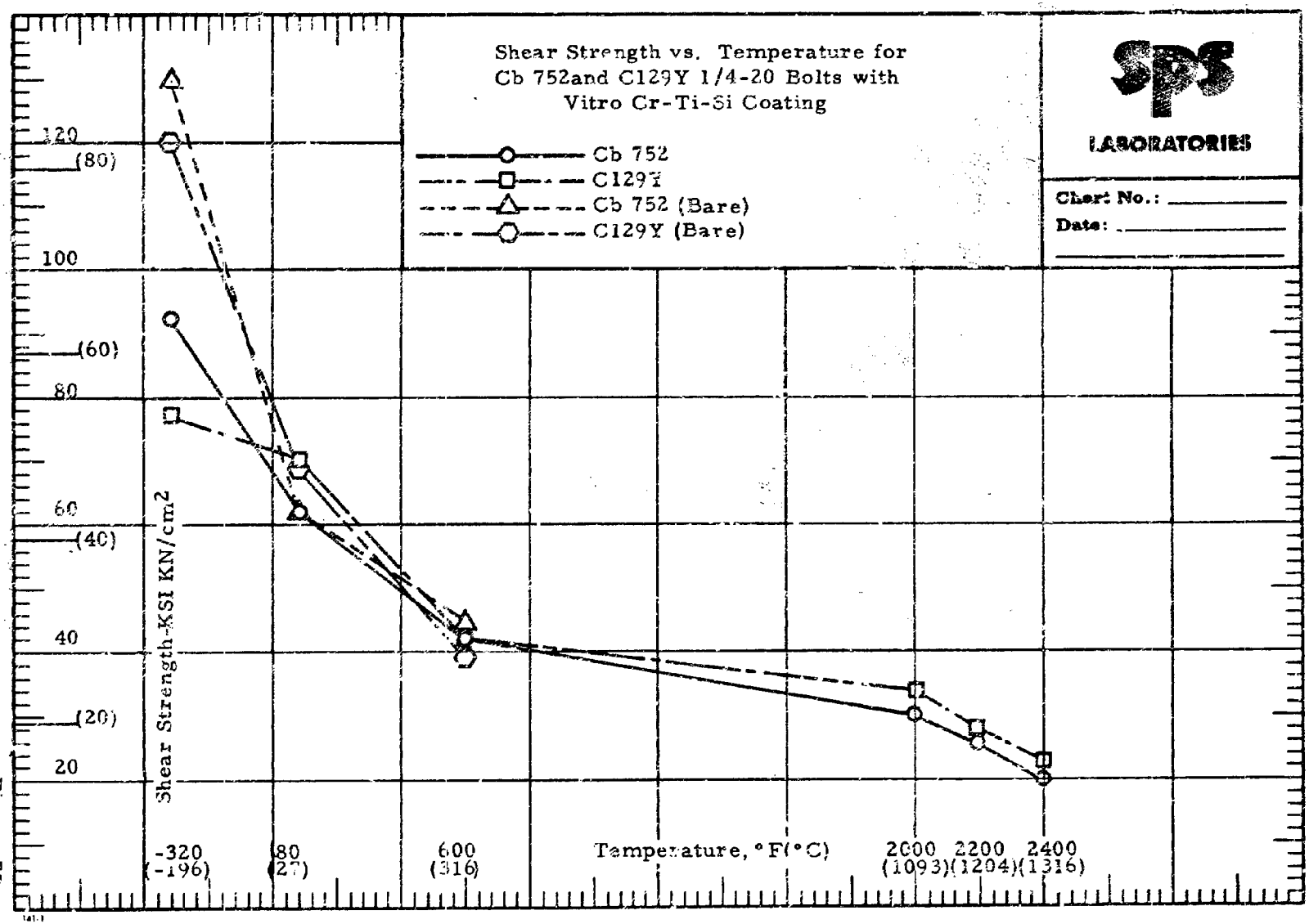

Shear Strength vs. Temperature for
Cb 752and C129Y 1/4-20 Bolts with
Vitro Cr-Ti-Si Coating
Cb 752
C129Y
Cb 752 (Bare)
C129Y (Bare)
SPS
LABORATORIES
Chart No.:
Date:
Shear Strength-KSI KN/cm2
120
(80)
100
(60)
80
60
(40)
40
(20)
20
-320
(-196)
80
(27)
600
(316)
Temperature, °F(°C)
2000
(1093)
2200
(1204)
2400
(1316)

Figure 77

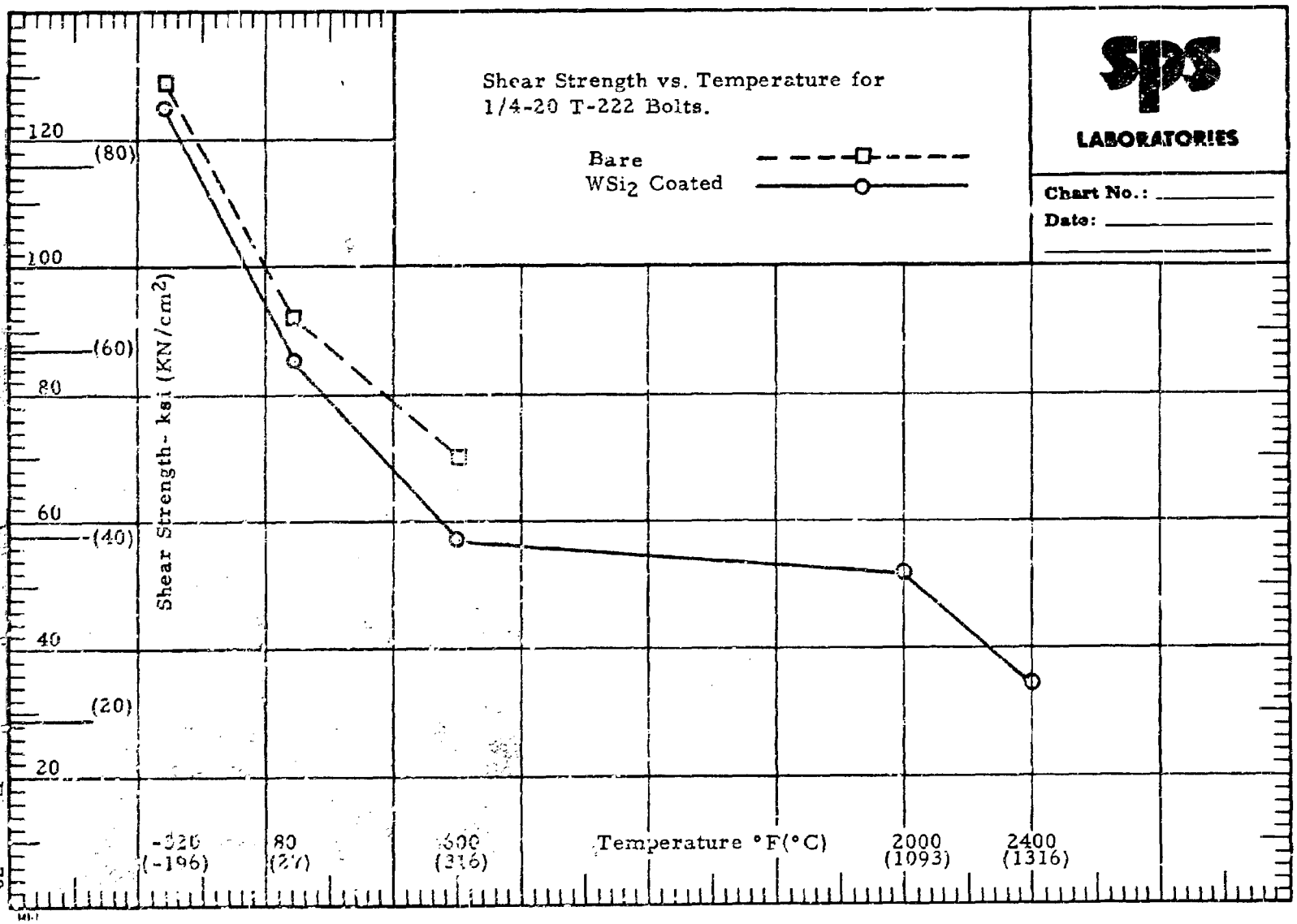

Shear Strength vs. Temperature for
1/4-20 T-222 Bolts.
Bare
WSi2 Coated
SPS
LABORATORIES
Chart No.:
Date:
Shear Strength - ksi (KN/cm2)
120
(80)
100
(60)
80
60
(40)
40
(20)
20
-320
(-196)
80
(27)
600
(316)
Temperature °F(°C)
2000
(1093)
2400
(1316)

Figure 78

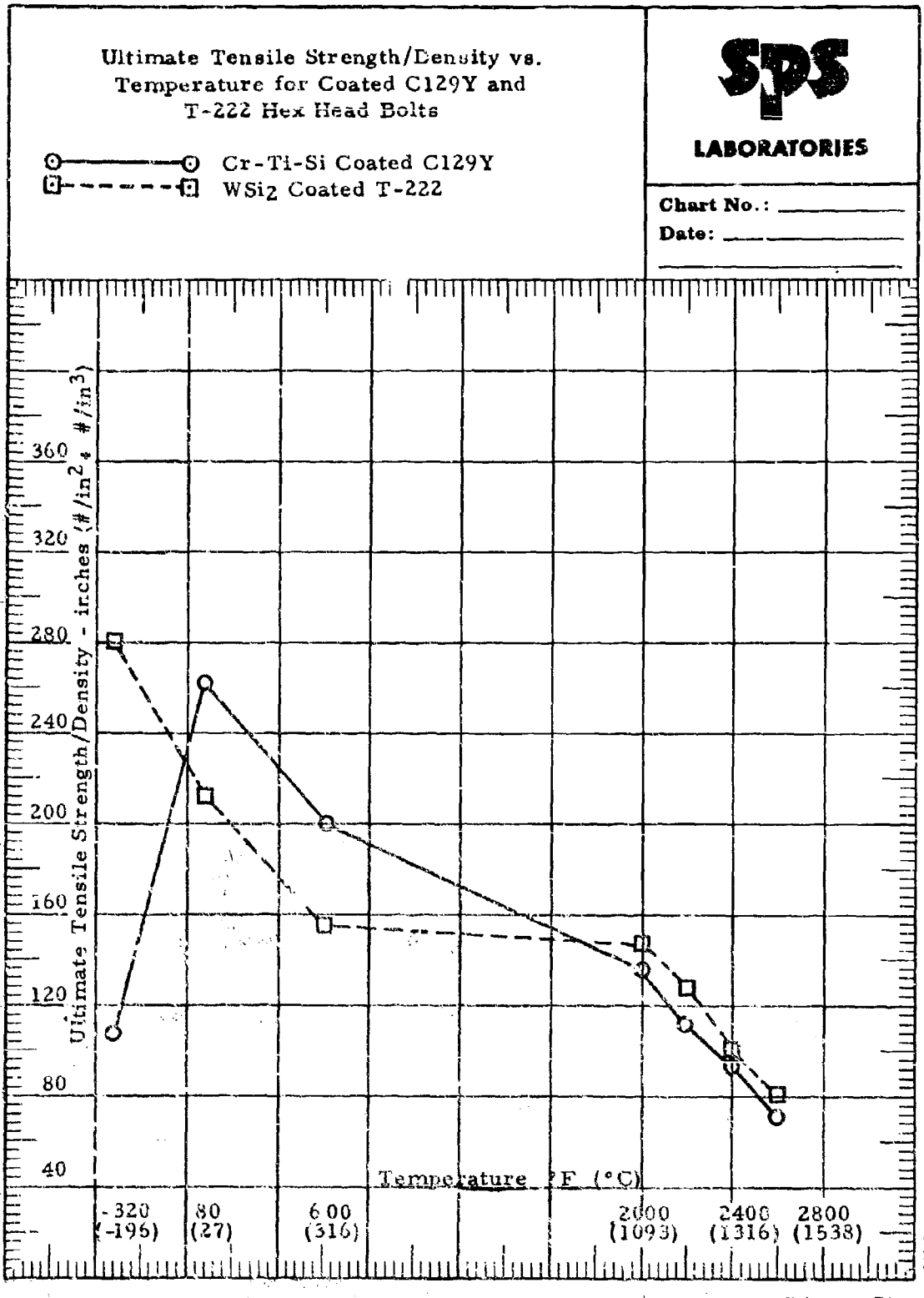
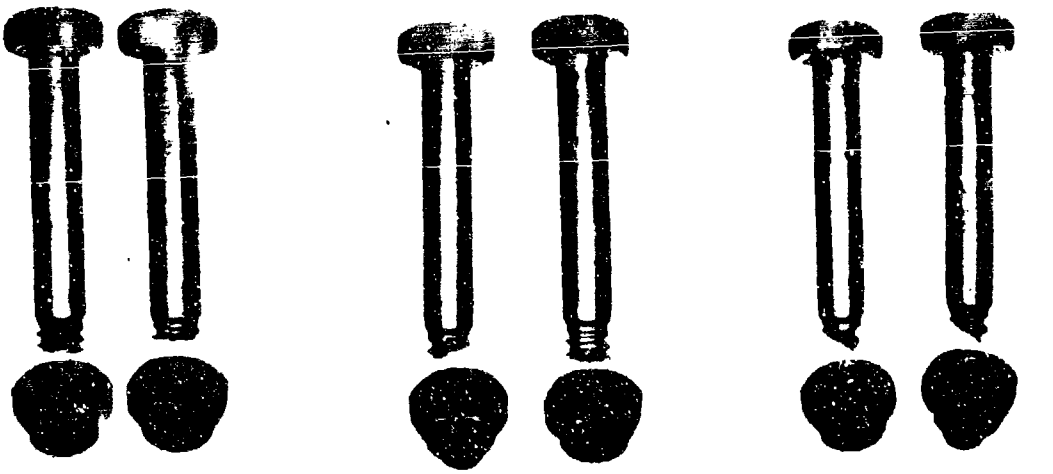
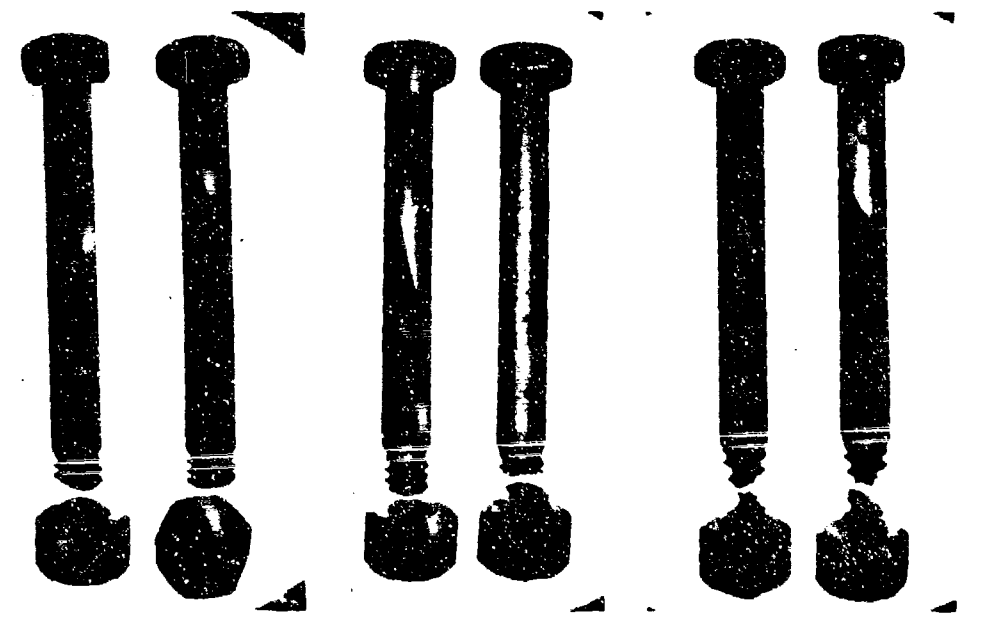

Ultimate Tensile Strength/Density vs.
Temperature for Coated C129Y and
T-222 Hex Head Bolts
Cr-Ti-Si Coated C129Y
WSi2 Coated T-222
SPS
LABORATORIES
Chart No.:
Date:
Ultimate Tensile Strength/Density - inches (#/in2, #/in3)
360
320
280
240
200
160
120
80
40
Temperature °F (°C)
-320 (-196)
80 (27)
600 (316)
2000 (1093)
2400 (1316)
2800 (1538)

Figure 79



-320°F (-196°C) 80°F (27°C) 600°F (316°C)

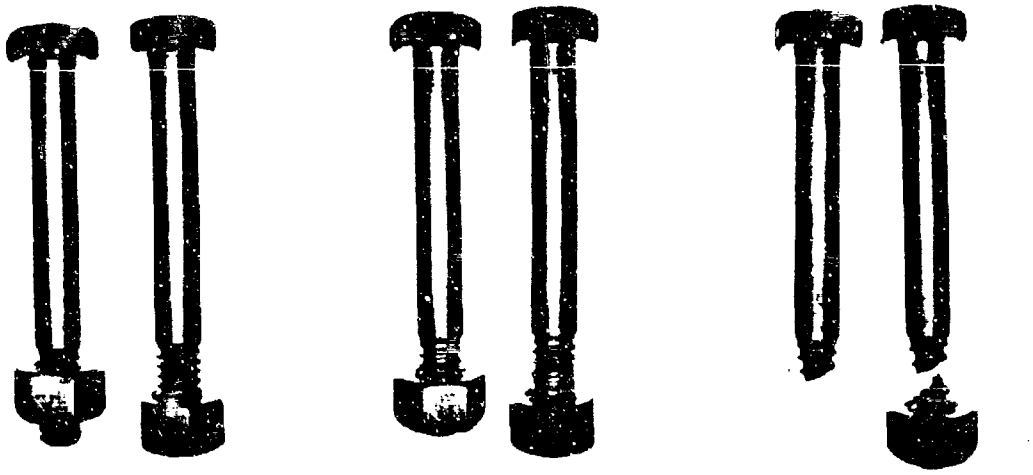
Bare



-320°F (-196°C) 80°F (27°C) 600°F (316°C)

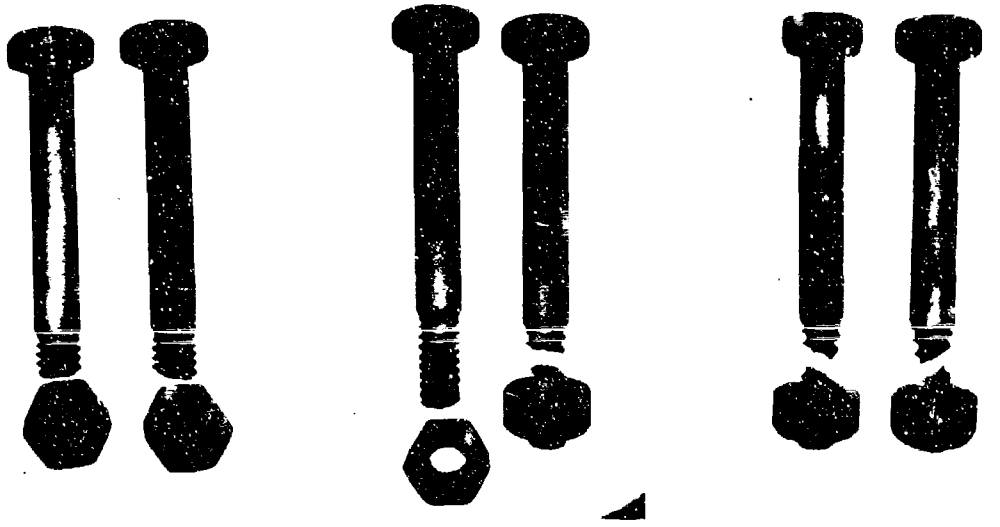
Vitro Cr-Ti-Si Coated

Figure 80. Cb 752 1/4-20 Bolts Tensile Tested at Temperatures Shown.



-320°F (-196°C) 80°F (27°C) 600°F (316°C)

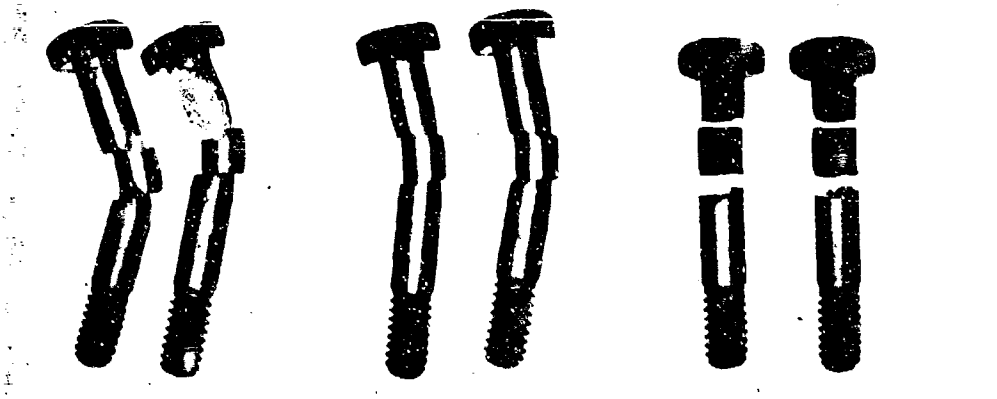
Bare



-320°F (-196°C) 80°F (27°C) 600°F (316°C)

Vitro Cr-Ti-Si Coated

Figure 81. C129Y 1/4-20 Bolts Tensile Tested at Temperatures Shown.



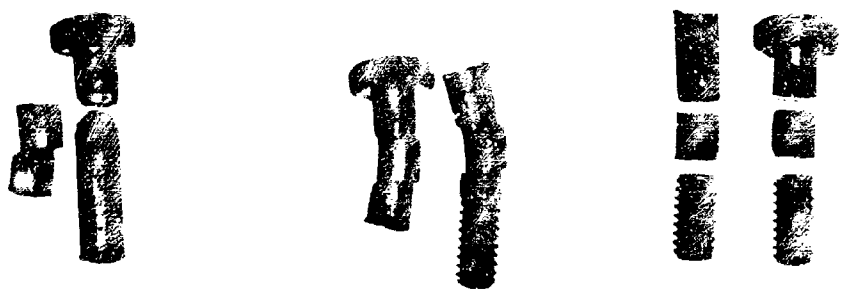
-320°F (196°C) 80°F (27°C) 600°F (316°C)

Bare

-320°F (-196°C) 80°F (27°C) 600°F (316°C)

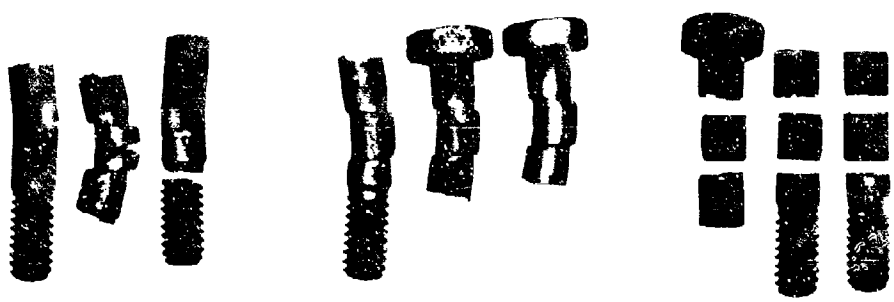
Vitro Cr-Ti-Si Coated

Figure 82. Cb 752 Shear Strength Specimens Tested at Temperature Shown.



-320°F (-196°C) 80°F (27°C) 600°F (316°C)

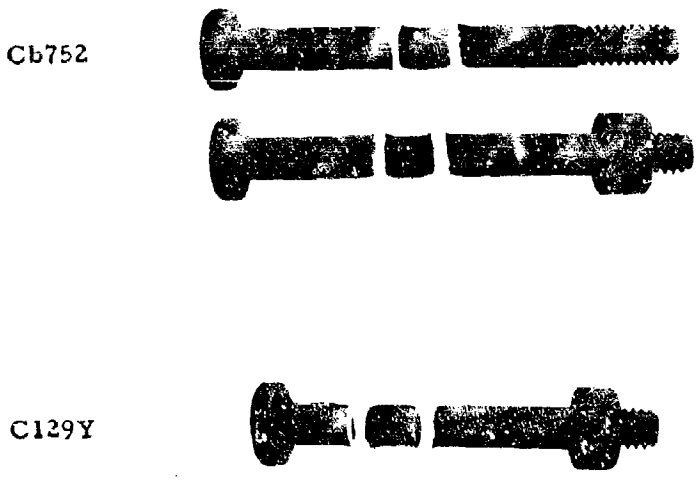
Bare



-320°F (-196°C) 80°F (27°C) 600°F (316°C)

Vitro Cr-Ti-Si Coated

Figure 83. C129Y Shear Strength Specimens Tested at Temperature Shown.



Typical 2000°F (1093°C) Shear Specimens Vitro Cr-Ti-Si Coated

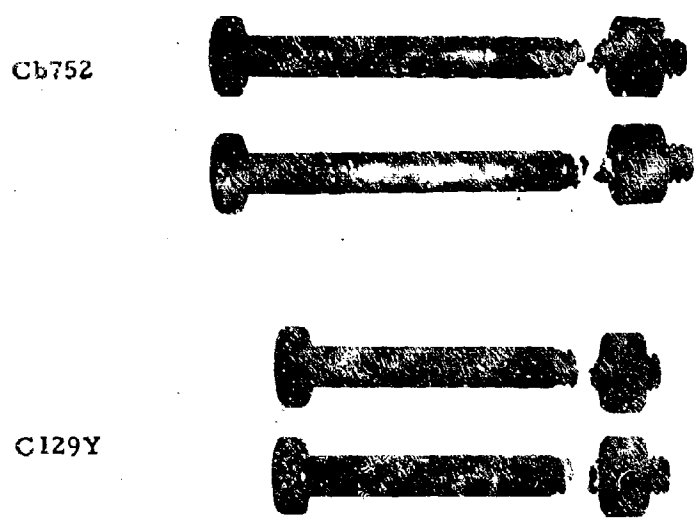
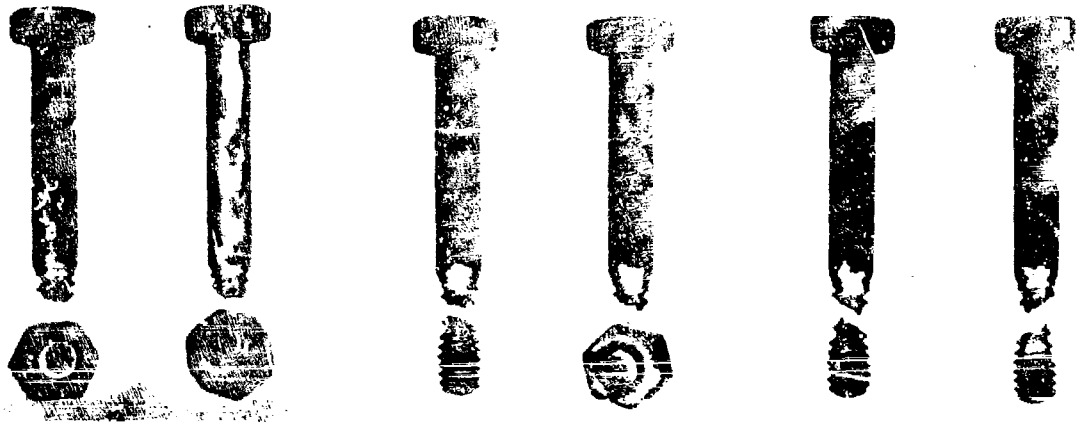


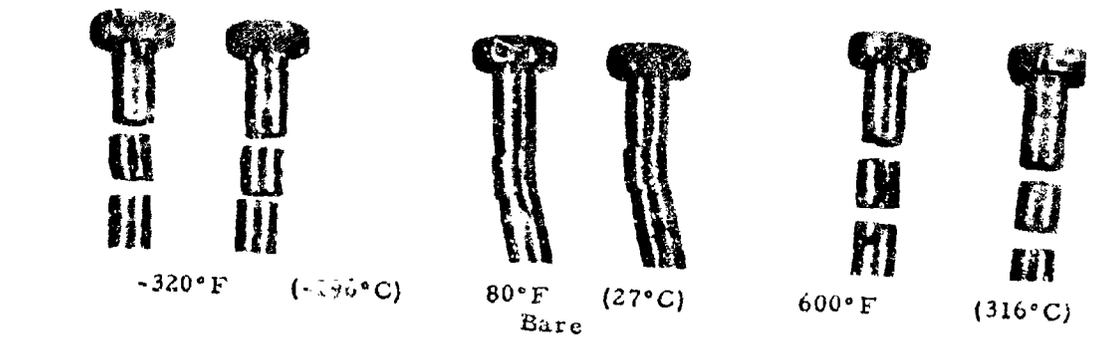
Figure 84. Typical 2000°F (1093°C) Tensile Specimens Vitro Cr-Ti-Si Coated.

-320°F (-196°C) 80°F (27°C) 600°F (316°C)
Bare



-320°F (-196°C) 80°F (27°C) 600°F (316°C)
Si/WSi_2 Coated

Figure 85. T-222 Ultimate Tensile Strength Specimens
Test Temperature and Conditions as shown.



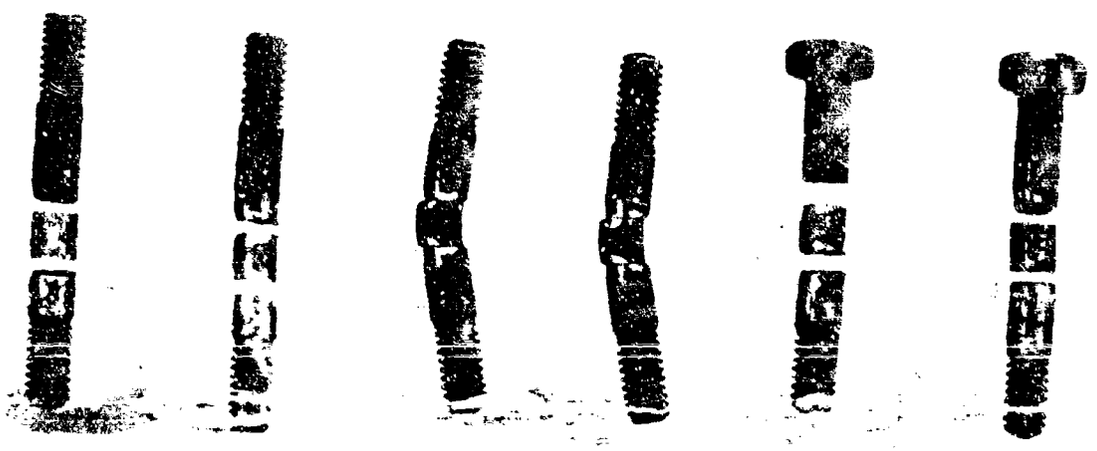


Figure 86. T-222 Shear Specimens. Test Temperature and Conditions as shown.

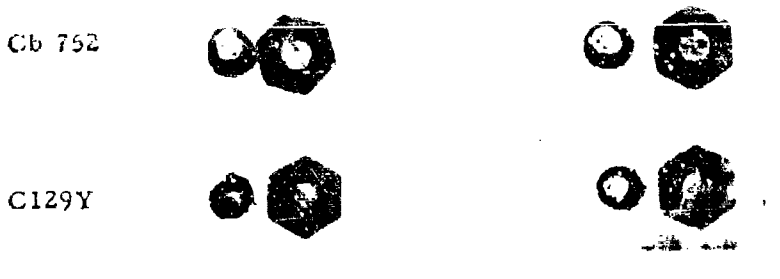


Figure 87. Typical Elevated Temperature Axial Fatigue Test Specimens.

Figure 88. Typical Elevated Temperature Joint Fatigue Test Specimens. Both Cb 752 (Nuts and heads damaged during disassembly.)

SECTION X

DEFORMABLE FASTENER DEVELOPMENT

One of the initial requirements of this program was the determination of the limits of deformability of the coating substrate systems evolving from coating studies and the subsequent application of this information to the design and manufacture of a deformable fastener. Accordingly, the work performed as part of this requirement was divided as follows:

A. Basic Deformability Tests on Columbium Alloys (Cb 752) - Bend Tests, etc.
B. Oxidation Tests on Bend Test Specimens
C. Blind Fastener Design Manufacture and Test
D. Basic Deformability Tests on Tantalum Alloys (T-222)

A. BASIC DEFORMABILITY TESTS ON COATED Cb752 SHEET

This work was performed using 1/2 x2 x(.012-.030) D43 and Cb752 sheet. The initial tests were conducted on test pieces coated with Vitro's Cr-$MoSi_2$ coating. The bending was performed initially in the "free bend" fixture shown in Figure 89. The first pieces had such low ductility that the substrate cracked with only slight bending. Some additional pieces were bent by hand around mandrels of varied sizes. Some cracking occurred on pieces bent around a 2-3/8 inch diameter mandrel. The results of these tests were as follows, the percent elongation shown representing the claculated outer fiber strain at maximum bending.

.012" Sheet	% Elong.	Mandrel Diameter	.030" Sheet	% Elong.
1-Failure	1.0	1 1/4" diameter	1-Failure 1-No Failure	2.3
1-Failure 1-No Failure	.6	2" diameter	2-No Failure	1.5
2-No Failure	.5	2 3/8" diameter	1-Failure 1-No Failure	1.2

Photographs of the tested pieces are shown in Figure 90. Bare pieces tested in the free bend test fixture are shown in Figure 91. None of these pieces cracked.

1 - Start of Test

2

3

4 -
End of Test

Figure 89. Free Bend Test Fixture Showing Bending Sequence.

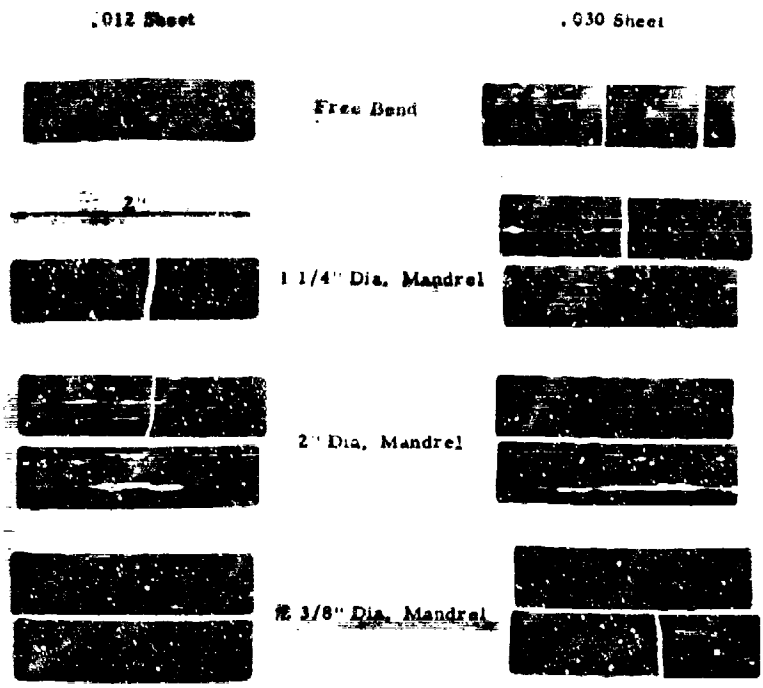
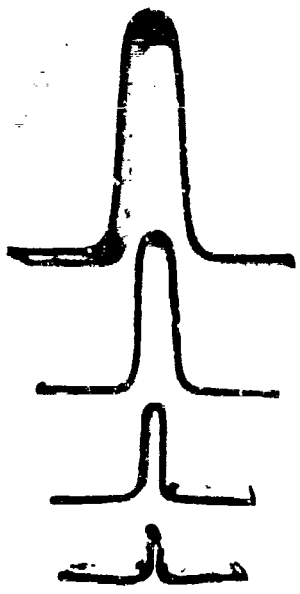
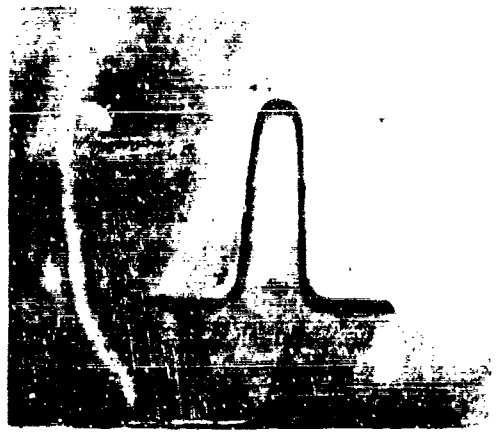


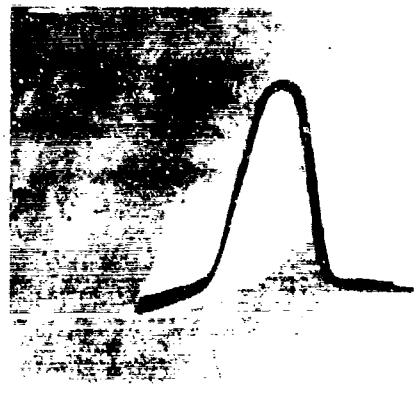
Figure 90. Vitro Coated (Cr-$MoSi_2$) D-43 Bend Test Results.





Cb 752 Material
.018 Gage

D-43 Material
.030 Gage



D-43 Material
.012 Gage

Figure 91. Bare Columbium Alloy Sheet, Bent in Free Bend Test Fixture.

Samples of Cb752 and D43 coated by Tapco with their Cr-Ti-Si coating were tested as follows:

All specimens were bent using the Free Bend Fixture. The first tests were run using 2" long specimens. All survived the most severe bend.

Additional specimens were prepared with a 1 in. overall length. These also survived the most severe bend attainable. All these specimens exhibited excellent ductility in the base metal, however, cracks occurred in in the coating on the tension side of the specimen and most of the coating spalled off the compression side. The results of these tests are shown in Figure 92.

Computed elongation for these specimens shows approximately 50% elongation at the outer fibers.

Additional samples of D 43 were coated by Vitro using varied chromium diffusion times. These specimens were chromized at 2500°F for 15 minutes, 30 minutes, and one hour. These specimens were tested in the free bend fixture and exhibited some improvement in ductility in the specimens diffused at 2500°F for 15 minutes. These specimens are shown in Figure 93.

Bend tests conducted on Cb752 specimens chromized at 2500°F for 3 hours exhibited good ductility.

At this point a program was undertaken at Vitro to investigate the cause of the embrittlement. The parameters investigated were time, temperature, atmospheric purity and pressure, and alloy composition. The experimental conditions and results are summarized in Table XLVII.

Photomicrographs of the D36 in the as-received condition and after a 3 hour heat treatment in argon and in vacuum are shown in Figure 94. Some grain boundary contamination is evident in the annealed, as-received, D36 specimen. This contamination was reduced and ductility maintained by the vacuum treatment, but contamination increased and ductility was lost after heat treatment in argon. When the argon was purified in a regenerated train of hot titanium chips some ductility was retained by the D36 and no surface discoloration was noted. In subsequent experiments with D36, chromium was applied in a purified argon atmosphere (dewpoint -90°F, O_2N_2 <5ppm) for one hour at temperatures ranging from 2200° to 2500°F and in a vacuum of 10^{-5} Torr for 3 hours at 2500°F. None of these conditions yielded ductile specimens. The Cb752 alloy, on the other hand, acted quite differently. Ductility was maintained after chromium diffusion in purified argon for one hour at temperatures between 2200 F and 2500°F. A subsurface band of chromium or columbium chromide is formed in specimens heated at 2400°F and 2500°F.

TABLE XLVII

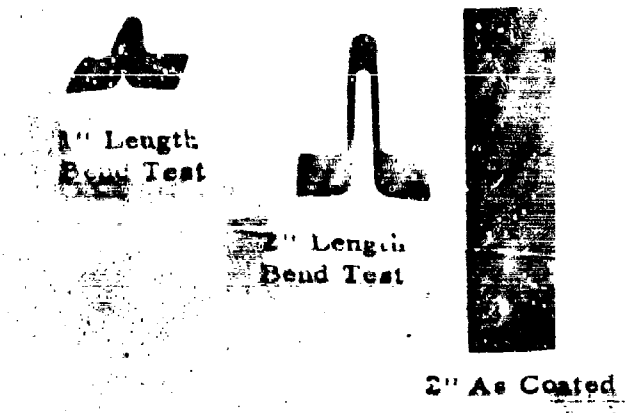
EFFECT OF TIME, TEMPERATURE, ATMOSPHERE, AND CHROMIUM DIFFUSION ON BEND DUCTILITY OF D-36 AND Cb-752 ALLOY

Alloy	Chromium Coated*	Temp. °F	Time (hrs)	Atmosphere	Results
D-36	No	2500 (1371°C)	3	Argon	Slight discoloration, brittle
Cb-752	No	2500	3	Argon	Slight discoloration, ductile
D-36	No	2500	3	Argon**	Slightly ductile
D-36	No	2500	3	Argon***	Discolored, Brittle
D-36	No	2500	3	Vacuum (10^{-5}torr)	Ductile
Cb-752	No	2500	3	Vacuum (10^{-5}torr)	Ductile
D-36	Yes	2500	3	Vacuum (10^{-5}torr)	Brittle
D-36	Yes	2500	1	Argon**	Slightly ductile
D-36	Yes	2400 (1316°C)	1	Argon**	Slightly ductile
D-36	Yes	2300 (1260°C)	1	Argon**	Slightly ductile
D-36	Yes	2200 (1204°C)	1	Argon**	Slightly ductile
Cb-752	Yes	2500 (1371°C)	1	Argon**	Ductile
Cb-752	Yes	2400 (1316°C)	1	Argon**	Ductile
Cb-752	Yes	2300 (1260°C)	1	Argon**	Ductile
Cb-752	Yes	2200 (1204°C)	1	Argon**	Ductile

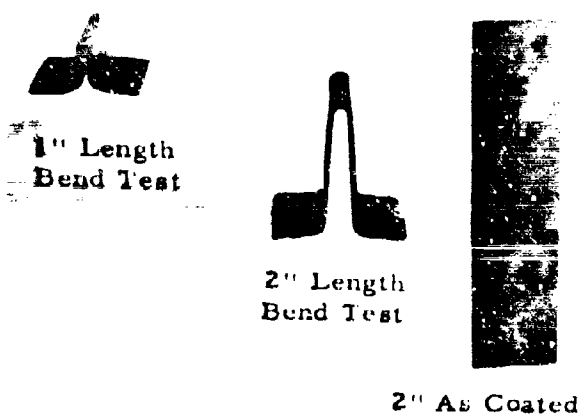
* Chromium applied by embedding specimen in $67Al_2O_3$-33Cr bed.

** Argon passed through regenerated purification train of titanium chips at 700°C.

*** Argon used directly from tank.



Cb 752

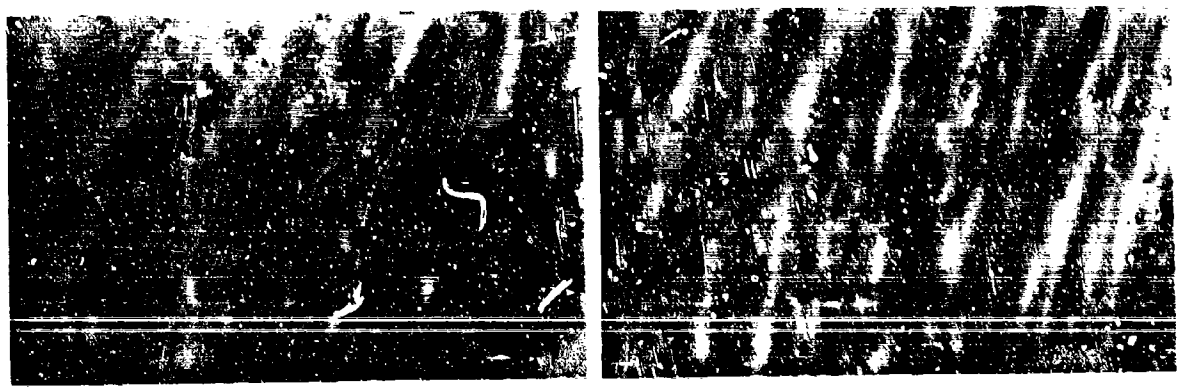


D 43

Figure 92. Cb 752 and D 43 Tapco Cr-Ti-Si Coated Bend Test Results.

Figure 93. D 43 Chromized at Various Diffusion Times -2500°F.

D-36 As-Received (400X)



D-36 Held for 3 Hours @ 2500° F at 10^{-5} Torr (400X)

D-36 Held for 3 Hours @ 2500° F in Argon (400X)

Figure 94. Effect of Three Hour Heat Treatment at 2500° F in Vacuum and Argon on D-36 Alloy.

These experiments indicated that minute amounts of contaminants in the argon atmosphere or the chromium contribute to embrittlement of Cb 752 and D36. The Cb 752 alloy is, however, much less sensitive to the effects of these contaminants.

Subsequent to the above tests, a set of ten 2 in. x1/2 in. x0.030 in. Cb 752 bend test panels were coated with Cr-$MoSi_2$ in purified argon to a thickness of 2.5±0.4 mil and were bend tested in the free bend test fixture. The specimens survived the 180° bend with some substrate cracking occurring on bends of 90° or more. Cracking of the coating occurred on the compression side of the bend at 20-30° of bend. The coating on the tension side cracked at approximately 90° of bend but continued to adhere to the substrate. Typical specimens are shown in Figure 95.

Following completion of the electrophoretic adaptation of the Tapco Cr-Ti-Si coating (See Section VI) a set of bend specimens was coated with that coating and bend tests were performed.

The bend test specimens survived the 180° bend with no significant substrate cracking. The coating spalled off the compression side at approximately 20° of bend. Cracks developed in the coating on the tension side at 120° bend, but the coating remained in place through the complete 180° bend. Typical specimens are shown in Figure 96.

Figure 95. Bend Tests on Vitro Cr-$MoSi_2$ coated Cb752.

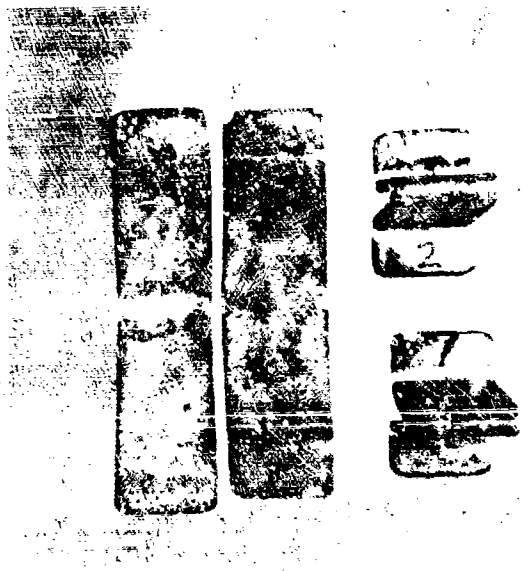


Figure 96. Bend Tests on Vitro Cr-Ti-Si coated Cb752.

B. OXIDATION TESTS ON DEFORMED SPECIMENS

In order to determine the degree to which oxidation protection is impaired by deformation, several tests were conducted using Vitro Cr-Ti-Si coated Cb752 sheet specimens. These specimens were bent in the free bend test fixture then heated to 2500° F in static air. The results of these tests are shown in Table XLVIII and pictures of the specimens are shown in Figures 97, 98 and 99.

Examination of the results reveals the following:

1. The 2500° F oxidation resistance of the compression side of bends is poor once the overlay portion of the coating has been removed.

2. The slight cracks which occur on the tension side of the coating under bending are not self-healing at 2500° F.

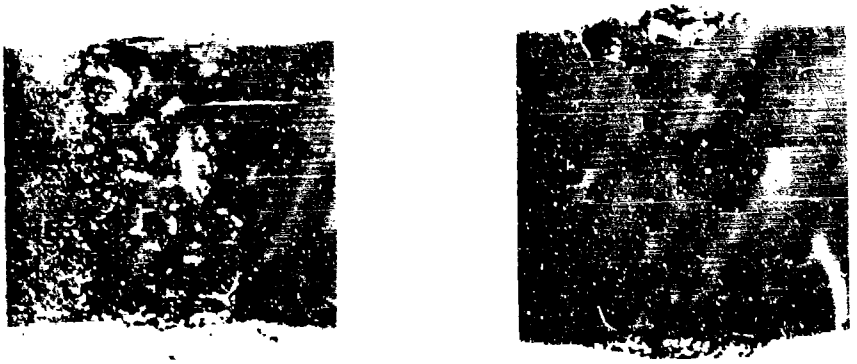
3. The 2500° F oxidation resistance of the tension side of moderately deformed sheet is considerably better than that of the compression side.

TABLE XLVIII

OXIDATION TESTS ON COATED AND DEFORMED Cb 752 SHEET

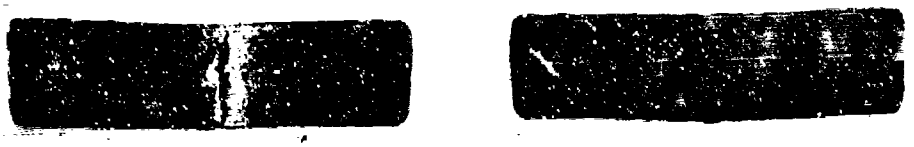
Spec. No.	Degree of Bend	Time at 2500°F	Condition Before Test	Condition After Test
1	180	2 hrs.	Compression side of bend bare of coating. Tension side of bend had severe coating cracks.	Severe substrate oxidation on both sides of bend. Specimen cracked upon cooling.
2	75	1 hr. 2 hrs.	Compression side of bend bare of coating. Tension side of bend had small coating cracks.	Slight substrate oxidation on compression side. No substrate oxidation evident on tension side. Severe substrate oxidation on compression side. Slight substrate oxidation on tension side with oxide projecting through coating cracks.
3	20	2 hrs.	Compression side of bend bare of coating outer layer. Tension side of bend had no evidence of cracks.	Severe substrate oxidation on compression side. Slight oxidation on tension side with oxide projecting through cracks in coating.

Figure 97. Specimen #1 - 180° Bend - 2 hrs. at 2500°F
Vitro Cr-Ti-Si coated Cb 752.



Compression Side Tension Side

Figure 98. Specimen #2 - 75° Bend - 2 hrs. at 2500°F
Vitro Cr-Ti-Si coated Cb 752.



Compression Side Tension Side

Figure 99. Specimen #3 - 20° Bend - 4 hrs. at 2500°F
Vitro Cr-Ti-Si coated Cb 752.

Following the completion of the sheet metal tests, cylinders of Cb752 were manufactured to the following dimensions, .210 ID::, 262 ODx, 50 long. These were coated with Cr-Ti-Si coating or with Cr-Ti omitting the siliconization treatment. A few of each were oxidation tested at 2400°F in static air in the as coated, undeformed condition. The remainder of the Cr-Ti-Si coated pieces were flared to various degrees by inserting to various depths a mandrel with a 20° point angle and a highly polished surface. Permanent deformation was measured by change in diameter at the end of the cylinder after removal of the expanding tool. The expanded cylinders were then oxidation tested at 2400°F in static air.

The results were as follows:

1. The oxidation tests on as coated cylinders resulted in the following:

   a. Cr-Ti coated cylinders failed in less than one hour.
   b. Cr-Ti-Si coated cylinders failed in 24-41 hours and in 41-64 hours.

2. Deformation tests produced cylinders with .007, .011, .013 and .015 increase in outside diameters. Some coating spalled off in all cases. Expansion beyond this point produced base metal splitting.

3. Oxidation tests on deformed cylinders resulted in all pieces failing through oxidation in1-2.5 hours.

Photographs of the above specimens are shown in Figures 100 and 101.

24-41 hrs. 41-64 hrs.

Figure 100. Vitro Coated Cb 752 Deformation Cylinders Oxidation Tested at 2400°F as Coated, Undeformed. Times to failure indicated.

.077 .011 .013 .015

Figure 101. Vitro Coated Cb 752 Deformation Cylinders Oxidation Tested at 2400°F after Deformation. Ends expanded to permanent diameter increase as shown. All failed in 1-2.5 hours.

C. BLIND FASTENER DESIGN, MANUFACTURE AND TESTING

Some hope was revived for a deformable blind fastener with the discovery that a somewhat successful patch technique had been used on Tapco Cr-Ti-Si coated Cb 752 assemblies by the Martin Co. The possibility therefore arose that the deformable portion of a fastener might be coated with this patch material then deformed while the coating was wet. While this patch coat was not expected to equal the oxidation protection of the remainder of the fastener, the area in which the deformable portion is located would probably not be subjected to the extreme environmental conditions and may therefore perform satisfactorily.

A few prototypes were coated with the electrophoretically applied Cr-Ti-Si coating and installed using the $MoSi_2$ + Synar Binder + H_3PO_4 patch coat. Some degree of success was attained; however, several problem areas existed.

Among the problems were:

1. High friction between mating surfaces during installation causes high variable torque for deformation. Since torque is the best available indication of complete installation, a problem in determining whether the deformation is complete exists.

2. As coating cracks and comes off the substrate during deformation, it takes some of the patch with it, thereby leaving areas with only diffusion zone protection.

3. Tension required for deformation may damage the coating on the threads.

A modified configuration of the deformable fastener was chosen for the continuation of the test program. Several parts were manufactured from Cb 752 rod. These were then coated with the electrophoretically applied Cr-Ti-Si coating. No special effort was made to coat the inside of the fastener since previous tests had shown that thin coating layers had less tendency to crack and would most certainly provide lower installation torques.

A drawing of the final configuration is shown in Figure 102.

These fasteners were tested as follows:

In order to reduce installation torques to an acceptable level, two pieces were preoxidized at 2000°F for 15 minutes. Premature failures occurred on the inside of the fasteners. Three pieces were installed at room temperature in cylinders of coated Cb 752. Complete spalling of the coating occurred and the deforming area cracked with only slight deformation.

Attempts were then made to install a few pieces at elevated temperatures. These were heated to 1200-1300°F by induction then installed in cylinders before the temperature had dropped to 1000°F. No improvement in the deformability of the coating or the substrate was noted.

At the completion of the above tests, the following problems were still seen to exist:

1. Deformability of the Cr-Ti-Si coating is virtually non-existant.

2. Embrittlement of the substrate by the coating makes reproducible deformation difficult to attain.

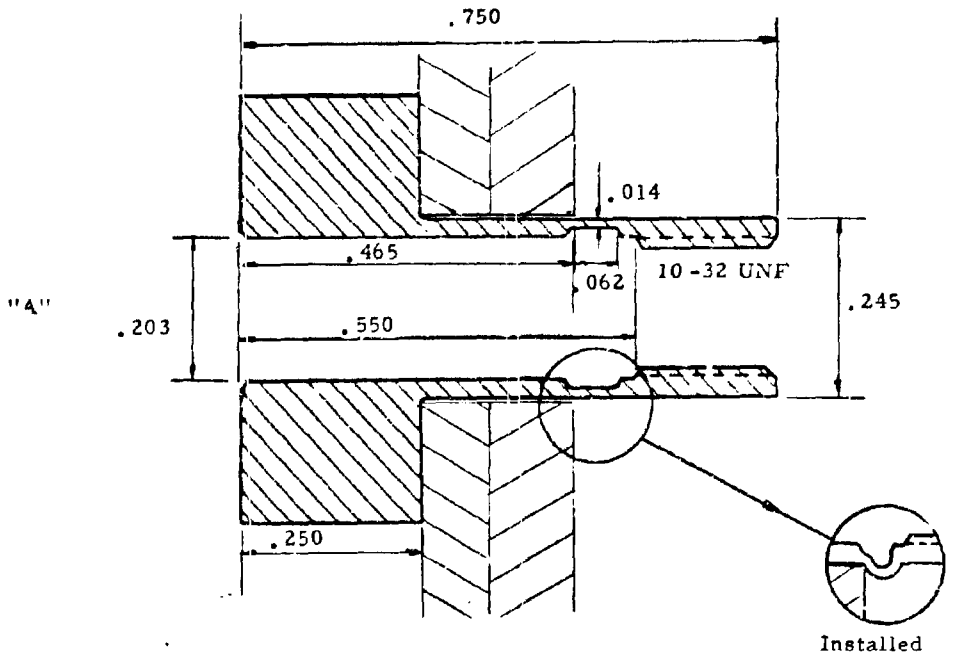
3. A slurry patch coating applied to a deformable fastener immediately prior to installation does not reduce the tendency of the coating to spall.

4. Heating within practical temperature ranges prior to installation does not improve the deformability of the coating and eliminates the possibility of installation with a wet slurry of patch coating material.

5. Because of the rough nature of the coating, torques required to deform a blind fastener are excessive and can cause severe damage to the coating.

6. The manufacture and installation of a bare deformable fastener is possible in a wide variety of configurations and these may prove useful in an application where post installation coating is possible.

REVISION AND DATE											



Deformation accomplished by tightening a smooth steel bolt into the threaded end from end "A". The steel bolt is then removed. Shear strength may then be increased by the insertion of a 10-32 coated refractory alloy bolt.

Figure 102

Deformable Fastener	TOLERANCE UNLESS SPECIFIED	STANDARD PRESSED STEEL COMPANY JENKINTOWN, PENNSYLVANIA	
	FRACTIONS ±	DRAWN BY T. Roach	MATERIAL AND HEAT TREAT Refractory Alloy
	DECIMALS ±	DATE 10-1-65	
	ANGLES ±		
	SURFACE FINISH		

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D. BASIC DEFORMABILITY TESTS ON COATED T-222 SHEET

Samples of T-222 sheet were coated with the WSi_2 coating and bend tested to determine the relative ductility of WSi_2 compared to the Cr-Ti-Si coating on columbium alloys. When these pieces were bent over a 1 1/4" diameter cylinder all coating on the compression side of the bend spalled off in large sections. The tension side of the bend did not spall off, but did exhibit numerous small cracks. A photograph of some of the test pieces is shown in Figure 103.

By comparison with the original tests conducted on Cb752 sheet Cr-Ti-Si coated, the spalling described above is more severe, indicating that the probability of achieving success with a tantalum alloy deformable fastener was less than that of achieving success with the columbium alloys.

Therefore, no further effort was expended on the development of a tantalum alloy deformable fastener.

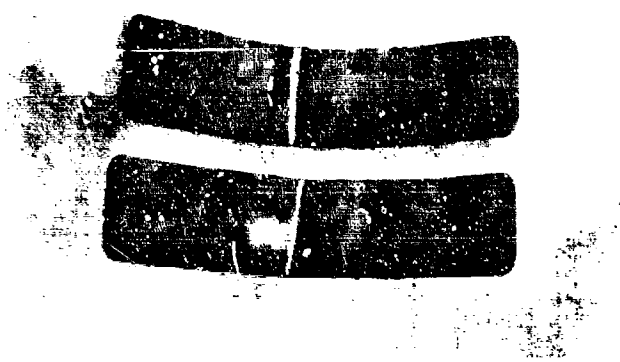


Figure 103. Bend Test Specimens of WSi_2 Coated T-222.

SECTION XI

DISPERSION STRENGTHENED METALS

A. OBJECTIVE AND BACKGROUND

The Dispersion Strengthened Metals portion of this program originally incorporated the following two principal objectives:

1. Manufacture and test two materials in three fastener configurations; flush head bolts and two blind or semi-blind types. The tests were to consist of tensile, shear, and creep on fasteners and bend and impact on specimens.

2. Determine the compatability of the dispersion strengthened metal fasteners with coated columbium parts; expose assemblies containing representative materials to elevated temperatures and observe any reactions or interactions.

At the start of the program the only dispersion strengthened metal commercially available was TD Nickel. While this material possesses moderate oxidation resistance to 2200° F and retains 7 - 10 Ksi ultimate strength at 2400° F, it does not possess acceptable low temperature strength nor does it possess the required oxidation resistance to 2400° F.

For this reason DuPont, Curtiss-Wright, and Vasco Metals were contacted, and all expressed an interest in supplying more advanced materials for the program. Accordingly the following actions were taken:

1. Vasco Metals - An order was placed for 10 feet of Ni-15% Mo-ThO_2. The material was to be made and extruded at New England Materials Laboratory and finished by Vanadium Alloys Steel Co. prior to its shipment to Standard Pressed Steel Company.

   The first material produced was not of acceptable quality and was scrapped prior to shipment.

   A subsequent attempt produced material which Vasco Metals considered acceptable and this material was finished and shipped to Standard Pressed Steel Company. Twenty 1/4-28 hex head bolts were manufactured with forged heads and rolled threads. These were fluorescent penetrant inspected with the result that six pieces were rejected for cracks and open seams in the threads, underhead fillets, and in the head. The acceptable pieces were tensile tested at both room temperature and elevated temperatures as discussed in Section C.

2. Curtiss-Wright - An order was placed with Curtiss-Wright for 100 feet of .270 diameter thoriated nickel-chromium. Approximately 75 feet of this material was shipped to Standard Pressed Steel Company. Forty bolts were fabricated and prepared for testing. Prior to the start of elevated temperature testing, Curtiss-Wright notified Standard Pressed Steel Company that the properties of the material were not satisfactory at temperatures of 1800°F and above. Consequently no elevated temperature mechanical property data on this material is reported. The room temperature tensile strength was 154,000 psi.

3. DuPont - The Metals Department of DuPont supplied a research sample of TD Ni C (TD Nickel-Chromium) 54 inches long and .270 inches in diameter at no charge. This material was used to fabricate 1/4-28 bolts which were subsequently tested at room temperature and at several elevated temperatures.

B. TEST PROGRAM

Tensile tests were conducted on the bolts described above using TD Nickel nuts which were available from a previous, Standard Pressed Steel Co. sponsored, TD Nickel program. The fixtures were similar to those described in Section VIII except that they were made of TD Nickel. The results of the tensile tests are contained in Table XLIX and photographs of untested parts are shown in Figure 104.

A comparative oxidation test program was conducted on the four materials (using TD Nickel as a standard). Finished rod material specimens, 1/4 in. diameter by 1/2 in. long, were exposed to temperatures of 1800°F, 2000°F, and 2200°F in static air for 100 hours. Periodic weight checks were made for weight change data throughout the 100 hours. The data are plotted in Figures 105, 106, and 107 and photographs of representative specimens are shown in Figure 108.

It is significant to note that the weight gain of TD Nickel shown by the data is also evident in the photographs by reason of a glass-like coating formation. The high weight loss experienced by Vasco's Ni + 15 Mo + ThO_2 is also evident in the photograph by the flaking oxide which is apparent. The thoriated nickel-chromium from both Curtiss-Wright and DuPont exhibits a tightly adherent thin greenish-black oxide film. The slight weight loss experienced by the TD Ni C and the Curtiss-Wright thoriated nickel-chrome is apparently due to the volatilization of part of the oxidation products.

Since the amount of useful material was severely limited, the complete test program desired could not be conducted.

TABLE XLIX

TENSILE STRENGTH OF DISPERSION STRENGTHENED
1/4-28 HEX HEAD BOLTS

Test Temperature		Material					
		DuPont TD Ni C		Vasco Ni-Mo-ThO_2		DuPont TD Nickel	
°F	°C	PSI	N/cm^2	PSI	N/cm^2	PSI	N/cm^2
80	27	145 000	100 000	110 000	75 700	77 500	53 400
1600	870	35 200	25 300	- - -	- - -	- - -	- - -
1800	982	23 700	16 350	10 500	7 240	14 500	10 000
2000	1093	16 800	11 600	5 500	3 790	10 600	7 300
2400	1316	8 120	5 600	- - -	- - -	4 700	3 240

DuPont - TD Ni C

Curtiss-Wright - Thoriated Nickel-Chromium

Vasco - Thoriated Ni-15% Mo

Figure 104 Dispersion Strengthened Metal Bolts, 1/4-28, Untested

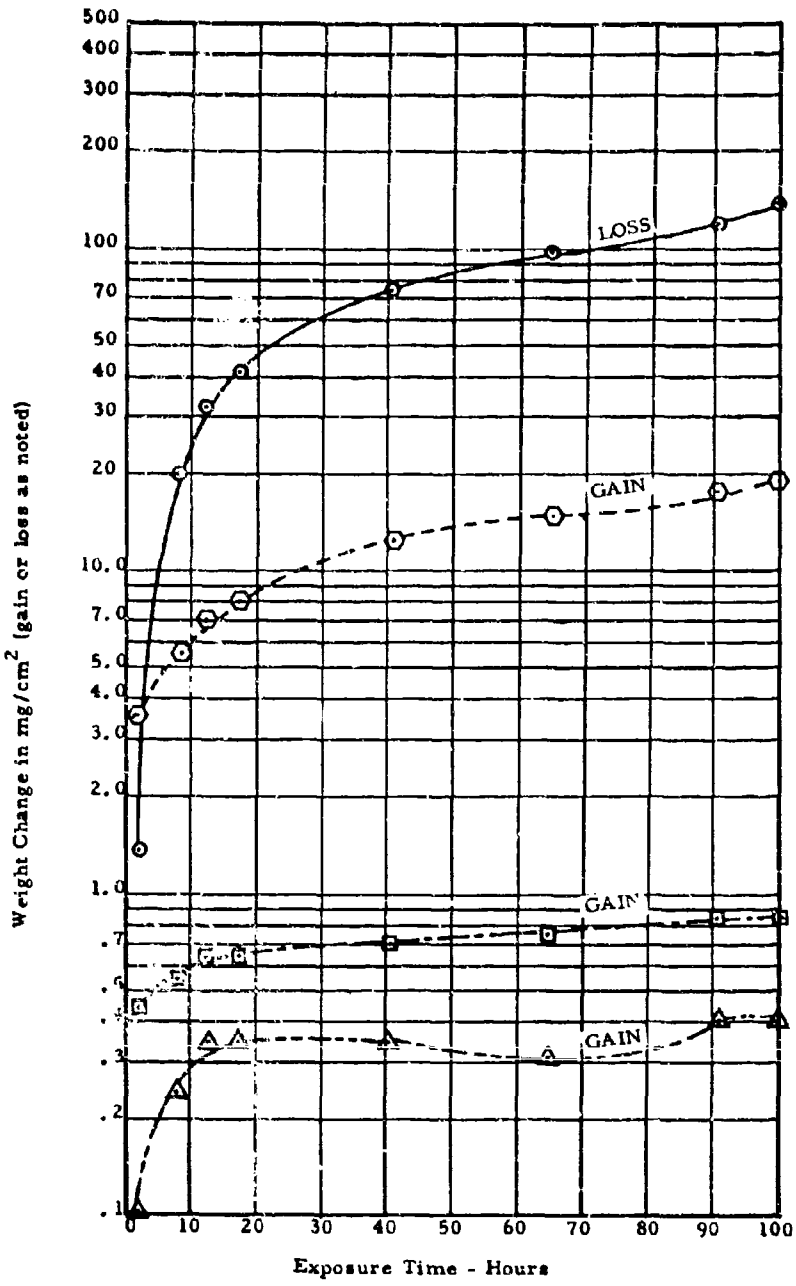


Figure 105. Oxidation Rate for Dispersion Strengthened Metals Tested at 1800°F (982°C) in Still Air

- Vasco Ni-15% Mo-ThO_2
- DuPont TD Nickel
- Curtiss Wright Thoriated Nickel-Chromium
- DuPont TD NiC

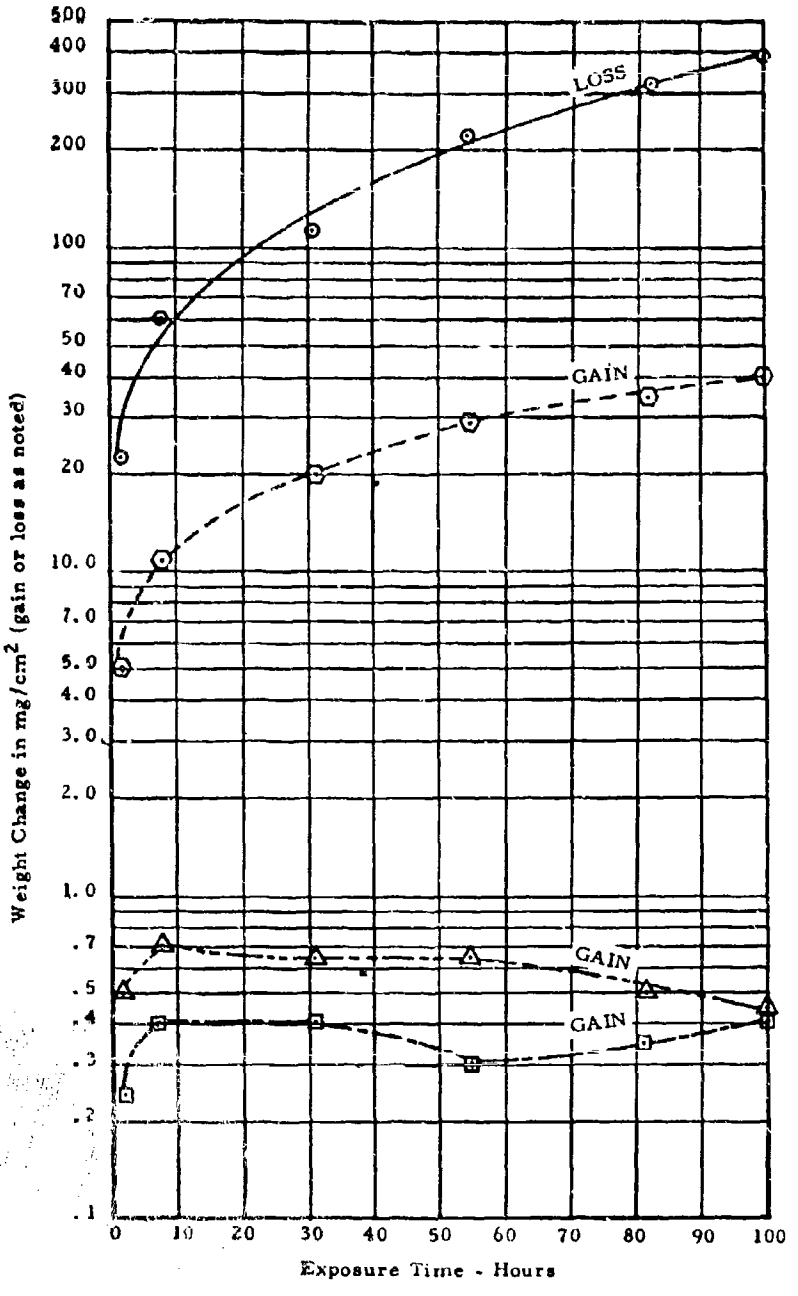


Figure 106. Oxidation Rate for Dispersion Strengthened Metals Tested at 2000°F (1093°C) in Still Air

- Vasco Ni-15% Mo-ThO_2
- DuPont TD Nickel
- Curtiss Wright Thoriated Nickel-Chromium
- DuPont TD NiC

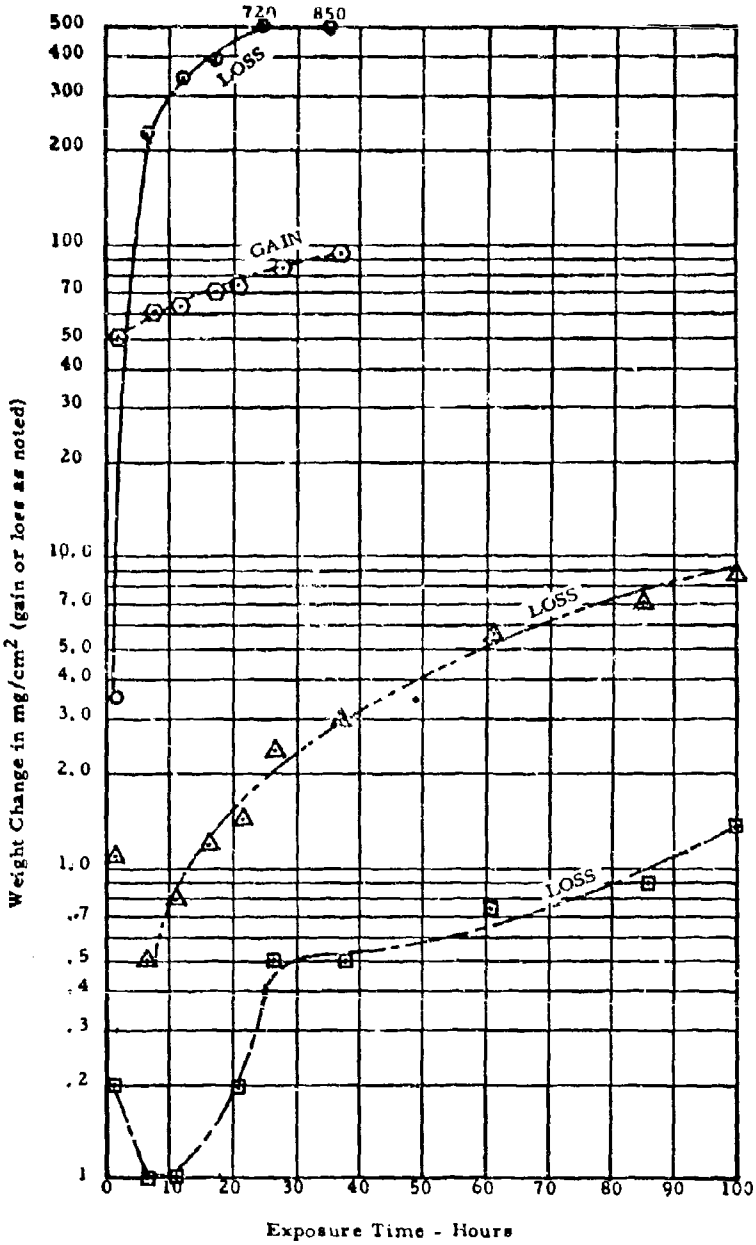


Figure 107. Oxidation Rate for Dispersion Strengthened Metals Tested at 2200°F (1204°C) in Still Air

- Vasco Ni-15% Mo-ThO_2
- DuPont TD Nickel
- Curtiss Wright Thoriated Nickel-Chromium
- DuPont TD NiC

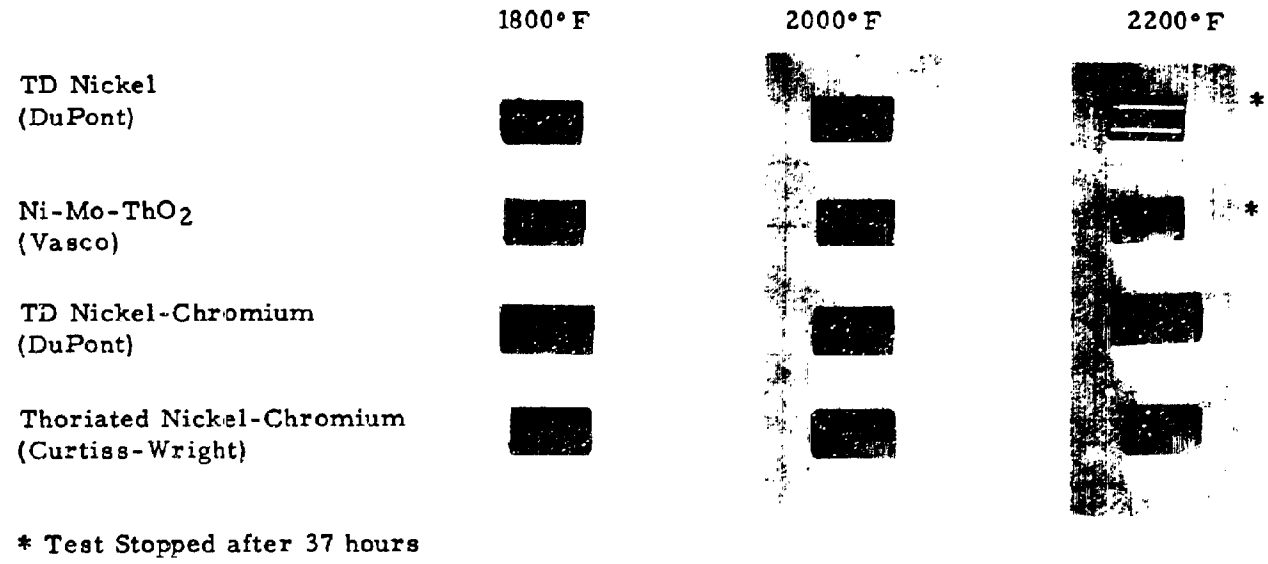


Figure 108 Typical Oxidation Test Specimens of Dispersion Strengthened Materials - 100 hours exposure at temperature indicated

SECTION XII

METALLOGRAPHY

Throughout the course of this program certain metallographic studies were carried out to determine:

a. Conformance of materials in the as received condition to the requirement that they be 100% recrystallized following final reductions at the mills.

b. General characteristics of the as received microstructures.

c. Effect of the coating process on the microstructure.

Specimens of the three representative materials were examined in the as received and as coated conditions. Tranverse and longitudinal sections were examined in each case.

Photomicrographs of the pieces examined are contained in Figures 109 through 114.

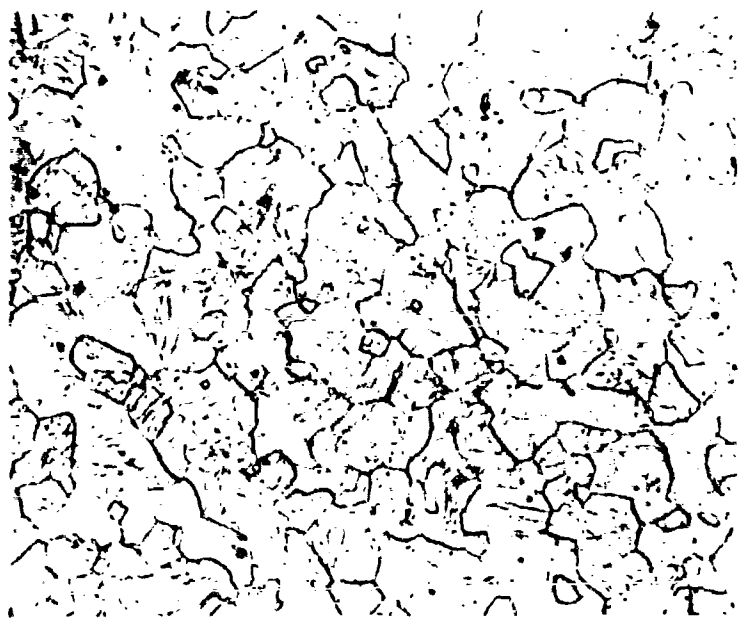
Study of the microstructures reveals the following:

1. All materials were 100% recyrstallized when received from the material suppliers. They therefore all fulfilled the recyrstallization requirement set forth in the survey conclusions.

2. No significant change in grain size or other microstructural characteristics occurred in the columbium based alloys during the coating process.

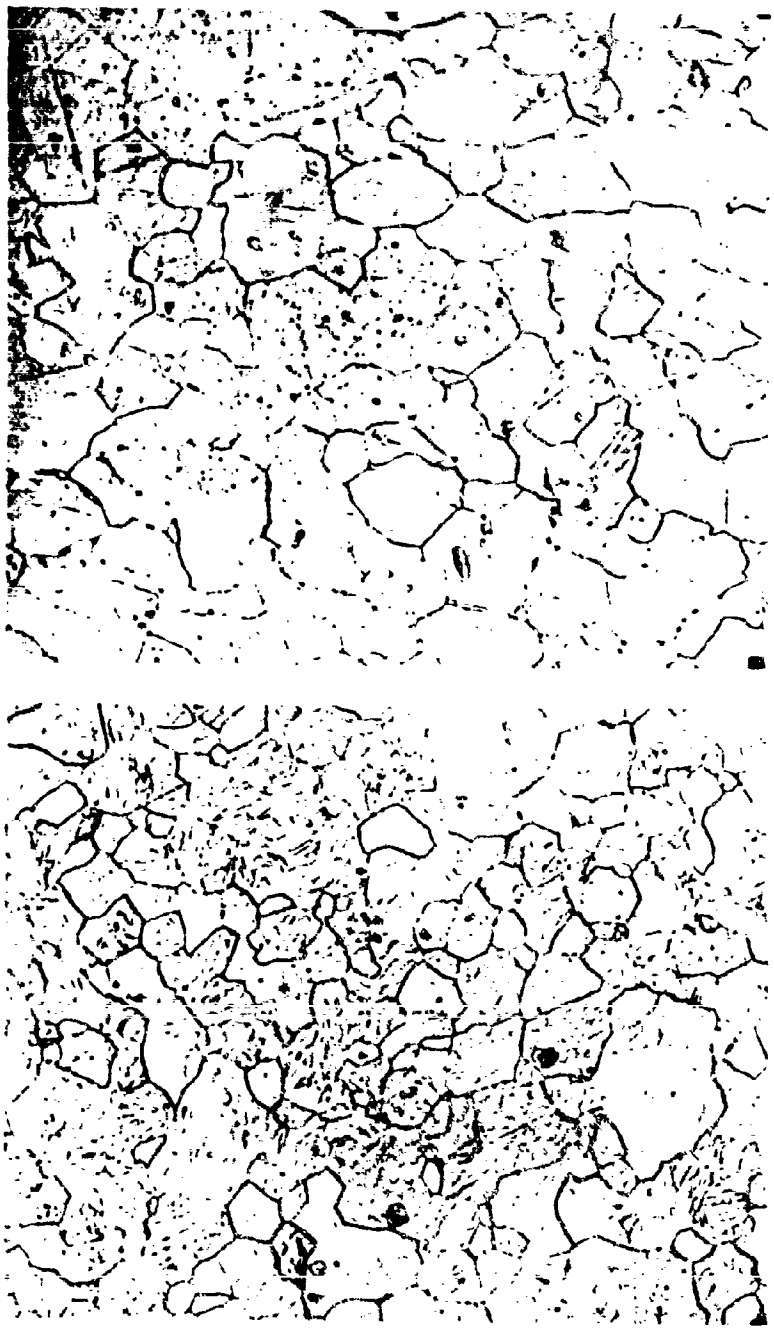
3. A considerable increase in grain size occurred in the T-222 during the coating process.

Longitudinal



Transverse

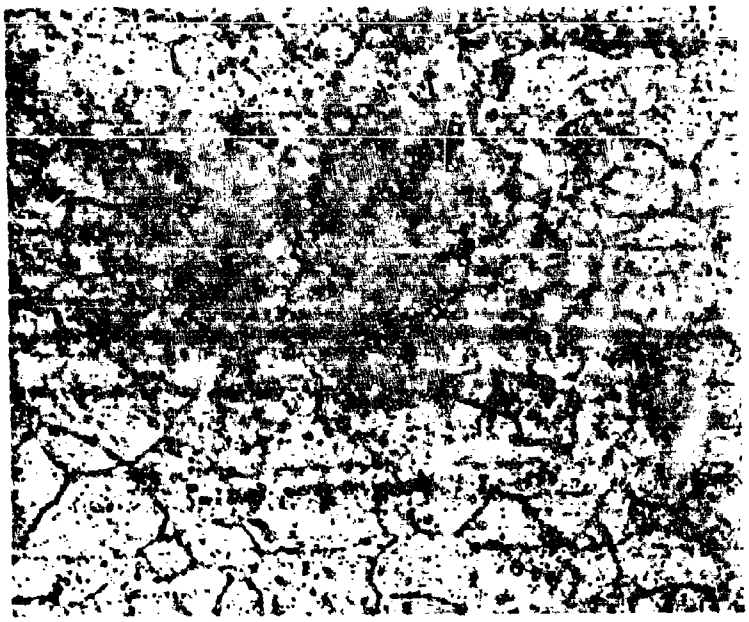
Figure 109 Microstructure of Cb752 in the As-Received Condition - Mill Recrystallized
Etchant: 48% H_2SO_4, 48% HNO_3, 4% HF, Immersion 500X



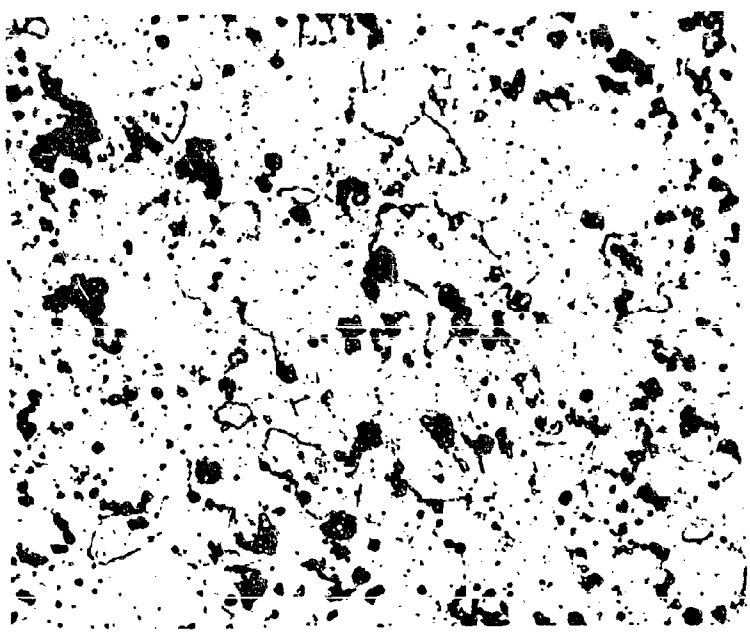
Longitudinal

Transverse

Figure 110 Microstructure of Cb752 in the As Coated Condition
Etchant: 48% H_2SO_4, 48% HNO_3, 4% HF, Immersion 500X

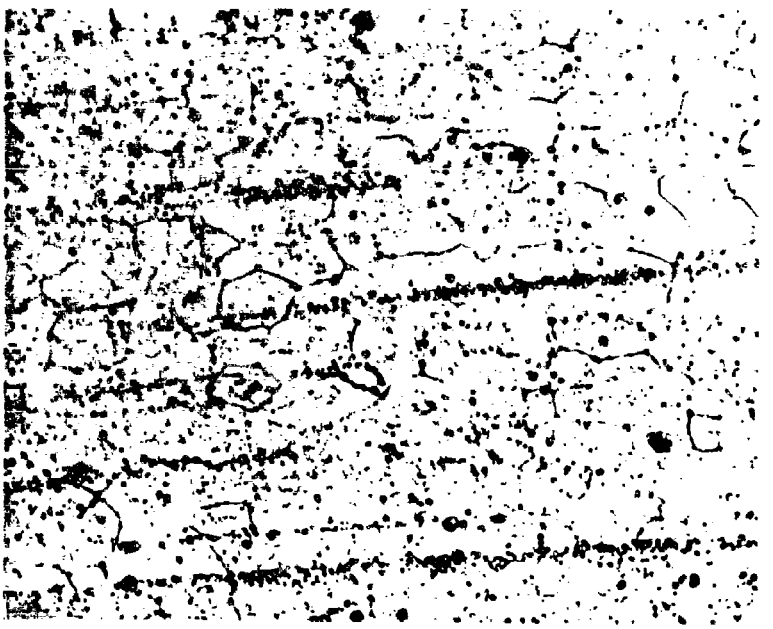


Longitudinal

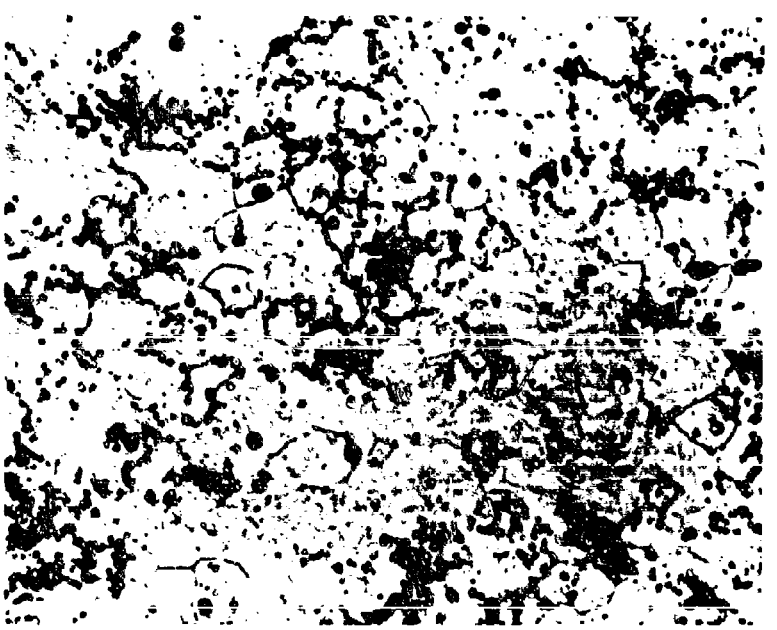


Transverse

Figure 111 Microstructure of C129Y in the As-Received Condition - Mill Recrystallized
Etchant: 48% H_2SO_4, 48% HNO_3, 4% HF, Immersion 500X

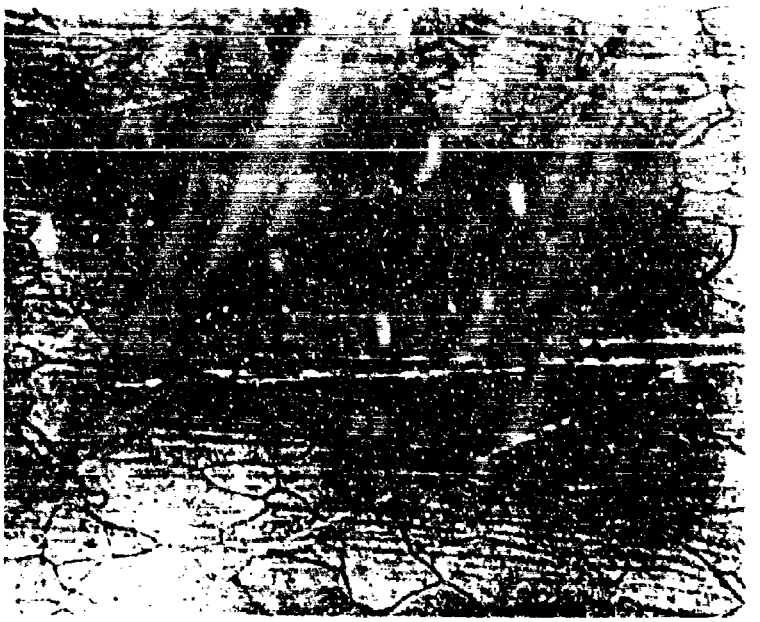


Longitudinal



Transverse

Figure 112 Microstructure of C129Y in the As Coated Condition
Etchant: 48% H_2SO_4, 48% HNO_3, 4% HF, Immersion 500X

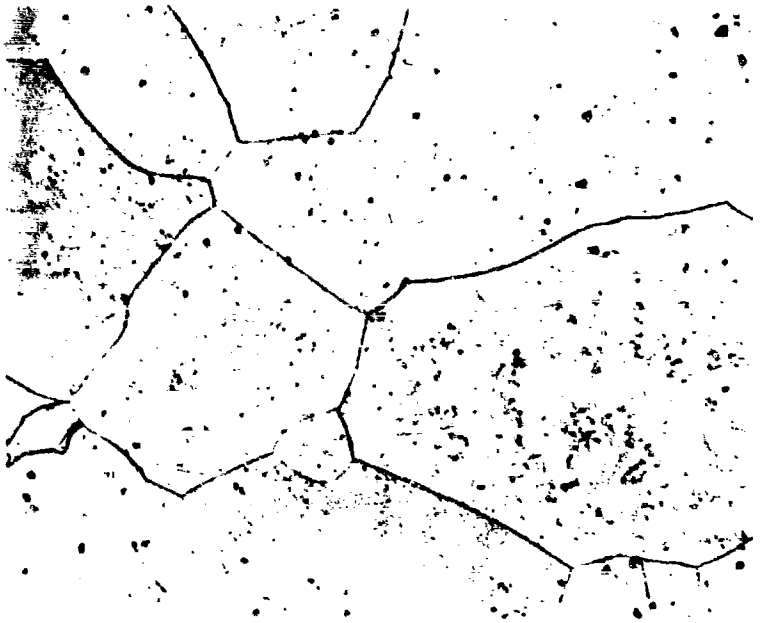


Longitudinal

Transverse

Figure 113 Microstructure of T-222 in the As-Received Condition - Mill Recrystallized
Etchant: $NH_4F + H_2O$, Immersion 500X

Longitudinal



Transverse

Figure 114 Microstructure of T-222 in the As Coated Condition
Etchant: $NH_4F + H_2O$, Immersion 500X

SECTION XIII

CONCLUSIONS

The following conclusions were reached on the basis of the results of this program:

1. The electrophoretic coating process is readily adaptable to the application of a variety of coating compositions on threaded fasteners.

2. The tolerance control attained by electrophoretic deposition coating is superior to any heretofore applied to fasteners. The control attained permitted the maintaining of complete interchangeability of parts with tolerances equivalent to those applied to precision high strength aircraft fasteners.

3. The electrophoretically applied Cr-Ti-Si coating possesses properties comparable to those of the pack applied Cr-Ti-Si coating.

4. The survival potential of coated refractory alloy fastener systems is not impaired by the use of a truncated thread form on the internally threaded member.

5. Oxidation resistance of Cr-Ti-Si coating is essentially the same on Cb 752 as it is on C129Y. An exception lies in the partial pressure behavior, the Cb 752 experiencing some degradation of the coating at 2000°F or 2400°F and 1 torr or 10^{-2} torr. The C129Y experiences no noticable degradation at these temperature and pressure levels. Preoxidation of the coating prior to partial pressure exposure contributes to the degradation, but is not an essential requirement for degradation.

6. Partial pressure degradation of preoxidized Si/WSi_2 coating on tantalum alloy is significant to temperatures as low as 2200°F at 1 torr and 10^{-2} torr. The result of this degradation is the reduction of 2400°F static oxidation life to the levels attainable by this system without preoxidation.

7. It is not feasible at this time to produce a coated deformable fastener because of the limitations imposed by the ductility of present coatings.

8. The tightening torque which may be applied to coated fasteners is limited to approximately 50 inch-pounds due to the lack of ductility in the coating.

9. Threaded fasteners may be removed and reused after exposure at up to 2200° F. Beyond this temperature chipping of the coating occurs on removal and reusability is not possible without a repair operation on the coating. At 2600° and above, fusion of the coating produces sufficient resistance to removal that shearing of the bolt generally occurs.

10. The program has helped to answer many questions and to make refractory alloy fasteners more usable however, many questions remain to be answered. The limited investigation conducted on dispersion strengthened metals indicates that further effort is certainly warranted in order to explore and determine their full potential.

APPENDIX I

SURVEY

A. REFRACTORY ALLOY USERS SURVEY

1. General Review of Information Sought

The following companies were surveyed for comment on their future refractory fastener requirements:

Astronautics Division of General Dynamics

Boeing, Seattle

Chance Vought, Dallas

Convair, Fort Worth

Douglas, Santa Monica

Lockheed, Palo Alto

Martin, Baltimore

Marquardt, Van Nuys

McDonnell, St. Louis

North American, Downey

Republic Aviation, Farmingdale.

The major programs which are currently utilizing coated refractory metal structural fasteners in research vehicles or in test structures are :

ASSET at McDonnell Aircraft

DYNASOAR at Boeing

SLAM at Chance Vought

Foil Gage Heat Shield Panels at Bell Aerosystems Co.

Columbium Alloy Test Panels at Martin Company, Baltimore

High Temperature Fastener Program at Republic Aviation.

Threaded fasteners for use in these programs have been fabricated from molybdenum and columbium alloys in sizes up to 3/4 inch diameter x 4 1/2 inches long, and various types of rivets have been investigated in sizes up to 5/16 inch diameter.

Because of the diversity of background, requirements, and approach to the problem, several questions were asked of each firm to get on a common ground. The questions to each of the user companies were:

a. What was the choice of

   a. molybdenum based alloy?
   b. columbium based alloy?
   c. tantalum based alloy?

b. Would these alloys be used in the recrystallized condition?

c. What coating is preferred on each of the above-mentioned alloy systems?

d. How did coating fit into the construction process?

e. Were sections recoated?

f. Were patch techniques anticipated or used?

g. What was the choice of fastener

   1. threaded?
   2. locknuts?
   3. thread form?
   4. rivets?
   5. deformable blind and semi-blind?
   6. Unique or other special fasteners?

h. What were installation considerations?

i. What were the main design criteria for the structure?

j. What temperature ranges were anticipated on the fasteners?

k. Static or moving air?

l. What atmospheric pressure considerations are made in designing the joint?

m. What non/refractory materials were in the joint?

n. What are the other compatibility problems?

o. What are current plans for fastener reusage?

p. Are current tolerances sufficient?

Not all companies were in position to answer all these and other questions at the time of the survey, but a good deal of information was compiled.

2. Materials

Surprisingly, most of the companies interviewed had no strong feeling on alloy selection. The choice of TZM in molybdenum based alloys was unanimous with everyone who expressed an opinion. The first choice in columbium alloys was Cb-752 which was mentioned by everyone having a choice. Two of the companies had no particular columbium alloy preference at this time. The second place columbium alloy was B-66 which was named by four of the ten as their first choice. After Cb-752 and B-66 came D-43, C-129Y, and FS-85 in that order. Only two companies were ready to mention a tantalum alloy, 90 Ta-10 W and T-111.

Most of those surveyed said that the recrystallized mechanical properties would be used in determination of design allowables. No one was firmly against this.

The accumulated comments of all parties are listed below:

Company	Molybdenum Alloy Choice	Columbium Alloy Choice	Tantalum Alloy Choice	Recrystal-lization
Astronautics	None	B-66, D-43, Cb 752	None	Yes
Boeing	TZM	Cb 752, C129Y	Not ready	Yes
Chance Vought	TZM	D-43, C 129, Cb 752, B-66	Will use tungsten first	Yes
Convair	Not ready	B-66, D-43, Cb 752, FS 82	Not yet made	Yes
Douglas	TZM	B-66, FS 85, Cb 752, C 129Y	No choice	Not decided
Martin	TZM	D-43, C 129Y Cb 752	T-111	If forced
Marquardt	No choice	No choice	No choice	No choice
McDonnell	TZM	Cb 752, B-66 D-43, FS-85	90-10, T-111 Ta-30 Cb-7 1/2V	Yes
North American	No preference	No preference	No preference	Yes
Republic	Will not use	B-66, Cb 752, C 129	No Preference	Yes

While the Lockheed facility at Palo Alto was included in the survey, they have no products and therefore no preferences in hardware. Their work is primarily aimed at determination of the basic mechanism of coating oxidation and failure. For these reasons they were not included in the breakdown lists.

The choices above were not as decisive as they appear. The Boeing selections of columbium alloys were based on availability rather than technical considerations. McDonnell lists TZM as the choice of molybdenum alloy, but their intended usage is for above 2600° F only. The McDonnell usage of materials versus temperature range is:

1.	Ceramics	above 3000° F
2.	Tantalum based	above 3000° F
3	Molybdenum based	to 3000° F
4.	Columbium based	to 2600° F

The McDonnell columbium alloy selections were based on strength. Martin, Baltimore took the economic approach to refractory fastener design. Their choice of fasteners for their Test Panel Program is predicated on the cost of the raw material. For this reason Martin has considered TZM fasteners in the columbium structure. Also, C 129Y rates high with them because this alloy has been quoted at 60% of the cost of the other main second generation columbium alloys.

The Republic Aviation choice in columbium alloys was somewhat qualified since they preferred the C129 for the high temperature ranges (2600-3000° F). Republic did not intend to use coated molybdenum based alloy fasteners in future structural work.

While Astronautics Division of General Dynamics had a preference in columbium alloys, they had no immediate plans to use any refractory alloy fasteners.

The selections of Chance Vought, Convair, and Douglas were based on future work. Marquardt had no choice because the bulk of their refractory structures were in bare tungsten alloys.

The North American engineers had no particular preference because they felt that refractory fasteners are coating critical, and that most coatings impart such great property loss that alloy selection is not of prime importance.

3. Coatings

Probably the strongest indication received from the users was that they preferred their own proprietary refractory coatings. Three of the firms contacted had coatings and others were working on their own coatings. Most felt that today's coatings were not sufficient and that future fastener coatings would be tailored more toward the exact application. Answers to direct questions were:

	Preferred Coating			
Company	Mo	Cb	Ta	Usage Comments
Astronautics	None	Tapco	None	
Boeing	Boeing	Boeing	Boeing	Have not run compatibility with other coatings

Company	Preferred Coating Mo	Cb	Ta	Usage Comments
Chance Vought	Chance Vought			Wants coated fasteners to be post-coated in structure
Convair	None	Tin-Aluminum	None	Want slurry coating
Douglas	None	Tapco	None	
Martin	None	Tapco	None	Any other coating should be compatible with Tapco
Marquardt	None	Durak B	None	
McDonnell	None	None	None	Prefer LB-2 slurry which they put on themselves. Want to see new coatings
North American	North American			NAA coatings causes no loss in properties. Pest condition under 2000° F
Republic	No preference			Want smooth coatings. Use coated fasteners, recoat structure, then patch critical areas.

All the companies with their own coating expressed intentions to buy uncoated fasteners. For the most part the remaining companies preferred to purchase coated fasteners. For the most part even companies which showed a preference are not completely firm on fastener coating so long as fastener coating is compatible to structure coating.

The bulk of the people contacted want coated fasteners which will be recoated after installation. Heads, nuts, and bucked portions of rivets will be patched and coated by most of the participants.

4. Fasteners

Everyone contacted had quite a bit to say about fasteners. Threaded fasteners were most popular with everyone having a certain amount of plans for them. Nine of the ten wanted rivets. The deformable

blind and semi-blind fasteners were more controversial. Five of the companies wanted them while two would not use them. The design philosophy varied from using deformable fasteners from minimal load (20 pounds) to the full strength of the material. Locknuts were wanted by most companies, but the inherent difficulties were recognized. Specific fastener requirements were:

Company	Threaded Designs Required	Thread Form	Size Range	Deformable Designs Required	Special Considerations
Astronautics	None	None	-	None	None
Boeing	Hex heads Flush heads Nuts (no lock) Dome nuts	Boeing spec. #10- (equal root & crest). Flat internal crests acceptable.	3/8	Rivets only. Will not use deformable or breakoff types.	To drive in flush heads.
Chance Vought	Hex & flush heads. Locknuts.	No choice	to 3/8	Rivets. Would use good ones.	Are now using own design of shear pin.
Convair	Hex & flush heads. Nuts.	No choice	No choice	No comment.	
Douglas	Hex & flush heads. Nuts.	No choice	No choice	Will use any	PLI washers considered.
Martin	Hex heads. Point drive bolts. Smooth flush heads. Nuts (locking).	Coarse preferred. No other choice	3/16 & 1/4	Rivets. Explosive rivets.	Want locking device.
Marquardt	No choice	No choice	No choice	Rivets & blind parts.	
McDonnell	Hex & flush heads. Dome nuts. Locknuts. Plate nuts.	Fine thread. 65% version	#10- 1/2	Any blind part. Rivet upset at room temp.	Will use jam nuts if must. Want stamped parts. Quick disconnect fastener

Company	Threaded Designs Required	Thread Form	Size Range	Deformable Designs Required	Special Considerations
North American	Hex heads. Flush heads. Nuts.	Standard-ized coarse		Rivets blind	
Republic	Flush heads. Hex heads. Nuts.	Coarse 65%		Rivets blind bolts	Clips

Astronautics, Lockheed, and Marquardt had no particular fastener requirements at that time. Marquardt did have future requirements for blind-type fasteners, but probably of a tungsten alloy.

Convair and Douglas had no present refractory structural program, but were in the concept stage of future projects. They had no firm requirements at that time.

Boeing was making use of more or less standard threaded fastener configurations in the Dynasoar effort. Their engineering evaluations had shown no need for locking devices as the coating itself acts as a lock. This is most particularly true after elevated temperature exposure. Boeing did not consider jam nuts at that time. The feeling at Boeing was quite negative on deformable type blind fasteners. They considered any effort expended as wasted.

Chance Vought had incorporated fasteners in their structural program. They had difficulties in the bucking of molybdenum based alloy rivets. For this reason they had reservations on rivet usage. One interesting design unique to Chance Vought was a threadless shear pin held in the joint by a cotter pin.

Martin Co., Baltimore expressed a desire for almost every type of fastener. The first attempt at a semi-blind fastener combination was the point drive bolt with a smooth countersunk head and a conventional threaded nut. The Martin desire for explosive rivets was the only one encountered in the survey. The engineers at Martin did indicate a strong interest for a locking device of some type.

The only company showing a preference for the fine thread series was McDonnell. They did express a willingness to go along with

any industry standards. A preference was stated for some type of locking device on either member. They had had previous bad experiences with coated locknuts which lost locking torque after one or two applications. McDonnell wanted to use both threaded and blind fasteners to their maximum capacity. A quick disconnecting coated refractory fastener would be used at McDonnell.

North American had successfully used deformable type blind bolts in their previous refractory structural effort. They were very much interested in deformable fasteners. They were in fact replacing spot welds with coated refractory rivets. Here again, North American was very interested in thread standardization.

The future usage at Republic Aviation fell in line with other people's thinking. They wanted to design around deformable type fasteners, but when forced to use them they would minimize the load to 20 - 50 pounds. During the course of the Air Force contract on "High Temperature Fasteners" Republic had decided on the 65% rounded refractory thread form. They did not have a long range commitment to any thread form.

5. Temperature and Atmospheric Conditions

The most popular temperatures were all under 2500° F. The discussion of temperatures at 3000°F and above was all in the future, and no firm commitment could be made at this time.

Many of the companies desired to use coated refractories at temperatures of less than 2000° F. These people would all like to see oxidation testing in the lower ranges because of the pest condition prevalent with some of the coatings.

The latest studies showed that coating breakdown is accelerated with lowered pressure. For this reason the consensus of opinion was that partial pressure studies should be added to the program to get meaningful data.

Some of the opinions of the survey participants were :

Company	Operating Temp. °F for Refractory Fasteners Max	Min	Atmospheric Pressures
Boeing	2700-1/2 hr		.5 torr-3000°F - 40 min.
Chance Vought	2300	1400	Partial. See Lockheed study
Convair	2300-Mo 2000-Cb		No comment
Douglas	2400-1/2 hr	1400	10^{-1}, 10^{-3}, 10^{-10} torr
Martin	2450-Cb, Mo 3000-Ta	2000	No comments
McDonnell	3000	1400	Room to: 3000°F-30 min-70 micron then: 1400°F-30 min-11 torr
North American	2500	2000	Partial pressures
Republic	2400	1000	No comment

Astronautics, Marquardt, and Lockheed personnel had nothing direct to contribute because they did not have refractory fastener requirements. Lockheed did have a basic study (23) in which the mechanism of coating failure was being studied. This could have been generally applied to fasteners, but fasteners had no direct part in the program.

The 2700°F-1/2 hour condition mentioned by Boeing was a static air, ambient pressure test for coated fasteners. The 1/2 mm of mercury test was an evaluation of the coating whether on fasteners or other structures. This was a test to meet specific Boeing requirements. The feeling of the people at Boeing was that partial pressure studies should be added to the program to get usable data.

While Chance Vought and Douglas had had no trouble with fasteners, their interest in the Lockheed studies led to their separate requests that partial pressure studies be added to the program.

The low pressure, high temperature cycle referred to by McDonnell was a test that duplicates flight conditions. These people felt that

temperatures lower than 2000° F should be thoroughly investigated.

Republic had a couple of temperature ranges of interest under 2000°F; these were 1500-1600°F for 100 hours and -423°F.

6. Applications

The information received here was both extensive and varied. Five companies expressed the desire to retighten the nut and bolt combinations as much as one hundred (100) times without impairing oxidation resistance. In addition, most of these same people wanted ten (10) to one hundred (100) missions at maximum temperature exposures. One company will not reuse fasteners.

Installation of all fasteners with existing tooling was high on the list of desirable features. Each company had its own comments peculiar to in-house procedures.

Some direct requirements were:

Company	Temp. Exposure Number	Room Reusability Number	Compatibility Coatings and Materials	General
Astronautics			Tapco coating	
Boeing	None	None	All refractory coatings. Boeing Disil especially. Super alloys	
Chance Vought	Unspecified		Vought coating	
Convair	10	Unspecified		Might use ablative fasteners
Douglas	Unspecified		Tapco	
Martin	100	100	Tapco Haynes 25 Hastalloy	
McDonnell	10	Unspecified	Lb-2	Need resistance to high torque. Water or acetone as tightening lubricant.

Company	Temp. Exposure Number	Room Reusability Number	Compatibility Coatings and Materials	General
North American	None	None	NAA coating Super alloys	
Republic	100	100	T. D. Nickel Gaseous hydrogen	Coating should prevent gas diffusion.

Most of the companies that had unspecified requirements felt that they were necessary, but that they were not ready to specify exact limits.

Boeing and North American felt that refractory alloy fasteners could not be reused, neither after tightening at room temperature, nor after elevated temperature exposure. All the others would expect reusable fasteners out of the program.

B. REFRACTORY ALLOY PRODUCERS SURVEY

The ultimate selection of refractory alloys to be used was based primarily on the requirements of the end item users and the desires of the Air Force based on future needs. Several materials vendors were surveyed, however, to determine such factors as new alloys, availability and price of established alloys, and working specifications. There was no attempt to conduct a mechanical and physical property study during the survey, as most of the intended fastener users are up to date already The material suppliers contacted during the refractory alloy survey were:

Armetco Inc., Wooster, Ohio

Astro Metallurgical Corp., Wooster, Ohio

Climax Molybdenum Co. of Michigan

E I duPont de Nemours & Co.(Inc.), Wilmington, Delaware

Fansteel Metallurgical Corp , North Chicago, Illinois

General Electric Co., Cleveland, Ohio

Kawecki Chemical Co., Boyertown, Pennsylvania

National Research Corp

Stauffer Metals Division, Richmond, California

Sylvania Electric Products Co., Towanda, Pennsylvania

Union Carbide Stellite Co., Kokomo, Indiana

Wah Chang Corp , Albany Oregon

Westinghouse Electric Corp , Blairsville, Pennsylvania.

1. Molybdenum Based Alloys

There had been no recent advances in molybdenum based alloys which were immediately pertinent to fastener manufacture. The alloys Mo-.5 Ti and TZM (Mo-.5 Ti-.08 Zr) appeared to be the best for fasteners. These were readily available with a certain amount of shelf stock, a price list, and various specifications written by both vendors and customers. The TZC alloy (Mo-1.25 Ti-.3 Zr-.15C) was still a development item.

2. Columbium Based Alloys

As a result of interest exhibited by aircraft companies, detailed information was sought on only five columbium base alloys, Cb 752 (Cb-10W-2.5 Zr), B-66 (Cb-5Mo-5V-1Zr), D43 (Cb-10W-1Zr-.1C), FS 85 (Cb-11W-27 Ta-.8Zr), and C-129-Y (Cb-10W-10Hf-.4Y). Surveys by other organizations have also included Scb 291 (Cb-10W-10Ta) and AS 55 (Cb-8W-1Zr-.7Y) in the classification of "second generation" columbium alloys. Recent noteworthy developments were the elevation of duPont's experimental alloy, X-110, to a commercial status as D43 and the improvement of Wah Chang's C-129 by the addition of yttrium. Of course, numerous older columbium base alloys were readily available, but they were of little interest as high strength fastener material.

Of the five columbium alloys of interest, only the Stellite Division of Union Carbide Corporation had a complete, detailed specification for bar and rod stock of its Cb 752 alloy. Even this was a tentative specification. Some of the alloys had specifications for sheet material only. Generally, the suppliers were willing to meet any reasonable special requirements. In order to have a common ground for comparison purposes, a brief tentative specification for columbium alloys was prepared at SPS. This specification accompanied requests for quotes on price and delivery of representative amounts of the alloys of interest.

3. Tantalum Based Alloys

Because of the relative newness of tantalum alloy development, the attempt in this program was to delay as long as possible any final decision on a tantalum based alloy. Some information was sought from suppliers, but this will not be the last because of constant development. Alloys immediately available were Ta-10W (90-10) and T-111 (Ta-8W-2Hf). In development are Ta-8W-2Re, Ta-5W-2.5 Mo, Ta-10W-2.5Mo, Ta-17W, Ta-9.6W-2.4 Hf-.01C. It was reported (1)* that Ta-30cb-7.5V alloy has had difficulties because of vanadium segregation.

C. REFRACTORY ALLOY COATERS SURVEY

1. General Review of Requirements

At the inception of this program, the following individuals and organizations were visited or contacted to determine current and future requirements for coated fasteners and comments regarding potentially useful coating compositions:

Thompson Ramo Wooldridge, Inc.	R. Jeffreys
Chance Vought Corp.	W. L. Aves, K. P. O'Kelley
McDonnell Aircraft Corp.	C. W. Neff, R. E. Jackson, J. D. Culp, D. Grimm
Boeing Co.	J. Stacey, D. Honebrink, R. Gunderson, C. Boese
Atomics International	J. P. Page, G. V. Sneesby, E. V. Kleber
Solar	A. Stetson
Chromizing Corp.	M. Commandy
IITRI	J. Rausch

The areas of information which were discussed included:

1. Current programs involving coated refractory alloys.
2. Coating requirements (time, temperature, pressure, flow).
3. Coating chemistries and application techniques.
4. Coating problems peculiar to structural fasteners.
5. Test and inspection procedures.

This section summarizes the comments of these individuals as well as the author's opinion of some of the factors to be considered in the choice of refractory alloy-coating systems for use as structural fasteners.

The objective of this survey was to determine which of the available state-of-the-art coatings for molybdenum, columbium, and tantalum alloys offered the most promise for application to threaded fasteners by means of the electrophoretic technique. The survey was performed originally in 1963 and early 1964 and, for the purpose of this report, has been updated to cover current research and development efforts. The conclusions reached in 1963 - 1964, however, with respect to the selection of coatings for study have not changed as a result of continuing development effort during the period 1964 - 1965. During the course of this program every effort was made to keep abreast of developments in the field, and the co-operation afforded by numerous individuals and organizations in this regard is hereby acknowledged.

The choice of the refractory alloy-coating combination for each application were governed by many interrelated factors such as:

1. Anticipated exposure conditions of the joint (time, temperature, pressure, and tensile and shear stress levels).

2. Fabricability of the alloy for the joint under consideration.

3. Compatibility requirements for alloys coated with different materials.

4. Applicability of the coating to difficult areas as recesses, faying surfaces, and thread elements.

5. Cost which, in addition to raw materials, is determined by the fabricability of the alloy and the complexity and reliability of the coating process.

6. Applicability of a given coating system to a particular alloy composition.

The general considerations enumerated were further complicated by design problems imposed upon the fastener itself by the limitations of the available coating systems. Some of these problems are the choice of thread form (i.e., refractory,

truncated, or "semi-refractory"), head design, assembly tools which will not damage the coating, logical design of blind or semi-blind mechanical fasteners which are adaptable to coating, tolerances allowed on bare threaded elements so that they will mate after coating, etc.

Despite this multitude of problems, a great deal of progress has been made in the utilization of coated refractory metal structural fasteners as exemplified by the recent flight of the first ASSET vehicle, and the assembly and testing of structures such as McDonnell's fin-rudder assembly and simulated leading edge assemblies at Chance-Vought and at other organizations. A great deal of work remains to be done, however, to develop dimensional, mechanical, and compositional standards for coated refractory alloy fasteners comparable to those which exist for bare fasteners, to develop coatings with sufficient ductility so that post-coating treatments after joint assembly becomes unnecessary and the use of deformable fasteners becomes practicable, and to extend the range of utilization of coated fasteners to temperatures above 3000°F at pressures below 5 Torr.

Since this is not intended to be a comprehensive survey on coatings for refractory alloys, the reader is referred to several excellent existing bibliographies and reports on the subject (15 - 21) which cover the older literature.

The first consideration in the choice of a refractory alloy-coating system for use as a structural fastener is the temperature-time-pressure-load-vibration requirement for the particular joint under consideration. These requirements will vary with the flight profile of the vehicle and with the position of the joint on the surface of the vehicle. Some typical anticipated equilibrium temperatures for re-entry of radiation-cooled orbital and super-orbital vehicles of the glider and lifting body design are summarized in Table L.

TABLE L

EQUILIBRIUM TEMPERATURES FOR RADIATION COOLED RE-ENTRY VEHICLES

Location	Orbital (°F)		Superorbital (°F)	
	Glider	Lifting Body	Glider	Lifting Body
Nose	3600-4000		6800-8300	7000-8500
Leading edge	2700-3000	-	4500-5200	-
Lower surface	1700-2400	2300-2700	2700-3750	4000-4500
Upper surface	1500-2000	2000-2500	1800-3000	3400-4000

The dynamic conditions which exist during re-entry of a glider have been treated analytically by Perkins and by others (22) Perkins' calculation of the temperature-pressure-time variations of a frontal section for one possible re-entry trajectory are shown in Figure 115. For this case, peak heating from 2700° to 4500°F occurs at a pressure of 0.0085 mm Hg for a period of 25.33 min. The less severe conditions which exist at the stagnation line, and upper and lower surfaces of the leading edge during re-entry are shown in Figure 116. Here, the temperature is relatively constant for about 11 minutes of the re-entry period, and peak heating occurs at a pressure of 0.1 to 1.0 mm Hg.

Based upon calculations of this type and, taking into consideration the limitations of currently available coatings, materials for operational glide re-entry vehicles such as ASSET were chosen as follows (23):

Nose Cap - Zirconia

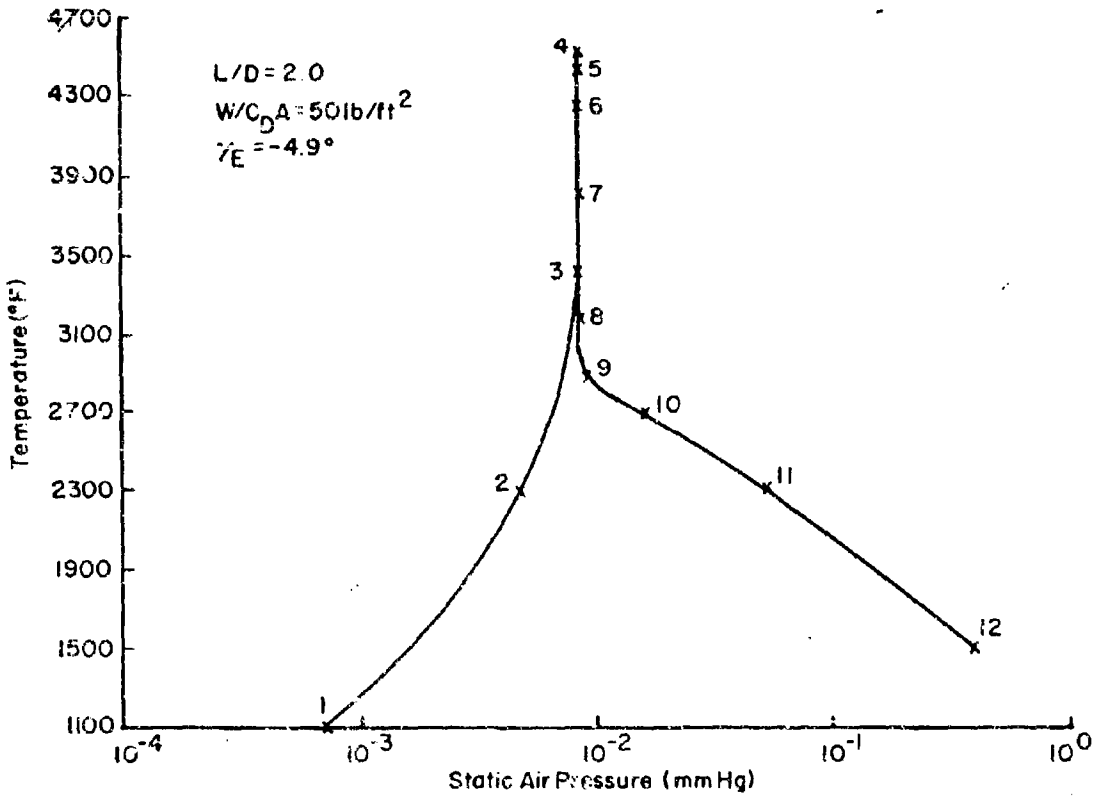
Forward Leading Edges - Siliconized Graphite

Structural Members, Lower Forward Body Panels, etc., - W-3 Coated TZM (Max. Svc. Temp. 3000°F)

Lower Aft Body Panels - LB-2 Coated D-14 (Max. Svc. Temp. 2500°F)

Structural Fasteners, Tubing, etc. - TAPCO Coated Cb Alloys (Max. Svc. Temp. 3000°F)

Low Temperature Body Panels - Uncoated L-605



Point No.	Elapsed Time (min.)
1	0.66
2	1.00
3	1.33
4	1.66
5	2.50
6	5.00
7	10.00
8	20.00
9	26.66
10	33.33
11	41.66
12	50.00

Figure 115. Typical Reentry Conditions at Stagnation Point of Frontal Section of Orbital Glider (22)

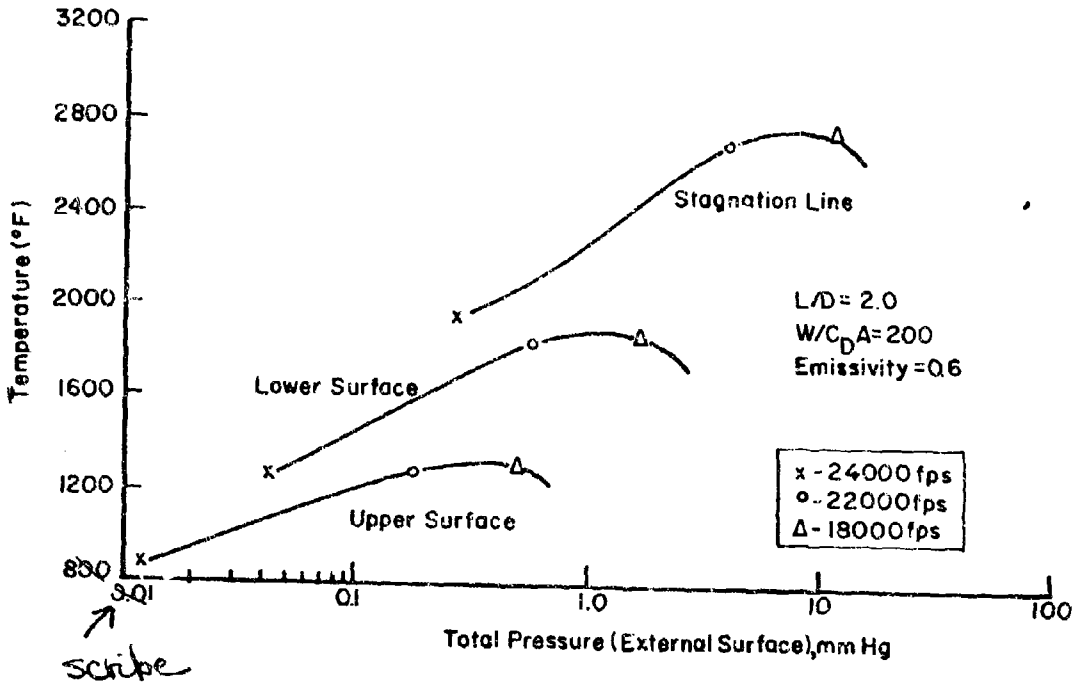


Figure 116. Typical Reentry Conditions Along Leading Edge of Orbital Glider. (Total elapsed time ~20 min.)

The designer, faced with a choice of the various coatings available for the refractory metals will consider, in order of decreasing importance, test data available for the coating systems - processing requirements which vary with the coating application method and therefore affect cost - and the composition of the available coatings. Consideration of the details of the available coating chemistries is not productive of much useful information since virtually all available coatings for columbium and molybdenum alloys contain silicon as a major constituent plus metal additives such as Cr, Ti, B, Mo, V, Al and Cb. The principal effect of the metal additives is to vary the composition and relative proportions of the intermetallic compounds formed in the coating and thereby modify the viscosity, stability, and thermal expansion of the glassy film which is formed during oxidation. Although the composition of the coatings formed by the various application techniques may be revealed by electron microprobe analysis, and calculations may be made of the strains existing in the coating due to thermal expansion mismatch (24), theory is not sufficiently advanced so that the oxidation resistance of a specified metal-modified silicide coating can be predicted without actually performing the experiment.

A common denominator for the variety of coating application techniques is the necessity of preparing the surface of the substrate for coating.

While the surface preparation procedure adopted by various coating vendors differ in detail, they generally consist of the following steps:

a. Edge radiussing of sharp corners by hand grinding and polishing or by tumbling in an abrasive powder.

b. Removal of organic contaminants by solvent or detergent cleaning, followed by an acetone or water rinse.

c. Acid pickling to a maximum metal removal per surface of 0.002 in. A typical pickling solution for columbium alloy parts which is operated at 70° - 90°F contains the following (27)

H_2SO_4 (66° Be)	- 15 vol. %
HNO_3 (42° Be)	- 10 vol. %
HF (50% Tech)	- 20 vol. %
H_2O	- 55 vol. %

Variations on this procedure which have been utilized by TAPCO (25), Pfaudler (26), and McDonnell (23) are described in the literature.

Edge radiussing is a particularly time consuming and costly operation on large panels, and the necessity for radiussing is reflected in the use of thread forms for refractory metal structural fasteners with rounded crests and roots. The use of a truncated thread form, particularly for internal threads, would be an important advance in the state-of-the-art and this possibility was investigated in the present program.

Some important characteristics of the most widely used coating application techniques for columbium and molybdenum alloys are summarized in Table LI. In addition to the methods listed in Table LI, a variety of programs are in progress or have been completed on alternative methods of preparing coatings of the metal-modified silicide type. These programs include fluidized bed processing at Boeing (28), chemical vapor deposition at Texas Instruments, Inc. (29) fused salt plating at Pfaudler (30), slip-pack deposition at Ling-Tempco-Vought (31) spray-diffusion processing at TRW (32), and electrophoretic deposition at Vitro.

None of the processes listed in Table LI is a panacea for the problems involved in costing refractory metal structures. The major advantages enjoyed by each of the techniques listed are as follows:

1. Vacuum Slurry	a) Applicable to faying surfaces and recessed areas.
	b) Coating defects relatively easily repaired.
2. Pack Processes	a) Good reliability and high temperature performance.
	b) Low cost for high volume of small parts.
3. Electrophoresis	a) Good control of coating thickness
	b) Flexible with respect to coating composition.
4. Fluidized bed	a) Short cycle - good control.
	b) Amenable to scale-up.

TABLE LI

CHARACTERISTICS OF SELECTED COATING APPLICATION TECHNIQUES FOR Mo AND Cb ALLOYS

Coating Type	Application Method	Nominal Coating Composition	Typical Coating Cycle	Process Characteristics	Critical Parameters	Notes and Parameters	Reference
Boeing Disil (27)	Fluidized powder bed and gas carrier.	Unmodified silicide	1.5 hrs at 1450°F 2.0 hrs at 1850°F	Low temperature process. Rapid cycle. No packing and unpacking of retort with powder.	Particle size. Gas flow rate. Fixturing for parts. Temperature uniformity	Fluidized bed process being developed for Cb and Ta alloys (28)	
Pfaudler PFR-6 (33, 34)	Atmospheric pressure pack cementation.	Cb-modified silicide	5 hrs heat up to 2050°F 7 hrs at 2050°F	Slow cycle, inert filler and activator in pack.	Particle size and homogeneity of pack. Heat up time and time at temperature. Temperature uniformity in retort.	W-3, Durak B and Chance Vought processes are similar.	
T.R.W.	Two-cycle, vacuum, pack cementation	$CbCr_2$ + Overlay of Cr and Ti silicides	50Cr-50Ti; 8 hrs, 0.01-1.5 torr, 2300°F. Si + 1% KF, 6 hrs, 0.01 torr, 2100°F	2-cycle. No inert filler. Good reliability.	Same as PFR-6	(35)	
G.E. or McDonnell LB-2 (mod.)	Vacuum slurry impregnation.	Al-10Cr-2Si ($CbAl_3$)	Double Coat. Dry. Anneal 1 hour 1900°F.	Applicable to faying surfaces. Recessed areas. Amenable to repair. Thick Coating	Surface preparation. Viscosity and composition of slurry. Control of drying and annealing.	(36)	Anneal
Vitro	Electrophoretic deposition.	Cr/Ti-Si	43Cr-57Ti, 1 hr 2550°F 1 atm. Argon, Si, 6 hrs at 2370°F, 0.01-1 torr.	Rapid coating cycle. Flexible with respect to coating chemistry. High uniformity of coating thickness.	Coating bath composition. Particle size. Sintering conditions.	(20)	

2. Coatings For Molybdenum And Columbium Alloys

In the previous section some general requirements for coatings for refractory alloys were reviewed, and some characteristics of the various coating application techniques which are employed for the formation of such coatings were discussed. In this section typical performance data is presented for the oxidation resistance of the various available coatings for molybdenum and columbium.

The most extensive evaluations of coatings for molybdenum and columbium base alloys have been performed by Solar on foil gage materials (37) and by the University of Dayton on 10-12 mil sheet specimens (38) Solar's data for the 2500°F, 1 atmosphere cyclic oxidation life of a variety of coatings on TZM foil is shown in Figure 117, and University of Dayton data for the probable cyclic oxidation life at 2600°F of many of the same coatings on TZM sheet is listed in Table LII. Among the coatings tested by both groups, the Durak B coating gave the best results with Chromalloy, G. T. E., and Pfaudler yielding approximately equivalent life equal to about 50% of the life of Durak B. It should be noted that with the exception of the G. T. and E. tin-aluminum coating, each of the other systems are metal-modified silicides or unmodified silicides which are prepared by a variety of techniques. The oxidation resistance of the Vitro nickel-$MoSi_2$ coating was outstanding in the Solar test.

TABLE LII

PROBABLE CYCLIC OXIDATION RESISTANCE AT 2600°F OF COATED TZM FOR VARIOUS LEVELS OF RELIABILITY (38)

	Coating Life (hrs) at Specified Level of Reliability		
	70%	90%	95%
Chromizing Durak B	25	18	15
LTV Single-Cycle Silicide	22	14	9
Boeing Disil	14	10	7
Chromalloy W-3	9	4	3
GT and E Sn-Al	8	5	4
PFR-6	5	< 1	< 1
LTV Two-Cycle Silicide	1	< 1	< 1
GTC Modified Silicide	< 1	< 1	< 1

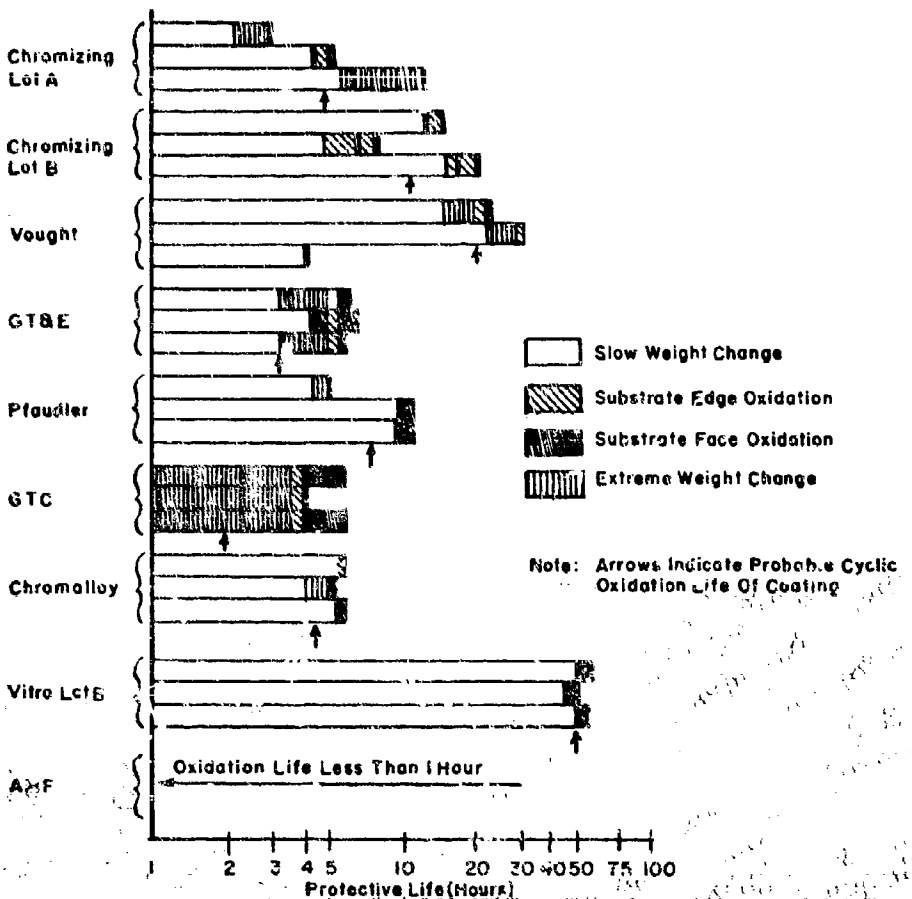


Figure 117. Cyclic Oxidation Test at 2500°F of Various Coatings on 6 Mil TZM Foil (37)

Data gathered from the older literature (39, 40, 41) for the oxidation resistance of a variety of coatings on columbium alloys is shown in Table LIII and data obtained by Solar and by the University of Dayton in the previously mentioned programs (37, 38) is shown in Figure 118 and in Table LIV, respectively.

TABLE LIII

CYCLIC OXIDATION RESISTANCE OF SELECTED COATINGS ON VARIOUS COLUMBIUM ALLOY SHEET SPECIMENS (39, 40, 41)

Protective life[a] in cyclic oxidation[b], hours												
	2300°F(1260°C)						2500°F(1371°C)			2600°F(1427°C)		
Coating	D-31	D-14	F-48	D-43	Cb	B-66	D-31	F-48	Cb	D-14	D-43	B-66
Sylcor	50	43	> 300	-	28	-	20	12	24	17	-	-
	> 300	150	> 300	-	-	-	24	12	40	24	-	-
GE-McDonnell	176	5	24	-	12	-	24	4	2	2	-	-
	296	16	30	-	-	-	24	5	3	2	-	-
Vought	7	17	7	-	7	-	2	1	2	6	-	-
	12	18	12	-	-	-	2	2	8	13	-	-
Chromalloy	12	5	7	-	2	-	20	1	2	1	-	-
	12	16	12	-	-	-	24	1	2	9	-	-
Chromizing	7	-	24	-	24	-	6	2	2	-	-	-
	12	-	24	-	-	-	20	(c)	2	-	-	-
TRW	> 300	150	> 300	102	> 300	> 150	123	146	171	21	24	24
	> 300	150	> 300	148	-	-	> 200	> 200	> 200	37	-	49
Pfaudler	-	1	-	54	-	5	-	-	-	9	5	2
	-	17	-	72	-	7	-	-	-	11	-	24

(a) First observed external rupture of the coating.

(b) 24-hr. cycles to R. T. in the first 24 hr. of test, 8 cycles to R. T. in every 24-hour period thereafter, at 2600°F, specimens cycled to R. T. each hour to failure.

(c) Specimen not returned.

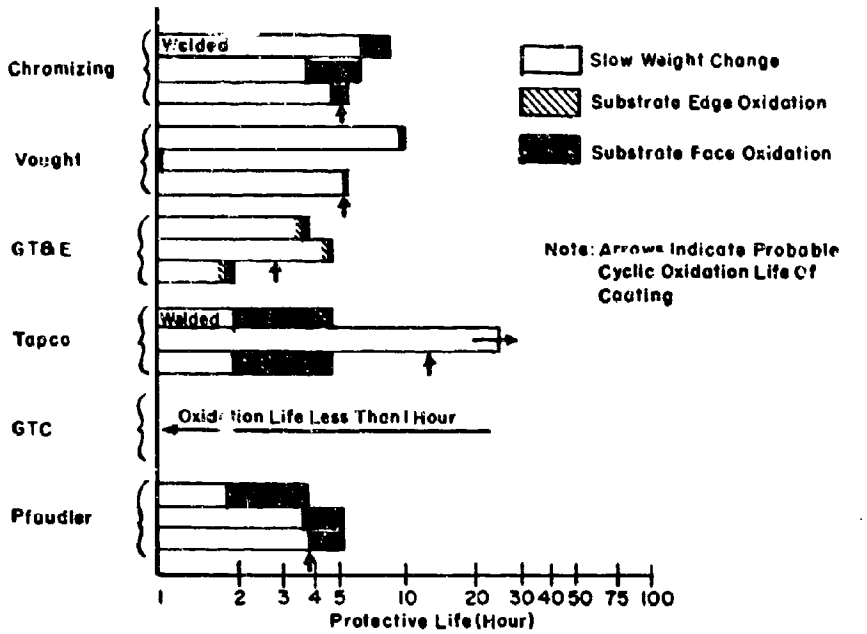


Figure 118. Cyclic Oxidation Resistance of Various Coatings at 2500°F on 6 MIL B-66 Foil (37)

TABLE LIV

PROBABLE CYCLIC OXIDATION LIFE OF COATED B-66
FOR VARIOUS LEVELS OF RELIABILITY

Coating		2600°F (1427°C) Coating Life (hours) At Specified Level Of Reliability		
		70%	90%	95%
TRW Cr/Ti-Si	Batch 1	24	15	11
	Batch 2	15	8	6
Chromizing Durak KA	Batch 1	3	1	< 1
	Batch 2	< 1	< 1	< 1
Pfaudler PFR-30 Modified Silicide		13	8	7
LTV - Cr-B-Silicide		18	9	6
GT & E - Cr/Ti - Modified Silicide (R-513)		65	10	3
Boeing Disil		25	21	19

Again, the data indicates the superiority of the metal modified silicide coatings such as TRW, Disil, Durak KA, and GT & E's R-513. In a more detailed comparison of the TRW Cr-Ti-Si coatings and Durak KA conducted at Solar (37), the former coating was found to provide the best protection for B-66 alloy, however, the coating life was seriously degraded by prestraining, and some problems were noted with respect to reliability.

It was indicated in the survey that an external coated refractory metal structural part, during reentry, may be exposed to low partial pressures of oxygen (0.002-0.2 mm Hg) for periods of time up to about an hour at temperatures up to 3200°F. It was first pointed out by Perkins (22) that under these conditions a silicide base coating might degrade rapidly through the loss of volatile SiO instead of protecting the substrate through the formation of solid SiO_2. Supporting data from Lockheed on the performance of four silicide-type coatings on molybdenum as a function of pressure are summarized in Table LV where it is indicated that all but the Chance Vought coating suffer a decrease in maximum temperature - 30 minute oxidation life of about 450°F as the oxygen pressure is reduced from 160 torr to 0.2 torr.

TABLE LV

MAXIMUM TEMPERATURE (^{o}F) FOR 30 MINUTE LIFE
AT INDICATED OXYGEN PRESSURE

Coating	Coating Thickness (mils)	Partial Pressure O_2 (mm Hg)					
		160	21	10	5	1	0.2
Durak B	2.8	3170	3100	-	-	2975	2815
Disil II	1.5	3280	3240	-	3225	2975	2815
PFR-6	2.6	3250	-	3200	3185	2850	2800
Chance-Vought	3.0	3000	-	-	-	-	2950

The Chance-Vought reduction was about 50^{o}F, however, its maximum temperature capability for 30 minute life was some 200^{o}-250^{o}F lower than the other coatings. More recently (42), Lockheed has shown that the oxidation life of the Chromizing and TRW coatings on B-66 and Cb-752 alloys is also drastically reduced in a low pressure environment. It is apparent, therefore, that the low pressure behavior of the currently available coatings is a serious problem which must be investigated in any comprehensive program involving the application of coatings to aerospace structural parts.

One of the problems in the use of coatings, which has not been widely studied but which is nevertheless serious, is the compatibility of the various coating systems with one another. In structures such as ASSET special problems such as accessibility, high temperature-low pressure performance, and coating uniformity, require that two or more coating systems be used in various parts of the structure. When these coatings vary widely in their chemical makeup, each coating may be degraded by the other if they are exposed to oxidation while in contact. For example, McDonnell reported that the LB-2 and the Tapco-coatings for columbium are incompatible with the PFR-6 coating for molybdenum, based upon the results of exposure of a joint containing the three systems in contact which was exposed to short time oxidation at 2000^{o} - 2500^{o}F. It is possible that cooler parts of a refractory structure where uncoated superalloy components are in contact with coated molybdenum or columbium parts might also evidence the same behavior.

This situation is one of several serious problems which point up the necessity for standardization in the testing and in the application of coatings for refractory structures.

3. Coatings For Tantalum Alloys

Investigation of coatings for tantalum-base alloys began about five years ago with the study of pack silicide or metal-modified silicide coatings at Battelle (43) and spray-diffused tin-aluminum coatings at General Telephone and Electronics Labs (44).

Typical lives of the first-generation aluminide and silicide coatings at various temperatures are summarized in Table LVI. The aluminide coatings, consisting of Sn-50Al (designated 34S) or Sn-25Al (40S), were prepared by hot dipping at 1700°-1900°F or by spraying the tin-aluminum in a lacquer vehicle and then diffusing at 1900°F. The pack cementation silicide coatings were generated in mild steel retorts containing 10-40 wt.% silicon plus modifier elements, 0.5 - 3% halide carrier, and the balance -100 + 140 mesh alumina filler. Vapor-phase coating from the pack was accomplished at 2000°F-2200°F for 4-12 hours in argon.

The most serious deficiency of the first-generation Sn-Al coatings was the formation of excessive liquid phase upon heat-up to temperatures above 1200°F which led to "run-off" of the coating and severe diffusion interaction between the coating and the substrate. To reduce the fluidity of the coating, tantalum and molybdenum powders were added to the basic Sn-Al compositions in an attempt to form the solid aluminides $MoAl_3$ and $TaAl_3$ which would support the coating (45). Typical oxidation lives of the modified aluminide coatings are shown in Table LVII. A scale-up program for the tin-aluminum coating was then initiated under Air Force sponsorship (46), since this system was one of the few available compositions which was ductile, as applied. Representative furnace oxidation test data for the intermetallic compound-modified tin-aluminum coating is summarized in Table LVIII.

TABLE LVI

SUMMARY OF OXIDATION PERFORMANCE DATA FOR COATED TANTALUM ALLOYS (46)

Alloy Substrate	Coating Designation	Coating Thickness, mils	Oxidation life at indicated temperature (°F), hours							
			1200	1800	2000	2500	2700	2800	3000	3500
Ta	BMI, Si-Al, Si-Mn	2.9 9.7	100 >100	20 3		6.5 11.	2 4			
Ta-10W	GTE, Al-Sn BMI, Si-Al, Si-Mn	4 3.5 7.3	>100 40	10 3		100. 3.7 >20.	4.2 10	29	>10	?
Ta-10Hf-5W	GTE, Al-Sn BMI, Si-Al, Si-Mn	- 2.8 8.4	100 >100	>100 1	4-8	1-4 9.5 15.	4 7.5			
Ta-30Cb-7.5V	GTE, Al-Sn BMI, Si	- 4.2	>100	>100			9 -	8 -	2 -	

TABLE LVII

OXIDATION LIVES OF Sn-Al COATINGS
ON Ta-10W AND Ta-30Cb-7.5V ALLOYS[a] (47)

Substrate	Coating	Oxidation Temperature,	Coating Life hr.[b]
Ta-10W	(Sn-25Al)-10$TaAl_3$	1100°F, 593°C	21 - 162
Ta-10W	(Sn-50Al)-10$TaAl_3$	1100	44 - 63
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$TaAl_3$	1100	> 100
Ta-10W	(Sn-25Al)-10$TaAl_3$	1400°F, 760°C	23 - 157
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$TaAl_3$	1400	> 100
Ta-10W	(Sn-25Al)-10$TaAl_3$	2000°F, 1093°C	> 100
Ta-10W	(Sn-50Al)-10$TaAl_3$	2000	71 - 96
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$TaAl_3$	2000	> 100
Ta-10W	(Sn-25Al)-10$TaAl_3$	2500°F, 1371°C	16 - 77
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$TaAl_3$	2500	43 - 87
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$MoAl_3$	2500	> 100
Ta-10W	(Sn-25Al)-10$TaAl_3$	2800°F, 1538°C	3 - 15
Ta-10W	(Sn-25Al)-10$MoAl_3$	2800	21 - 51
Ta-10W	(Sn-50Al)-10$TaAl_3$	2800	6 - 7
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$TaAl_3$	2800	7 - 31
Ta-30Cb-7.5V	(Sn-50Al-Si)-10$MoAl_3$	2800	24 - 40
Ta-10W	(Sn-25Al)-10$TaAl_3$	3000°F, 1649°C	3 - 10

(a) Tests conducted in still air in a furnace. Specimens generally cycled to room temperature ten times each 24 hours at and below 2500°F, and once each hour above 2500°F.

(b) Range of coating lives obtained with coatings of varying thickness in multiple tests.

TABLE LVIII

OXIDATION RESISTANCE OF
TYPICAL Sn-Al TYPE COATINGS (49)

Substrate	Coating	Coating Weight (mg/cm^2)	Test Temp. °F (°C)	Length of Cycle (hrs)	Coating Life (hrs)
Ta-10W	90(Sn-25Al)-10$MoAl_3$	80	2800 (1538)	1	20
Ta-10W	90(Sn-25Al)-10$MoAl_3$	80	2800	12	70
Ta-10W	90(Sn-25Al)-10$TaAl_3$	35	3000 (1649)	-	3-4
Ta-10W	90(Sn-25Al)-10$TaAl_3$	70	3000	-	7-8
Ta-30Cb-7.5V	90[Sn-50(Al-Si)]-10$TaAl_3$	45	2800 (1538)	-	8-30

In a more severe test of the Sn-27Al-5.5 Mo coating on Ta-10W by NASA-Langley, specimens were exposed at 2600°F and 2900°F to a mass flow of air of 0.4 lb/ft^2/sec for repetitive 6 minute cycles (50). In this test the samples were found to ignite after approximately 30 minutes at 2600°F and 15 minutes at 2900°F, indicating the weakness of a liquid phase coating in a high shear environment.

A second serious deficiency of the tin-aluminum base coating in low pressure environments was reported recently by Sylcor (51) in a follow-on of an earlier development program (52). In this study, hot-dipped Sn/25-50Al coatings, Si and Cr-Ti modifications of Sn-Al, and Al-5 La, Al-5Cr-5Ti, and Al-10Cr coatings on T-111 alloy were exposed for 30 minutes at either 2500°F and 0.2 torr or 2800°F and 1 torr with the following results:

a) All coatings failed in the 30 minute-2800°F - 1 torr exposure test.

b) After each exposure, no $TaAl_3$ remained in any of the coatings containing Sn.

c) All coatings except Al-5Cr-5Ti suffered gross microstructural damage after the 2500°F exposure. The Al-5Cr-5Ti coating caused substrate damage after 2800°F exposure.

Based upon the results reviewed above, it is evident that all aluminide-base coatings examined to date exhibit poor behavior in low pressure or high shear environments, even at temperatures as low as 2800°F.

In the Battelle program, vanadium, boron, aluminum, and manganese were evaluated as modifiers for pack silicide coatings on Ta-30 Cb-7.5V, Ta-10W, and Ta-8W-2Hf alloys (53). The pack compositions consisted generally of 10-40 wt. percent halide carrier, with the balance -100+100 mesh alumina. The samples were packed in small, mild steel cans which were heated to 2000°F -2200°F for 4 to 12 hours in argon. The vanadium-modified silicides provided good oxidation protection on Ta-10W (6 - 10 hours in cyclic oxidation and 100 hours in static oxidation at 2700°F) but severely embrittled the substrate (due to the presence of a calcium contaminant). Boron additions also resulted in substrate embrittlement. Manganese improved the self-healing properties of the coating, but decreased coating life at 1800°F, while aluminum modifications showed no significant improvement over unmodified silicide.

The best compromise between retention of mechanical properties and good oxidation life was obtained with an unmodified silicide coating on Ta-30 Cb-7.5V. Typical oxidation lives and mechanical properties of this system are summarized in Table LIX.

TABLE LIX

CYCLIC OXIDATION LIFE* OF UNMODIFIED 4-6 MIL SILICIDE COATINGS ON Ta-30 Cb-7.5V PANELS(53)

Exposure Temperature	Oxidation Life(hrs.)
1200°F, 649°C	>100
1500°F, 816°C	>100
1800°F, 982°C	>100
2000°F, 1093°C	25-75
2200°F, 1204°C	>100
2500°F, 1371°C	> 24
2700°F, 1482°C	2 -12
2900°F, 1593°C	6 -17
3000°F, 1649°C	2

*Cycles were 25 hours at temperatures to 2200°F, 4 hours at 2500°F, 1 hour at 2700° and 2900°F, and 1/2 hour at 3000°F.

Battelle's data indicated that the tensile strength and the bend ductility of the Ta-30Cb-7.5V substrate were not impaired by the coating, and that the yield strength decreased only slightly in the coated condition. The coating also remained protective during 1.5 percent tensile deformation at 2200°F.

The coatings listed in Table LIX were prepared in a pack of 81Al_2O_3-17 Si-2NaF under argon in two steps of 4 hours and 12 hours at 2200°F. The coating was single phase, and its composition by electron probe analysis corresponded to the pseudo-compound $MSi_{2.8}$ where M represents the Ta-30Cb-7.5V composition. Pest failure at 1800°F was considerably improved for the silicide coated Ta-30Cb-7.5V as compared to silicide-coated Ta-10W or T-111, but the coated Ta-30Cb-7.5V was susceptible to relatively early failure at 2000°F. General Telephone has shown that pest failures at 1800°F on Ta-10W may also be eliminated by precoating the substrate with titanium before siliconization. This coating, designated R-506, yields about 200 hours life at 1800°F(45).

Investigation of pack silicide coatings, modified by additions of vanadium, chromium, titanium, tungsten, molybdenum, manganese, boron, and aluminum, was continued by Solar (54). In initial studies using conventional packs, chromium-vanadium and chromium-titanium modified silicides were the most successful for Ta-10W, providing up to five hours life at 2700°F. Boron, vanadium, and molybdenum modifiers were found to produce silica glasses of high fluidity, whole tungsten and titanium modifiers resulted in glasses of high viscosity. All modifiers but chromium reduced the softening point of silicon to below 2700°F. Chromium alone severely embrittled the Ta-10W substrate and degraded the oxidation resistance of the silicide coatings while chromium plus titanium or vanadium produced a crystalline, refractory, silicide coating which was not fluid at 2700°F. The performance of these coatings was considerably improved by changing to a 2-cycle process in which the substrate surface was first heavily modified (20-50 mg/cm^2) with Ti-W, Ti-V, Ti-Cr, or Ti and then silicided. The coatings were produced from active metal packs with all inert material removed from the retort and the alumina liner of the retort replaced by graphite. These modified silicide coatings increased the 2700°F cyclic oxidation life of Ta-10W from 6 to 26 hours and the 2700°F life of Ta-30Cb-7.5V from 22 to 42 hours.

Surface modification of a tantalum alloy prior to siliconization yields two effects. First, the characteristics of the glass formed in oxidation are changed and, more importantly, interdiffusion between the silicon and the alloy is reduced. For example, direct siliconization of unalloyed tantalum yields a non-protective silicide layer which continuously grows and oxidizes due to diffusion at a rate of about

0.04 mil/hr. at 2500°F (Reference 21, p. 186). Diffusion, however, is considerably reduced when the bulk tantalum is alloyed with tungsten or vanadium, or when the tantalum surface is alloyed with the same elements.

The same effect is noted when beryllide coatings are compared on Ta-10W and on unalloyed tantalum (55). If beryllium is diffused into Ta and Ta-10W at 2500°F in vacuum, the depth of penetration after 10 hours is 5 mils in Ta-10W, and 9 mils into pure tantalum. The oxidation resistance of the beryllide-coated Ta is also inferior to that of Ta-10W.

An important incentive for the study of metal-modified surface coatings for tantalum has undoubtedly been the excellent high temperature performance evidenced by the pack silicide coating for tungsten reported by Thompson-Ramo-Wooldridge (56, 57). The Si-W coating on tungsten in thicknesses of 4-5 mils has yielded the following results:

a) 96 ± 1% probability at 99% confidence level of surviving 5 hours cyclic oxidation in one atmosphere of air at 3500°F with ultimate capability to 3600° - 3650°F.

b) Average protective life at one atmosphere of 20 hours at 3300°F. 25 hours at 3000°F, 50 hours at 2500°F, and 40 hours at 1800°F.

c) Slow deterioration at pressures less than 15 torr, but coatings generally survive 1 hour exposure at pressures between 0.025 and 15 torr at 3400°F.

d) Resistant to erosion for one hour when exposed to a flow of 2000-2500 f.p.s. of hot gas at 2900° - 3400°F and a partial pressure of 16-20 torr of air.

e) No creep or failure when subjected simultaneously to a tensile stress of 20% of the yield strength of tungsten and exposed in air for one hour at 3350°F.

It would appear, therefore, that if a tungsten surface could be formed upon a tantalum alloy, then subsequent W-Si treatment would yield a coating with properties equivalent to those obtained on tungsten. Unfortunately, however, the rate of transfer of tungsten from various packs to tantalum have been too low to produce the desired surface modification (54), attempts to deposit tungsten on tantalum by vapor deposition or fused salt plating have not been successful, and no solution to the low temperature (1600°-2500°F) oxidation problem has been forthcoming.

The best example of the failure of pack methods to produce a heavily modified tungsten surface on tantalum alloys is contained in a recent report from TRW (58) in which an attempt was made to extend the excellent results obtained in their tungsten program (57) to tantalum. In this program 0.1-0.3 mil barrier layers of molybdenum or tungsten were formed on Ta-10W by pack methods (6 hours at 2500°F), and the barrier coatings were then silicided. The results of cyclic oxidation tests on coating systems of this type are summarized in Table LX, where it is seen that the protection achieved for Ta-10W is far less than that obtained for silicided tungsten.

The present status of pack silicide and spray or dip-diffused aluminide coatings for tantalum alloys was well-summarized in a recent direct comparison of the Sn-Al-Mo and (Ti + W)-Si systems on 6 and 12 mil T-111 foil. (59) Some typical test results for the coatings are summarized below.

	Sn-Al-Mo	(Ti-W)-Si
Bend ductility on 6 mil foil	ok	Failed 60° bend
Bend ductility on 12 mil foil	ok	ok
Stress-oxidation* 12 mil foil	ok - 22 cycles	3 cycles to failure, creep rate double that of Sn-Al-Mo
1800°F cyclic oxidation life (hrs. at 95% reliability)-12 mil foil	100	4
2600°F cyclic oxidation life (hrs. at 95% reliability)-12 mil foil	25	< 1
2800°F cyclic oxidation life (hrs. at 95% reliability)-12 mil foil	1	3.7

*800°-2700°-800° cycle in one hour at one atmosphere pressure and stress of 4-6 ksi.

The results indicate that neither of these coatings, in its present state of development, would be suitable for the protection of tantalum alloy structural fasteners at temperatures up to 3200°F.

TABLE LX

CYCLIC OXIDATION LIFE OF BARRIER COATINGS ON Ta-10W(58)

Coating System	Thickness (mils)	Hours at Indicated Temperature					
		2500°F (1371°C)	2700°F (1482°C)	3000°F (1649°C)	3250°F (1788°C)	3300°F (1815°C)	3500°F (1926°C)
W-Si	2.8-3.0	6,6	1,4	1,1-1/2	0.2	0.2	0.1
W-Si(W)	2.8-3.4	7,6	3,1	2,1-1/2	0.3	0.2	0.1
Mo-Si	2.4-2.6	3,3	1,2	1/2,1	0.1	0.1	0.1
Mo-Si(Mo)	2.4-2.6	1,1	2,2	1/2, 1/2	0.1	0.1	< 0.1
Si	2.0-2.4	5,5	2,2	1/2, 1	0.2	0.2	0.1
Si(W)	2.4-2.6	6,6	2,2	1/2, 1/2	0.3	0.2	0.1
Si(Mo)	2.0-2.2	5,5	2,2	1/2, 1/2	0.3	0.2	0.1

The most extensive work on coatings for tantalum for use at temperatures above 3000°F has been directed at the formation of adherent refractory oxide films on tantalum through the oxidation of reservoir alloys (Marquardt and IITRI), gradated mixed oxide-silicide composites (Vitro), and long range theoretical and experimental studies of oxides (as bulk materials) aimed at modification of their physical properties to provide a good thermal expansion match to tantalum and low diffusivity for oxygen (Solar).

Work at IITRI and at Marquardt has identified alloys such as Hf/20Ta (60) and Hf-19Ta-2.5Mo(61) which oxidize rapidly at elevated temperatures to produce an adherent scale of the probable composition $6HfO_2$ Ta_2O_5, and a subscale containing a mixture of metal and oxide. The difficulty with these alloys is their very high rate of growth of scale plus subscale (typically 0.3 mil/min at 3200°F and 3 mil/min at 4000°F) which mitigates against their use as thin coatings. The Hf-Ta alloys, however, show great promise as claddings for rocket nozzle applications, and work along these lines is now underway.

The principal achievement of the long-range Solar program to date has been the identification of the mixed oxide composition $94HfO_2$-$3ZrO_2$-$3Y_2O_3$ which provides a close thermal expansion match to tantalum and to Ta-10W(62). Suitable methods for applying this material as a coating, however, have not yet been developed and it is likely that a barrier layer, less reactive than Ta, will be required to prevent interaction between the tantalum substrate and the ceramic coating. In addition, basic studies performed by GTE indicate the probability that this system will suffer from rapid oxygen diffusion(63).

In summary, consideration of the systems studied to date for the protection of tantalum alloys at temperatures to 3200°F indicates that only tungsten modified silicides offer any promise for application to structural fasteners. Methods are required, however, which yield heavy tungsten modifications of the tantalum surface. Hafnium-tantalum alloys are excluded as coatings because of the thickness of the alloy required to achieve protection, and coatings of the modified aluminide type cannot provide the required dimensional uniformity and, in addition, will degrade rapidly in a high shear or a low pressure environment at temperatures above 2800°F.

APPENDIX II

RIVET PROGRAM

A supplemental effort to this program consisted of the manufacture, coating and testing of Cb 752 rivets in several sizes from 1/16 inch diameter to 5/32 inch diameter. All rivets were tested in joints of Cb 752 sheet.

A. MANUFACTURING

The rivets were manufactured from bar stock by hot forging the head and grinding the bodies and underhead areas, employing techniques similar to those employed for the manufacture of threaded fasteners. The rivets were pickled to remove the oxide formed during hot forging and to present a clean uniform surface for coating.

The sheet metal parts were made from .030 inch thick Cb 752 by milling the desired outline and drilling the appropriate holes. All specimens were made with sufficient length to provide protrusion from the ends of the test furnace so as to simplify the fixturing. By using this technique, sheet metal clamp fixtures were used to support the parts, thereby greatly reducing the fixture expense.

An e/D ratio (e=edge distance, D = rivet diameter) of 2 was used for all parts in accordance with Federal Test Method Standard 151.

The joint pieces were prepared to test the rivets in single lap shear.

Several tensile specimens were made from the Cb 752 sheet to determine the tensile properties of the sheet material.

B. COATING

All parts, including both rivets and sheet metal specimens, were coated by TRW with their Cr-Ti-Si coating to a thickness of .0025-.003 inches.

C. ASSEMBLY OF JOINTS

All test assemblies were prepared by cold upsetting the "formed" heads of the rivets at a slow rate of deformation in a tensile machine. As anticipated, some "flaking" of the coating occurred during deformation, however, no cracking was seen in the parent metal of the rivets.

All coated assemblies were patched using the $MoSi_2$ - Colloidal Silica patch coating. Photographs of assembled joints are shown in Figure 119 prior to patching and after patching.

D. TEST PROGRAM AND RESULTS

Four sizes of rivets, 1/16 inch, 3/32 inch, 1/8 inch and 5/32 inch were tested in the coated condition at room temperature, 2000°F and 2400°F. All sizes were tested in the bare condition at room temperature. The sheet material property specimens were tested in the bare condition at room temperature and in the coated condition at 2000°F and 2400°F.

All tests were conducted as described in Section IX.

The results of these tests are shown in Tables LXI and LXII and Figure 120.

E. DISCUSSION OF RESULTS

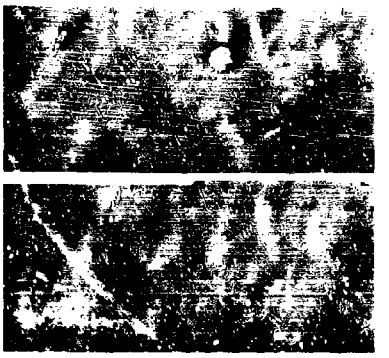
The tests conducted on riveted joints show significant differences in shear strength between the various sizes.

The high values for the 1/16 inch diameter rivets are evidently due to the fact that the coating overlay the diffusion zones represent a greater percentage at the cross sectional area for the smaller diameter parts. The strengthening effect of the coating therefore varies inversely with the diameter of the rivet. This strengthening effect is evident only in shear since it is accompanied by a loss of ductility which has an adverse effect on tensile properties due to the increased notch sensitivity.

All elevated temperature rivet failures were by shear at the sheet interface as would be expected.

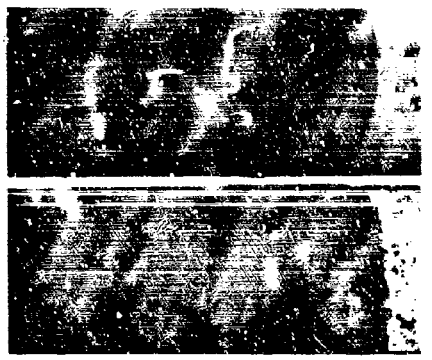
At room temperature, the rivets failed by the popping of the manufactured head.

Manufactured Head

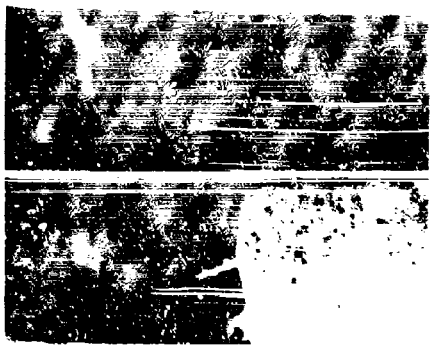


Upset Head

Before Patching



Manufactured Head



Upset Head

After Patching

Figure 119. Cb 752 Rivet Joints, Before and After Application of $MoSi_2$ - Colloidal Silica Patch Coat.

TABLE LXI A

STRENGTH OF RIVETED CB 752 JOINTS AT VARIOUS TEMPERATURES
BARE AND CR-TI-SI COATED -BRITISH UNITS

Test Temperature and Condition	1/16"Dia. Rivet		3/32"Dia. Rivet		1/8"Dia. Rivet		5/32"Dia. Rivet	
	Ultimate Load Lbs.	Shear* Strength PSI	Ultimate Load Lbs.	Shear* Strength PSI	Ultimate Load Lbs.	Shear* Strength PSI	Ultimate Load Lbs.	Shear* Strength PSI
Room Temperature (Bare)	155 185 190	57 600	355 318 300	47 000	550 750 670	53 500	672 725 715	36 700
Room Temperature (coated)	263 340 210	88 000	487 334 315	55 000	490 505 680	45 500	500 630 750	32 700
2000°F (coated)	168 176 154	54 000	254 297 268	39 600	350 384 428	31 600	550 534 555	28 500
2400°F (coated)	103 128 148	40 000	228 191 183	29 200	285 278 298	23 400	382 392 418	20 700

*Based on load/rivet cross sectional area

TABLE LXI B

STRENGTH OF RIVETED CB 752 JOINTS AT VARIOUS TEMPERATURES
BARE AND CR-TI-SI COATED - INTERNATIONAL UNITS

Test Temperature and Condition	1/16" Dia. Rivet		3/32" Dia. Rivet		1/8" Dia. Rivet		5/32" Dia. Rivet	
	Ultimate Load Newtons	Shear* Strength N/cm^2	Ultimate Load Newtons	Shear* Strength N/cm^2	Ultimate Load Newtons	Shear* Strength N/cm^2	Ultimate Load Newtons	Shear* Strength N/cm^2
Room Temperature (bare)	689 823 845	39 700	1580 1415 1335	32 400	2450 3340 2980	36 900	2990 3230 3180	25 300
Room Temperature (coated)	1170 1515 935	60 600	2170 1490 1400	37 900	2180 2250 3030	31 300	2230 2810 3340	22 500
2000°F (coated)	747 782 685	37 200	1130 1320 1190	27 300	1560 1710 1910	21 800	2450 2370 2470	19 600
2400°F (coated)	458 570 658	27 600	1015 850 814	20 100	1270 1240 1325	16 100	1700 1745 1860	14 250

*Based on load/rivet cross sectional area

TABLE LXII

TENSILE STRENGTH OF CB 752 SHEET SPECIMENS
.030 THICK X .250 WIDE - CR-TI-SI COATED

Test Temperature and Condition	Lbs.	PSI	Newtons	Newtons/cm^2
Room Temperature (bare)	630 630 635	84 000	2800 2800 2830	57 800
Room Temperature (coated)	559 570 560	75 000	2490 2540 2490	51 600
2000°F (coated)	271 260 264	35 400	1205 1155 1175	24 400
2400°F (coated)	152 200 203	24 700	675 889 902	17 000

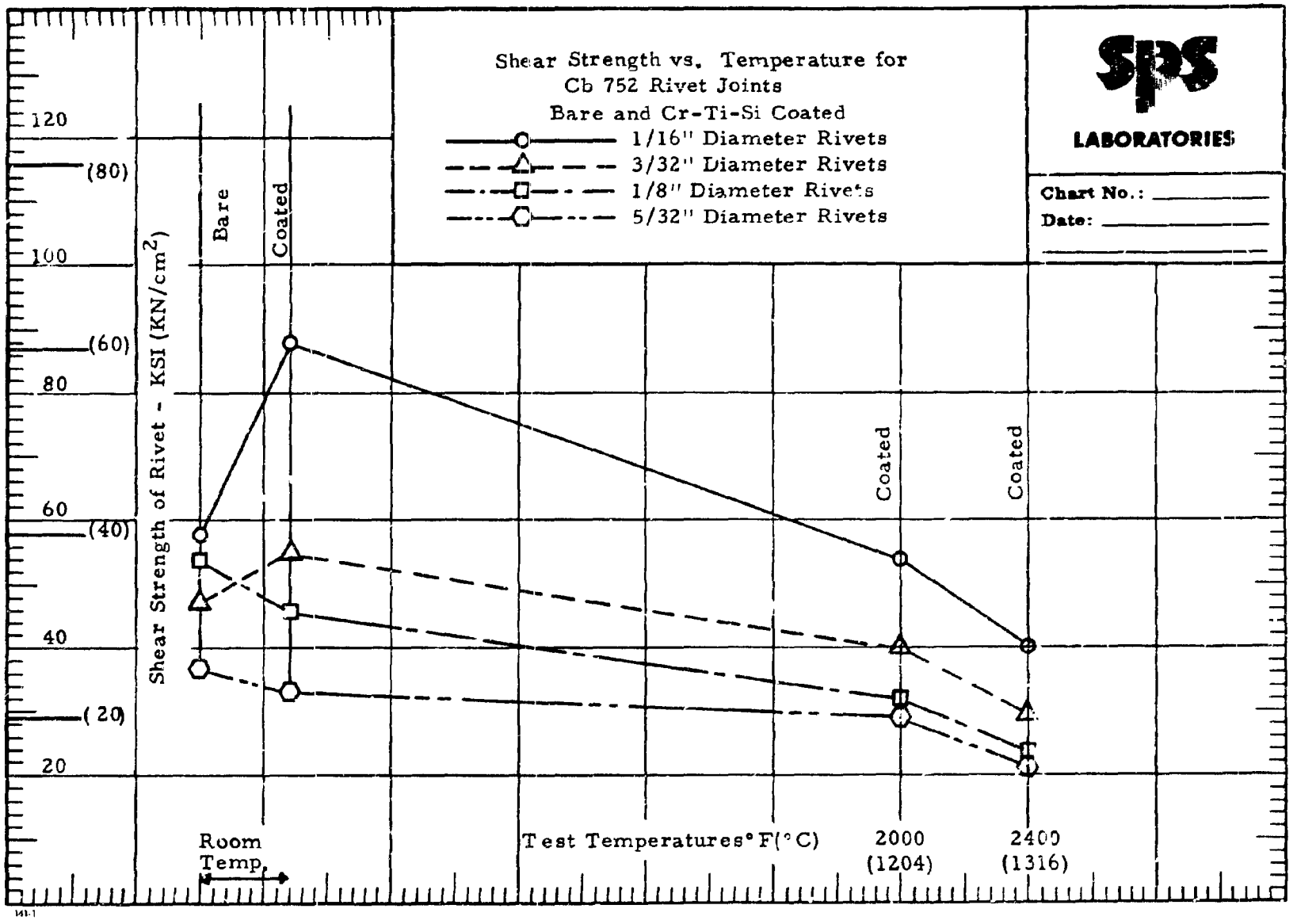

Shear Strength vs. Temperature for
Cb 752 Rivet Joints
Bare and Cr-Ti-Si Coated
1/16" Diameter Rivets
3/32" Diameter Rivets
1/8" Diameter Rivets
5/32" Diameter Rivets
SPS
LABORATORIES
Chart No.:
Date:
Shear Strength of Rivet - KSI (KN/cm²)
120
(80)
100
(60)
80
60
(40)
40
(20)
20
Bare
Coated
Coated
Coated
Room Temp.
Test Temperatures °F(°C)
2000 (1204)
2400 (1316)

Figure 120

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13. ABSTRACT Fasteners of several materials and configurations were developed, manufactured, coated and tested in various modes of oxidation and mechanical properties were characterized by extensive testing. The materials utilized were molybdenum alloy TZM, columbium alloys Cb752 and C129Y, tantalum alloys T-222 and 90 Ta-10W, and several dispersion strengthened metals. Protective coatings were adapted to fasteners, the columbium coating being an electrophoretically applied adaption of the Tapco Cr-Ti-Si coating and the tantalum coating being an electrophoretically applied WSi_2 coating. A facility for dynamic oxidation testing was developed capable of exposing small parts to 3200 degrees F. in air moving at 250 ft. /second. The deformability limits of the coating-substrate "systems" were established. Deformability of the systems was found to be insufficient to permit the development of a deformable blind fastener. Threaded fasteners were manufactured from a limited number of dispersion strengthened nickel base metals and were tested. Results indicate the feasibility of fastener manufacture from these materials and show considerable promise for their use in the 1800 degree F. to 2200 degree F. temperature range.

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