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OXIDATION RESISTANT HIGH TEMPERATURE PROTECTIVE COATINGS FOR TUNGSTEN

Technical Documentary Report No. ML-TDR-64-227

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JULY 1964

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

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Project No. 7312, Task No. 731201

Prepared under Contract AF 33(657)-1
By Thompson Ramo Wooldridge Inc., Clevela o,
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H. J. Nolting, R. A. Jefferys, Authors

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FOREWORD

This report was prepared by Materials Processing Department, TRW Electromechanical Division, Thompson Ramo Wooldridge Inc. under USAF Contract No. AF 33(657)-11151. This contract was initiated under Project No. 7312 "Finishes and Materials Preservation", Task No. 731201, "Surface Treatments and Coatings". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Mr. N. M. Geyer acting as Project Engineer.

This report describes the results of the program conducted during the period 15 May 1963 to 15 May 1964.

The report was managed and directed by R. A. Jefferys and H. J. Nolting was in charge of conducting the technical effort. H. Tolchinsky assisted in the experimental work.

ABSTRACT

A controlled process has been established for application of (silicon-tungsten) and titanium + zirconium + (silicon-tungsten) coatings to tungsten sheet. Protective capabilities of these coatings on arc cast and powder product tungsten sheet have been determined at one atmosphere (air) from 1600 to 3600°F under cyclic conditions. Exposure at static pressures below 15 mm Hg (air) at 3400-3500°F resulted in varying degrees of deterioration of the (silicon-tungsten) and titanium + zirconium + (silicon-tungsten) coatings. Under dynamic low pressure conditions (2000-2800 ft/sec simulated air flow) at 16-20 mm Hg both coatings were protective to tungsten and resisted erosion in the temperature range of 2900-3400°F (180 to 325 BTU/ft^2/sec heat flux range).

Various refractory compound mixtures plasma sprayed on tungsten sheet were not protective at elevated temperatures in air. A silicon-tungsten + titanium nitride-boron nitride coating combination protected tungsten for short periods of time at 3700°F.

Tensile properties were determined for silicon-tungsten and titanium + zirconium + (silicon-tungsten) coated arc cast tungsten sheet at various temperatures to 3300°F. In stress oxidation tests the same systems loaded at 20 percent of the yield strength showed essentially no creep after 1 hour at 3350°F in air. The coatings were completely protective at this stress level.

The future potential of the coating systems developed for tungsten during this program has been demonstrated on experimental and prototype tungsten hardware.

This technical documentary report has been reviewed and is approved.

I Perlmutter
I. PERLMUTTER
Chief, Physical Metallurgy Branch
Metals and Ceramics Division
Air Force Materials Laboratory

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1. INTRODUCTION

Protection of tungsten from catastrophic oxidation in air at high temperatures has been achieved through the use of protective coatings. In work carried out under Contract AF 33(616)-8188 two coating systems were initially developed that protected tungsten 60 mil powder product sheet in air to 3600°F. Preliminary process techniques were developed to apply these coatings to tungsten sheet material.

As a result of the success realized under the initial effort a new program was sponsored by the Air Force Materials Laboratory (ASRCM33). The purpose of this program was to further develop protective coating systems and improve tungsten coating technology with respect to standardization of process techniques for application of the two existing coating systems to arc cast as well as powder product tungsten sheet. This phase of the work included evaluation of coated tungsten systems in air at full or partial atmospheric pressures at elevated temperatures. Other phases of study consisted of determining the scale-up potential of one coating system and investigating new coating concepts.

2. SUMMARY

During the initial portion of the program a laboratory scale study was made of process parameters for coating tungsten by the vacuum pack process. As a result of this study optimum coating parameters were established for application of oxidation resistant (silicon-tungsten) and titanium + zirconium + (silicon-tungsten) coatings to arc cast and powder product tungsten sheet. The coated systems were designated as W (base metal) + (Si-W) (coating) and W (base metal) + Ti-Zr-(Si-W) (coating).

In the latter portion of the program scale-up potential of the (Si-W) coating process was demonstrated by applying the coating in (1) a retort ten times the size of the laboratory size retort, and (2) in three different furnace units. In each case the (Si-W) coatings produced were comparable with respect to structure thickness and protective characteristics.

The vacuum pack process was also utilized to form two coating systems containing hafnium on tungsten sheet. These systems were identified as W+Hf-Si and W+Hf-(Si-W). The Hf-Si coating was not oxidation resistant at 3200°F in air. The Hf-(Si-W) coating was protective to tungsten to 3600°F in air but the ultimate time-temperature capabilities were no better than the (Si-W) coating alone.

Refractory compound coatings were formed by plasma spraying refractory compound mixtures directly on tungsten. These coatings were not gas tight and did not protect tungsten from catastrophic oxidation in air at 3000°F. A titanium nitride-boron nitride refractory mixture sprayed on (Si-W) coated tungsten resulted in a coating complex protective to tungsten for short periods at 3700°F in air.

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Oxidation tests were conducted on W+(Si-W) and W+Ti-Zr-(Si-W) systems at full and reduced atmospheric pressures. Coated systems were tested in air at one atmosphere at temperatures from 1600 to 3600°F under cyclic conditions. Both coatings were protective to the tungsten substrate for periods of time in excess of 25 hours at temperatures from 1600-3000°F and 20 hours at 3300°F. The ultimate temperature capability of both systems in air was 3600-3650°F. A reliability study determined that the W+(Si-W) system has a 96 ± 1% probablility at a 99% confidence level of surviving five hours of cyclic exposure at 3500°F in air.

Static oxidation tests of W+(Si-W) and W+Ti-Zr-(Si-W) systems were conducted at reduced pressures of 0.025, 0.100, 1, 5, 10 and 15 mm Hg. W+(Si-W) coated systems were exposed at these pressures in the as-coated condition and also after oxidation at elevated temperatures in air. W+Ti-Zr-(Si-W) systems were exposed in the as-coated condition, after conversion, and also after conversion and oxidation at one atmosphere. Exposure of all coated systems at reduced pressures resulted in varying degrees of coating deterioration at pressures below 15 mm Hg.

Oxidation tests were also conducted at reduced pressures under dynamic conditions. (Si-W) and Ti-Zr-(Si-W) coated tungsten specimens were exposed in a plasma flame (simulated air) at pressures of 16-20 mm in the temperature range of 2900-3400°F. Both coating systems protected the tungsten substrate and were resistant to erosion under these conditions.

Tensile properties of (Si-W) and Ti-Zr-(Si-W) coated arc tungsten sheet were determined under vacuum and argon at temperatures to 3300°F. Stress oxidation tests at 3350°F in air for 1 hour periods were conducted on coated arc cast sheet under loads approximating 20 percent of the yield strength of each system. Essentially no creep was observed and the protective nature of the coatings was not affected by stress at this level.

The procedures used for operating the high temperature oxidation furnace are outlined. This equipment was in nearly continuous operation for over 30 months. A description of procedures and equipment used to conduct the dynamic low pressure phase of testing is presented.

The coating technology developed during the program was utilized to coat experimental and prototype tungsten hardware for the aerospace industry. A modification of the coatings for tungsten has protected molybdenum to 3500°F under cyclic conditions in air.

3. MATERIALS

Tungsten test specimens used in experimental studies during the program were fabricated from three different lots of 60 mil sheet stock. These lots were:

1. Wah Chang Lot II - Powder product sheet remaining from Contract AF 33(616)-8188. Initially 5 Kg of this material was purchased

in sections 3 to 8 inches wide and lengths varying from 6 to 12 inches. Approximately 3 Kg of this sheet was in-house at the start of the program.

2. Wah Chang Lot III - Powder product sheet (5 Kg) purchased during the third quarter of the program. Sheet was received in sections having the same dimension as Wah Chang Lot II.

3. Universal Tungsten Sheet - Arc cast sheet received from the Air Force sponsored sheet rolling program at Universal Cyclops. This material was received in one section having a total area of 287.5 square inches.

Table 1 lists the analyses of the tungsten powder lots used in fabrication of Wah Chang sheet material and Table 2 lists the analysis of the Universal arc cast sheet material. These analyses were supplied by the vendors.

Hardness of arc cast tungsten sheet ranged from 498-526 Knoop as compared to 512-522 Knoop for the powder metallurgy sheet (Wah Chang Lot II). Measurements were made on transverse sections of representative specimens of both types of tungsten sheet parallel to the rolling direction. Figures 1 and 2 illustrate the structure of the arc cast and powder product sheet respect showing the areas in which hardness measurements were taken.

Materials used for application of coatings to tungsten sheet by the vacuum pack process were:

1. Titanium sponge - Grade A-1 (DuPont Corporation), screened to -8+30 mesh

2. Zirconium sponge - Reactor grade (Wah Chang Corporation), screened to -8+30 mesh

3. Hafnium sponge - Reactor grade (Wah Chang Corporation), screened to -8+30 mesh

4. Silicon powder - 0.5% maximum iron grade (Electromet Division of Union Carbide Corporation), screened to -8+30 mesh

5. Tungsten powder - High purity (Firth Sterling Corporation) 5 to 10 micron size

Prior to use, all silicon powder was leached in concentrated HCl, rinsed and air dried. The silicon powder was then mixed with a small amount of sodium fluoride (1-2 w/o) and the mixture heated under vacuum at 2300°F for 6-7 hours

Materials used in application of plasma spray coatings to tungsten sheet included spray grade boron nitride (Carborundum Co.) titanium hydride (Giannini Scientific Corp.), zirconium oxide and thorium oxide (Metco Corp.). In addition, hafnium diboride was available from in-house stock

TABLE 1

Analyses of Tungsten Powder Used in Fabrication of Wah Chang Lots II and III 60 Mil Tungsten Sheet

Element	Analyses in PPM	
	Lot II	Lot III
Al	<10	<10
C	4	14
Co	<10	<10
Cr	<10	<10
Cu	<10	<10
Fe	2	<10
Mg	<10	<10
Mn	<10	<10
Mo	< 2	50
Ni	2	10
O	400	180
Pb	<10	<10
Si	<10	<10
Sn	10	<10

TABLE 2

Analysis of Universal Cyclops 60 Mil Arc Cast Tungsten Sheet

Element	Analysis in PPM
Al	<10
C	10
Co	< 5
Cr	<10
Cu	< 1
Fe	2
H	< 1
Mg	< 1
Mn	<10
Mo	<10
N	2
Ni	< 1
O	9
Pb	<20
Si	<20
Sn	<20
Ti	< 1
V	10

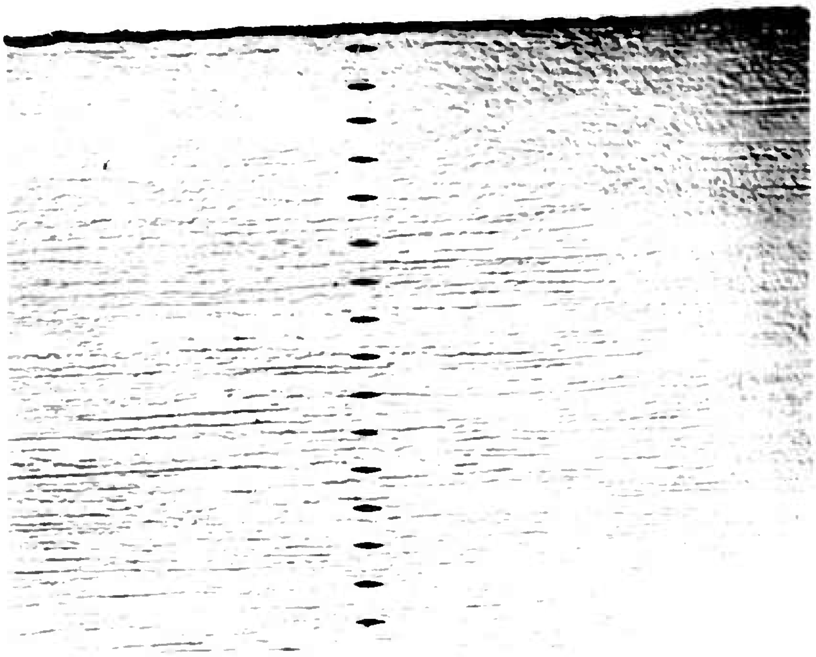


Figure 1 Microstructure of Arc Cast 60 Mil Tungsten Sheet in the As-Received Condition 100X

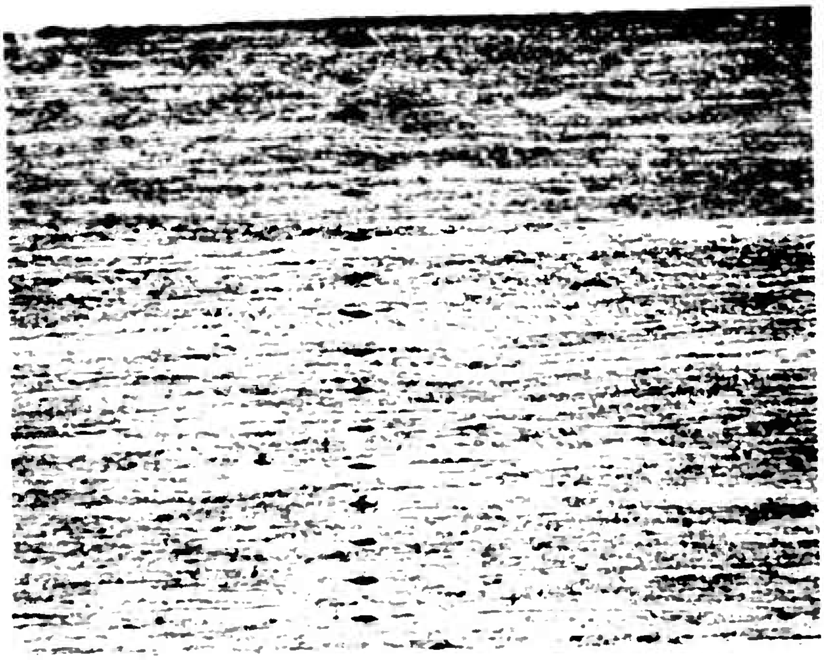


Figure 2 Microstructure of Powder Product (Wah Chang Lot II) 60 Mil Tungsten Sheet in the As-Received Condition 100X

4. EXPERIMENTAL WORK

4.1 Fabrication of Tungsten Specimens

The scope of coating and evaluation studies required fabrication of large quantities of specimens from the 60 mil arc cast and powder product sheet stock. Five types of specimens were used, these being:

1. Coupons 1/2 inch square - employed for coating studies and cyclic oxidation tests.
2. Strips 1/2 inch wide x 3 inches long - employed for static low pressure tests.
3. Strips 1 inch wide x 2 inches long - employed for dynamic low pressure testing. Specimens were curved to simulate a leading edge section by heating to 1200-1300°F under a partially protective atmosphere and bending to a 3/16" radius along the 2" axis.
4. Strips 1/2 inch wide x 12 inches long - used for process scale-up studies.
5. Tensile specimens - 1.9 inches long with a 0.125 inch x 0.5 inch gage.

All of the above specimens were fabricated from the tungsten sheet stock in the same manner. The tungsten sheet was mounted in a slotted metal back up holder. This holder supported the sheet firmly on both sides and the slot was positioned to allow a shallow surface cut of the desired length. The sheet was cut, in one direction only, to a depth of 0.005 inch per pass with a silicon carbide cutting wheel. The radial speed of the cutting wheel was controlled between 10-50 ft/sec and large volumes of coolant were used. The 60 mil sheet was cut halfway through one surface and then turned over and the cut completed from the opposite side. This fabrication technique minimized chipping or delamination of the tungsten stock and resulted in approximately 60 percent of specimens fabricated from powder product sheet and 70 percent of specimens fabricated from arc cast sheet being acceptable for use. Specimens were considered as acceptable for use if, by visual observation, all corners and edges free from any indication of chipping or delamination. Representative quantities of specimens were also etched and examined under 10X magnification.

4.2 Coating Studies

During work performed under Contract AF 33(616)-8188 two coatings, silicon-tungsten and titanium + zirconium + silicon-tungsten, were developed that protected 60 mil powder product tungsten sheet in air to temperatures of 3600°F. Cryptic designation for these coatings as applied to tungsten metal are: W (base metal) + (Si-W) (coating); and W (base metal) + Ti-Zr-(Si-W) (coating). The vacuum pack coating process was found to be the most suitable technique for application of both coating systems. Basically, the process consisted of embedding tungsten specimens in a pack of the metal to be deposited and heating under vacuum or reduced pressure. Alkali metal halides were used as pack activators to facilitate coating element transport.

Evaluation of (Si-W) and Ti-Zr-(Si-W) coated tungsten specimens at high temperatures in air showed that, with respect to ultimate time-temperature capabilities, (Si-W) coatings 4-5 mils thick and Ti-Zr-(Si-W) coatings 3.0 to 3.5 mils thick were best. Conditions necessary to apply coatings of the desired thickness were identified. These studies were conducted using a cylindrical coating retort, 2 3/4 inch diameter x 7 inches tall, having a capacity of approximately 2 liters of pack material. Application of the (Si-W) coating to tungsten sheet required one coating cycle. Application of the Ti-Zr-(Si-W) coating required three separate cycles; titanium, zirconium and silicon-tungsten being deposited in successive order. Various surface preparations were given to the tungsten test specimens used in the coating investigation. The most reliable, from processing and coating considerations, proved to be a light etching treatment in a $HF-HNO_3-H_2SO_4$ mixture prior to coating. The combination of surface preparation and optimum conditions of coating were arbitrarily defined as standard coating procedures. These procedures were standard insofar as the coating applications were made in the 2 3/4 inch diameter x 7 inch coating retort using powder product tungsten sheet as the base material.

In studies conducted during this program, the (Si-W) coating, the Ti-Zr-(Si-W) coating, hafnium containing coatings and plasma sprayed refractory compound coatings for tungsten were investigated. The initial coating studies were primarily concerned with establishing a laboratory scale process for application of the (Si-W) and Ti-Zr-(Si-W) coatings to both arc cast and powder product tungsten sheet.

4.2.1 Development of a Standard Laboratory Scale Process for Application of (Si-W) and Ti-Zr-(Si-W) Coatings to 60 Mil Tungsten Sheet

The standard procedure developed during the preceeding program for application of the (Si-W) coating to 60 mil powder product tungsten sheet was carried out in one coating cycle in a 2 3/4 inch diameter x 7 inch coating retort. Specimens, after this coating treatment, could be exposed at high temperatures in air. Procedures for application of the Ti-Zr-(Si-W) coating to powder product sheet required three separate coating cycles. These cycles were carried out in the following order:

1. titanium and zirconium were applied in successive order to form the W+Ti-Zr base metallic system. The Ti-Zr diffusion alloy layer was termed the base metallic coating,

2. silicon-tungsten was added to the Ti-Zr base metallic coating to form the Ti-Zr-(Si-W) coating complex.

Prior to exposure in air at high temperatures Ti-Zr-(Si-W) coated specimens required a pre-oxidation or conversion treatment. This was accomplished by exposing the coated specimens at 2250°F in a water saturated (Dew Point + 72°F) hydrogen atmosphere for 2 hours. The resulting system was designated as the W+Ti-Zr-(Si-W)-O coated system.

As previously stated, the initial coating studies in this program were directed toward establishing a standard laboratory scale process (vacuum pack technique) for application of such coatings to arc cast and powder product tungsten sheet. In chronological order, the studies were carried out by first applying the Ti-Zr base metallic layer to both types of tungsten sheet. This was followed by addition of (Si-W) to the W+Ti-Zr base metallic system and also to unalloyed tungsten. The description of the procedures and results are reported in this order.

4.2.1.1 Base Metallic Coating

Coating characteristics of arc cast and powder metallurgy tungsten sheet were compared by applying the Ti-Zr base metallic layer to both types of sheet under standard coating conditions established for powder product sheet. Briefly, these conditions consisted of a 1 hour hold treatment at 1600°F followed by a 5 hour cycle at 2000°F for each coating step. The coating steps were carried out at a system pressure of 25-75 microns using 15 grams of a 70 w/o NaF-30 w/o KF mixture as the pack activator. The retort used for these depositions was 2 3/4 inch diameter x 7 inches tall and had a capacity of two liters of pack material. Test specimens were the standard 1/2 inch square size. Average coating thickness (0.6-0.7 mil), weight addition of coating materials (25-30 mg/in.^{2}) and gross appearance of the coatings on arc cast and powder product specimens were essentially identical. The arc cast material, however, exhibited a partially recrystallized base metal structure after application of the Ti-Zr layer while the powder product sheet retained a cold worked structure.

A series of coating runs were then made in a larger retort. This retort measured 3 1/4 inches diameter x 10 inches tall and had a capacity of five liters of pack material. The Ti-Zr base metallic layer was applied to both arc cast and powder product sheet in this retort. Coating temperature and time for both the 1600 (1 hour) and 2000°F (5 hours) steps was held constant for these applications while type and amount of activator used and system pressure was systematically varied. Five liters of metallic sponge were used in each coating application and test coupons (1/2 inch square) were placed at regular positions in the pack starting at 1 inch from the bottom and extending to 1 inch from the top. The following conditions were found to have the greatest effect on the Ti-Zr coatings applied with respect to coating thickness and continuity:

1) system pressure

2) position (vertical) of test coupons in pack

3) amount of activator used

The most reproducible results were obtained when a system pressure of 200-300 microns was maintained throughout the coating step at 2000°F and the test coupons were positioned in a vertical 5 1/2 inch zone in the coating pack. This centrally located zone extended 2 inches from the bottom of the retort to within 2 1/2 inches of the top. Specimens in this zone were separated from the side walls of the retort by at least 1/8 inch. Varying quantities (10-30 grams) of the 70 w/o NaF-30 w/o KF activator mixture were used. Eighteen grams of this mixture was found to be the best quantity. With lesser amounts the 200-300 micron system pressure was difficult to maintain and with larger amounts constant adjustment of the system pressure was required.

Coating thickness differed slightly between arc cast coupons and powder product coupons coated under the above conditions. The Ti-Zr layer on the arc cast coupons was somewhat thinner, averaging 0.5 mil thick, while the Ti-Zr layer on powder product coupons was 0.7 to 0.75 mil thick. Figures 3 and 4 illustrate the Ti-Zr base metallic layer on an arc cast and powder product substrate, respectively.

The above conditions used to apply the Ti-Zr base metallic layer to 60 mil arc cast or 60 mil powder product tungsten sheet were considered as standard for a laboratory scale operation. They are outlined in Figure 5.

4.2.1.2 Silicon-Tungsten Coating

Addition of (Si-W), by the vacuum pack process, was made to the following tungsten sheet specimens:

1) arc cast coupons (1/2 inch square) which had the Ti-Zr base metallic layer applied under standard conditions in the 2 3/4 x 7 inch retort;

2) powder product coupons (1/2 inch square) which had the Ti-Zr base metallic layer applied in the same retort;

3) arc cast coupons (1/2 inch square) which had no prior coating treatment;

4) powder product coupons (1/2 inch square) which had no prior coating treatment.

The (Si-W) addition was made under conditions previously identified as standard for powder product 60 mil tungsten sheet. This coating cycle

Figure 3 The Ti-Zr Base Metallic Layer on Arc Cast Tungsten Sheet 250X

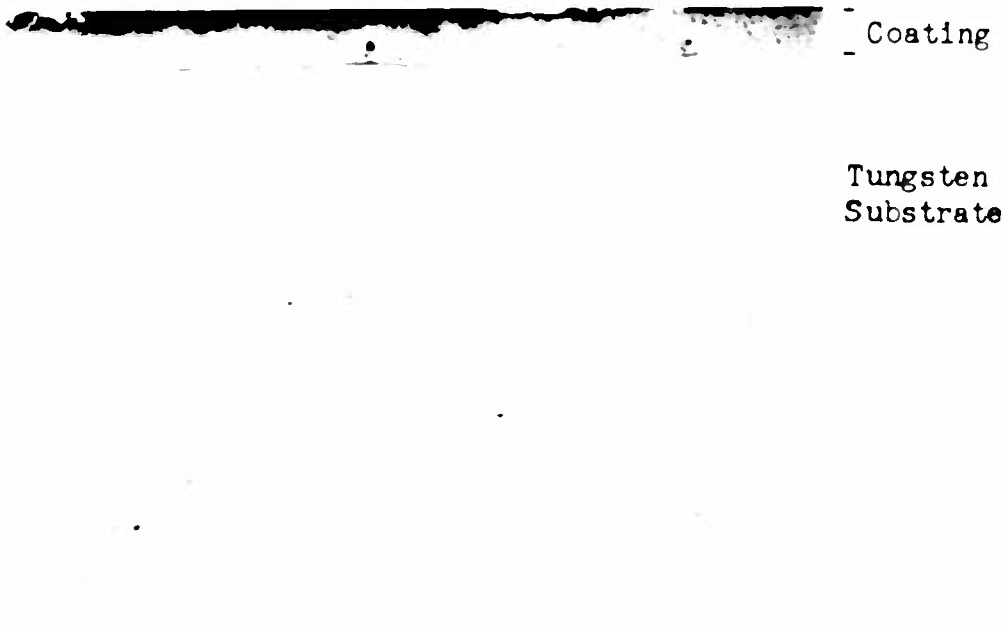


Figure 4 The Ti-Zr Base Metallic Layer on Powder Product Tungsten Sheet 250X

Pack Material	Ti Sponge (-8+30 Mesh) (Titanium Cycle) Zr Sponge (-8+30 Mesh) (Zirconium Cycle)
Pack Activator	Sodium Fluoride + Potassium Fluoride (Both Cycles)
Coating Retort	Columbium Can 3 1/4 Inches Diameter x 10 Inches High (Both Cycles) (Maximum Size)
Coating Cycle	1 Hour at 1600°F Under Vacuum + 5 Hours at 2000°F Under 200-300 Microns System Pressure (Both Cycles)

Figure 5 Vacuum Pack Process for Application of Ti and Zr in Successive Coating Cycles to Tungsten Sheet

consisted of an initial temperature step at 1600°F for 1 hour immediately followed by a 4 hour treatment at 2200°F. A mixed NaF-KF pack activator was used. The system was evacuated during the 1600°F temperature step and a partial pressure of 25-75 microns maintained for the 2200°F step.

Coating thickness of the Ti-Zr-(Si-W) layer formed on arc cast coupons by the above conditions varied from 3.0 to 3.25 mils. On powder product coupons the thickness varied from 2.75 to 3.0 mils. Coating thickness on both types of tungsten substrates were slightly irregular. The gross appearance and metallographic structures were identical, both being typical of the complex coating system. The substrate of the arc cast material was completely recrystallized except for a thin layer of apparently retained cold worked structure directly underneath the coating layer. This is illustrated in Figure 6. A completely cold worked structure was retained by the powder product tungsten after formation of the Ti-Zr-(Si-W) coating complex from the above coating treatments.

After conversion of all W+Ti-Zr-(Si-W) coated systems to the W+Ti-Zr-(Si-W)-O system, the powder product substrate was completely recrystallized. On powder product specimens examined after conversion, only slight traces of a cold worked layer beneath the coating layer was observed. This layer was not as uniform or accentuated as the layer observed in the substrate of Ti-Zr-(Si-W) coated arc cast material which was present both before and after the conversion treatment.

Addition of (Si-W) to arc cast and powder product test coupons to form the W+(Si-W) system produced smooth and uniform coatings on both types of substrates. The (Si-W) layer on arc cast coupons averaged 4.5 mils thick. Complete recrystallization of the substrate had occurred and no retention of the cold worked layer seen in the Ti-Zr-(Si-W) coated coupons was observed in the (Si-W) coated coupons. Figure 7 shows the coating layer and a portion of the substrate directly underneath the coating layer. The (Si-W) layer on powder product coupons averaged 4.0 mils thick and the substrate retained the cold worked structure. Figure 8 illustrates the coating and a portion of this substrate.

Application of (Si-W) to the W+Ti-Zr base metallic system (both arc cast and powder product coupons) was made in the larger 3 1/4 by 10 inch coating retort. Time and temperature for this application were held constant (standard conditions) and the amount of activator and operating pressure were systematically varied. The most reproducible results were achieved when 25 grams of a 70 w/o NaF-30 w/o KF mixture, blended with 10 grams of tungsten powder, was used as the pack activator for five liters of silicon powder. The system was under constant evacuation during the 1 hour 1600°F step and a pressure of 100-300 microns was maintained during the 2200°F cycle.

Figure 6 The Ti-Zr-(Si-W) Coating on Arc Cast Tungsten Sheet 250X

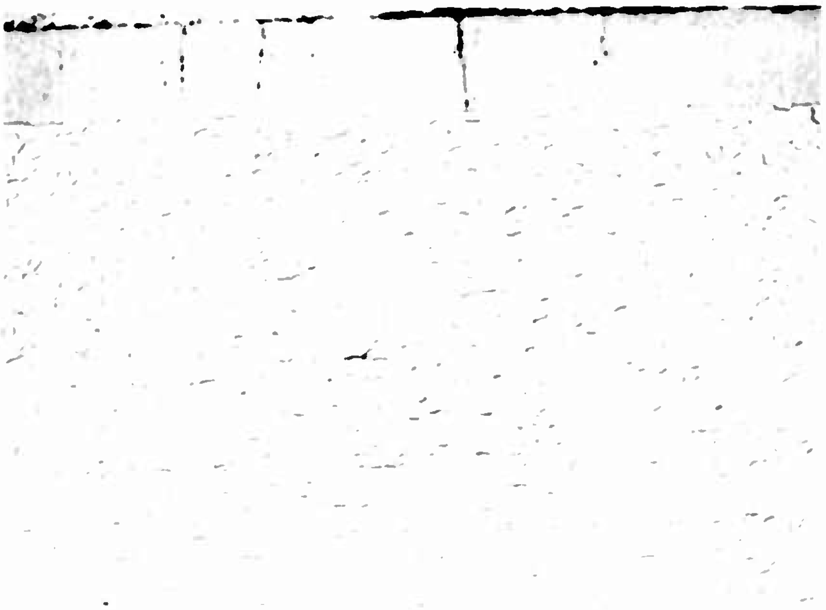


Figure 7 The (Si-W) Coating on Arc Cast Tungsten Sheet 100X

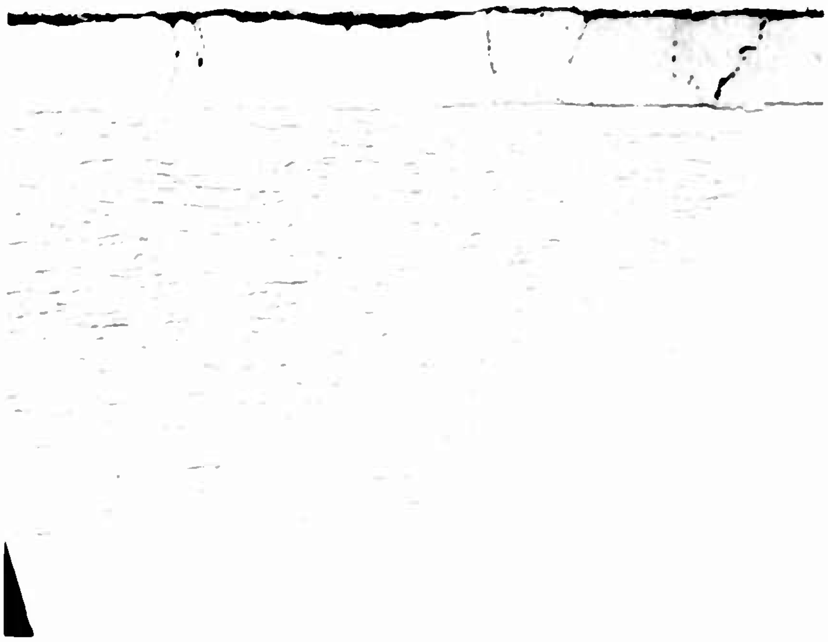


Figure 8 The (Si-W) Coating on Powder Product Tungsten Sheet 100X

Coating thicknesses of 2.75 to 3.0 mils were produced on Ti-Zr base metallic coated coupons placed within the previously described 5 1/2 inch vertical zone of the retort. No significant differences were observed between the Ti-Zr-(Si-W) coatings on arc cast or powder product tungsten coupons. The same effect as in the smaller coating retort, recrystallization of the arc cast substrate and a peripherial cold worked layer, was also observed on coupons coated in the larger retort.

Addition of (Si-W) to arc cast and powder product tungsten test coupons were made under identical conditions in the same retort. Coupons placed within the 5 1/2 inch zone of the retort exhibited coating thickness of 4.0 mils. Essentially no variation of this coating thickness was observed between arc cast or powder product coupons.

Figure 9 outlines the above coating procedures used for application of (Si-W) to the W+Ti-Zr base metallic system and to unalloyed tungsten. These coating conditions have been established as the standard laboratory scale process for (Si-W) additions.

After the standard laboratory scale processes for formation of the W+Ti-Zr-(Si-W) and W+(Si-W) coated systems had been established, additional studies were conducted. Mixtures of LiF-KF and BaF_2-KF were used instead of the NaF-KF mixture for pack activators. All coating cycles were carried out under standard time-temperature-system pressure conditions. Coating results with respect to thickness and uniformity of the applied coatings were the same when LiF-KF, BaF_2-KF, or NaF-KF mixtures were used. Some adjustment of weight ratios of LiF-KF and BaF_2-KF were required. Approximately 50 w/o less of LiF and 50 w/o more of BaF_2 than the weight of NaF used in each of the coating cycles gave the most consistent results. However, subsequent evaluation of the protective nature of the coatings applied using these activators did not show any advantage over NaF. There was no indication that any significant amount of the cation of the activator was incorporated into the coating.

4.2.2 Limited Scale-Up of the Silicon-Tungsten Coating Process

The scale-up potential of the (Si-W) coating process was investigated during the program. The objective of this study was to establish conditions for application of uniform and protective (Si-W) coatings on tungsten sheet by the vacuum pack process using a 7 1/2 inch diameter x 18 inch tall coating retort.

The capacity of this size of retort was approximately ten times that of the retorts used for standard laboratory scale coating studies. Although this increase in size does not represent a major scale-up, the problems encountered during this study were of the same nature as those anticipated for much larger units.

A (Si-W) coating thickness of 2.0 mils was selected as the minimum in order to expect protection for reasonable periods of time at elevated tempera-

Pack Material	Silicon Powder (-8+30 Mesh) + Tungsten Powder (5-10 Micron)
Pack Activator	Sodium Fluoride + Potassium Fluoride
Coating Retort	Columbium Can 3 1/4 Inches Diameter x 10 Inches High (Maximum Size)
Coating Cycle	1 Hour at 1600°F Under Vacuum + 4 Hours at 2200°F at 100-300 Micron System Pressure

Figure 9 Vacuum Pack Process for Application of (Si-W) Coatings to the W+Ti-Zr-Base Metallic System to Form the W+Ti-Zr-(Si-W) System and to Unalloyed Tungsten to Form the W+(Si-W) System

tures in air. In addition, previous experience with (Si-W) coatings on sheet stock material had indicated the desirability of limiting the maximum coating thickness to 5.0-5.5 mils. (Si-W) coatings thicker than this tended to split or "ear" on edges and corners of test specimens. These thicker coatings when exposed in air at elevated temperatures were protective, but premature failures could be induced at specimen edges and corners by thermal cycling. Thus, the range of (Si-W) coating thickness established as optimum for applications carried out in the 7 1/2 inch diameter x 18 inch coating retort was from 2.0 to 5.5 mils.

Another problem anticipated in this study was the volume of the 7 1/2 inch diameter x 18 inch retort that could be utilized for coating applications. Earlier coating studies on an associated program had shown that position of specimens in the retort was very important due to vertical and horizontal temperature gradients. Specimens, in coating packs, positioned anywhere in a vertical zone extending 1 1/2 inches from the retort bottom to within 4 inches of the top were observed to have less variation in coating thickness than specimens positioned outside of this zone. Coatings generally tended to be thicker on specimens from bottom and edge positions. In addition, a separation of at least 1/4 inch between specimens and the retort walls was also found to be necessary.

Using these data as a guide, four (Si-W) coating applications were carried out in the 7 1/2 inch diameter x 18 inch coating retort. The purpose of these runs was primarily to establish conditions for application of protective (Si-W) coatings, however a minimum coating thickness of 2.0 mils was also set as a goal. Standard 1/2 inch square tungsten coupons (fabricated from Universal Cyclops arc cast 60 mil sheet) were used as the test specimens. Four test specimens were placed in each of the following positions in the coating pack for each coating run:

1) in the bottom center and edge of the pack, 1 1/2 inches from the retort bottom;

2) in the middle center and edge of the pack, 9 inches from the retort bottom;

3) in the top center and edge of the pack, 14 inches from the retort bottom.

Table 3 lists the coating conditions for Runs 1 through 4. Chronologically this portion of the investigation was carried out by conducting the coating run, testing the coated specimens (from each position) in air at elevated temperatures and, if necessary, adjusting the parameters for the succeeding run. One furnace unit was utilized for these coating applications.

Evaluation of coated coupons from Run 1 was conducted at 3300°F in air.

TABLE 3

Conditions For (Si-W) Coating In The 7 1/2 Inch Diameter x 18 Inch Retort

Coating Run	Activator Mixture	Pack	Process Parameters Coating Temp. °F	Time Hrs.	Operating Pressure Microns
1	50g NaF + 20g KF + 20g W Powder	Si Powder (-8+30 mesh)	1800 + 2200	2 + 5	10 100-300
2	50g NaF + 20g KF + 20g W Powder	Si Powder (-8+30 mesh) + 50g W Powder	1800 + 2250	2 + 5	10 100-300
3	100g NaF + 50g W Powder	Si Powder (-8+30 mesh) + 50g W Powder	2300 + 2300	4 + 2	100-300 10
4	100g NaF + 50g W Powder	Si Powder (-8+30 mesh) + 50g W Powder	1500 + 2250 + 2250	1 + 4 + 2	10 100-300 10

Every specimen exhibited surface melting and failed after very short periods of exposure. This condition indicated excess amounts of silicon present in the coating which upon exposure to air at 3300°F formed molten SiO_2. Evaluation of specimens from coating Runs 2 and 3 was carried out at 3400°F in air. Specimens from each position from Run 2 showed some surface melting after exposure but all specimens survived. Adjustment of the coating parameters in Run 3 resulted in all specimens surviving a 15 minute exposure at 3400°F with only specimens from the top positions exhibiting indications of surface melting. Coatings deposited on specimens in Run 4 were protective to 3600°F in air, giving the same protection as (Si-W) coatings deposited under standard conditions established for a laboratory scale process. These results showed the the process parameters controlled the coating composition. Identification of the correct process parameters resulted in (Si-W) coatings of the proper composition and best protective qualities.

Thickness of coatings on specimens in different pack positions varied in each of the coating runs. Table 4 lists the coating measurements made on specimens from Runs 2, 3 and 4. Coupons from Run 1 were measured for dimensional changes only. Coating conditions used in Run 4 not only resulted in protective (Si-W) coatings being applied to the tungsten specimens but the minimum thickness of at least 2.0 mils was achieved. Figure 10 shows the (Si-W) coating on the tungsten coupons from each pack position in coating Run 4. Although the minimum coating thickness desired (2.0 mils) was achieved in Run 4 coatings deposited on coupons in the bottom edge and center positions exceeded the arbitrarily selected 5.5 mils maximum thickness. One additional (Si-W) coating application (Run 5) was carried out under the same conditions as Run 4 to verify results. Standard 1/2 inch square tungsten coupons were placed in the same positions as Run 4 and the same furnace unit was used. Results from coating Run 5 with respect to the protective nature of the applied coatings and variations in coating thickness were identical to those of Run 4. Variations in coating thicknesses from Run 5 as a function of position in the coating retort are graphically presented in Figure 11.

At this point in the investigation conditions for applying protective (Si-W) coatings to tungsten sheet using the 7 1/2 inch diameter x 18 inch retort were considered as being initially established. The next objective was to minimize variations in the coating thickness observed in Runs 4 and 5 and to determine the zone of the retort in which coatings of the desired thickness (between 2.0 and 5.5 mils) could be applied. In past work, the thickness of (Si-W) coatings was generally controlled by the temperature of application. Thus in the large retort where coatings were in excess of 6.0 mils in the bottom portion of the coating pack as compared to less than 2.5 mils in the top center portion, the following was indicated:

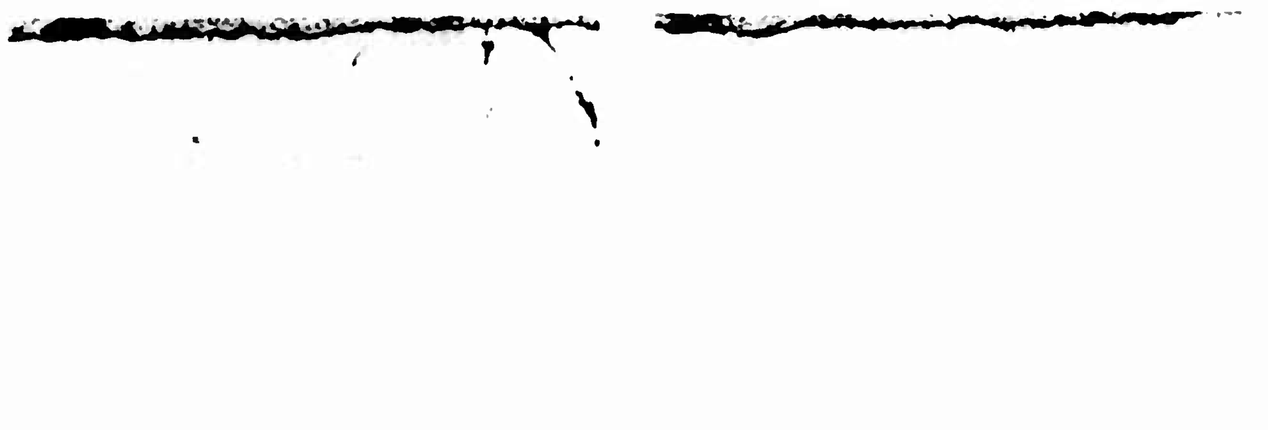
1) a thermal gradient existed from the bottom to the top of the retort during the coating operation, the top temperature being considerably lower than the middle or bottom;

2) a thermal gradient also existed from the edge to the center of the retort. This gradient was apparently not severe and remained

TABLE 4

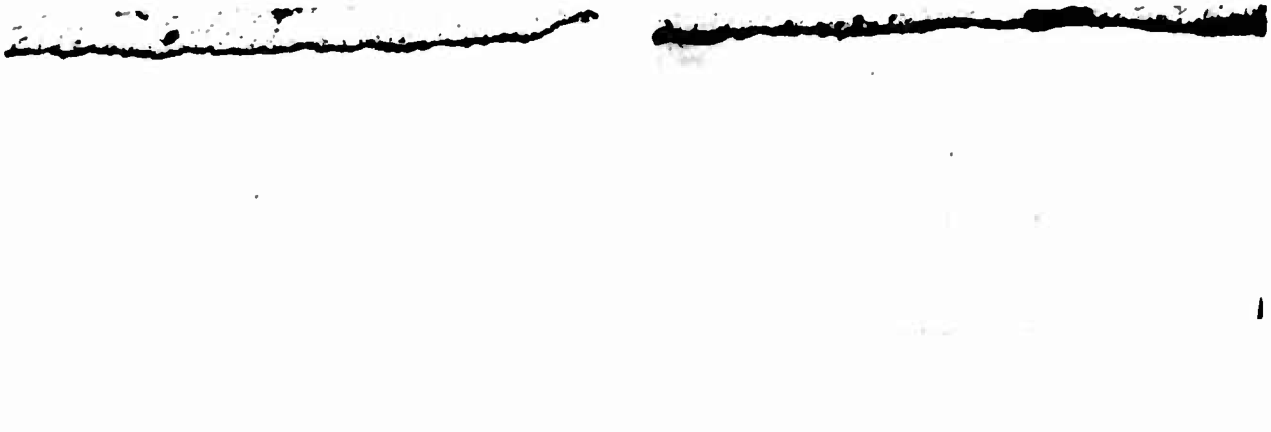
Thickness Of (Si-W) Coating Deposited Using 7 1/2 Inch Diameter x 18 Inch Retort

Specimen Location In Pack	(Si-W) Coating Thickness (Mils)			
	Run 1	Run 2	Run 3	Run 4
Top Edge	-	2.5	2.5	3.2
Top Center	-	1.6	1.5	2.4
Middle Edge	-	4.0	4.5	5.4
Middle Center	-	2.5	2.8	5.0
Bottom Edge	-	2.7	5.5	6.4
Bottom Center	-	2.8	4.0	6.0



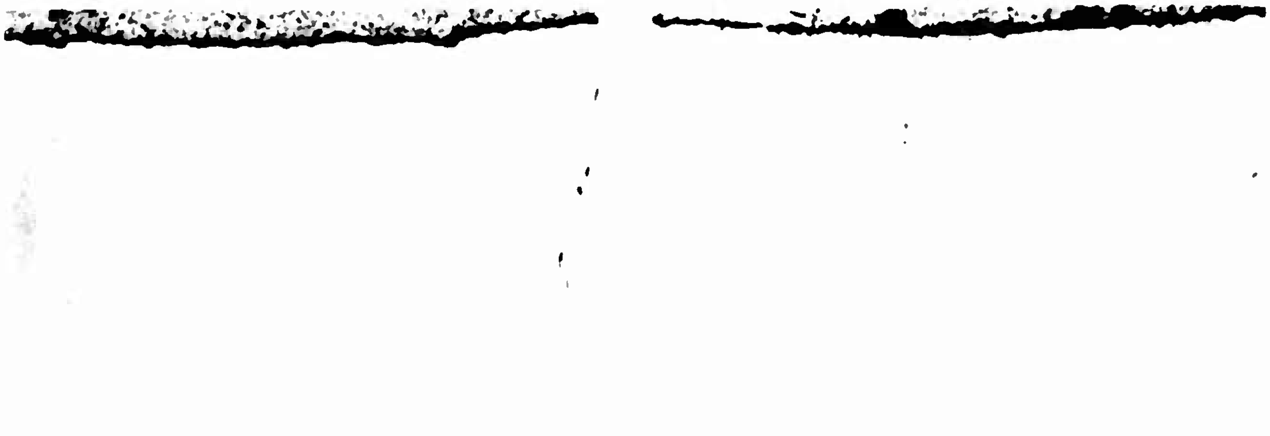
Top Center

Top Edge



Middle Center

Middle Edge



Bottom Center

Bottom Edge

Figure 10 (Si-W) Coating on Tungsten Coupons from Coating Run 4 Using 7 1/2-Inch Diameter x 18-Inch Retort 250X

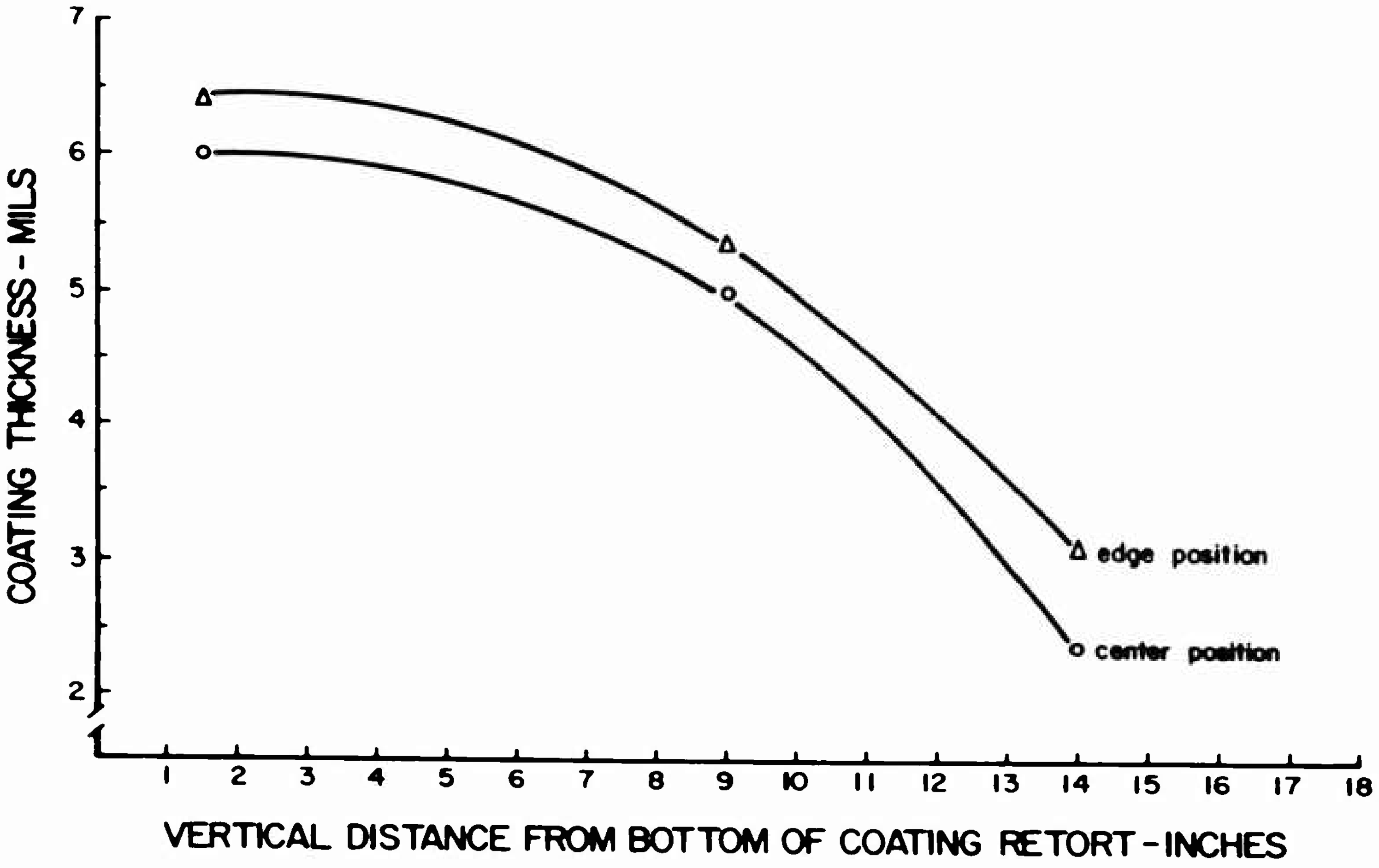


Figure 11 (Si-W) Coating Thickness on Tungsten Coupons from Run 5 as a Function of Vertical Position in 7 1/2-Inch Diameter x 18-Inch Retort

constant for the 12 1/2 inch vertical zone in which coupons were positioned.

Temperature of the coating run was measured on the outside wall of the retort 9 inches from the bottom. From the variation in coating thickness, pack temperature apparently exceeded 2250°F below this point and was lower than 2250°F above this point.

The next coating run (Run 6) in the 7 1/2 inch diameter x 18 inch retort was carried out using larger tungsten specimens. It was reasoned that a larger mass in the coating pack would improve heat transfer characteristics and reduce the vertical thermal gradient. The specimens used were fabricated from Wah Chang Lot II 60 mil sheet and measured 1/2 inch wide by 11 inches long. Four specimens were placed vertically at equidistant points around the edge of the coating pack. The wide face of each specimen was parallel to, and 1/2 inch away from, the retort wall. The bottom of each strip was 3 inches from the retort bottom and the top 14 inches from the bottom. Sheet coupons, 1/2 inch square, were positioned adjacent to the bottom, middle and top of each strip specimen. The coating run was carried out under the same conditions as Run 5. All strip specimens and a representative number of sheet coupons were examined metallographically after coating, the remainder of the (Si-W) coated coupons were exposed in air at temperatures up to 3600°F for 30 minute periods. Coating measurements were made along the entire length of each strip specimen and also on one coupon from each position to these strips. The average values of these measurements are presented in Figure 12 as a function of vertical distance from the retort bottom. These data indicated that the heat transfer characteristics of the coating pack were improved through the use of the larger specimens. Variation in (Si-W) coating thickness, 6.8 mils maximum to 4.2 mils minimum for strips and 6.9 mils maximum to 4.6 mils minimum for coupons adjacent to strips, was less severe than in previous applications in this retort. However, a significant increase in the overall thickness of coatings applied in this application was not particularly desirable. Splitting and earing of the (Si-W) coating at the edges and corners of the bottom portion of the strip specimens and also on coupons from bottom positions was quite evident. The (Si-W) coatings on all coupons tested (one from each position) were protective in air to 3600°F, however corner and edge failures could be induced on coupons from the bottom positions by repeated thermal cycling between room temperature and 3600°F.

Coating Run 7 in the 7 1/2 inch diameter x 18 inch retort was carried out under the same time, temperature and operating pressure conditions as Runs 4, 5 and 6. However, the following changes were made:

1) the activator mixture used consisted of 75 grams of sodium fluoride and 50 grams of tungsten powder instead of 100 grams of sodium fluoride and 50 grams of tungsten powder,

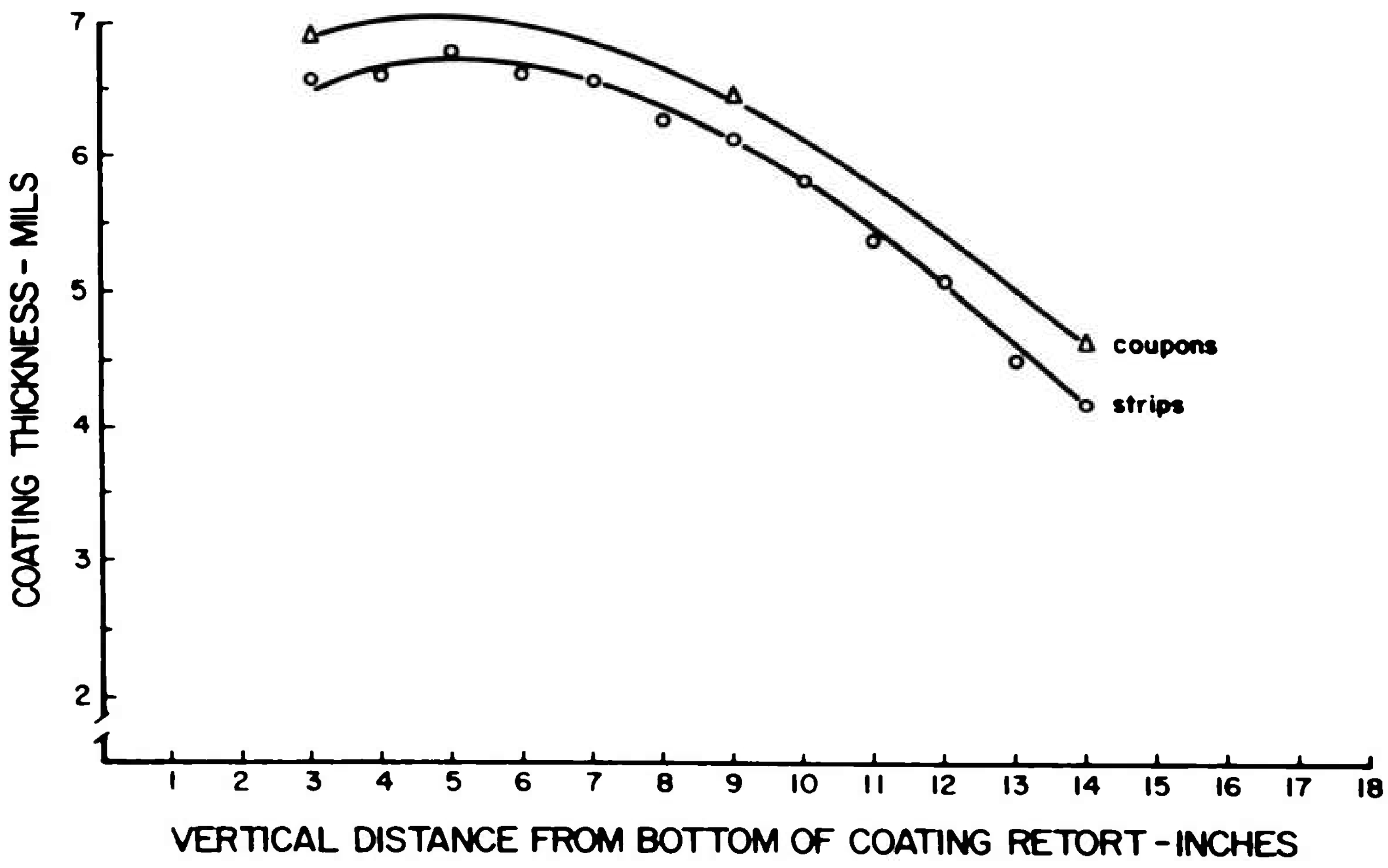


Figure 12 (Si-W) Coating Thickness on Tungsten Strip and Coupon Specimens from Run 6 as a Function of Vertical Position (Edge) in the 7 1/2-Inch Diameter x 18-Inch Retort

2) a different coating furnace was used for the application. This furnace had the same design and construction as the furnace used in Runs 1 through 6. The same coating retort was utilized, however the position of the retort in this furnace chamber was slightly lower than in the furnace originally used. Thus, the only change affected was to vertically raise the heat zone in the coating pack. Temperature of the coating run was measured 9 inches from the bottom of the retort,

3) strip specimens 1/2 inch wide by 12 inches long were positioned in the edge and center of the coating pack between 2 and 14 inches from the retort bottom. Sheet coupons, 1/2 inch square, were placed adjacent to the bottom, center and top of each strip specimen.

Variations in coating thickness from bottom to top of specimens were minimized as illustrated in Figures 13 and 14. The maximum coating thickness on strip specimens from the edge of the coating pack was 5.3 mils and the minimum 3.4 mils. A very uniform coating on strip specimens and sheet coupons was observed for all three coupon positions in the coating pack. There was no splitting or separation of the (Si-W) coating on edges and corners of specimens from the center of the pack. Specimens from the edge of the coating pack did exhibit this effect to a somewhat minor degree.

The protective nature of the (Si-W) coating applied under the above conditions was evaluated by exposing coated sheet coupons from each pack position at 3600°F in air for 15 minutes. All coupons survived this exposure without failure. Based on previous experience, if the coating survived exposure at 3600°F, protective life at lower temperatures would be normal.

An additional series of (Si-W) coating applications (Runs 8, 9 and 10) using the 7 1/2 inch diameter x 18 inch coating retort were carried out in a newly constructed furnace unit. The purpose of these coating runs was to determine the effect of the heating characteristics of the furnace unit upon the limited scaled-up (Si-W) coating process. Conditions for Run 8 were identical to those used in Run 7. Briefly these conditions were:

1) time, temperature and system pressure of application - 1 hour at 1500°F (vacuum) + 4 hours at 2250°F (100-300 microns) + 2 hours at 2250°F (5-10 microns),

2) activator mixture - 75 grams NaF + 50 grams W powder,

3) pack composition - 50 liters of silicon powder (-8+30 mesh).

Strip specimens 1/2 inch wide x 12 inches long were positioned at the edge and center of the pack between 2 and 14 inches from the retort bottom. Sheet coupons were placed adjacent to the bottom, center and top of each strip. Measurements of the coated strip specimens and sheet coupons after the (Si-W) coating cycle showed a very wide variation in coating thickness.

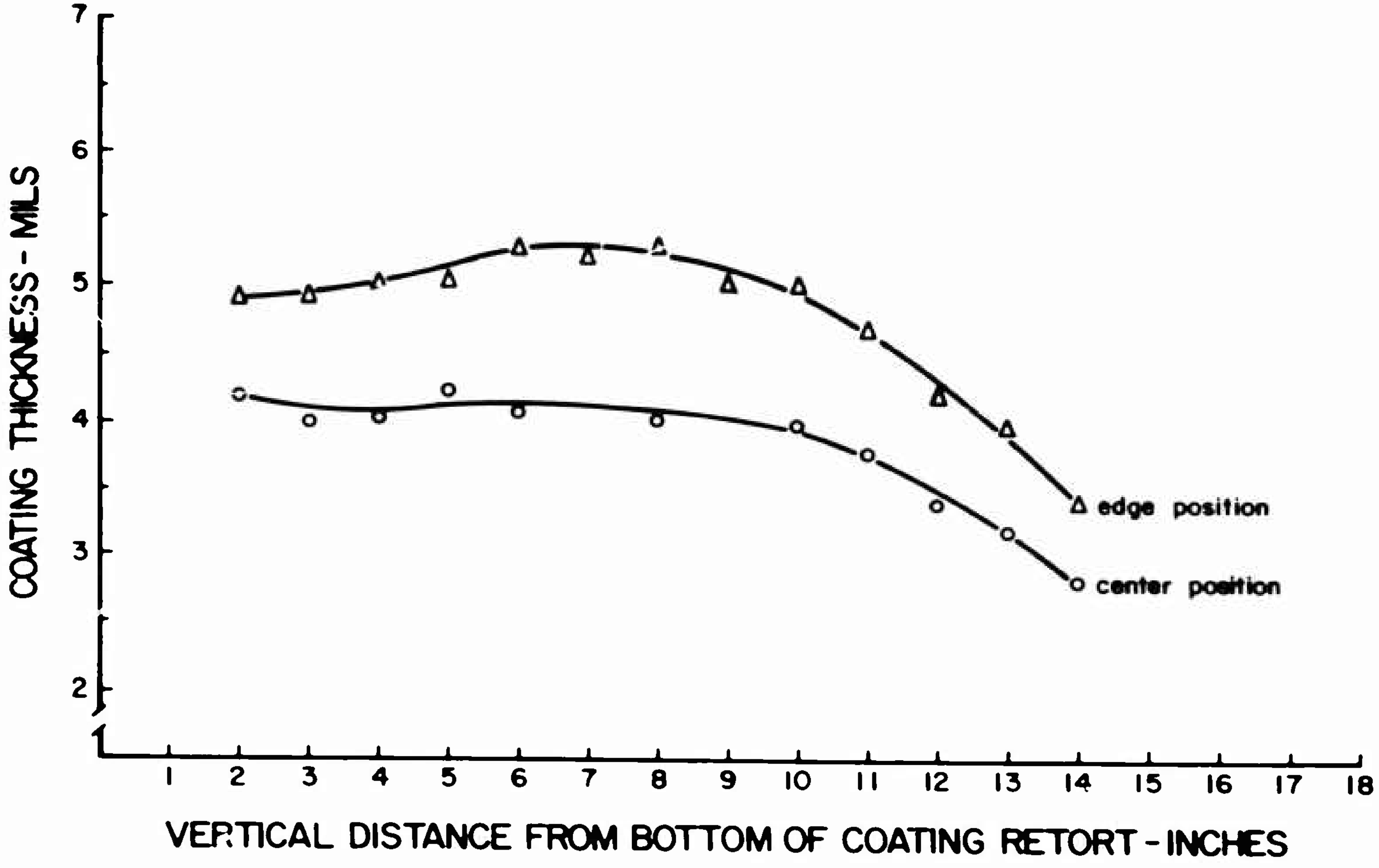


Figure 13 (Si-W) Coating Thickness on Tungsten Strip Specimens from Run 7 as a Function of Vertical Position in the 7 1/2-Inch Diameter x 18-Inch Retort

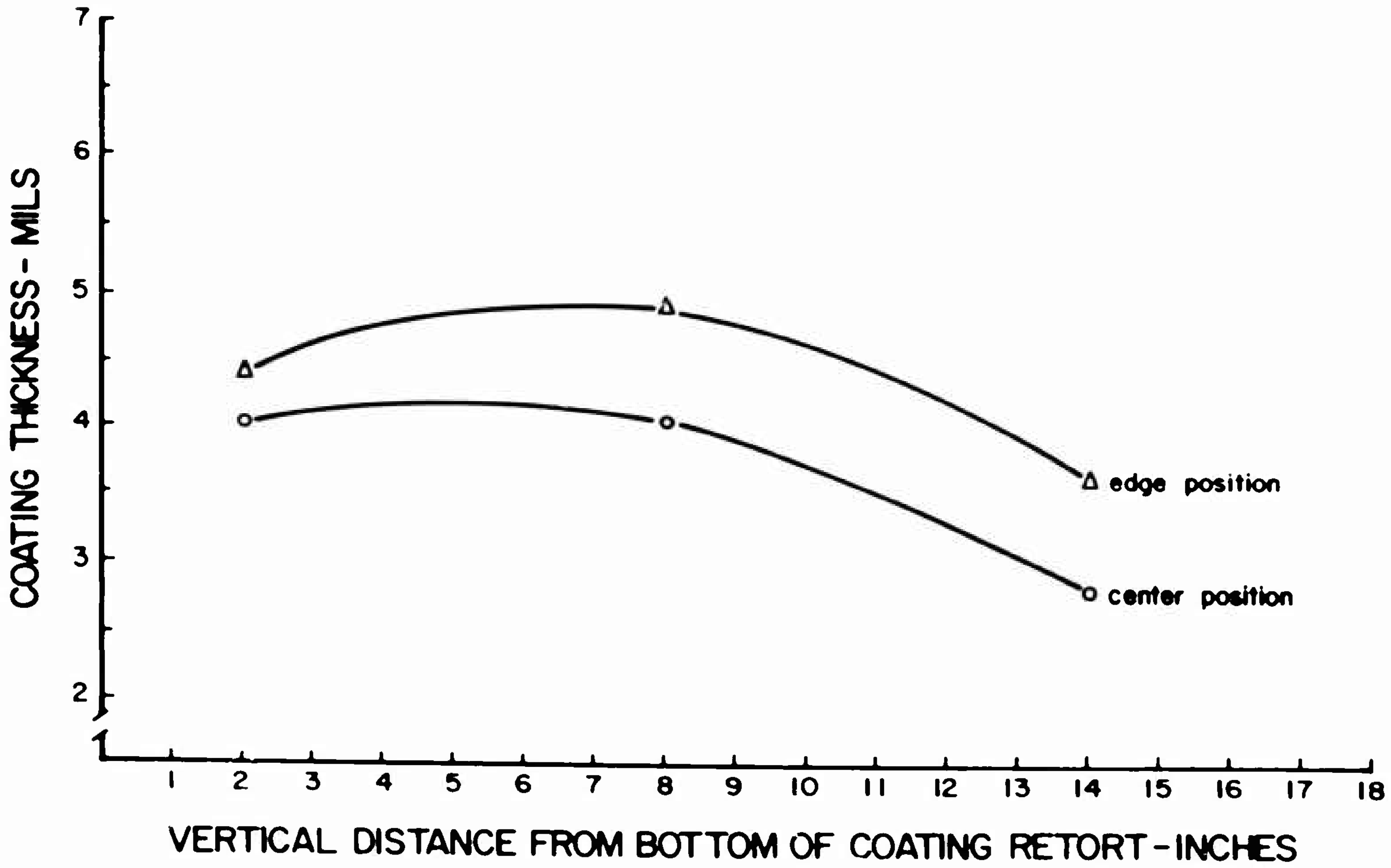


Figure 14 (Si-W) Coating Thickness on Tungsten Coupons (Adjacent to Strips) from Run 7 as a Function of Vertical Position in the 7 1/2-Inch Diameter x 18-Inch Retort

Strip specimens located at the edge of the pack had a maximum thickness of 9.0 mils on the bottom areas. Coating thickness at the top of these specimens was 4.2 mils, with the rate of decrease to this value from 9.0 mils being almost linear. The same effect was observed on strip specimens from the center of the pack. Coatings were somewhat thinner having a maximum thickness at 8.5 mils on bottom areas, this decreasing at a linear rate to 3.0 mils at the top. Coating thickness on coupons from each position adjacent to the strip specimens were the same as that area of the strips. Although splitting of the (Si-W) coating on edges and corners was quite evident on coupons from bottom positions the coatings were protective. None of the coupons exposed in air at 3500° F failed (providing they were not thermal cycled excessively) and one specimen survived 16 hours at 3500° F without failure.

The wide variations in coating thickness observed on specimens from Run 8 were attributed to a severe vertical temperature gradient in the new furnace unit. Temperature measurements, as in all previous runs, were made at a point 9 inches from the retort bottom. From the results of the coating application a temperature much higher than the recorded 2250° F was apparently attained during the coating cycle. In order to minimize this gradient the induction heating coils on the furnace unit were re-spaced and the whole coil raised 3 inches. To determine the effect of this furnace modification, the next coating application (Run 9) was carried out under the conditions used in Run 8. The same number and size of strip specimens and sheet coupons were employed and positioned exactly as in Run 8. (Si-W) coatings applied to specimens in Run 9 were uniform but the thickness generally exceeded the desired 5.5 mils maximum. Figure 15 graphically presents the measured (Si-W) coating thickness on strip specimens as a function of vertical position. Coupons adjacent to the bottom, middle and edge of the strips had the same coating thickness as the corresponding area of the strip specimens.

One additional (Si-W) coating application (Run 10) was carried out using the same coating furnace. The number and position of strip specimens and sheet coupons was the same as in Runs 8 and 9. Coating conditions were also the same as in Runs 8 and 9 with the exception of the second temperature step in the coating cycle. The temperature was dropped 50° F from 2250° F to 2200° F. Thus the temperatures of the coating cycle consisted of a 1 hour treatment at 1500° F followed by 6 hours at 2200° F (4 hours at a system pressure of 100-300 microns and 2 hours at 5-10 microns). The results of this coating run are presented in Figure 16. Coatings on specimens from both edge and center positions were within the desired thickness range (2.0 to 5.5 mils) and the gradient (bottom to top) was not severe.

The results of these studies indicate that the vacuum pack process for application of the (Si-W) coating to tungsten has definite scale-up potential. The major problem in any scaled-up coating operation will be in achieving a uniform heat zone over the entire coating retort during the coating cycle.

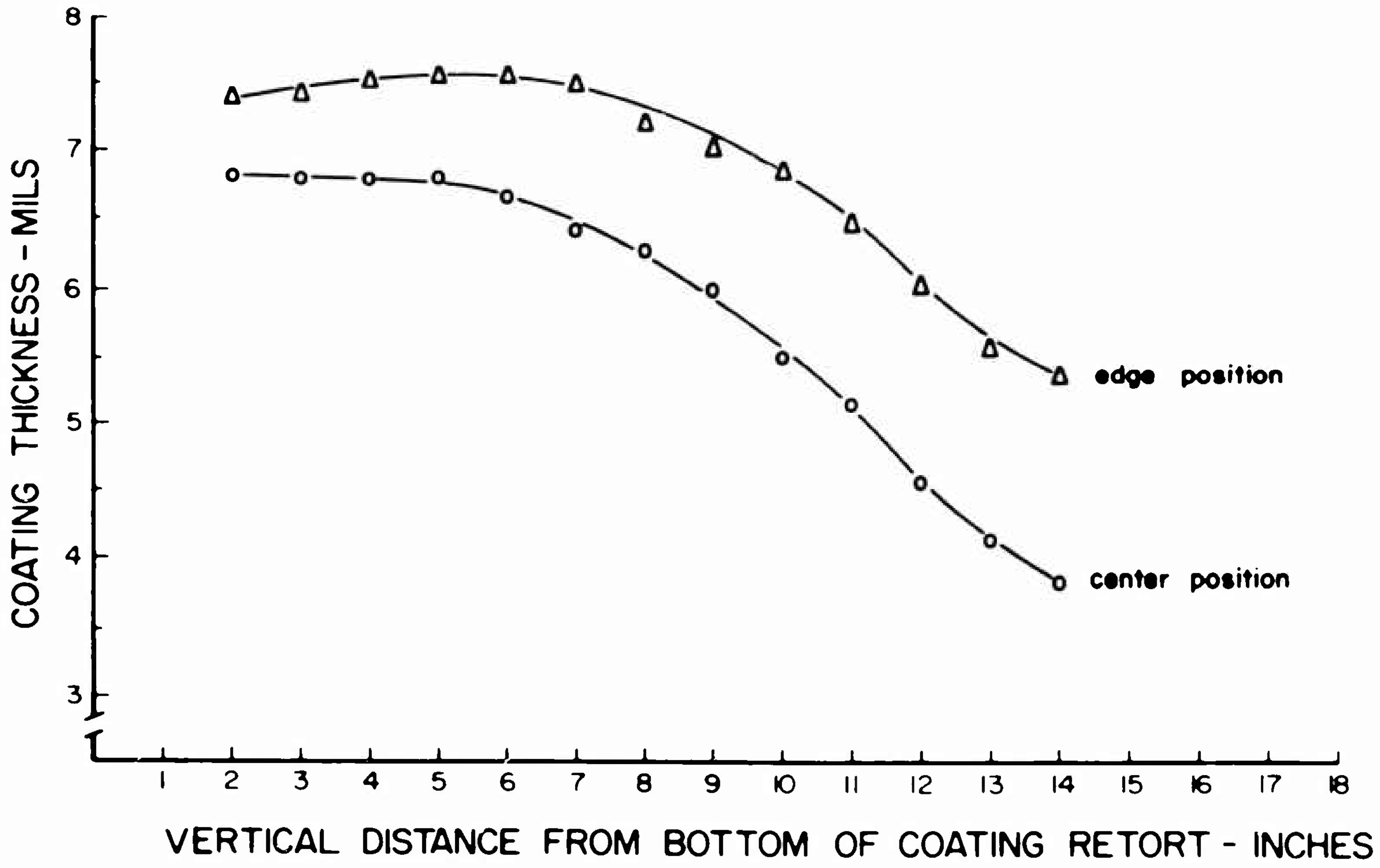


Figure 15 (Si-W) Coating Thickness on Tungsten Strip Specimen from Run 9 as a Function of Vertical Position in the 7 1/2-Inch Diameter x 18-Inch Retort

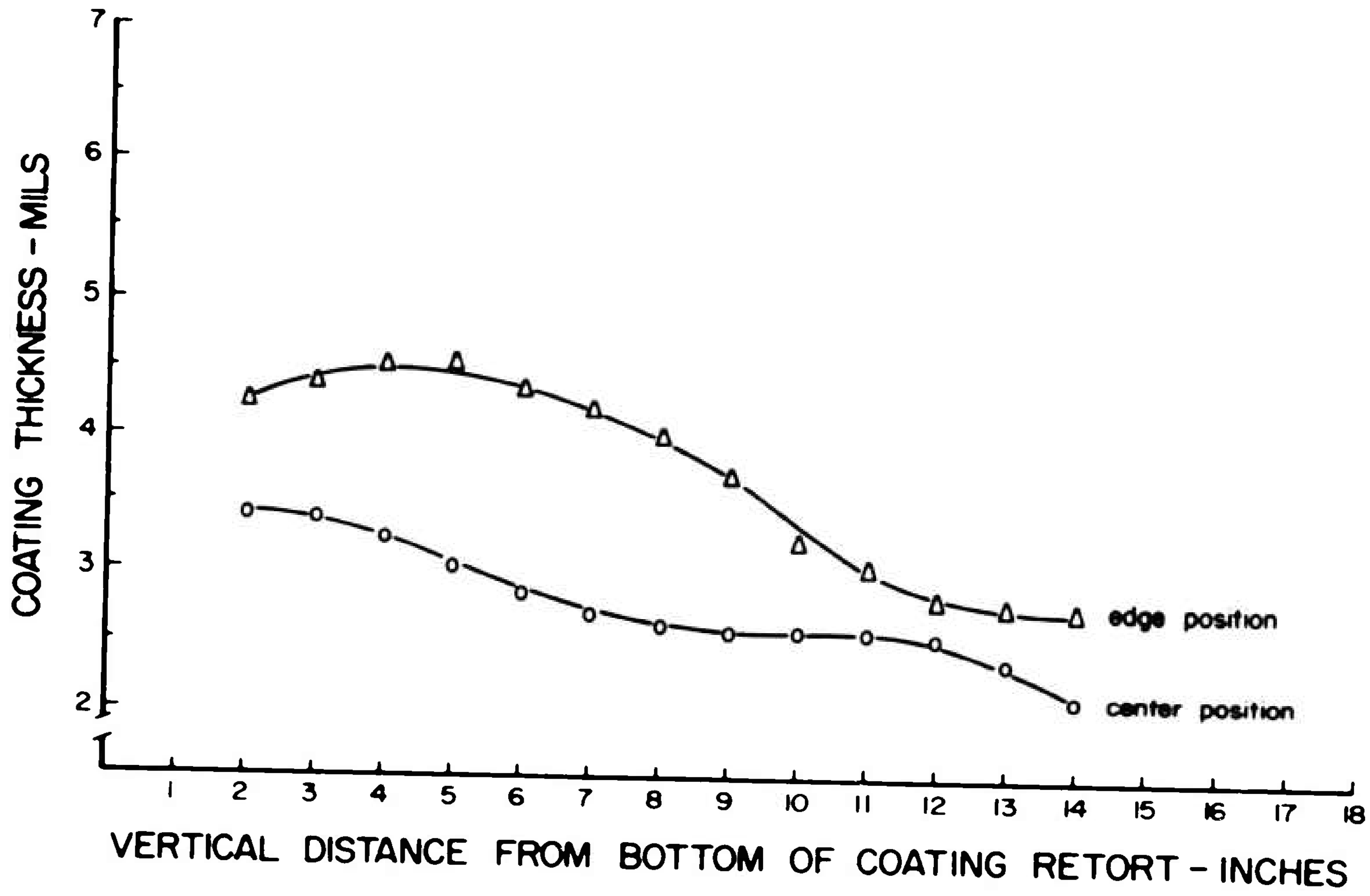


Figure 16 (Si-W) Coating Thickness on Tungsten Strip Specimens from Run 10 as a Function of Vertical Position in a 7 1/2-Inch Diameter x 18-Inch Coating Retort

4.2.3 Hafnium Coating

Deposition of hafnium on tungsten was carried out by the vacuum pack process. Two coating depositions were made using the 3 1/4 inch diameter x 10 inch coating retort. Twenty five (25) grams of a 70 w/o NaF-30 w/o KF mixture was used as pack activator for approximately 2.5 liters of -8+30 mesh hafnium sponge in each coating deposition. Standard 60 mil thick, 1/2 inch square tungsten coupons, both powder product and arc cast material, were used as the test specimens.

A two temperature cycle was employed for each deposition. Coating packs were heated to 1600°F under vacuum and held for a 1 hour period. The temperature was then raised to 2300°F. In the first deposition a system pressure of 100-300 microns was maintained for a 6 hour period during the 2300°F temperature step. After this time the system was evacuated to less than 10 microns and the run continued for an additional 2 hours. Hafnium coatings deposited on both types of tungsten were very thin. Figure 17 shows the hafnium layer on powder product tungsten and Figure 18 show the hafnium layer on arc cast tungsten. These coating layers were 0.1-0.2 mil thick. A second coating deposition was conducted during which the system pressure was maintained at 100-300 microns for 10 hours at 2300°F in an effort to increase the coating thickness. However, the hafnium layer on both powder product and arc cast test specimens after this coating treatment was still 0.1-0.2 mil thick.

Addition of Si and (Si-W) was made to the W+Hf system. Formation of the W+Hf-Si system was carried out by treating the W+Hf specimens in a silicon powder pack for 1.5 hours at 2250°F under vacuum. No activator was employed. Very thin coatings (0.4 mil thick) were produced under these conditions. Figure 19 shows the Hf-Si coating on a powder product tungsten substrate. The W+Hf-(Si-W) coated system was formed by depositing (Si-W) on the W+Hf system under the same conditions employed for (Si-W) additions to form the W+(Si-W) or W+Ti-Zr-(Si-W) systems. The Hf-(Si-W) coating formed was essentially the same in appearance as the (Si-W) or Ti-Zr-(Si-W) coatings, however it was thinner, averaging 2.0-2.2 mils in thickness. Figure 20 shows a representative area of this coating on tungsten.

Attempts were made to add boron to the hafnium system using the vacuum pack process. These were, however, unsuccessful due to a corrosive attack by pack activators on the hafnium coating layer.

4.2.4 Spray Coatings

A Metco plasma flame spray gun was used to apply a series of refractory coatings to tungsten sheet coupons. These refractory compound coatings were also applied to W+(Si-W) systems (1/2 inch square coupons) by the same techniques. Systems prepared for evaluation were:

$W+HfB_2$
$W+(TiN-BN)$

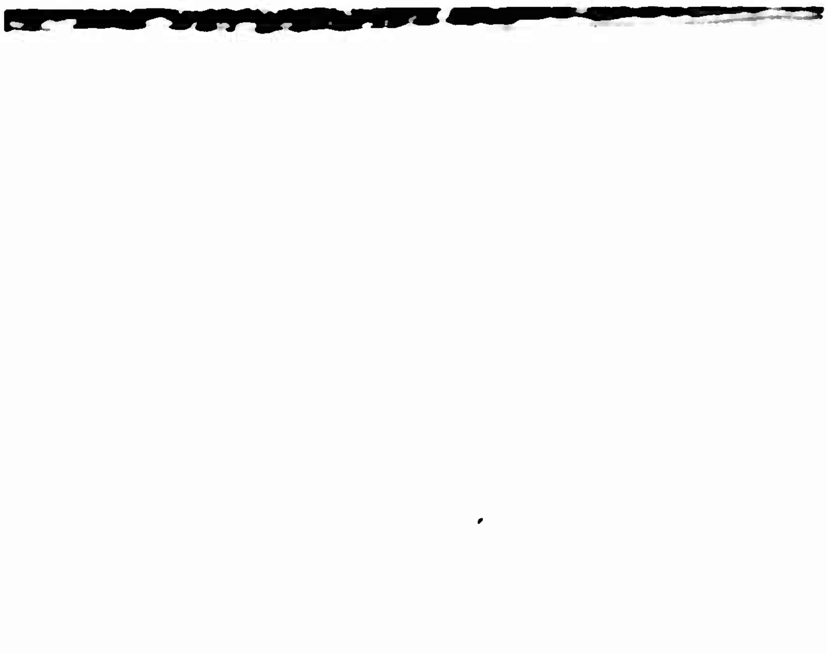


Figure 17 Hafnium Layer on Powder Product Tungsten Sheet 250X

Figure 18 Hafnium Layer on Arc Cast Tungsten Sheet 250X

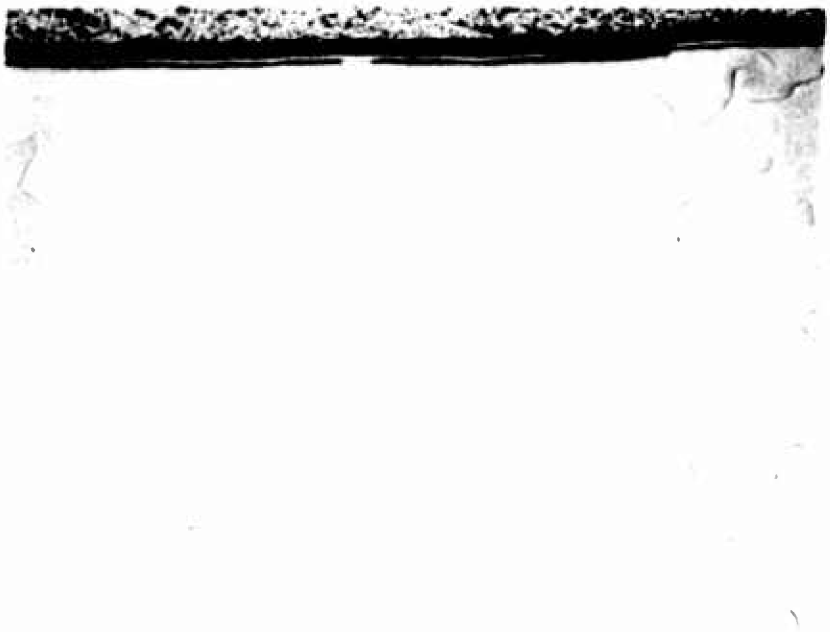


Figure 19 Hf-Si Coating on Tungsten 250X

Figure 20 Hf-(Si-W) Coating on Tungsten 250X

$W+(Si\text{-}W) + HfB_2$
$W+(Si\text{-}W) + BN$
$W+(Si\text{-}W) + (TiN\text{-}BN)$

Spray grade powder was used for every application. Tungsten and (Si-W) coated tungsten surfaces were prepared for coating by a light sandblast treatment followed by a mild etch in a $HF\text{-}H_2SO_4\text{-}HNO_3$ solution.

Adherence of sprayed coatings to tungsten sheet was generally good. Uniform 1.0 to 2.0 mils thick coatings (measured by dimensional change) were applied to all tungsten coupons. Best adherence of the sprayed coatings to (Si-W) coated tungsten was achieved when the thickness was held to less than 0.5 mil. Figure 21 shows the general appearance of a W+(Si-W) + (TiN-BN) coated coupon as compared to a W+(Si-W) coupon. Microstructures of both systems are shown in Figure 22.

Spray coatings of ZrO_2 were applied to tungsten sheet under the same conditions as described above. Rather uniform 1 to 2 mil coatings were obtained. Attempts to densify the ZrO_2 layer by conversion to a phosphate were unsuccessful. Upon heating in an atmosphere of P_2O_5 vapor (argon carrier) the zirconia layer spalled from the tungsten substrate.

4.3 Oxidation Studies

The following oxidation tests were conducted on (Si-W) and Ti-Zr-(Si-W) coated tungsten sheet specimens during the program:

1) atmospheric oxidation tests (cyclic) at temperatures from 1600 to 3600°F,

2) static low pressure oxidation tests at 3400-3500°F,

3) dynamic low pressure oxidation tests at measured heat fluxes of 180, 275 and 325 $BTU/ft^2/sec$.

Atmospheric oxidation tests were also conducted to evaluate the hafnium containing coatings and the plasma sprayed refractory compound coatings on tungsten. A portion of these tests were conducted at temperatures approaching 4000°F.

4.3.1 Atmospheric Oxidation Tests of the W+(Si-W) and W+Ti-Zr-(Si-W)-O Coated Systems

Atmospheric oxidation tests on (Si-W) and Ti-Zr-(Si-W)-O (converted) coated tungsten sheet were conducted at temperatures from 1600 to 3600°F.

Coated tungsten coupons 1/2 inch square were used in all of the atmospheric oxidation tests. Resistance type furnaces were employed for testing from 1600 to 2500°F and an induction heated furnace of special design was

A

B

Figure 21 (Si-W) Coated Tungsten Coupon (A) and (Si-W) Coated Tungsten Coupon After Plasma Spraying With (TiN-BN) Refractory Mixture (B) 1X

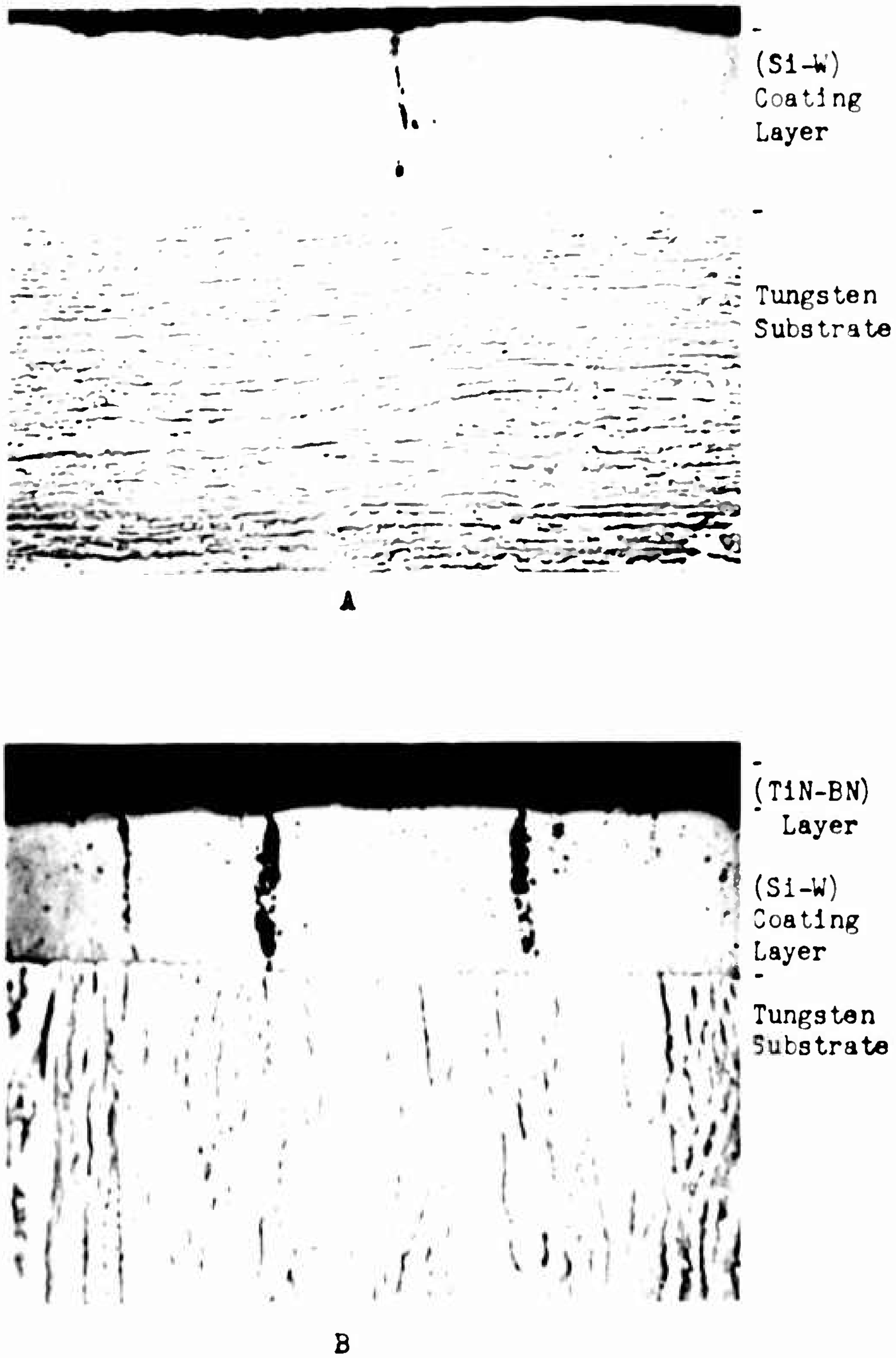


Figure 22 Microstructure of (Si-W) Coated Tungsten Specimen (A) and of (Si-W) Coated Specimen With (TiN-BN) Refractory Mixture Applied by Plasma Spraying (B) 250X

utilized for testing at 3000°F and higher. A description of this ultra high temperature oxidation furnace is presented in Section 5. Stabilized zirconia in the form of pads or discs was used to support specimens during the oxidation tests. At temperatures below 3000°F no reaction between zirconia and the coating was observed. However, at 3000°F after long periods of direct contact, zirconia reacted with the coating and eventually caused coating failure. Since the rate of this reaction was accelerated at temperatures above 3000°F sacrificial coupons were employed to circumvent premature coating failures. These sacrificial coupons (coated) were placed directly on the zirconia support and a second coated coupon (test specimen) placed on the sacrificial coupon. The top coupon was evaluated and the sacrificial coupon replaced when necessary.

During testing all specimens were thermal cycled. This consisted of removing the coated specimen directly from the hot zone of the furnace into the room atmosphere and air cooling. Upon inspection the specimens were placed directly into the furnace. The intervals between thermal cycles were based on the expected life of the coating. At higher temperatures specimens were cycled more frequently than at lower temperatures.

The first oxidation tests in air at one atmosphere were conducted at 3000°F to determine if an arc cast substrate had any effect on the protective nature of the coating system. Five (Si-W) and five Ti-Zr-(Si-W)-O (converted) coated arc cast coupons were exposed at 3000°F under cyclic conditions. These coupons had been coated in the 2 3/4 inch diameter x 7 inch coating retort under conditions defined as standard for the powder product tungsten sheet. Each coated arc cast specimen survived a minimum of 30 to 40 hours of cyclic exposure (1 thermal cycle every 5 hours) without failure. Cyclic oxidation tests of (Si-W)-O and Ti-Zr-(Si-W)-O powder product coupons coated along with the arc cast coupons gave the same results. In addition to the above tests one (Si-W) coated arc cast coupon and one (Si-W) coated powder product coupon were exposed in a prolonged test under cyclic conditions at 3000°F for in excess of 100 hours. The (Si-W) coated arc cast coupon failed sometime between the 102 and 105th hour of exposure due to reaction with the zirconia pad. This coupon was cycled to room temperature ten (10) times during the test. The (Si-W) coated powder product coupon survived 105 hours of cyclic exposure (10 cycles) before any indication of coating failure was observed. Figure 23 is a photograph of this specimen after exposure illustrating the initial stages of coating deterioration on edges and corners. Figure 24 is a photomicrograph of the coating structure after exposure.

Cyclic oxidation tests of the W+(Si-W) and W+Ti-Zr-(Si-W)-O (converted) coated systems prepared by the standard laboratory scale process were conducted at 1600, 1800, 2500, 3000, 3300, 3500 and 3600-3650°F. Five specimens of each coating system were exposed at each temperature and all specimens were thermal cycled as follows:

a) 1600°F - one cycle for each hour of exposure

b) 1800, 2500, 3000°F - one cycle for each five hours of exposure

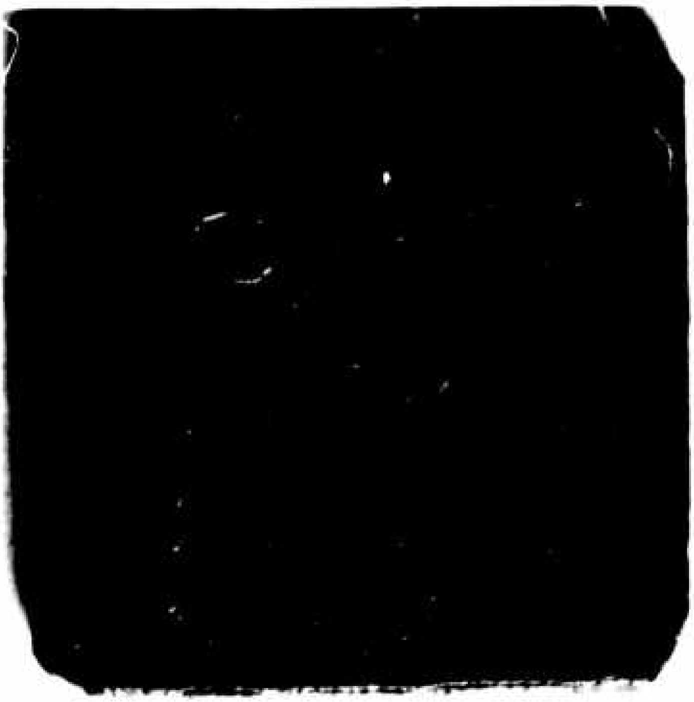


Figure 23 A (Si-W)-O Coated Tungsten Coupon After 105 Hours of Cyclic Exposure in Air at 3000° F 6X

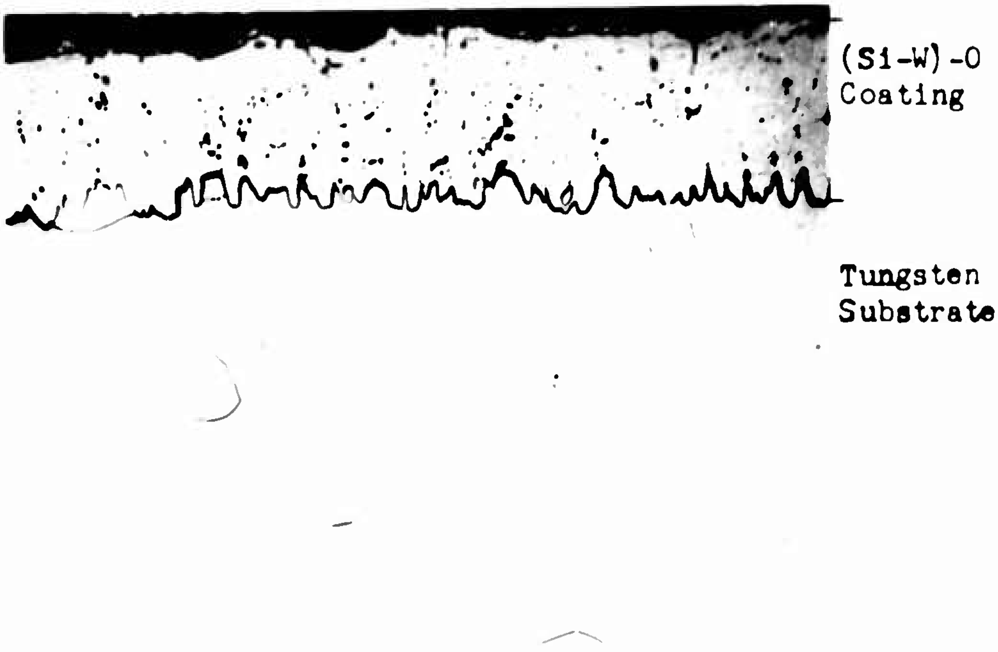


Figure 24 The (Si-W)-O Coating on Tungsten Sheet After 105 Hours of Cyclic Exposure in Air at 3000° F 100X

c) 3300 to 3650°F - one cycle for each hour of exposure

The results of these tests are graphically presented in Figure 25. A significant improvement in coating life at 1600°F over that reported during the last program was observed. The average life to failure of the five (Si-W) coated specimens tested at 1600°F was 40 hours and the Ti-Zr-(Si-W)-O (converted) coated specimen was 30 hours. In the previous program the average life of (Si-W) coated tungsten sheet at 1600°F was 1 hour and that of Ti-Zr-(Si-W)-O (converted) coated sheet 3.5 hours. Delamination of the powder product sheet used for those tests caused many premature failures at 1600°F since both coatings have essentially no selfhealing capabilities at this temperature. Coated arc cast specimens were used for all oxidation tests below 2500°F in the present program. This material exhibited much less tendency to delaminate upon thermal cycling than powder product sheet. The improvement in the protective capabilities of both coatings at 1600°F was partially attributed to this factor. Approximately equal quantities of coated arc cast and powder product sheet representative of both coating systems were used at temperatures of 3000°F and higher. Table 5 lists the type of coating failure observed for both systems at each of the test temperatures.

Cyclic oxidation tests were also conducted on the W+(Si-W) coated system at 3500°F in air. In order to obtain some indication of coating reliability at this temperature a random selection of twenty-five (Si-W) coated specimens was made from four separate lots. These lots had been coated by the standard laboratory scale process and contained approximately equal amounts of arc cast and powder product coupons. Each test coupon was exposed in air under cyclic conditions (approximately one cycle per hour) at 3500°F for five hours. A total of twenty-five (25) coated specimens were tested and twenty-four (24) survived the five hour exposure without failure. One specimen suffered a corner failure after three hours of exposure.

Based on the number of specimens tested the probability of a specimen surviving 5 hours of exposure at 3500°F is:

$$\text{Probability (P)} = \frac{\text{no. of specimens surviving (24)}}{\text{no. of specimens tested (25)}} \times 100 = 96\%$$

The confidence level on the probability was obtained from a standard table "Confidence Intervals for Proportions". The interval for the proportion $\frac{24}{25}$ is ± 1% to the probability for a 99% confidence level. Thus any (Si-W) coated tungsten specimen has a 96 ± 1% probability at a 99% confidence level of surviving five hours of exposure at 3500°F in air.

4.3.2 Atmospheric Oxidation Tests of Coating Systems Containing Hafnium

Evaluation of the W+Hf-Si and W+Hf-(Si-W) coated systems was made under

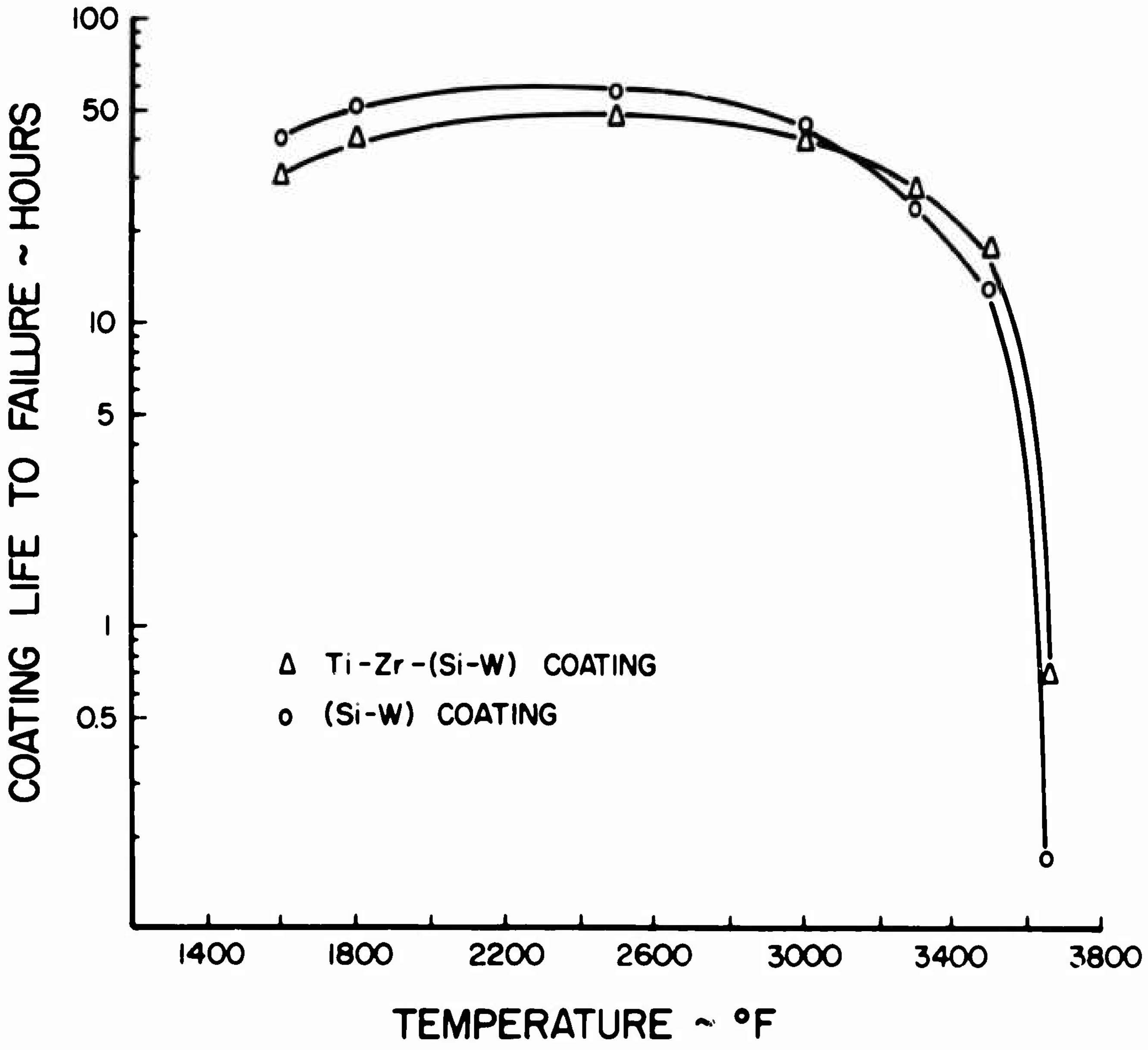


Figure 25 Average Life of (Si-W) and Ti-Zr-(Si-W) Coatings to Failure in Air at Temperatures from 1600 to 3600°F

TABLE 5

Type of Coating Failures on Tungsten Sheet Coupons Tested at Various Temperatures in Air

Temperature - °F	Type of Coating Failure
1600	Gradual breakdown of dense coating structure to porous friable structure. Initiated at outside surface and proceeds inward.
1800	Gradual breakdown of dense coating structure to porous friable structure. Proceeded more slowly than at 1600°F.
2500	Deterioration of coating at sharp edges and corners. Accelerated by thermal cycling because of poor selfhealing capabilities at this temperature.
3000	Gradual deterioration of coating at edges and corners of coupon.
3300	Gradual deterioration of coating at edges and corners of coupon.
3500	Gradual deterioration of coating at edges and corners of coupon.
3600-3650	Generalized melting of coating.

cyclic conditions in air. The W+Hf-Si coated system failed after very short periods of exposure at 3200°F. Failure was caused by a rapid deterioration of the coating at the corners and edges of the test coupons. The W+Hf-(Si-W) system, however, behaved essentially as the W+(Si-W) coated system with respect to the protective nature of the coating. The Hf-(Si-W) coating was protective to the tungsten substrate for 1.5 hours (3 thermal cycles) at 3550-3600°F. The ultimate temperature limit of this coating under atmospheric conditions was determined as 3625-3650°F. Incorporation of hafnium into the (Si-W) coating complex did not raise the ultimate temperature capability of the coating.

4.3.3 Atmospheric Oxidation Tests of Refractory Compound Coating Systems

Initial tests under atmospheric conditions quickly determined that hafnium boride and titanium boride-boron nitride refractory compound coatings applied to tungsten sheet by plasma spray techniques were not gas tight. Exposure at 3000 to 3300°F resulted in pinpoint coating failures on flat surfaces and edges of coupons. Every specimen tested failed catastrophically after less than 5 minutes exposure at these temperatures.

The W+(Si-W) test coupons having refractory compound coatings applied over the (Si-W) coating by plasma spray techniques were evaluated at temperatures from 3300 to 4000°F. The (Si-W)+HfB_2 and (Si-W)+BN combinations were not as protective as (Si-W) coatings alone. Both systems deteriorated below 3500°F after short periods of exposure. Higher temperature capability was demonstrated by the (Si-W) + titanium boride-boron nitride coatings. Test specimens were exposed to temperatures of 3650-3700°F for five minute periods before coating breakdown occurred. (Si-W) coated specimens failed almost immediately at this temperature due to melting and general coating deterioration. Additional tests on W+(Si-W)+(TiN-BN) coated systems were conducted to temperatures of 4000°F, however, 3700°F appeared to be the ultimate temperature capability of this coating. The very short period of exposure to failure of this coating at 3700°F did not indicate a significant advantage over the (Si-W) or Ti-Zr-(Si-W) coatings.

Lower temperature tests for longer periods of time were also conducted on this coating system. Figure 26 shows a coated coupon after 3 hours of cyclic exposure (three thermal cycles) at 3450-3500°F. A (Si-W)-O coated coupon is shown in Figure 27 after the same exposure at 3450-3500°F. Figures 28 and 29 illustrate the similarity in the microstructures of the (Si-W)+(TiN-BN)-O and (Si-W)-O coatings on these coupons.

4.3.4 Static Low Pressure Oxidation Tests of the W+(Si-W) and W+Ti-Zr-(Si-W) Coated Systems

Behavior of the (Si-W) and Ti-Zr-(Si-W) coatings under reduced pressures (air) was studied under static conditions at temperatures above 3000°F. Specimens for these tests were fabricated from Wah Chang Lots II and III 60

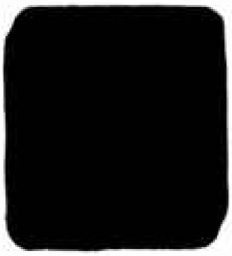


Figure 26 (Si-W)+(TiN-BN)-O Coated Tungsten Coupon after 3 Hours of Cyclic Exposure in Air at 3450-3500° F 1X

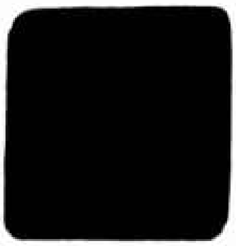


Figure 27 (Si-W)-O Coated Tungsten Coupon after 3 Hours of Cyclic Exposure in Air at 3450-3500° F 1X

Figure 28 Microstructure of (Si-W)+(TiN-BN)-O Coating after 3 Hours of Cyclic Exposure in Air at 3450-3500°F 250X

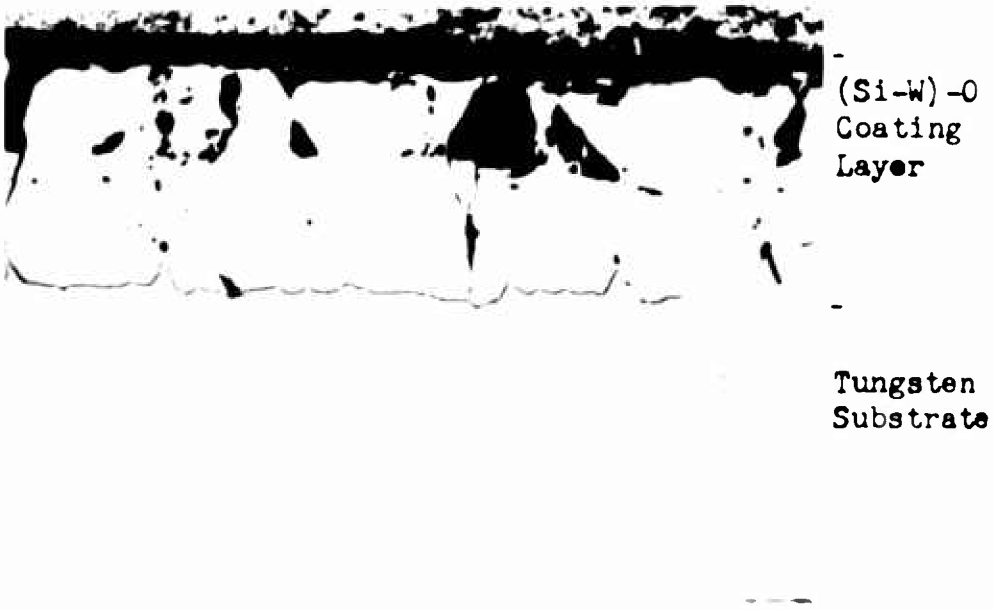


Figure 29 Microstructure of (Si-W)-O Coating after 3 Hours of Cyclic Exposure in Air at 3450-3500°F 250X

mil powder product sheet and from Universal Cyclops 60 mil arc cast sheet. The specimens were 3 inches long x 1/2 inch wide. All specimens were coated in the 2 3/4 inch diameter x 7 inch retort under conditions defined as standard for powder product sheet. Control coupons (1/2 inch square) were coated with each batch of low pressure test specimens. Prior to conducting the low pressure tests, the coated control coupons were exposed in air at 3000°F for 20 hours under cyclic conditions to ensure that the coatings applied were protective.

Specimens were tested by self-resistance heating in an evacuated chamber. This chamber was constructed so that the test specimen could be mounted and firmly clamped between two copper electrodes. A specimen, mounted in the chamber is shown in Figure 30. Figure 31 illustrates the specimen showing electrical contact areas and area achieving the highest temperature during test.

Static pressures in the chamber during testing were maintained by adjusting a series of bleed valves located between the chamber and pumping system. Prior to any test, the chamber was first evacuated to a pressure of less than 1 micron before the desired pressure of air was introduced. A McLeod gage was used to measure pressure. Figure 32 is a photograph of a specimen under test in the low pressure apparatus.

A number of attempts were made to make direct temperature calibrations by comparing optical measurements against readings from a W vs. W-26% Re thermocouple attached directly to the hot area of the specimen. These attempts were unsuccessful. An alternate method of temperature calibration for these tests was used. A temperature correction curve for optical readings on uncoated tungsten had been previously determined in this apparatus. This calibration curve covered the temperature range from 2000°F to the melting point of tungsten. Correlation between this curve and optical readings made on coated tungsten was accomplished in the following manner:

1) a strip of coating was removed from a Ti-Zr-(Si-W)-O (converted) and a (Si-W) coated specimen,

2) each specimen was heated under a vacuum of less than 1 micron to an optically measured temperature of 1800°F on the uncoated surface of the specimen. The optical temperature of the coated surface at the same vertical position was recorded,

3) temperature of the specimen was then raised in 100°F increments (for the uncoated surface) and optical readings at each increment made on the coated surface. These readings were made until the coating melted.

A temperature correction factor for optical readings on Ti-Zr-(Si-W)-O and (Si-W) coatings was calculated from these data. However, because of the indirect method that was utilized to obtain this calibration, all temperatures for low pressure tests are reported in ranges.

Figure 30 Vacuum Chamber Utilized for Low Pressure Tests. Coated Test Specimen is Mounted Between Copper Electrodes

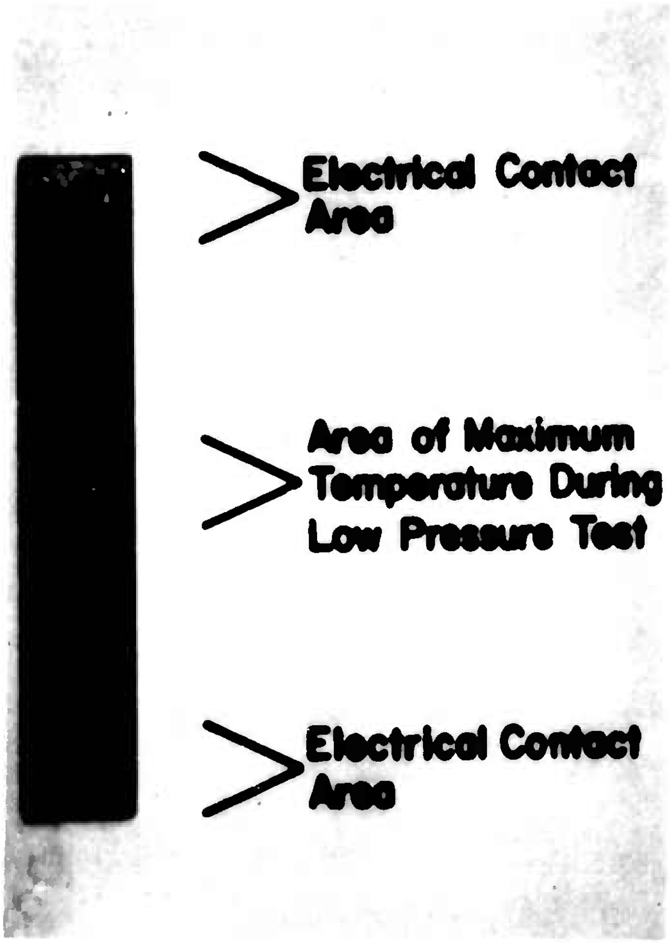


Figure 31 Coated Tungsten Test Specimen Used in Low Pressure Tests 1X

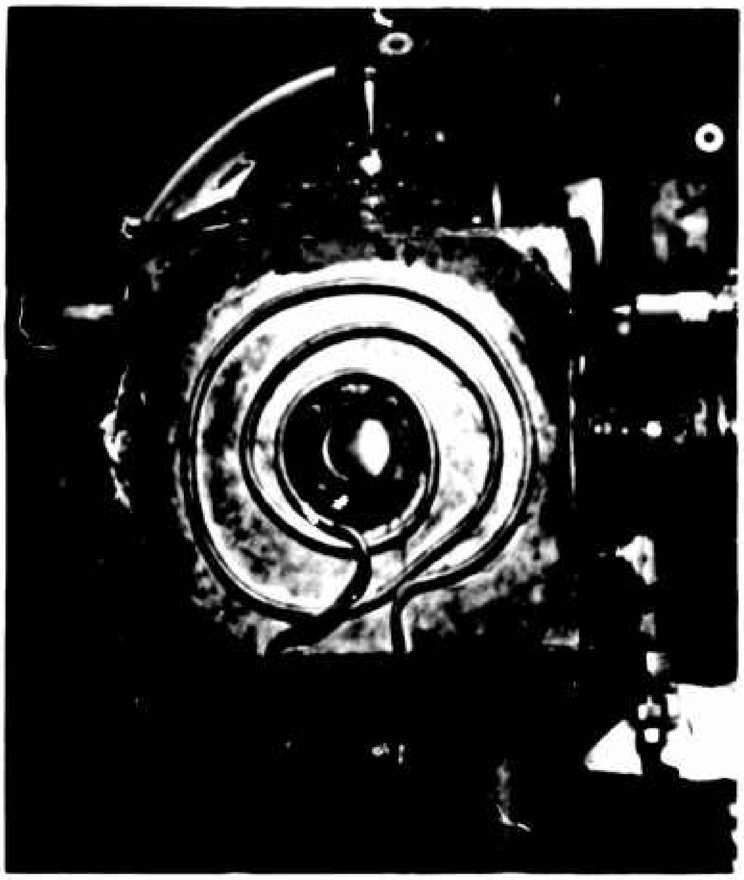


Figure 32 Low Pressure Test Apparatus Illustrating Specimen in Test

Preliminary tests on both the W+(Si-W) and W+Ti-Zr-(Si-W)-O tungsten systems were conducted at pressures of 0.001-0.003 mm Hg (1-3 microns), 0.025 mm Hg (25 microns) and 0.1 mm Hg (100 microns) of air. Specimens were heated to 2000°F rapidly and then the temperature was gradually increased until the coating was observed to melt. Slight variation of the melting points were observed at the different pressures. However, all values were in the range of 3700-3800 (corrected optical temperature). Figures 33 and 34, respectively, illustrate the appearance of the (Si-W)-O and Ti-Zr-(Si-W)-O coated specimens after exposure at 3700-3800°F under 0.1 mm Hg reduced pressure of air. The melting point of the coatings at these pressures was approximately 100°F higher than at one atmosphere.

Tests were also conducted in which coated specimens were heated under a vacuum to an optical temperature of 3000°F. Various pressures of air were then introduced into the test chamber. A change in temperature for a constant power setting was observed, the optical readings being slightly lower as the pressure was increased. The maximum pressure used was 0.1 mm Hg and the optical temperature reading at this pressure was 2970-2980°F. If the chamber was re-evacuated while the power source supplying electrical current to the specimen was held constant an optical reading of 3000°F was once again observed. This reversible change indicated that the variation in surface temperature of the specimen was due to heat convection at the higher pressure and did not result from a change in emissivity of the coating due to reaction with oxygen.

During these preliminary tests the coating was removed from both ends of coated specimens to allow good electrical contact. However, both the (Si-W) and Ti-Zr-(Si-W)-O (converted) coatings were found to be conductive and the procedure was eliminated whenever possible in subsequent testing.

Two series of tests were conducted to determine the behavior of the (Si-W) and Ti-Zr-(Si-W) coatings under reduced pressures of air at high temperatures. The standard test cycle for both test series was 1 hour at 3400-3500°F (corrected optical temperature). Because of overheating problems with the test apparatus the total time of exposure (1 hour) was accumulated in 15 to 20 minute cycles. In the first test series specimens were subjected to low pressure exposure without any prior one atmosphere oxidation exposure (except for the conversion of the Ti-Zr-(Si-W) coating system to the Ti-Zr-(Si-W)-O coating system). In the second test series specimens were pre-oxidized before low pressure exposure. Pre-oxidation consisted of exposure in air at one atmosphere at temperatures above 3000°F.

Table 6 lists pertinent data for Series I low pressure oxidation tests on the W+(Si-W) coated system. Figure 35 illustrates the appearance of all the specimens after testing. Figures 36 through 41 show the structure of the post test coatings at the pressures indicated in the table. As a basis for comparing coating structures, a section of the coating on the cold end of a tested specimen is shown in Figure 42. This is representative of all (Si-W) coated specimens used in the test. Figure 43 shows a protective (Si-W)-O coating after exposure at 3450°F for 1 hour at one atmosphere pressure (air).

Figure 33 The W+(Si-W)-O System After Exposure at 100 Microns Pressure of Air at 3700-3800° F Showing Melting of the Coating

Figure 34 The W+Ti-Zr-(Si-W)-O System After Exposure at 100 Microns Pressure of Air at 3700-3800° F Showing Melting of the Coating

TABLE 6

Series I Static Low Pressure Exposure of W+(Si-W) System - One Hour at 3400-3500°F (Corrected Optical Temperature)

Test Pressure (mm Hg)	Visual Appearance of Coating*	Appearance of Post Test Coating Structure
0.025	Dull-similar to as-coated appearance	Figure 36
0.1	Dull-smooth but darker than normal	Figure 37
1	Semi-glassy - smooth but much darker than normal	Figure 38
5	Glassy-very uneven surface with granular appearance	Figure 39
10	Glassy-rough, pitting of surface	Figure 40
15	Glassy-rough, pitting of surface	Figure 41

* Figure 35 Illustrates the appearance of all specimens after testing

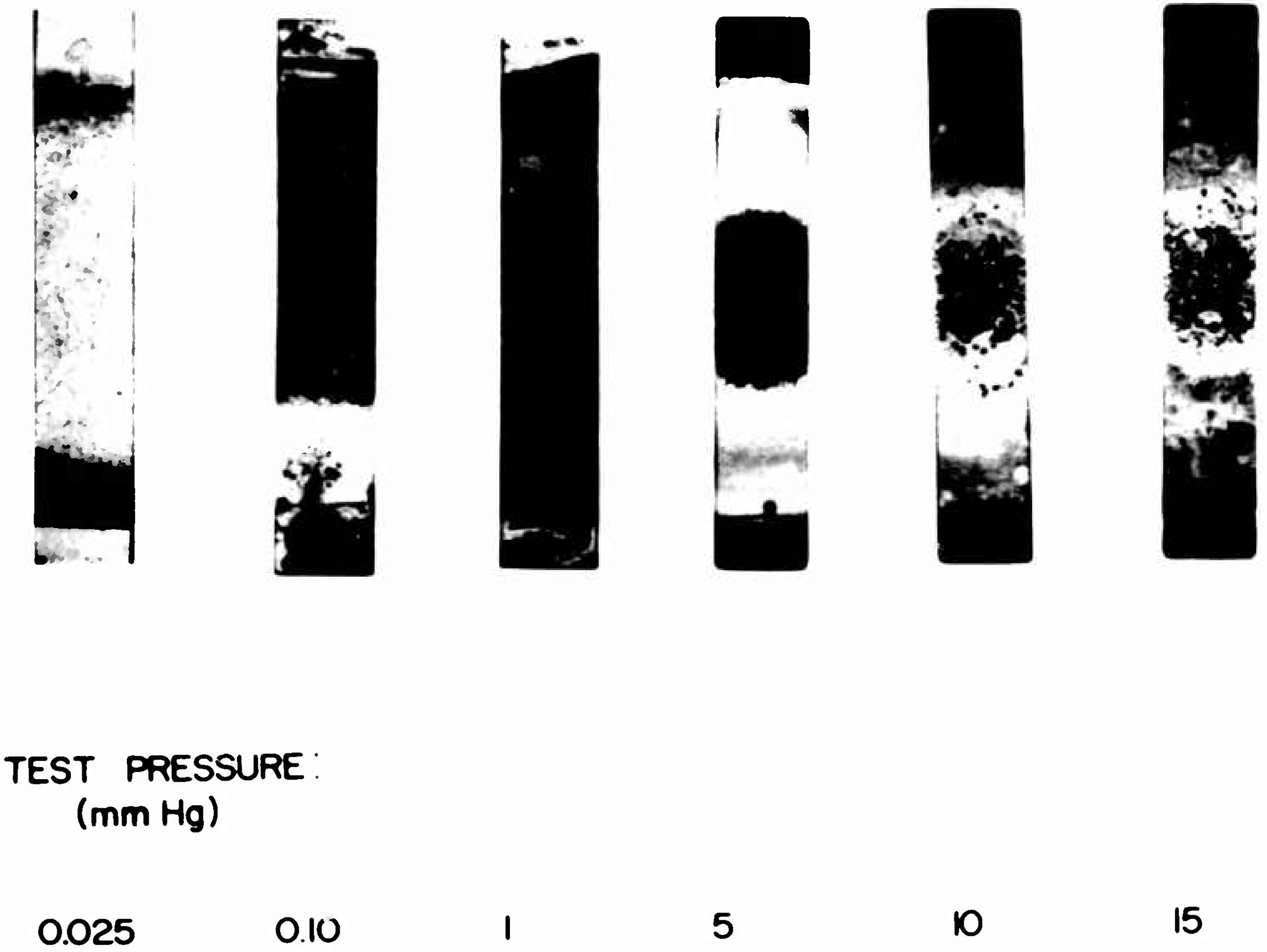


Figure 35 (Si-W)-O Coated Specimens After 1 Hour of Exposure at 3400-3500°F (Corrected Optical Temperature) at Pressures of 0.025, 0.1, 1, 5, 10 and 15 mm Hg

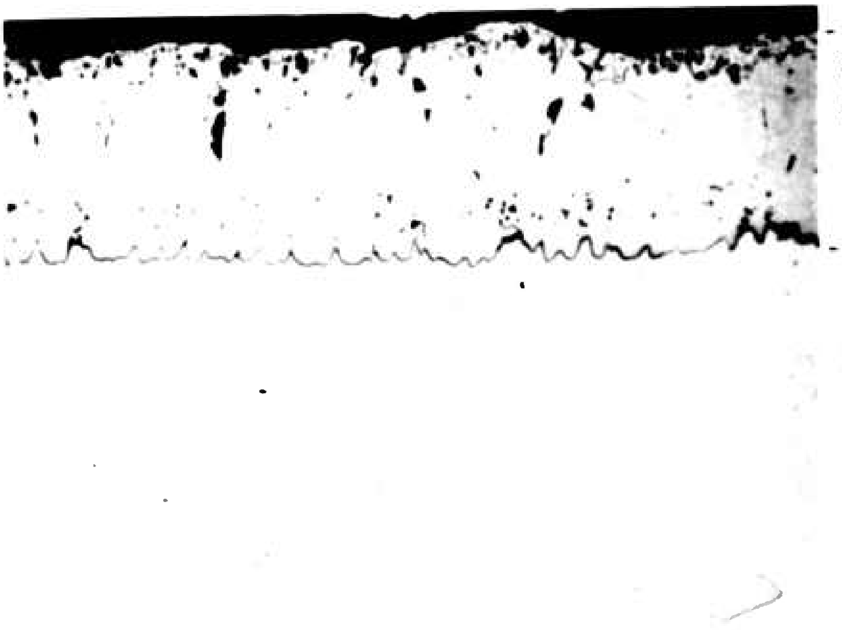


Figure 36 The (Si-W)-O Coating on Tungsten After 1 Hour Exposure at 3400-3500°F at 0.025 mm Hg Pressure 250X

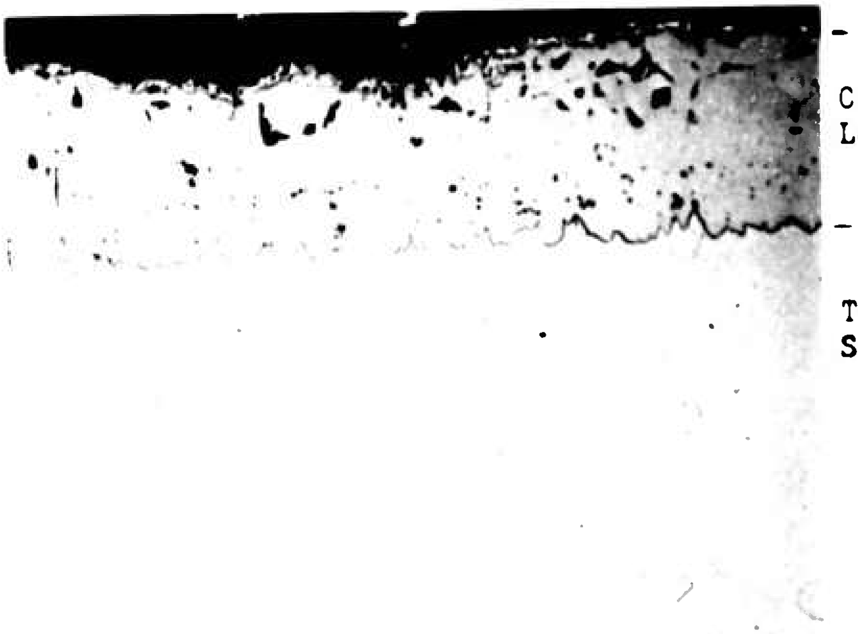


Figure 37 The (Si-W)-O Coating on Tungsten After 1 Hour Exposure 3400-3500°F at 0.1 mm Hg Pressure 250X

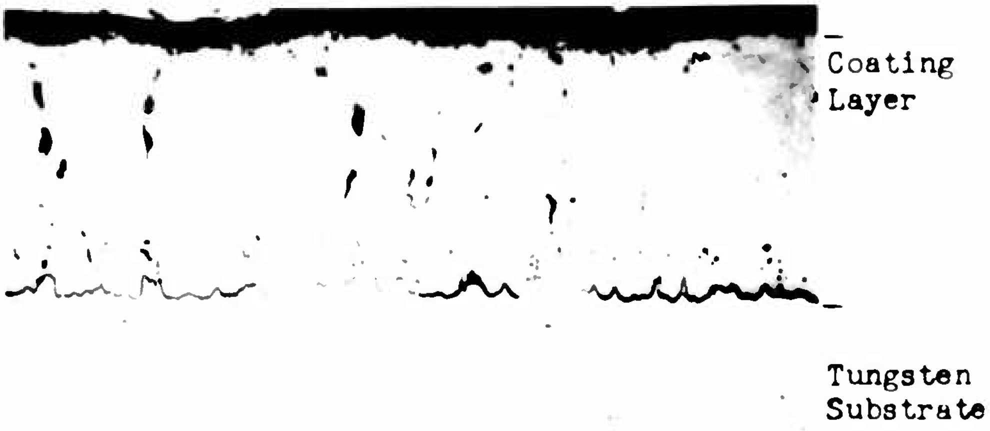


Figure 38 The (Si-W)-O Coating on Tungsten After 1 Hour Exposure at 3400-3500°F at 1 mm Hg Pressure 250X

Figure 39 The (Si-W)-O Coating on Tungsten After 1 Hour Exposure at 3400-3500°F at 5 mm Hg Pressure 250X

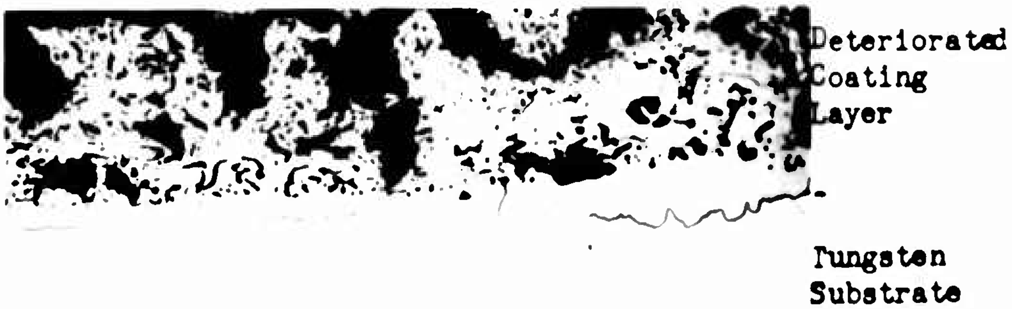


Figure 40 The (Si-W)-O Coating on Tungsten After 1 Hour Exposure at 3400-3500° F at 10 mm Hg Pressure 250X

Figure 41 The (Si-W)-O Coating on Tungsten After 1 Hour Exposure at 3400-3500° F at 15 mm Hg Pressure 250X

Figure 42 The (Si-W) Coating on Cold End of Low Pressure Test Specimen 250X

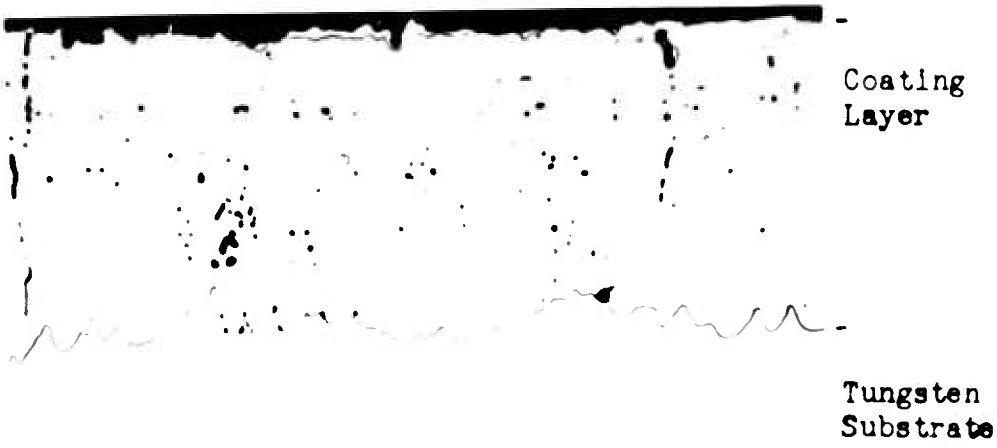


Figure 43 The (Si-W)-O Coating After 1 Hour Exposure at 3450°F at 1 Atmosphere 250X

The protective capabilities of the (Si-W) coating after low pressure exposure were determined by subsequent exposure at 3000°F at one atmosphere. Two tests were conducted in the following manner:

1) a (Si-W) coated system was exposed at 0.025 mm Hg (air) pressure for 15 minutes at 3400-3500°F. The entire specimen was then exposed at 3000°F at one atmosphere for 30 minutes,

2) a (Si-W) coated system was exposed at 0.1 mm Hg (air) pressure for 15 minutes at 3400-3500°F. The entire specimen was then exposed at 3000°F at one atmosphere for 30 minutes.

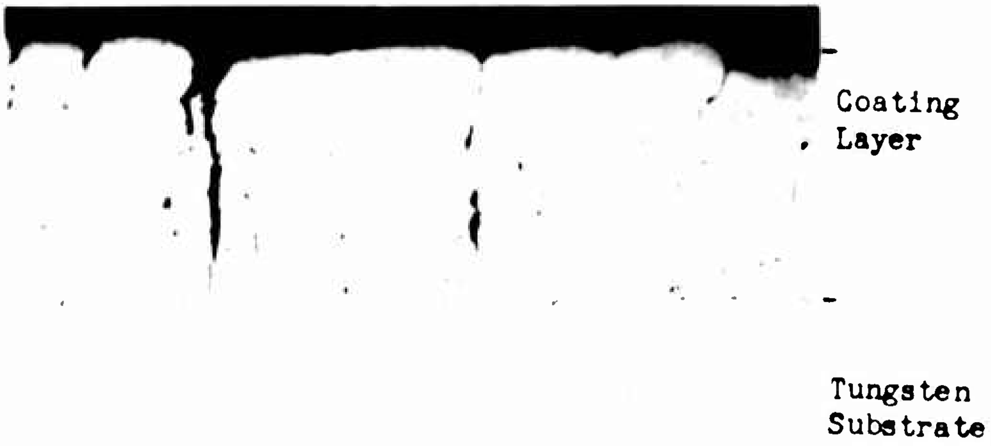
Both coated specimens survived this treatment without failure. Figure 44 shows the coating, initially tested at 0.025 mm Hg, after the atmospheric exposure and Figure 45 shows the specimen initially tested at 0.1 mm Hg, after the atmospheric exposure.

Additional tests in which coated specimens were exposed under low pressure conditions for longer periods before exposure in air at one atmosphere were attempted. However, a reaction between the coating and copper electrodes occurred in every case. Atmospheric exposure of the entire specimen resulted in rapid failure at these contact areas and evaluation could not be made.

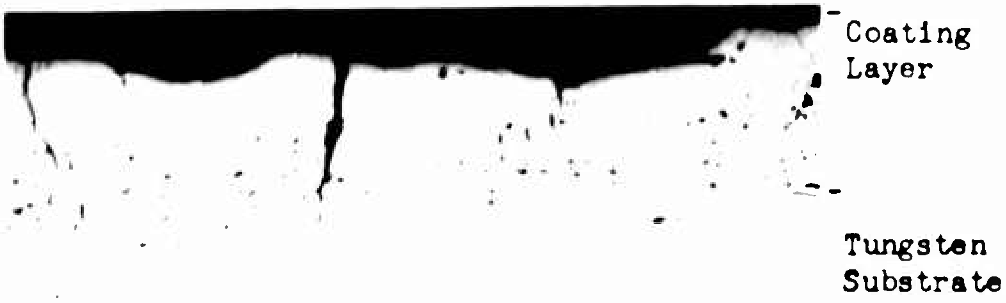
Table 7 lists the data for the Series I low pressure tests on the W+Ti-Zr-(Si-W)-O (converted) system. The entire series of specimens after testing is shown in Figure 46. Figures 47 through 52 (as indicated in the table) illustrate the coating structures after exposure. As a basis for comparison the Ti-Zr-(Si-W)-O coating on the cold end of a tested specimen is illustrated in Figure 53. This coating retained the as-coated structure. A Ti-Zr-(Si-W)-O coating after 1 hour exposure at 3450°F at one atmosphere is shown in Figure 54.

Three Ti-Zr-(Si-W)-O coated specimens were tested under low pressure for short periods of time and then exposed under atmospheric conditions at 3000°F to determine the protective quality of the coating. All specimens survived the two tests. The microstructure of the coated specimen initially exposed at 0.025 mm Hg pressure at 3400-3500°F for 15 minutes and then at one atmosphere at 3000°F for 30 minutes is shown in Figure 55. Figure 56 shows the microstructure of the coated specimen exposed at 0.1 mm Hg pressure for 15 minutes (3400-3500°F) after the atmospheric exposure. Figure 57 illustrates the coating structure initially exposed at 0.025 mm Hg pressure for 30 minutes after the atmospheric exposure.

Additional low pressure tests on the W+Ti-Zr-(Si-W) system were conducted to determine if the conversion treatment was detrimental to low pressure properties of the coating. One hour tests at 3400-3500°F at pressures of 0.025, 0.1 and 1 mm Hg pressure were carried out on Ti-Zr-(Si-W) coated specimens. Coatings on these specimens were not converted.

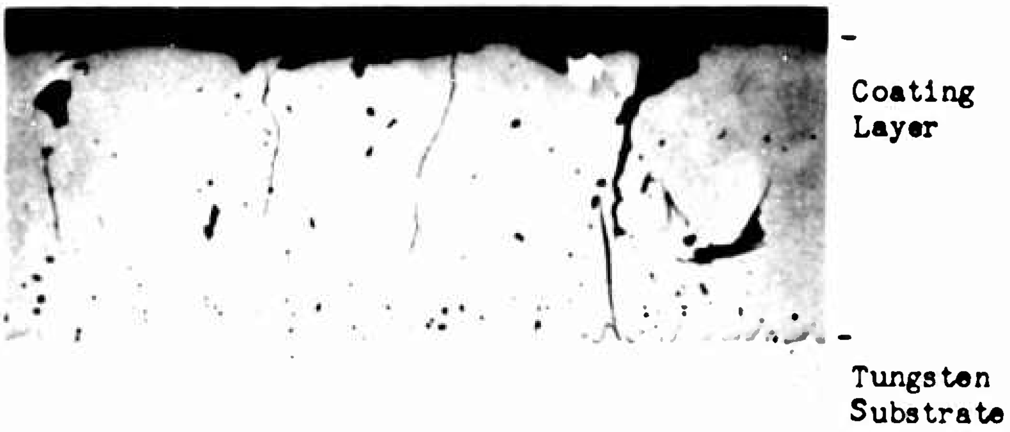


Coating on Cold Area of Specimen During Low Pressure Test



Coating on Hot Area of Specimen During Low Pressure Test

Figure 44 The (Si-W)-O Coating on Tungsten After an Initial Exposure at 3400-3500°F for 15 Minutes at a Pressure of 0.025 mm Hg Followed by a 0.5 Hour Exposure at 3000°F Under Atmospheric Conditions 250X



Coating on Cold Area of Specimen During Low Pressure Test

Coating on Hot Area of Specimen During Low Pressure Test

Figure 45 The (Si-W)-O Coating on Tungsten After an Initial Exposure at 3400-3500°F for 15 Minutes at a Pressure of 0.1 mm Hg Followed by a 0.5 Hour Exposure at 3000°F Under Atmospheric Conditions 250X

TABLE 7

Series I Static Low Pressure Exposure of W+Ti-Zr-(Si-W)-O (Converted) System - One Hour at 3400-3500°F (Corrected Optical Temperature)

Test Pressure (mm Hg)	Visual Appearance of Coating*	Appearance of Post Test Coating Structure
0.025	Dull-craze crack pattern	Figure 47
0.1	Dull-evidence of volatilization	Figure 48
1	Semi-glassy - smooth but some indication of volatilization	Figure 49
5	Glassy-granular appearance with some pitting	Figure 50
10	Glassy-granular appearance	Figure 51
15	Glassy-granular appearance	Figure 52

* Figure 46 Illustrates the appearance of all specimens after testing

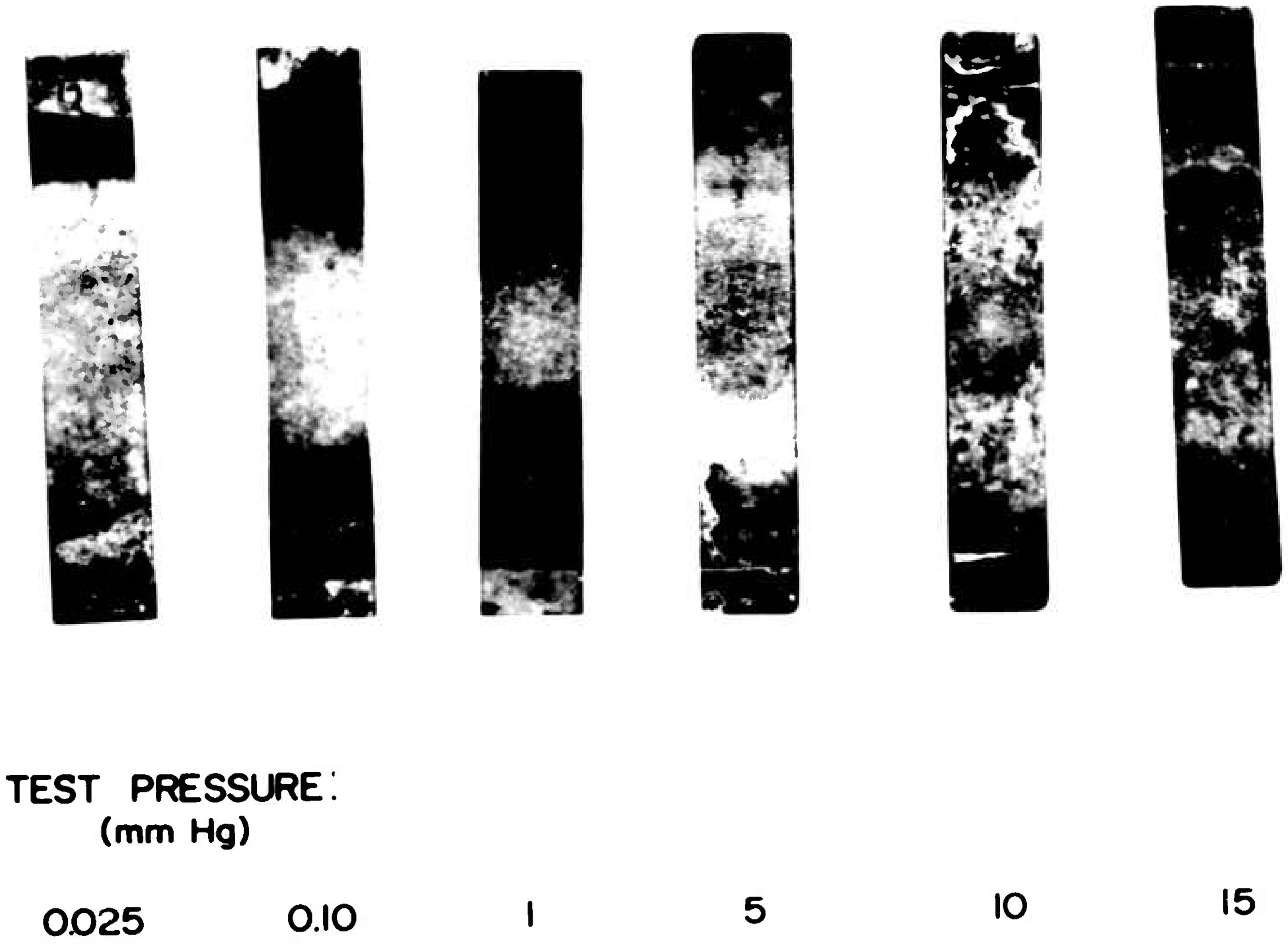


Figure 46 Ti-Zr-(Si-W)-O Coated Specimens After 1 Hour of Exposure at 3400-3500°F (Corrected Optical Temperature) at Pressures 25, 0.1, 1, 5, 10 and 15 mm Hg

Figure 47 The Ti-Zr-(Si-W)-O Coating on Tungsten After 1 Hour of Exposure at 3400-3500°F at 0.025 mm Hg Pressure 250X

Figure 48 The Ti-Zr-(Si-W)-O Coating on Tungsten After 1 Hour of Exposure at 3400-3500°F at 0.1 mm Hg Pressure 250X

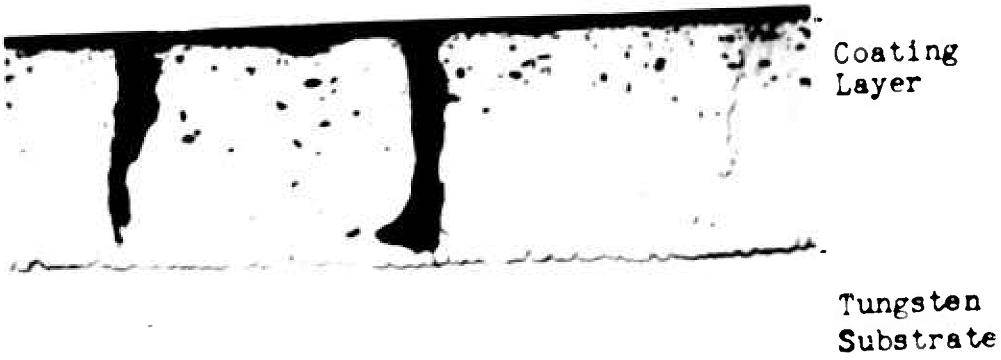


Figure 49 The Ti-Zr-(Si-W)-O Coating on Tungsten After 1 Hour of Exposure at 3400-3500° F at 1 mm Hg Pressure 250X

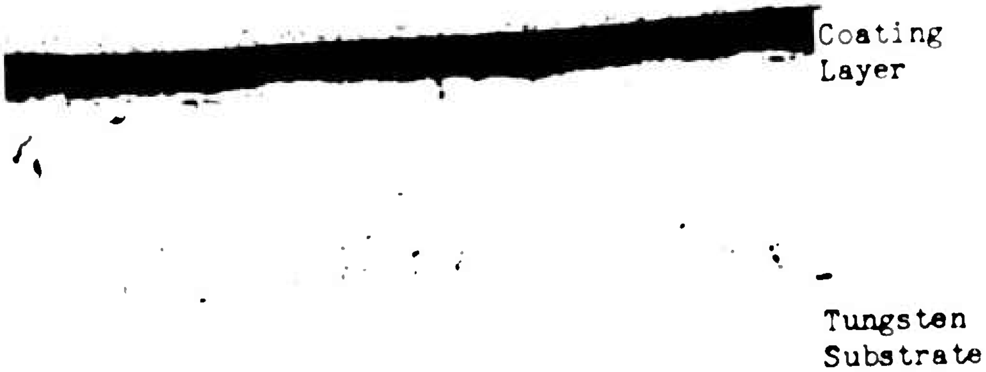


Figure 50 The Ti-Zr-(Si-W)-O Coating on Tungsten After 1 Hour of Exposure at 3400-3500° F at 5 mm Hg Pressure 250X

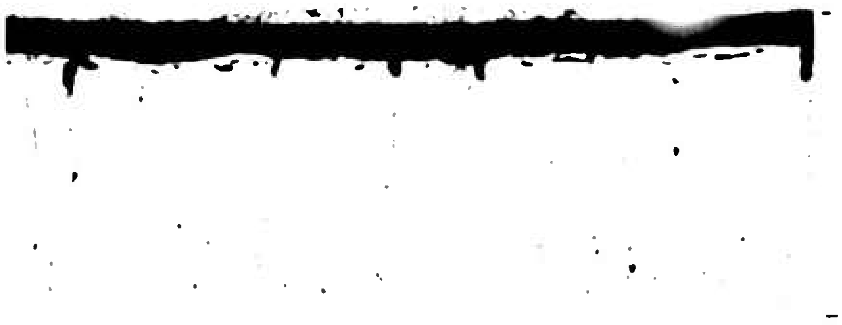


Figure 51 The Ti-Zr-(Si-W)-O Coating on Tungsten After 1 Hour of Exposure at 3400-3500°F at 10 mm Hg Pressure 250X

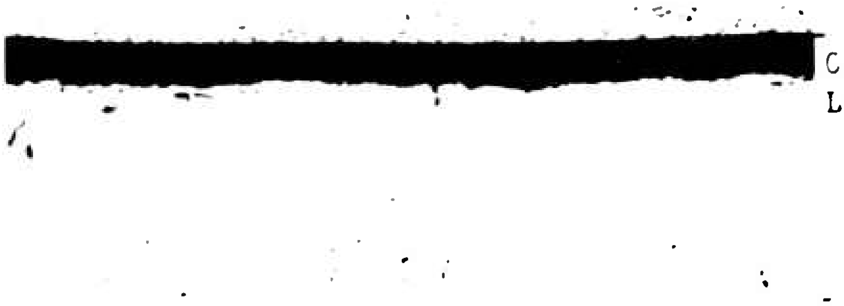


Figure 52 The Ti-Zr-(Si-W)-O Coating on Tungsten After 1 Hour of Exposure at 3400-3500°F at 15 mm Hg Pressure 250X

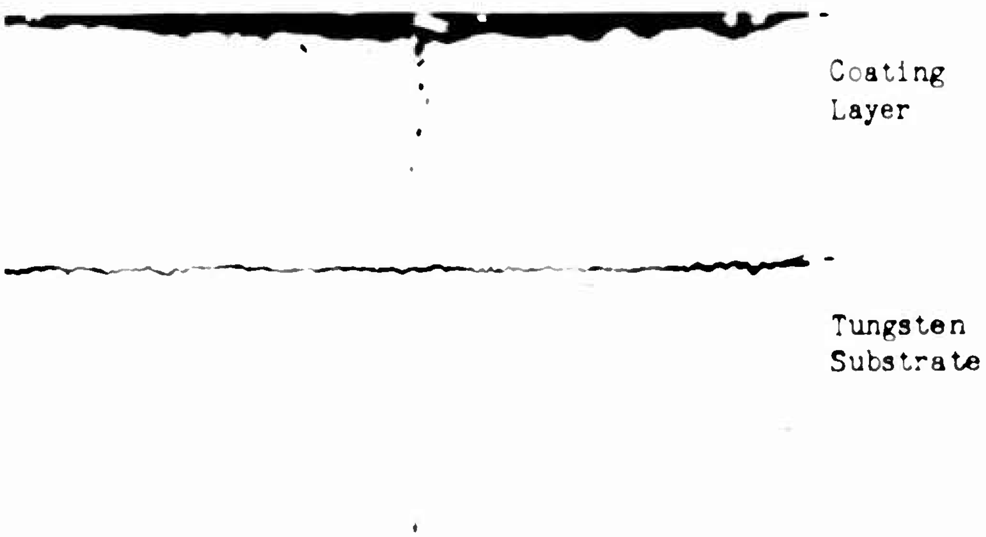


Figure 53 The Ti-Zr-(Si-W)-O Coating on Cold End of Low Pressure Test Specimen 250X

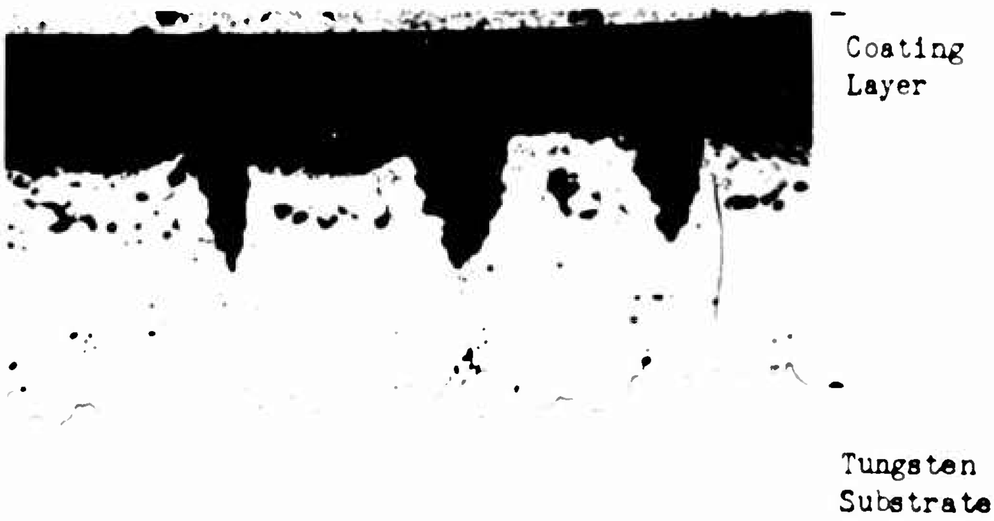
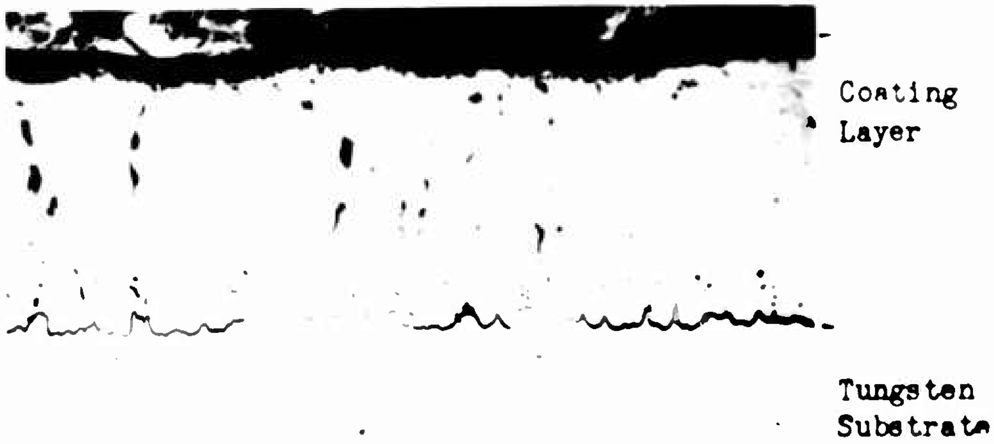


Figure 54 The Ti-Zr-(Si-W)-O Coating After 1 Hour Exposure at 3450°F at One Atmosphere 250X

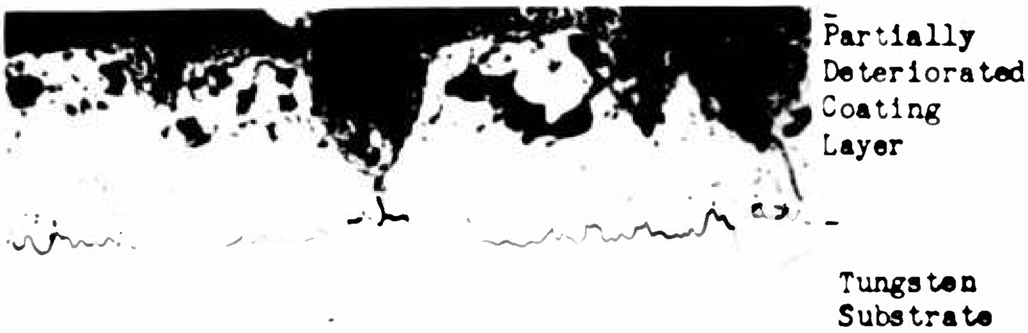
Coating on Cold Area of Specimen During Low Pressure Test

Coating on Hot Area of Specimen During Low Pressure Test

Figure 55 The Ti-Zr-(Si-W)-O Coating on Tungsten After an Initial Exposure at 3400-3500°F for 15 Minutes at a Pressure of 0.025 mm Hg Followed by a 0.5 Hour Exposure at 3000°F Under Atmospheric Conditions 250X

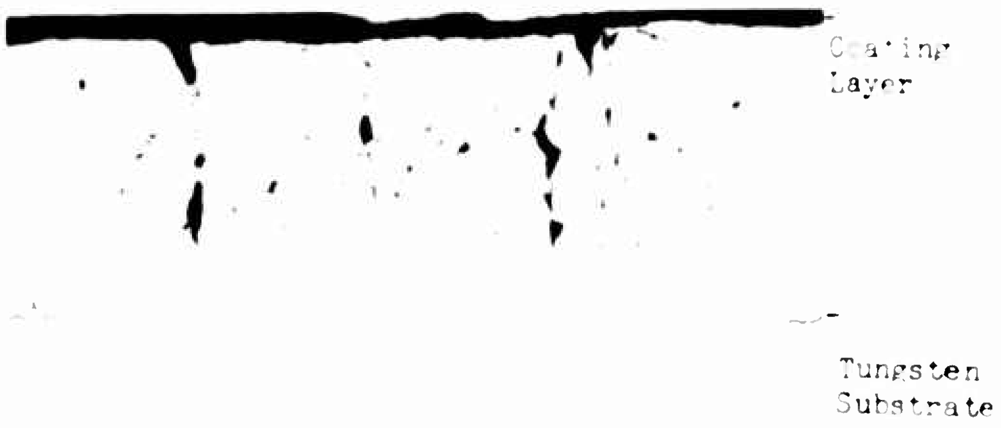


Coating on Cold Area of Specimen During Low Pressure Test

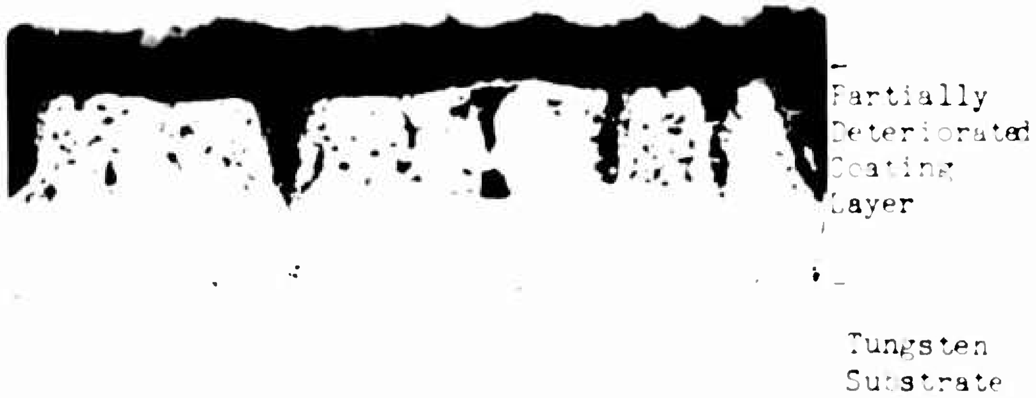


Coating on Hot Area of Specimon During Low Pressure Test

Figure 56 The Ti-Zr-(Si-W)-O Coating on Tungsten After an Initial Exposure at 3400-3500° F for 15 Minutes at a Pressure of 0.1 mm Hg Followed by a 0.5 Hour Exposure at 3000° F Under Atmospheric Conditions 250X



Coating on Cold Area of Specimen During Low Pressure Test



Coating on Hot Area of Specimen During Low Pressure Test

Figure 57 The Ti-Zr-(Si-W)-O Coating on Tungsten After an Initial Exposure of 3400-3500°F for 30 Minutes at a Pressure of 0.025 mm Hg Followed by a 0.5 Hour Exposure at 3000°F Under Atmospheric Conditions 250X

Figure 58 shows the structure of the coating exposed at 0.025 mm Hg pressure, Figure 59 shows the coating exposed at 0.1 mm Hg pressure and Figure 60 the coating exposed at 1 mm.

As indicated, some specimens from Series of the low pressure tests for both coating systems were evaluated by subsequent atmospheric exposure. This method of evaluation, which was carried out on specimens exposed under low pressure conditions for periods of time less than 1 hour, gave an indication of the degree of deterioration resulting from the low pressure exposure. All specimens exposed for 1 hour at reduced pressures of 0.025 to 15 mm Hg were evaluated by metallographic examination. The photomicrographs of the exposed coating structures which have just been presented give some indication of the varying degrees of coating degradation. To present this data in a more unified manner, three general types of conditions were used to classify the coatings after test. These conditions were:

1. general coating deterioration due to volatilization of oxidized coating products (worst condition),

2. little effect or partial coating deterioration due to volatilization of oxidized coating products,

3. formation of protective coating with essentially no volatilization of the oxidized coating products.

Figure 61 graphically presents in a generalized manner the condition of coatings after exposure for 1 hour at 3400-3500°F at the various reduced pressures. Deterioration of both types of coatings was attributed to volatilization of SiO formed from the breakdown of SiO_2 at the low pressures. This effect was particularly evident in the converted Ti-Zr-(Si-W)-O coating exposed at pressures below 1 mm Hg. The deterioration of the (Si-W) coating, particularly after exposure at 3400-3500°F at 5 mm Hg pressure, was also attributed to the volatilization of SiO. These tests also showed that the conversion treatment was detrimental to the low pressure properties of the Ti-Zr-(Si-W) coating at pressures below 1 mm.

Static low pressure oxidation tests in Series II were conducted by first pre-oxidizing coated specimens in air at one atmosphere at temperatures of 3000°F and higher. The specimens were then subjected to exposure at 3400-3500°F at reduced pressures from 0.025 mm Hg to 15 mm Hg.

Table 8 lists the conditions under which the W+(Si-W) system was pre-oxidized and exposed under reduced pressure. One control specimen was included as a basis for comparison. This specimen was pre-oxidized but not exposed at reduced pressures. The coating structure of this control specimen after pre-oxidation in air at 3350°F for 15 minutes is shown in Figure 62. The coating structure of specimens, pre-oxidized at 3350°F for 15 minutes and then exposed at the various reduced pressures are shown in the following figures:

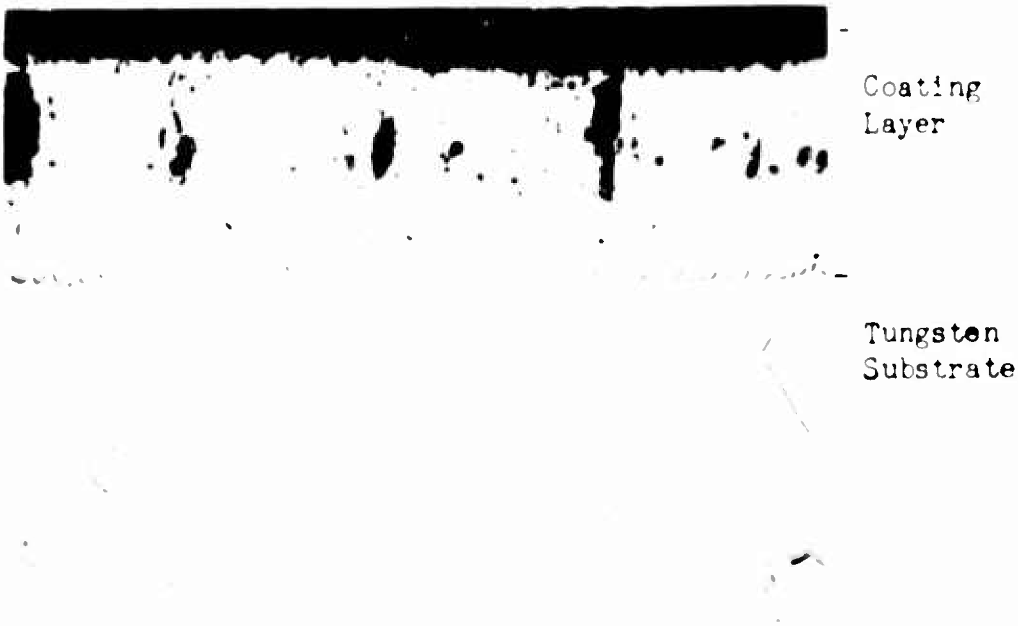


Figure 58 Ti-Zr-(Si-W) Coating (Not Converted) After 1 Hour Exposure at 3400-3500°F at a Pressure of 0.0.5 mm Hg 250X

Figure 59 Ti-Zr-(Si-W) Coating (Not Converted) After 1 Hour Exposure at 3400-3500°F at a Pressure of 0.1 mm Hg 250X

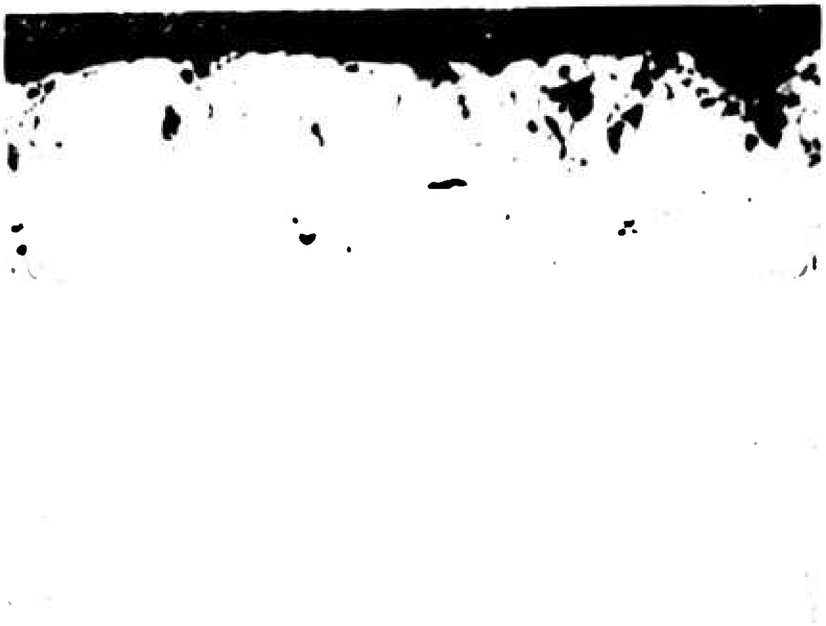


Figure 60 Ti-Zr-(Si-W) Coating (Not Converted) After 1 Hour Exposure at 3400-3500° F at a Pressure of 1 mm Hg 250X

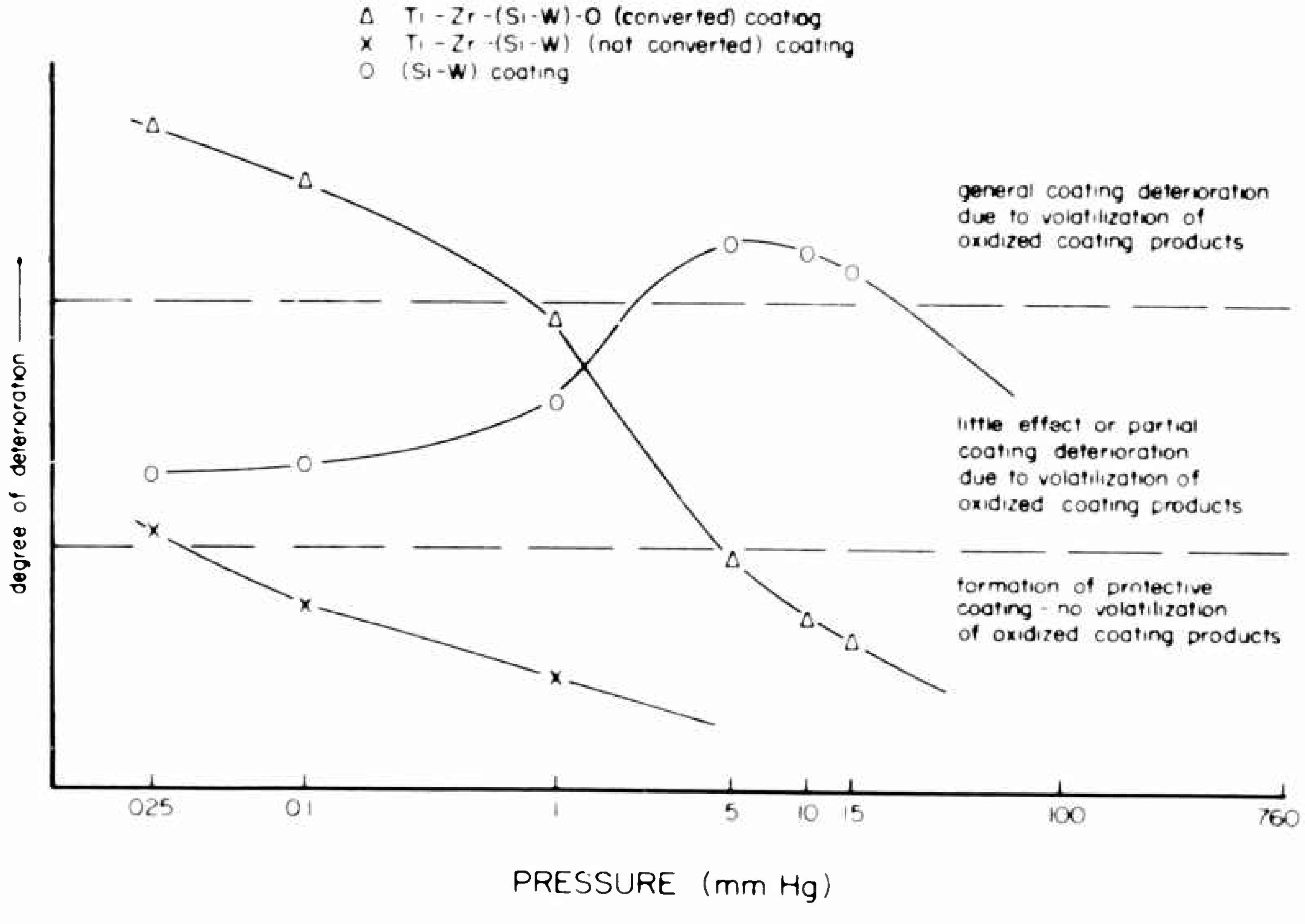


Figure 61 Degree of Coating Deterioration at 3400-3500°F After 1 Hour Exposure at Various Reduced (Air) Pressures

TABLE 8

Series II - Static Low Pressure Tests of Pre-Oxidized W+(Si-W) System

Pre-Oxidation Treatment*		Low Pressure Exposure			Post Test
Temp. - °F	Time - Min.	Temp. - °F	Pressure-mm Hg	Time-Min.	Coating Structure
3350	15	--------------Control----------------			
3350	15	3400-3500	0.025	60	Slight deterioration
3350	15	3400-3500	0.1	60	Moderate deterioration on periphery
3350	15	3400-3500	1	60	Severe deterioration
3350	15	3400-3500	5	60	Moderate deterioration
3350	15	3400-3500	10	60	Slight deterioration
3350	15	3400-3500	15	60	Essentially no deterioration
3000	15	3400-3500	0.025	60	Severe deterioration
3000	30	3400-3500	0.025	60	Severe deterioration

* One atmosphere pressure

Figure 62 (Si-W)-O Coating After 15 Minutes Exposure at 3350°F in One Atmosphere of Air 250X

Low Pressure Exposure	Figure No.
0.025 mm Hg	63
0.1 mm Hg	64
1 mm Hg	65
5 mm Hg	66
10 mm Hg	67
15 mm Hg	68

Table 9 lists the conditions of testing in Series II for the W+Ti-Zr-(Si-W)-O (converted) system. Three pre-oxidation temperatures were used. One control specimen was exposed at 3350°F for 15 minutes, Figure 69 shows the structure of this coating.

Severe coating deterioration was observed on all pre-oxided specimens exposed at 3400-3500°F at pressures lower than 5 mm Hg. Specimens pre-oxidized at 3350°F for 15 minutes and exposed at 3400-3500°F at pressures of 5, 10 and 15 mm, respectively, showed only moderate to slight coating deterioration. Figure 70 illustrates the coating structure of the specimen pre-oxidized at 3350°F for 15 minutes and exposed under 0.025 mm Hg reduced pressure at 3400-3500°F for 1 hour. The extent of deterioration in this structure due to volatilization of oxidized coating products was representative of all coatings which suffered severe deterioration. The pre-oxidized coating least affected by the low pressure exposure is shown in Figure 71. This specimen was pre-oxidized at 3350°F for 15 minutes and then exposed under a reduced pressure of 15 mm for 1 hour at 3400-3500°F.

Figure 72 graphically illustrates the generalized effect of low pressure exposure at 3400-3500°F for 1 hour on the (Si-W)-O and Ti-Zr-(Si-W)-O (converted) coatings pre-oxidized for 15 minutes at 3350°F. Classification of the condition of these coating structures was made on the same basis as was used to classify the coating structures from Series I of the low pressure tests.

Based on the plots presented in Figures 61 and 72 the following generalizations can be made:

1. The protective oxide ceramic layers formed at one atmosphere on both coating systems appear to become less stable at reduced pressures approaching 10 mm Hg,

2. In comparing the (Si-W) and (Si-W)-O (pre-oxidized) coatings the maxima in the curve (most severe coating deterioration) is shifted from 5-10 mm Hg for the (Si-W) coating to 1 mm for the (Si-W)-O (pre-oxidized) coating. This indicates pre-oxidation has extended the protective range for this system to a slightly lower pressure but does not eliminate the deterioration maxima,

3. This deterioration maxima apparently occurs in a pressure region which favors the formation and volatilization of SiO,

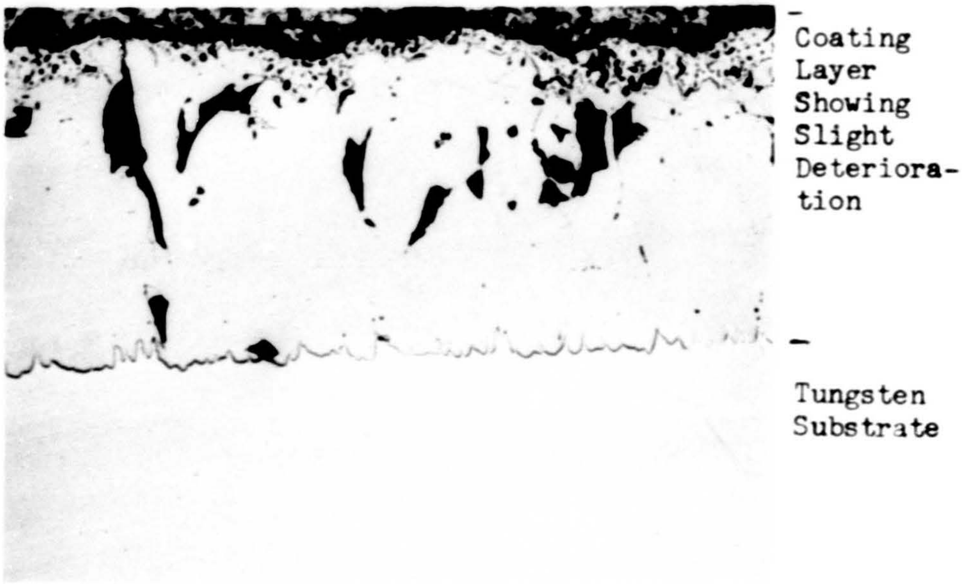


Figure 63 (Si-W)-O Coating (Pre-Oxidized at 3350°F) After 1 Hour Exposure at 3400-3500°F at a Pressure of 0.025 mm Hg 250X

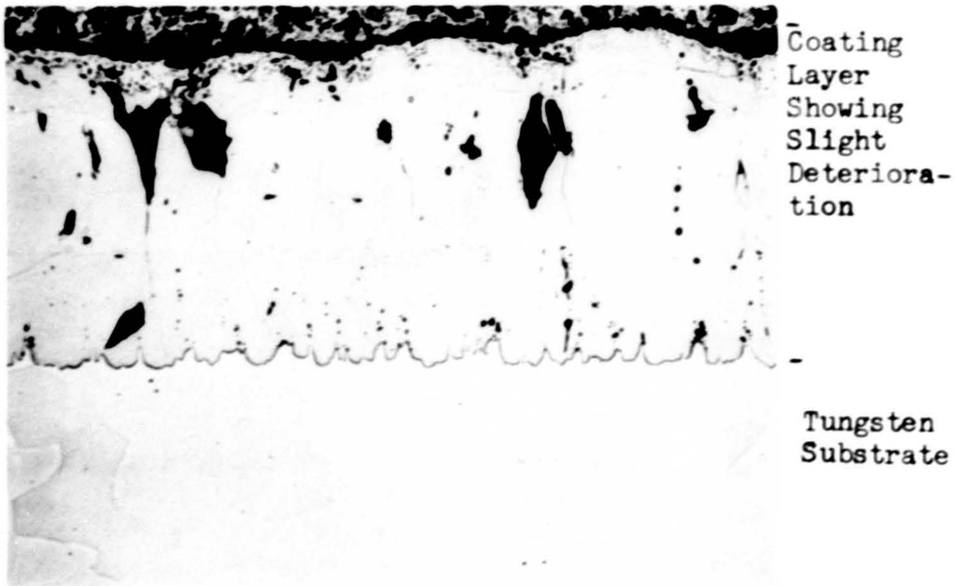


Figure 64 (Si-W)-O Coating (Pre-Oxidized at 3350°F) After 1 Hour Exposure at 3400-3500°F at a Pressure of 0.1 mm Hg 250X

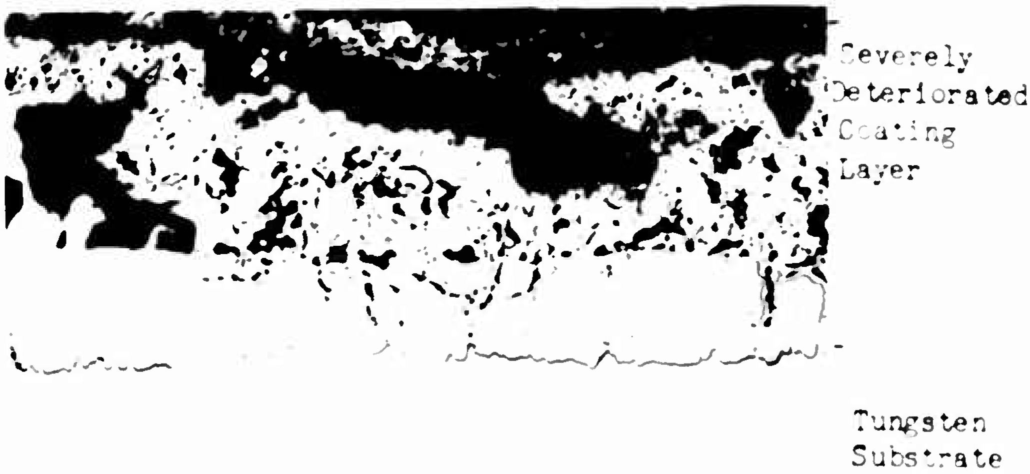


Figure 65 (Si-W)-O Coating (Pre-Oxidized at 3350° F) After 1 Hour Exposure at 3400-3500° F at a Pressure of 1 mm Hg 250X

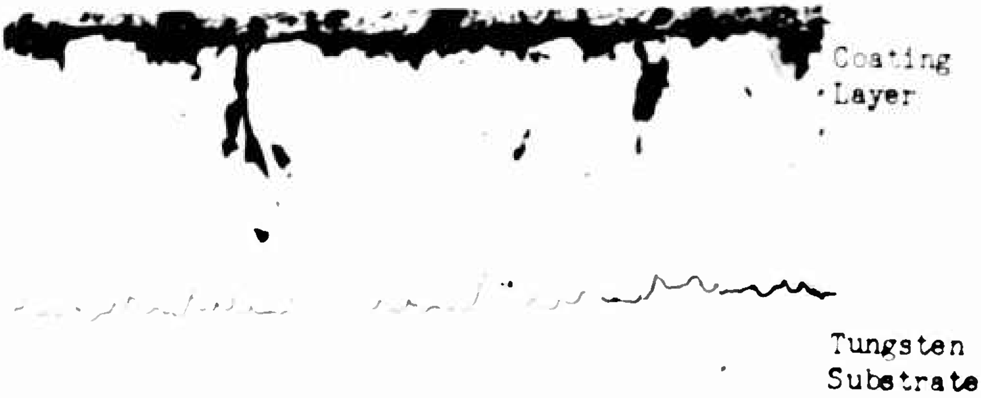


Figure 66 (Si-W)-O Coating (Pre-Oxidized at 3350° F) After 1 Hour Exposure at 3400-3500° F at a Pressure of 5 mm Hg 250X

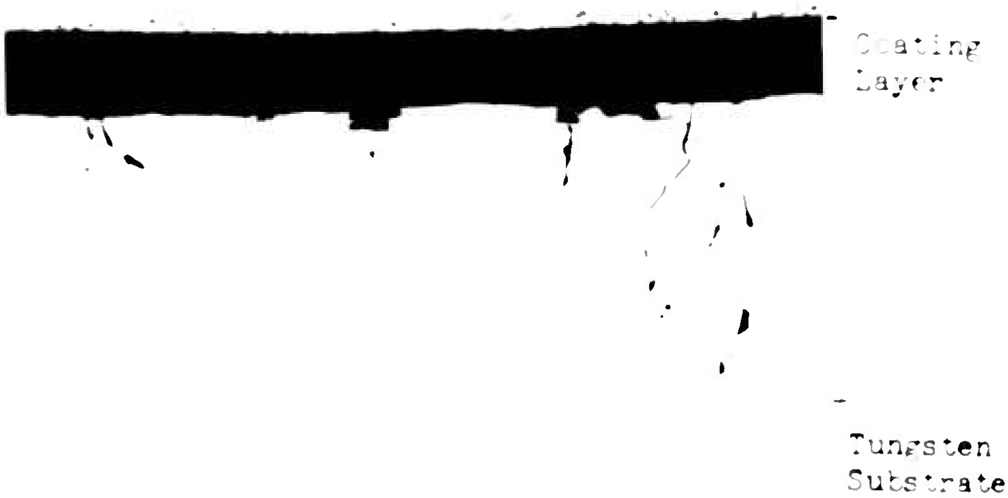


Figure 67 (Si-W)-O Coating (Pre-Oxidized at 3350°F) After 1 Hour Exposure at 3400-3500°F at a Pressure of 10 mm Hg 250X

Figure 68 (Si-W)-O Coating (Pre-Oxidized at 3350°F) After 1 Hour Exposure at 3400-3500°F at a Pressure of 15 mm Hg 250X

TABLE 9

Series II - Static Low Pressure Tests of Pre-Oxidized W+Ti-Zr-(Si-W)-O (Converted) System

Pre-Oxidation Treatment*		Low Pressure Exposure			Post Test
Temp. - °F	Time - Min.	Temp. - °F	Pressure-mm Hg	Time-Min.	Coating Structure
3350	15	Control			-
3350	15	3400-3500	0.025	60	Severe deterioration
3350	15	3400-3500	0.1	60	Severe deterioration
3350	15	3400-3500	1	60	Severe deterioration
3350	15	3400-3500	5	60	Moderate deterioration
3350	15	3400-3500	10	60	Slight deterioration
3350	15	3400-3500	15	60	Slight deterioration
3200	30	3400-3500	0.1	60	Severe deterioration
3200	30	3400-3500	1	60	Severe deterioration
3000	15	3400-3500	0.1	60	Severe deterioration
3000	30	3400-3500	1	60	Severe deterioration

* One atmosphere pressure

Figure 69 Ti-Zr-(Si-W)-O Coating After 15 Minutes Exposure at 3350°F in One Atmosphere of Air 250X

Figure 70 Ti-Zr-(Si-W)-O Coating (Pre-Oxidized at 3350°F) After 1 Hour Exposure at 3400-3500°F at a Pressure of 0.025 mm Hg 250X

Figure 71 Ti-Zr-(Si-W)-O Coating (Pre-Oxidized at 3350°F) After 1 Hour Exposure at 3400-3500°F at a Pressure of 15 mm Hg 250X

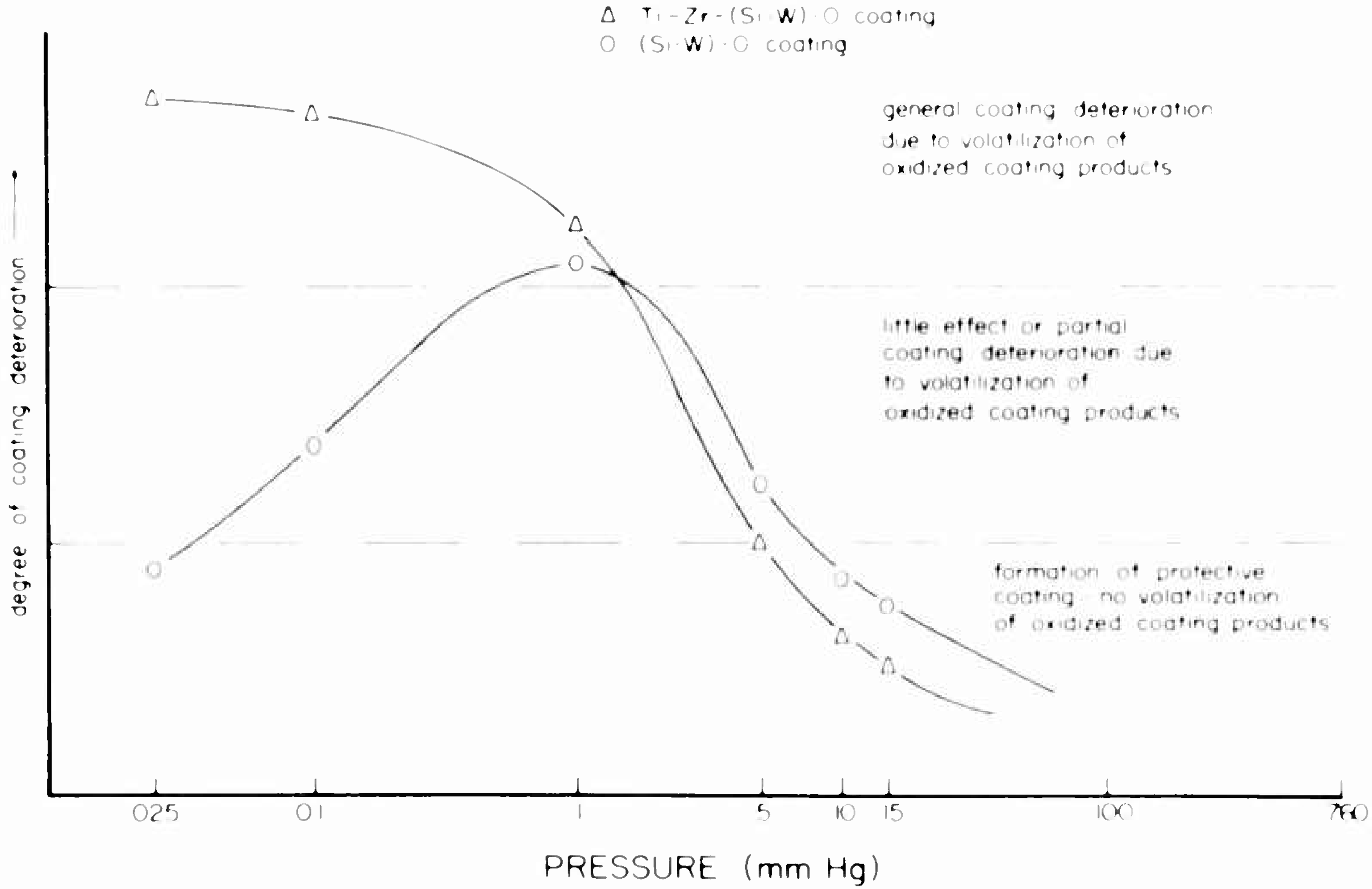


Figure 72 Degree of Coating Deterioration of Pre-Oxidized (15 Minutes at 3350°F at One Atmosphere) (Si-W)-O and Ti-Zr-(Si-W)-O Coatings at 3400-3500°F After 1 Hour Exposure at Various Reduced (Air) Pressures

4. At pressures below 0.1 mm Hg the (Si-W) and (Si-W)-O (pre-oxidized) coatings behave similarly. This must be a pressure region in which no appreciable volatile oxidation products are formed,

5. In comparing the curves for Ti-Zr-(Si-W) (non-converted) coatings with Ti-Zr-(Si-W)-O (either converted or pre-oxidized) it is apparent that conversion or pre-oxidation results in a significantly greater degree of coating deterioration at pressures of 5 mm Hg or less,

6. In the non-converted Ti-Zr-(Si-W) coating the activity of silicon is apparently low enough such that at reduced pressures neither SiO_2 or SiO are formed. Thus, in this condition the coating does not suffer deterioration in these low pressure ranges,

7. In the pre-oxidized or converted Ti-Zr-(Si-W)-O coatings at pressures below 5 mm Hg the complex oxide formed at one atmosphere appears to be unstable. It is most likely that one of the decomposition products is SiO_2 which in turn forms SiO. The volatilization of SiO results in severe coating deterioration indicated at pressures below 5 mm Hg.

4.3.5 Dynamic Low Pressure Oxidation Tests of the W+(Si-W) and W+Ti-Zr-(Si-W) Coated Systems

Dynamic low pressure oxidation tests were conducted on the W+(Si-W) and W+Ti-Zr-(Si-W)-O (converted) systems. Curved sheet specimens, 1 inch wide x 2 inches long, which simulated a leading edge configuration were used for these tests. Both coating systems were applied by the standard laboratory scale procedures. The 3 1/4 inch diameter x 10 inch coating retort was utilized for the coating application.

Testing was conducted in a large environmental chamber. A 60 KV Thermal Dynamic plasma flame gun, mounted in the chamber was used to obtain the high velocity simulated air (80% N_2-20% O_2) at reduced chamber pressures. Specimens were heated by exposure to the plasma flame. A more detailed description of this equipment is presented in Section 5.

Prior to conducting any oxidation tests, heat flux measurements were made of the plasma flame at three (3) fixed distances from the plasma gun at a chamber pressure of 5-10 mm. Exit gas velocities were in the range of 2000-2800 ft/sec. These values were:

Specimen Distance from Nozzle (Inches)	Heat Flux BTU/ft^2/sec
0.750	275
1.125	325
1.750	180

The apparent anomaly of the lower heat flux at a distance 0.75 inch from the gun nozzle as compared to that measured at 1.125 inches was attributed to the flame pattern under the reduced chamber pressure. Various methods (both optical and thermocouple) were tried to directly measure surface temperature of the specimens under test but none proved to be successful. Test temperatures were therefore estimated indirectly from heat flux measurements which could be made accurately at both one atmosphere and reduced pressure. In one atmosphere tests both heat flux and temperature measurements were made. It was assummed therefore that a comparable temperature would be reached in a specimen in the low pressure test for a comparable heat input. On this basis the following temperatures were estimated for the erosion area of specimens under low pressure test:

Specimen Distance from Nozzle (Inches)	Temperature °F
0.750	3200-3300
1.125	3300-3400
1.750	2900-3000

Pressure of the plasma flame was measured at each of the three fixed test distances from the gun nozzle in the flame center and 3/8 inch away from the center. At the 0.75 and 1.125 inch positions pressure in the flame center was 16-20 mm and pressure 3/8 inch away from the center was 40-45 mm Hg. At 1.750 inches from the gun nozzle a rather constant pressure of 16 to 19 mm was measured from the center to the outside (1" radius) of the flame. All measurements were made at a tank pressure of 5-10 mm.

The tests were carried out in the following manner:

1) curved sheet specimens were positioned in a specimen holder. This specimen holder was fixtured so that specimens could be moved in and out of the plasma flame from an external control,

2) the plasma gun, mounted in the chamber was ignited at atmospheric pressure. The specimen holder was positioned so that the specimen to be tested was not exposed to the plasma flame on start up,

3) the environmental chamber, with gun firing, was evacuated to a chamber pressure of 5-10 mm,

4) the specimen was introduced into the plasma flame at a fixed distance from the plasma gun nozzle. Each specimen was cycled to ambient temperature after every ten minute period of testing.

The complete series of tests on coated and control specimens conducted under the above conditions are listed in Table 10. One uncoated (control) tungsten specimen was exposed at each fixed test distance employed for the coated specimens. The very short time to complete burnthrough of the 60 mil control

TABLE 10

Dynamic Low Pressure Erosion Tests

System	Pre-Test Treatment	Gun Specimen Distance (Inches)	Heat Flux BTU/ft^2/sec	Exposure Time (Minutes)	Results
Uncoated tungsten (Control)	Etched	0.75	275	0.6 (35 seconds)	Burnthrough in high pressure areas of flame
W+(Si-W)	None (as-coated)	0.75	275	40	No coating failure
W+Ti-Zr-(Si-W)-O	Converted	0.75	275	45	No coating failure
Uncoated tungsten (Control)	Etched	1.125	325	0.5 (28 seconds)	Burnthrough in high pressure areas of flame
W+(Si-W)	None (as-coated)	1.125	325	60	No coating failure
W+Ti-Zr-(Si-W)-O	Converted	1.125	325	60	No coating failure
Uncoated tungsten (Control)	Etched	1.750	180	2	Burnthrough of specimen
W+(Si-W)	None (as-coated)	1.750	180	60	No coating failure
W+Ti-Zr-(Si-W)-O	Converted	1.750	180	60	No coating failure
W+(Si-W)-O	Exposed at 3200°F (0.5 hour) at one atmosphere	0.75	275	60	No coating failure
W+Ti-Zr-(Si-W)-O	Converted+exposed at 3200°F (0.5 hour) at one atmosphere	0.75	275	60	No coating failure
W+(Si-W)-O	Exposed at 3200°F (0.5 hour) at one atmosphere	1.125	325	60	No coating failure
W+Ti-Zr-(Si-W)-O	Converted+exposed at 3200°F (0.5 hour) at one atmosphere	1.125	325	60	No coating failure
W+(Si-W)-O	Exposed at 3200°F (0.5 hour) at one atmosphere	1.750	180	60	No coating failure
W+Ti-Zr-(Si-W)-O	Converted+exposed at 3200°F (0.5 hour) at one atmosphere	1.750	180	60	No coating failure

specimens (35 seconds at 0.75 inch, 28 seconds at 1.125 inches and 120 seconds at 1.750 inches) demonstrated the severity of the test conditions. In addition, the pattern of burnthrough also demonstrated the pressure profile of the plasma flame at the reduced pressure. Burnthrough occurred in the high pressure areas of the plasma flame.

Figure 73 illustrates the appearance of the control specimen and both coated specimens (not pre-oxidized) after exposure at the gun-specimen test distance of 0.75 inch. Figure 74 shows the same systems (control and coated specimens) after exposure at 1.125 inches from the gun and Figure 75 shows specimens after exposure at 1.75 inches. The portion of the coating on these test specimens in the erosion area of the plasma flame was glassy after exposure. Some discoloration was evident generally on all specimens but there was no indication of coating deterioration.

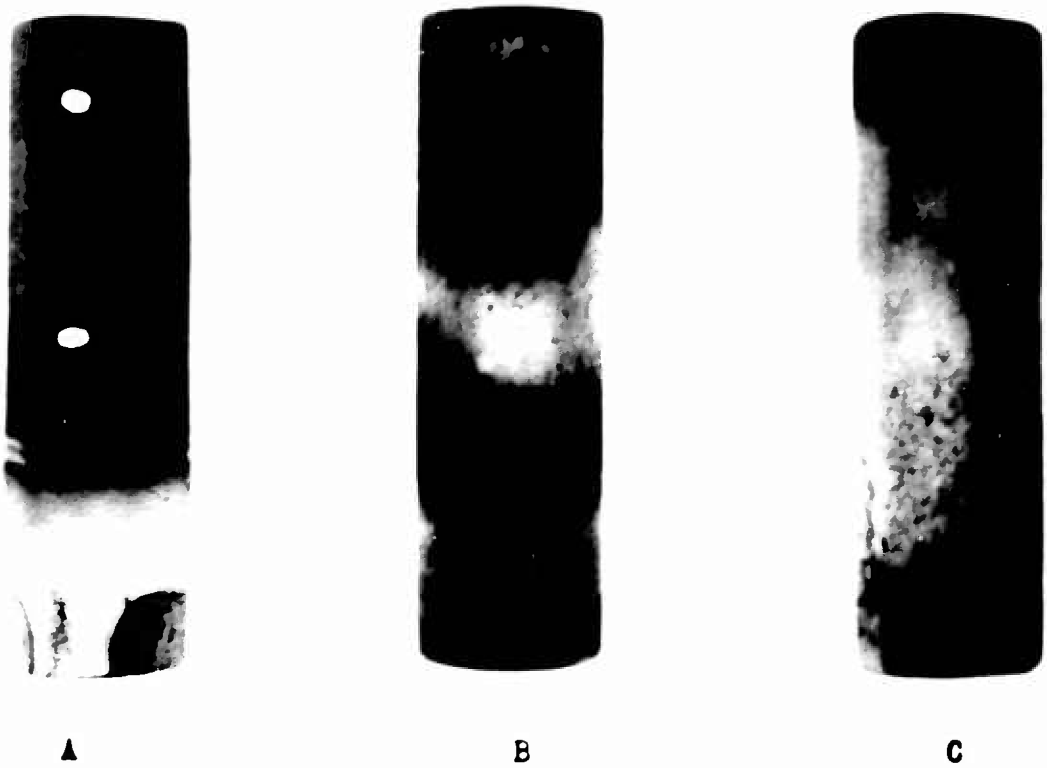
Coated specimens pre-oxidized at 3200°F for 0.5 hour at one atmosphere all survived the low pressure tests without failure. However, after testing, a loosely adherent layer was formed over the areas exposed to the plasma flame. Figure 76 shows the (Si-W)-O coated specimens and Figure 77 the Ti-Zr-(Si-W)-O coated specimens after test at the three gun-specimen distances.

4.4 Thermal Mechanical Tests

4.4.1 Tensile Properties of Coated Arc Cast Sheet

Tensile specimens were fabricated from the 60 mil arc cast sheet stock so that a comparison of the tensile properties of coated arc cast and coated powder product sheet could be made. Tensile properties of coated powder product sheet at various temperatures under vacuum, argon and in air had been determined and reported in Technical Documentary Report No. ASD TDR-63-459 (AF Contract 33(616)-8188). The presence of the coating layers had little or no affect on the tensile properties of the sheet. Major differences between tensile properties of coated and uncoated powder product sheet resulted from the effect of the coating heat treatment on the substrate. When the coating treatment recrystallized the base metal, the coated sheet had the same properties as uncoated recrystallized sheet. When the heat treatment did not recrystallize the base metal, tensile properties of coated sheet and uncoated sheet were the same. Tensile properties of coated powder product sheet were not significantly affected by the test atmosphere.

Figure 78 illustrates the arc cast tungsten sheet tensile specimen. This design was the same as used for the powder product sheet. Application of the (Si-W) and Ti-Zr-(Si-W) coatings to the arc cast tensile specimens was made by the standard laboratory scale process employing the 3 1/4 inch diameter x 10 inch coating retort for all coating cycles. Ti-Zr-(Si-W) coated specimens were converted after coating. Metallographic examination of control coupons showed the coating cycles necessary to apply both coating systems resulted in complete recrystallization of the arc cast sheet.

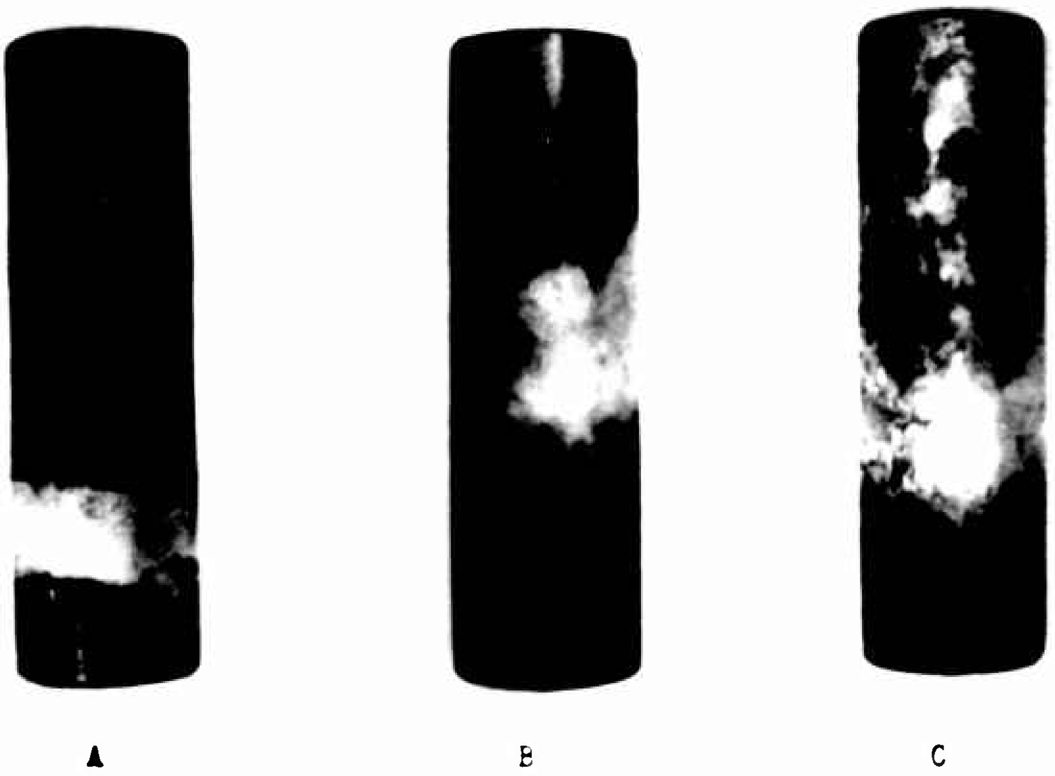


A. Uncoated Tungsten Specimen After 35 Second Exposure

B. (Si-W) Coated Tungsten Specimen After 40-Minute Exposure

C. Ti-Zr-(Si-W)-O Coated Tungsten Specimen After 45-Minute Exposure

Figure 73 Tungsten Specimens After Low Pressure Erosion Test at Gun-Specimen Distance of 0.75 Inch

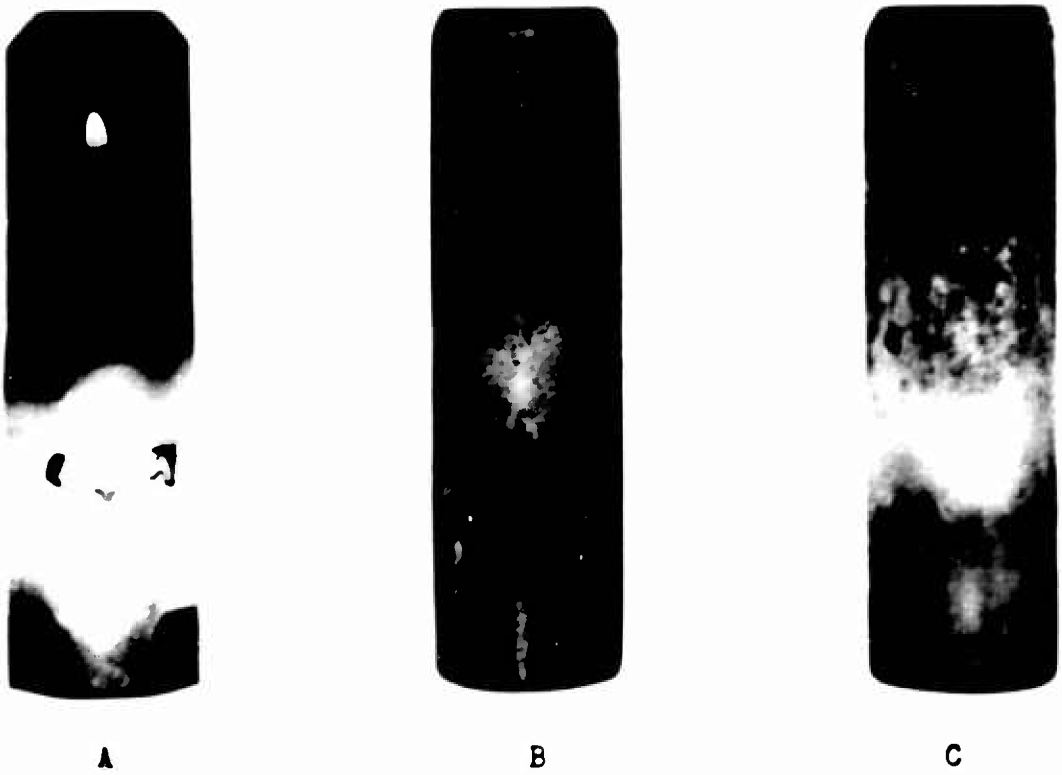


A. Uncoated Tungsten Specimen After 28 Second Exposure

B. (Si-W) Coated Tungsten Specimen After 1 Hour Exposure

C. Ti-Zr-(Si-W)-O Coated Tungsten Specimen After 1 Hour Exposure

Figure 74 Tungsten Specimens After Low Pressure Erosion Test at a Gun-Specimen Distance of 1.125 Inches

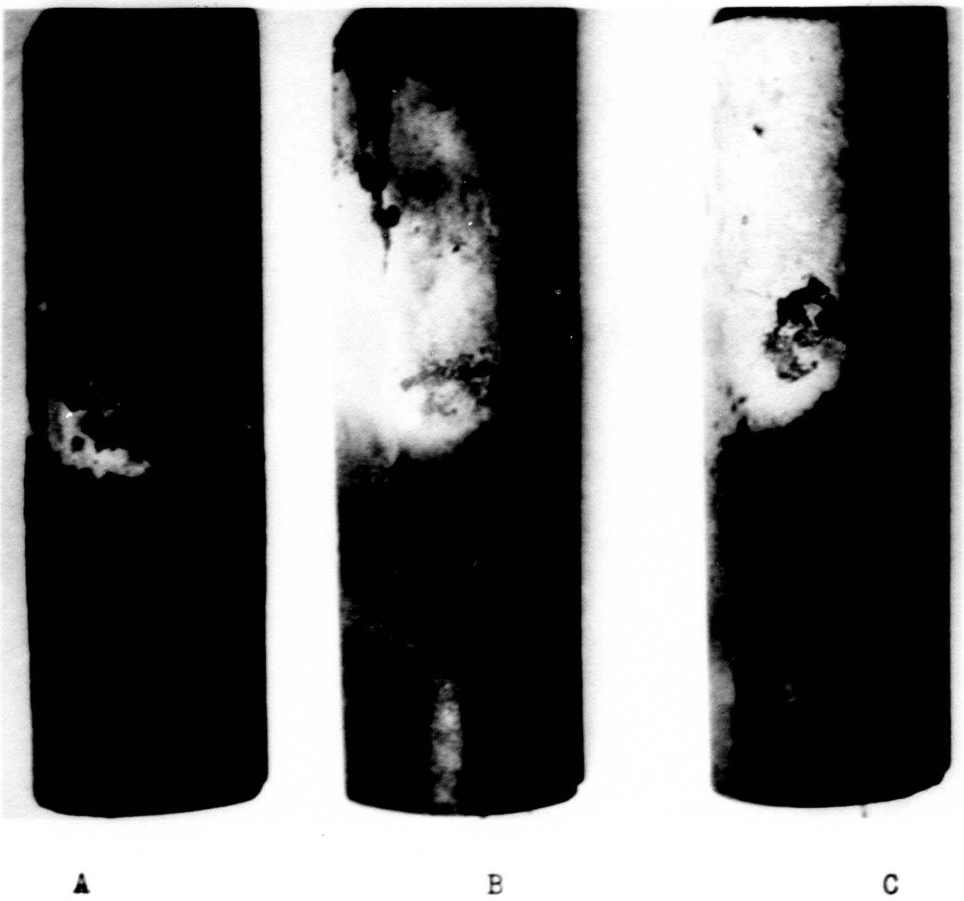


A. Uncoated Tungsten Specimen After 120-Second Exposure

B. (Si-W) Coated Tungsten Specimen After 1 Hour Exposure

C. Ti-Zr-(Si-W)-O Coated Tungsten Specimen After 1 Hour Exposure

Figure 75 Tungsten Specimens After Low Pressure Erosion Test at a Gun-Specimen Distance of 1.750 Inches

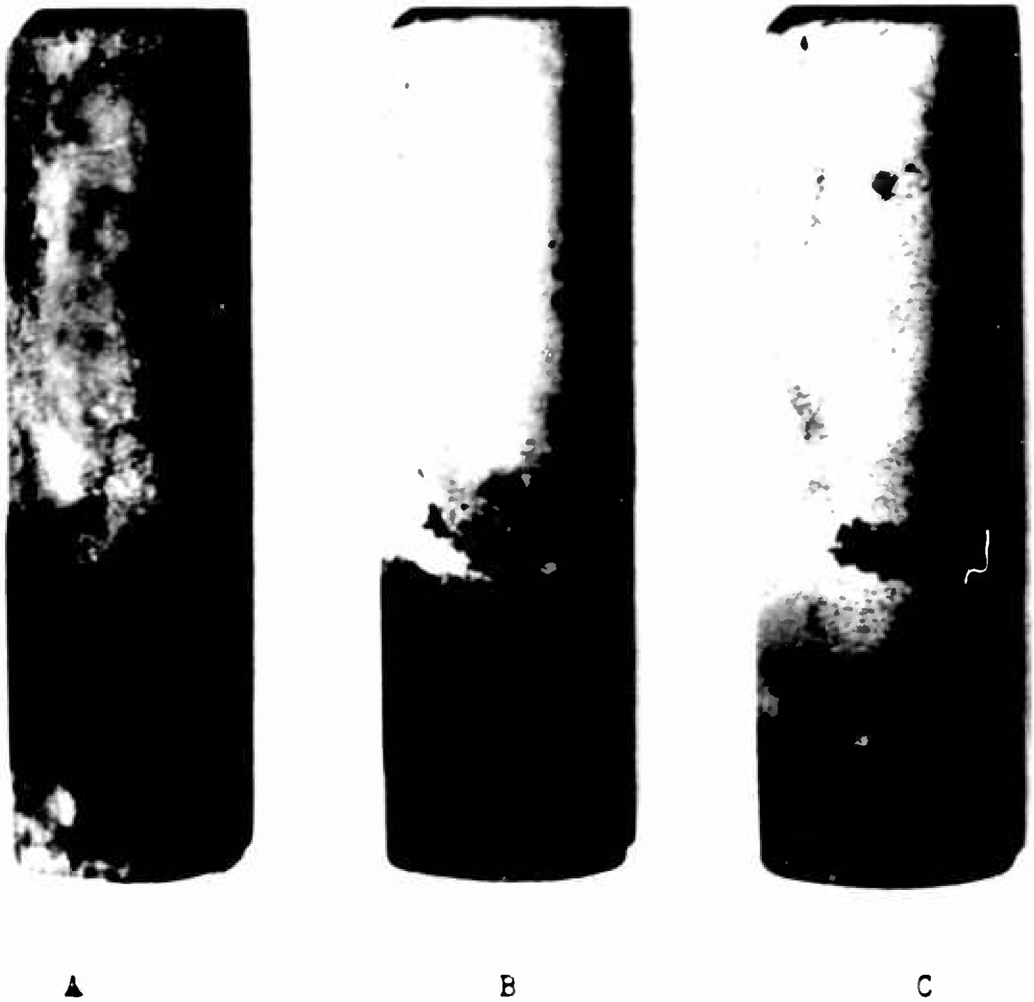


A. Plasma Gun Nozzle-Specimen Distance of 0.750 Inch

B. Plasma Gun Nozzle-Specimen Distance of 1.125 Inches

C. Plasma Gun Nozzle-Specimen Distance of 1.750 Inches

Figure 76 (Si-W)-O Coated Specimens (Pre-Oxidized at 3200° F) After Low Pressure Erosion Tests for 1 Hour. Note Loosely Adherent Layer Over Areas of Protective Coating Exposed to Plasma Flame



A. Plasma Gun Nozzle-Specimen Distance of 0.750 Inch

B. Plasma Gun Nozzle-Specimen Distance of 1.125 Inches

C. Plasma Gun Nozzle-Specimen Distance of 1.750 Inches

Figure 77 Ti-Zr-(Si-W)-O Coated Specimens (Pre-Oxidized at 3200° F) After Low Pressure Erosion Tests for 1 Hour. Note Loosely Adherent Layer Over Areas of Protective Coating Exposed to Plasma Flame

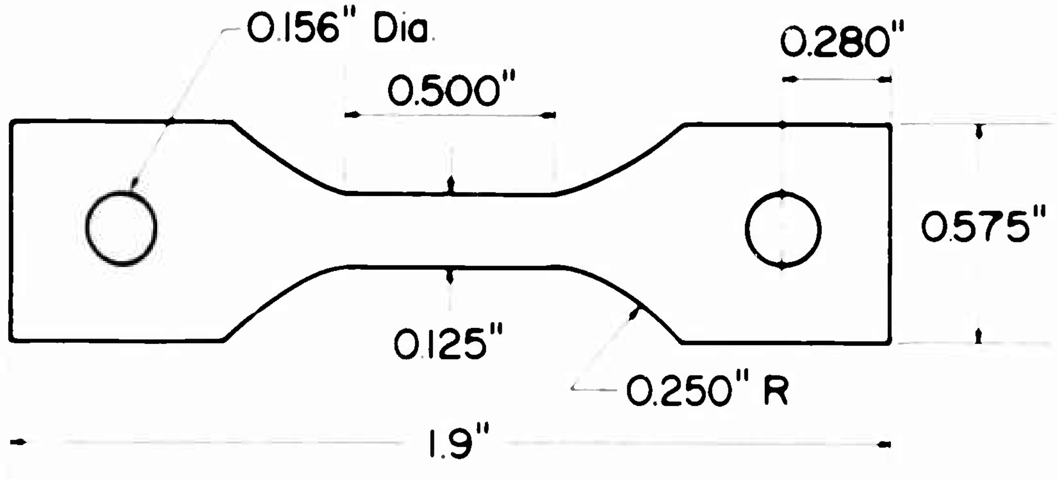


Figure 78 Schematic Drawing of the Arc Cast Tungsten Sheet Tensile Specimen

Coated specimens were tested under vacuum at 1000, 2000, 3000 and 3300°F using a Brew high temperature furnace mounted on an Instron tensile testing machine. The same apparatus was used to conduct tests under argon at 2000, 2800 and 3300°F.

Tensile properties of as-received sheet were determined (under vacuum) at 1000, 2000, 2800 and 3300°F to establish a baseline for comparison of coated sheet. Properties of uncoated sheet, given a 4 hour heat treatment at 2200°F (to simulate the (Si-W) coating cycle), were determined at the same temperatures. Table 11 lists the results of these tests. The ultimate and yield strengths of the arc cast sheet were slightly higher than that previously determined for powder product sheet.

Table 12 lists the results of the tensile tests under vacuum on coated and coated and oxidized sheet. Tensile properties of coated sheet were similar to recrystallized uncoated sheet at 2000°F and higher. This was expected since heat treatments necessary to apply the (Si-W) and Ti-Zr-(Si-W) coating to arc cast sheet caused recrystallization of the sheet. At temperatures below 2000°F in vacuum the recrystallized sheet exhibited greater ductility than the coated sheet. Tensile properties of (Si-W) coated and oxidized sheet and Ti-Zr-(Si-W)-O coated and oxidized sheet were similar at all temperatures tested. However, coated and oxidized sheet had lower ultimate and yield strengths than coated or recrystallized sheet at temperatures below 2000°F. Figure 79 graphically presents the ultimate strength of each system tested under vacuum between 1000 and 3000°F. Figure 80 graphically presents the yield tensile strength for the same systems under the same test conditions. As indicated by the curves, ultimate and yield tensile strengths of all systems (coated and uncoated) are very similar at temperatures of 2800°F and higher under vacuum.

Tensile properties of the (Si-W) coated, Ti-Zr-(Si-W)-O (converted) coated, and uncoated but recrystallized sheet were similar at 2000°F and higher under vacuum. The uncoated recrystallized sheet exhibited greater ductility but lower yield strength as compared to coated sheet at 1000°F. Table 13 lists the results of tensile tests made in argon on coated sheet. Tensile properties of coated sheet were, within experimental error, the same at comparable temperatures under either vacuum or argon.

4.4.2 Stress-Oxidation Tests of Coated Arc Cast Sheet

Stress oxidation tests of (Si-W) and Ti-Zr-(Si-W)-O (converted) coated arc cast sheet were conducted at 3350°F. Tensile type specimens were utilized for these tests. The coated systems were subjected to a load (700 psi) approximating 20 percent of the yield strength of each at 3350°F.

Testing was conducted in the high temperature oxidation furnace. The specimens were suspended in the hot zone of the furnace and the desired stress applied by means of weights attached to a series of tungsten support straps. This fixturing arrangement was illustrated in Technical Documentary Report No. ASD TDR-63-459 (Contract AF 33(616)-8188).

TABLE 11

Tensile Properties of 60 Mil Arc Cast Tungsten Sheet Under Vacuum
(0.040 in/in/min Strain Rate)

Uncoated As-Received Sheet

Test Temp. °F	U.T.S. PSI	0.2% Y.S. PSI	R.A. %	Elongation %
RT	164,800	-	-	-
1000	120,800	100,200	39	23
2000	72,600	68,500	67	16
2800	18,000	8,050	51	46
3300	9,330	3,880	42	72

Uncoated Heat Treated at 2200°F for 4 Hours in Vacuum

Test Temp. °F	U.T.S. PSI	0.2% Y.S. PSI	R.A. %	Elongation %
1000	66,500	17,900	71	66
2000	33,300	12,300	83	63
2800	18,300	8,260	85	66
3300	10,200	3,770	98	91

TABLE 12

Tensile Properties of Coated 60 Mil Arc Cast Tungsten Sheet
Under Vacuum
(0.040 in/in/min Strain Rate)

Test Temp. °F	U.T.S. PSI	0.2% Y.S. PSI	R.A. %	Elongation %
(Si-W) Coated Sheet				
1000	54,200	28,400	49	38
2000	30,900	18,800	51	46
3000	14,000	8,160	79	82
3300	8,440	4,050	72	73
Ti-Zr-(Si-W)-O Coated (Converted) Sheet				
1000	52,700	29,200	53	16
2000	30,900	23,400	40	32
3000	15,000	9,510	69	57
3300	8,740	4,670	98	98
(Si-W) Coated and Exposed in Air at 3300°F for 1 Hour				
1000	30,600	14,900	15	6
2000	25,300	14,500	43	38
3000	13,400	9,390	54	67
3300	8,790	5,190	98	103
Ti-Zr-(Si-W)-O Coated and Exposed in Air at 3300°F for 1 Hour				
1000	37,700	14,100	27	14
2000	*	*	*	*
3000	14,100	7,950	29	33
3300	8,280	5,250	98	49

* Specimen broke in pinhole

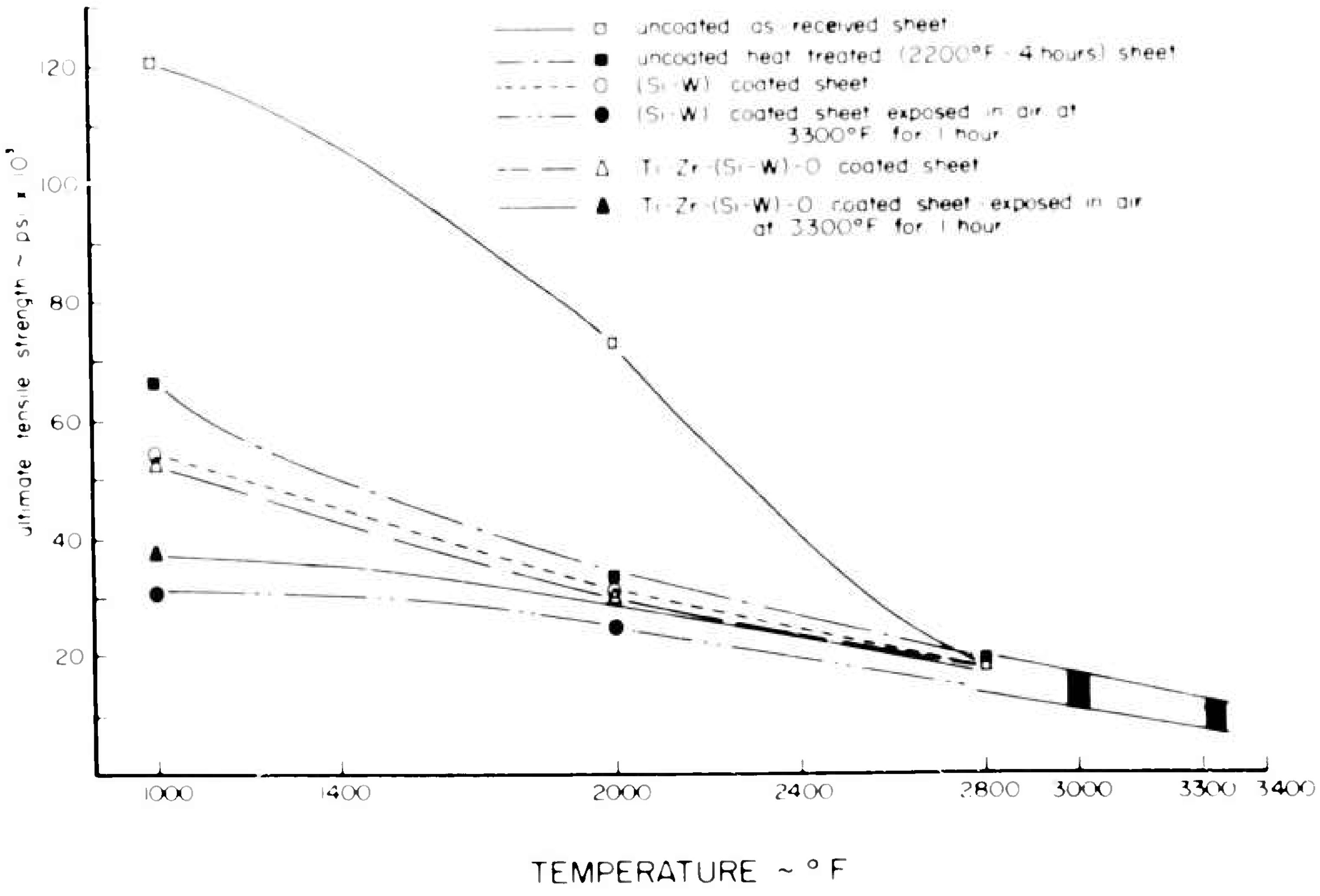


Figure 79 Ultimate Tensile Strength of As-Received, Recrystallized, Coated, and Coated and Oxidized 60 Mil Arc Cast Tungsten Sheet Under Vacuum

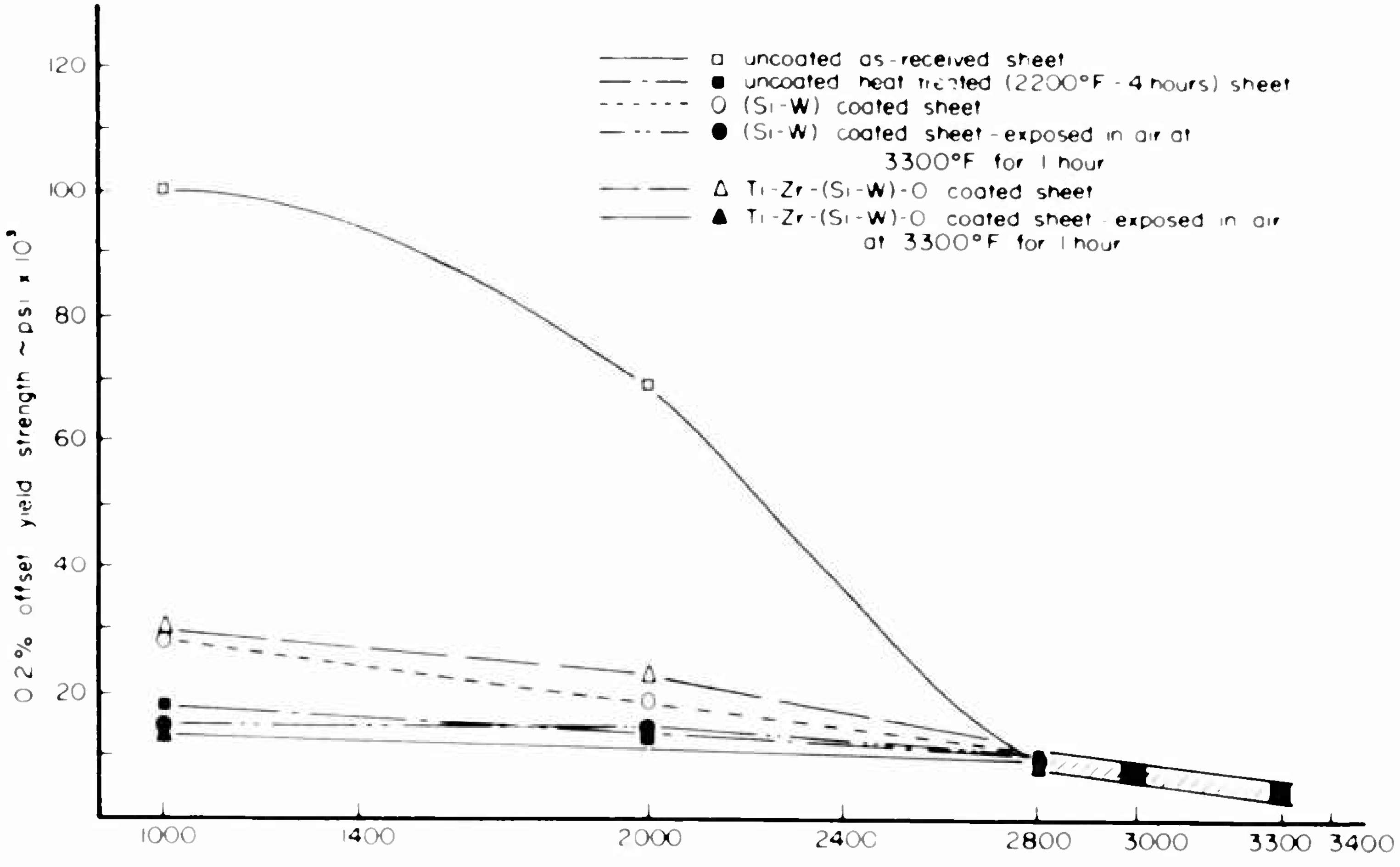


Figure 80 Yield Tensile Strength of As-Received, Recrystallized, Coated, and Coated and Oxidized 60 Mil Arc Cast Tungsten Sheet Under Vacuum

TABLE 13

Tensile Properties of Coated 60 Mil Arc Cast Tungsten Sheet
Under Argon
(0.040 in/in/min Strain Rate)

(Si-W) Coated Sheet

Test Temp °F	U.T.S. PSI	0.2% Y.S PSI	R.A. %	Elongation %
2000	34,200	22,800	63	37
2800	16,200	9,600	78	63
3300	10,240	5,570	77	71

Ti-Zr-(Si-W)-O Coated (Converted) Sheet

Test Temp °F	U.T.S. PSI	0.2% Y.S PSI	R.A. %	Elongation %
2000	31,100	21,300	56	27
2800	18,500	12,500	60	30
3300	10,375	4,610	75	85

Two specimens of each system were exposed at the 700 psi stress level for 1 hour at 3350°F. Three of the four specimens tested showed creep measuring less than 0.01 percent of the original gage length. During testing of one (Si-W) coated specimen, a support pin failed sometime during the 1 hour exposure. A bending moment caused by the failed support pin resulted in the specimen gage section being severely twisted. This amount of substrate deformation did not produce coating failure.

5. EXPERIMENTAL EQUIPMENT

The specialized experimental equipment used to conduct tests on coated tungsten systems during the program consisted of the following:

1) high temperature air oxidation furnace used for testing at one atmosphere at temperatures from 3000 to 4000°F,

2) vacuum chamber used for static low pressure tests at 3400-3500°F,

3) environmental chamber used for dynamic low pressure erosion tests.

The high temperature air oxidation furnace was constructed during the previous program (Contract AF 33(616)-8188). A complete description is presented in Technical Documentary Report No. ASD TDR-63-459. In review, this furnace is an induction heated unit. A calcia stabilized zirconia tube 20 inches long with an outside diameter of 2 inches and an inside diameter of 1 1/2 inches is used as the furnace muffle. This muffle is surrounded by a graphite susceptor, which in turn, is encapsulated in a quartz envelope. The induction coils are positioned outside of the quartz envelope or chamber. The graphite susceptor and lampblack insulation are protected from oxidation during operation by nitrogen gas flowing under a slight positive pressure through the quartz chamber. Loading and unloading of the furnace is accomplished through the use of a retractable bottom pedestal. This pedestal has a two-section shaft of calcia stabilized zirconia (1/2 inch diameter) capped with a 1/2 inch diameter zirconia disc. The disc is used as the specimen carrier. Alumina heat shields are used at the top of the zirconia muffle to operating temperatures of 3200°F, zirconia heat shields are used at temperatures above 3200°F. Free expansion of the zirconia muffle is allowed through the use of a bellows seal at the top portion. Figure 81 shows a schematic representation of this furnace unit.

Temperature measurements to 3000°F have been made using a Pt vs Pt+10% Rh thermocouple probe and to 3300°F using a W vs W+26% Re thermocouple probe. Above 3300°F temperatures are measured with a calibrated optical pyrometer (disappearing filament type). Towards the latter portion of the program an IDL Pyro-Eye two temperature pyrometer was employed to measure temperatures in the 3600 to 4000°F range. Figure 82 illustrates this pyrometer under actual use. Simultaneous temperature measurements

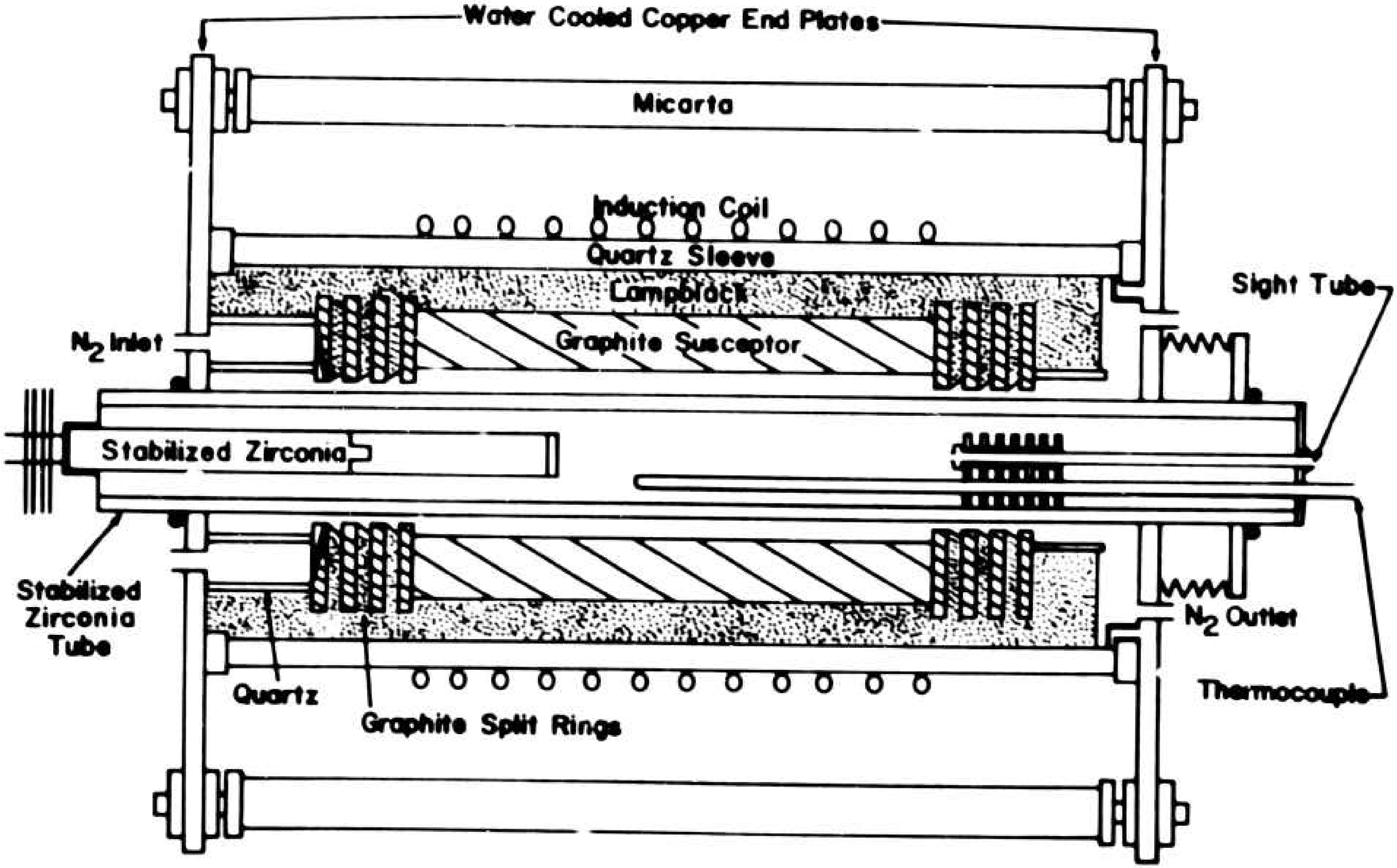


Figure 81 Schematic Drawing of the High Temperature Oxidation Furnace Used for Testing Coated Tungsten Coupons in Air to 4000°F

Figure 82 Two Temperature Optical Pyrometer (IDL Pyro-Eye) Used to Measure Temperatures Between 3600 and 4000°F in High Temperature Oxidation Furnace

were made between 3000 and 3600°F using this pyrometer and the regularly used disappearing filament type. Less than 15°F difference between measurements (direct readings from IDL Pyro-Eye versus corrected reading from disappearing filament type) was observed over the entire temperature range.

During the previous program an operating and maintenance schedule was established for this furnace in order to obtain the most efficient utilization. Because of the inherently poor shock resistance of zirconia, even stabilized zirconia, the furnace was maintained at operating temperatures for six week periods without shutdown. After six weeks the furnace was cooled and necessary maintenance on heat shields and accessory equipment carried out. The zirconia muffle (which always cracked during the cooling cycle) was replaced and the furnace returned to operation. Replacement of the susceptor, insulation and furnace seals were made after every twelve weeks of operation. The same maintenance schedule was continued throughout this program. Initially, in heating the furnace to operating temperature after shutdown, a 100-200 hour treatment at 3000°F was employed to condition the zirconia muffle for subsequent higher temperature use. If this conditioning period was omitted, atmospheric control of the test zone within the muffle could not be maintained. This was apparently due to porosity in the muffle which allowed diffusion of nitrogen through the walls. During the second quarter of the program a new type of zirconia muffle became available and was installed. This muffle permitted use of the furnace at 3400-3600°F immediately after a maintenance cycle with good control of the atmosphere in the test zone. These muffles were used for the remainder of the program.

The high temperature oxidation furnace was in almost continuous operation for thirty months during this and the preceding program. In addition to cyclic oxidation tests, stress oxidation tests were also conducted in this equipment. The dependability and versatility of this laboratory tool has been demonstrated during the extended period of operation.

The vacuum chamber used for static low pressure tests at 3400-3500°F was illustrated in Section 4.3.4. This equipment consisted of a vacuum chamber with internally mounted water cooled copper electrodes.

The equipment utilized for dynamic low pressure erosion tests consisted of the following:

1. environmental chamber and accessory vacuum equipment,
2. a 60 KV Thermal Dynamic plasma flame gun,
3. specimen holder with attached pressure probe,
4. button type calorimeter.

Figure 83 shows the environmental chamber in which the tests were conducted.

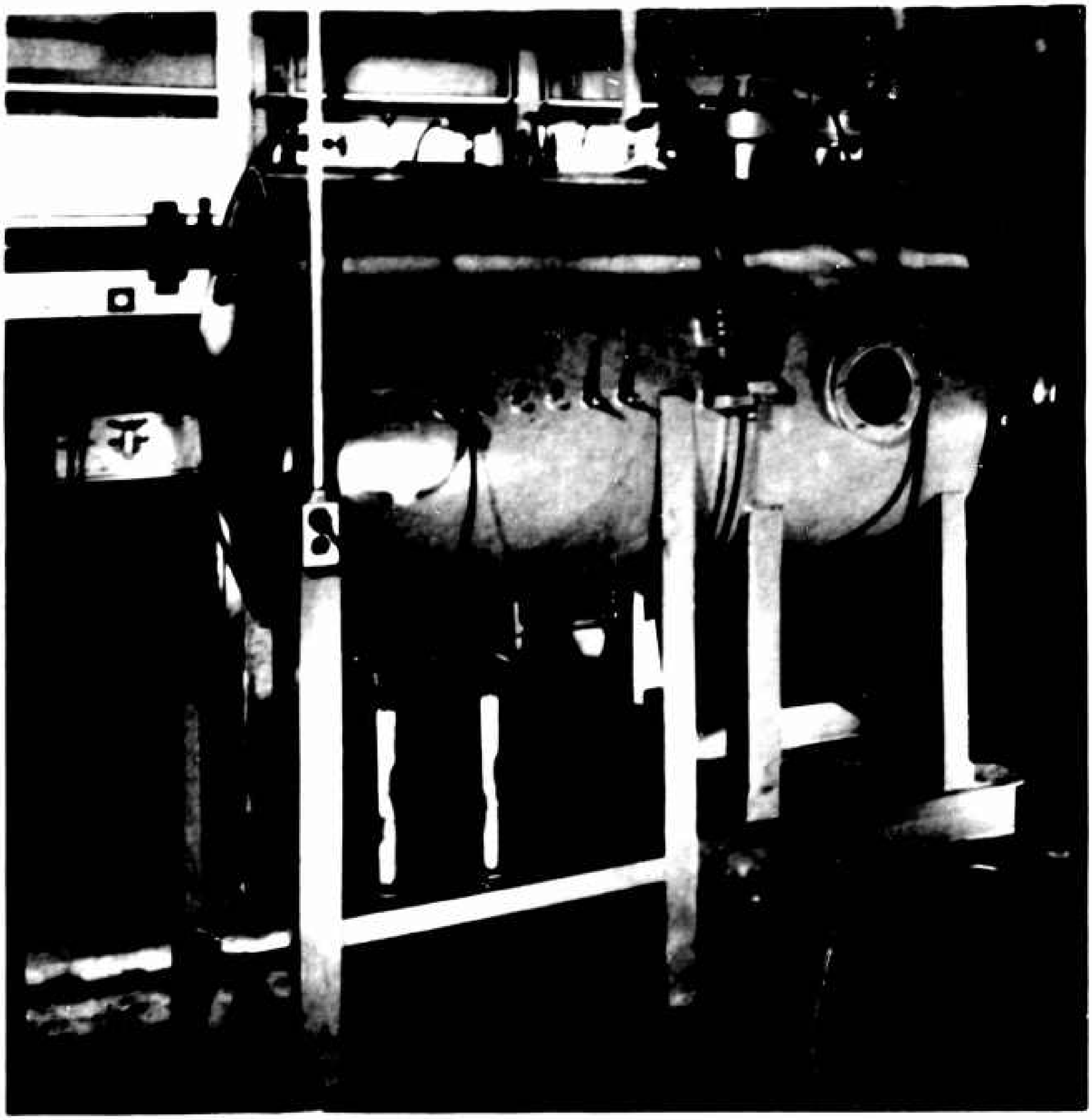


Figure 83 Environmental Chamber Used for Dynamic Low Pressure Erosion Tests

A Stokes Microvac vacuum pump having a pump capacity of 115 CFM was used to evacuate this chamber. During testing the plasma flame gun was rigidly mounted on the floor of the chamber directly between the side sighting ports. The plasma flame was directed at the end of the chamber containing the exhaust port. A water cooled specimen holder was fixtured so that the specimen could be introduced into the plasma flame by an external control (this is not seen in the photograph) while maintaining vacuum in the chamber. Pressure of the tank was measured with a McLeod gage at the chamber wall. A special probe, mounted in the specimen holder and connected to a McLeod gage, was used to measure the pressure at various points of the plasma flame.

6. APPLICATIONS

The most important application of the technology developed during this and the preceeding program has been the application of protective coatings to tungsten throat inserts used in liquid propellant reaction control rocket engines. Coated throats in these engines must operate under oxidizing conditions at temperatures greater than 3000°F and pressures greater than one atmosphere. Both types of coatings, (Si-W) and Ti-Zr-(Si-W), have been applied to this type of hardware and successful test firings made. However, the (Si-W) coating has found more general acceptance because of the relatively simple processing requirements. The slightly better capabilities of the more complex coating are outweighed by the more complex processing requirements. Figure 84 illustrates (Si-W) and Ti-Zr-(Si-W)-O (converted) coated tungsten inserts.

In addition to inserts, a number of tungsten leading edge configurations have been (Si-W) coated and used for experimental purposes. Figure 85 shows some types of these configurations that have been coated.

The Si-W coating developed for tungsten has been successfully modified to protect molybdenum. The coating is protective to molybdenum to temperatures of 3500°F in air. Molybdenum throat inserts protected with this modified coating have been extensively evaluated for liquid propellant reaction control engines. Currently such coated molybdenum inserts are being produced for the operational Saturn SIVB reaction control system. Figure 86 shows a SIVB molybdenum insert for a 150 lb. thrust engine before and after coating.

Figure 87 shows a coated prototype involving an integral molybdenum combustion chamber and throat.

7. CONCLUSIONS

Based on data presented in the preceeding sections, the following conclusions can be drawn:

1. Protective (Si-W) and Ti-Zr-(Si-W) coatings can be applied to 60 mil arc cast and powder product sheet by the vacuum pack process under standardized conditions on a laboratory scale basis.

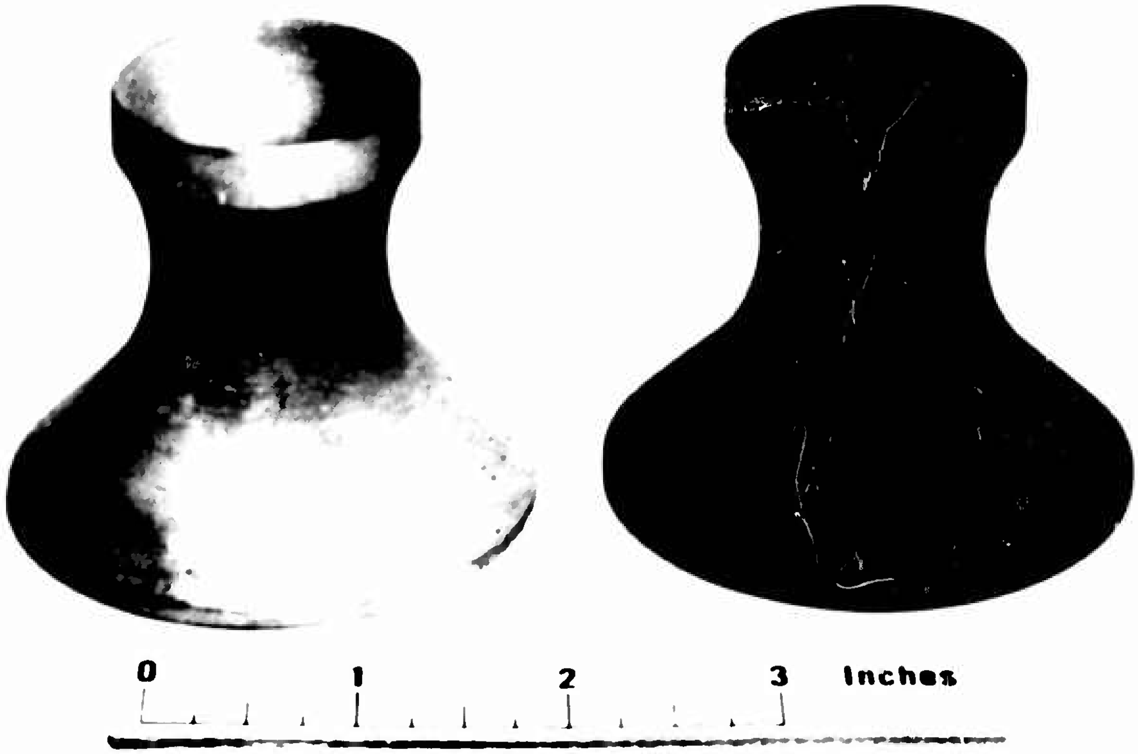


Figure 84 (Si-W) and Ti-Zr-(Si-W) Coated Tungsten Inserts for Liquid Propellant Reaction Control Rocket Engines

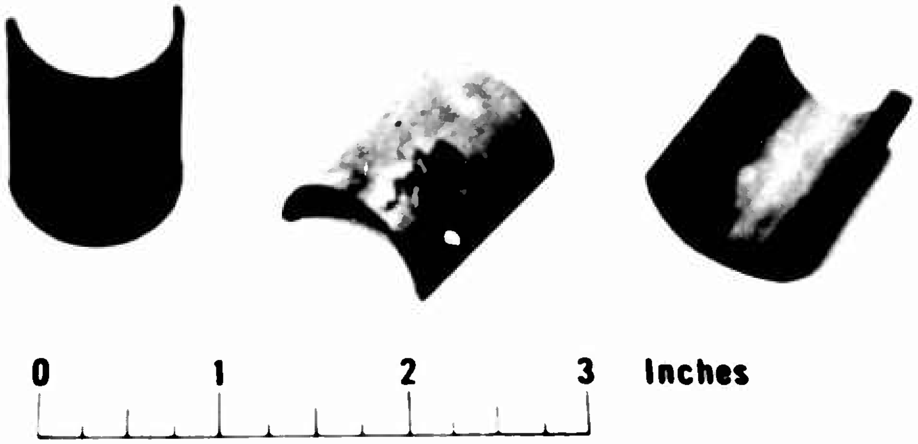


Figure 85 (Si-W) Coated Tungsten Leading Edge Configurations

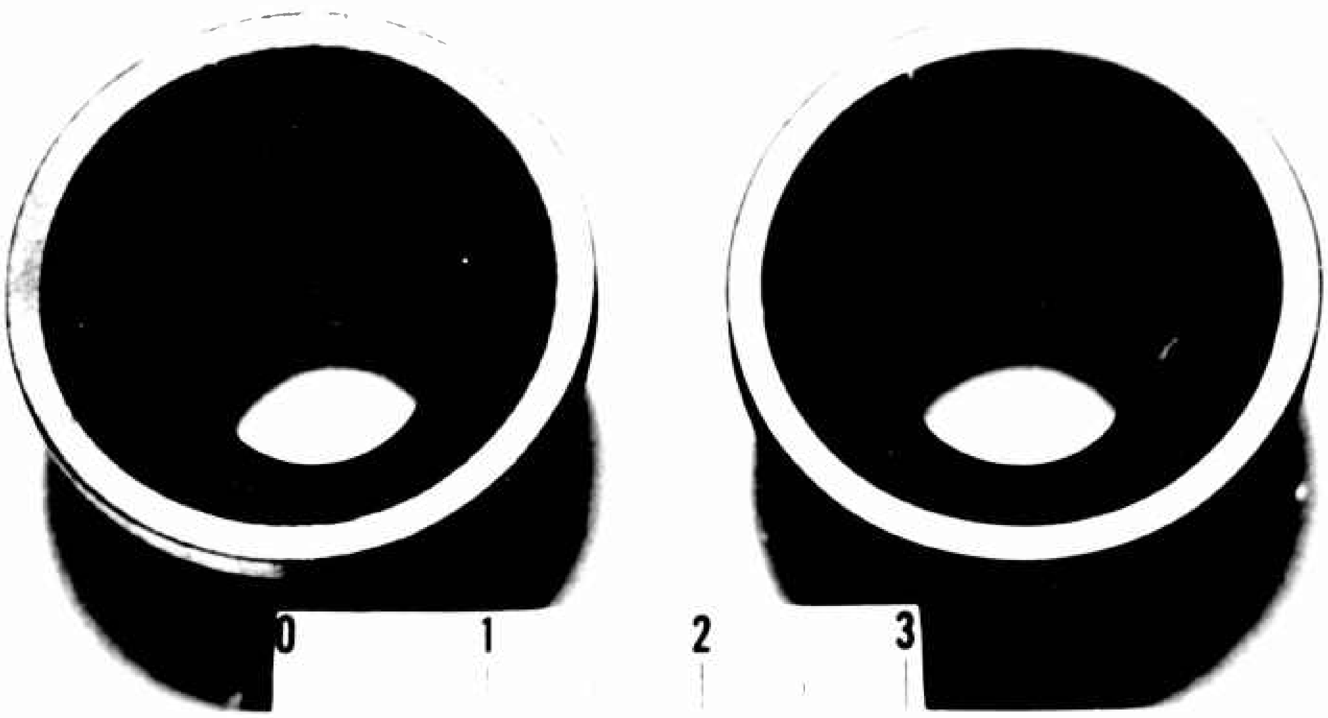


Figure 86 Molybdenum Insert for the Saturn SIVB Reaction Control Engine Before Coating (Left) and After Coating (Right)

Figure 87 Integral Molybdenum Combustion Chamber and Throat Protected by the Modified Tungsten Coating

2. The vacuum pack process can be utilized to apply protective coatings to tungsten in a coating retort 7 1/2 inches in diameter x 18 inches tall. This retort is approximately ten times larger than that used for laboratory scale work. Process parameters are well enough established so that use of different furnace units will result in comparable W+(Si-W) systems with respect to the thickness and protective nature of the coatings.

3. The protective capabilities of the (Si-W) and Ti-Zr-(Si-W) coatings in air at one atmosphere are the same on arc cast or powder product sheet.

4. The ultimate useful temperature capability of both the W+(Si-W)-O and W+Ti-Zr-(Si-W)-O coated systems in air at one atmosphere is 3600°F. Protective coating life at these temperatures is approximately 0.5 hours for both systems.

5. At temperatures below 3600°F in air substantially longer protective life of the coating systems can be expected. The (Si-W) coating has a 96 ± 1% probability at a 99% confidence level of being protective to tungsten in air for 5 hours at 3500°F under cyclic conditions. Both coatings are protective to tungsten for periods of time exceeding 20 hours under cyclic conditions in air at 3300°F.

6. The (Si-W)-O and Ti-Zr-(Si-W)-O coatings are protective to tungsten under cyclic conditions in air for periods exceeding 25 hours at 1600, 1800, 2500 and 3000°F.

7. Addition or incorporation of hafnium into the (Si-W) coating does not result in a coating system having a higher temperature capability than the (Si-W) system alone.

8. Refractory compound coatings plasma sprayed directly on tungsten sheet are not gas tight and are not protective to the tungsten substrate.

9. The (Si-W)-(TiN-BN) coating, formed by plasma spraying a (TiN-BN) refractory mixture on (Si-W) coated tungsten, is protective to tungsten in air for short periods of time at 3700°F. This coating exhibits the same protective capability to tungsten as the (Si-W) coating at lower temperatures.

10. The (Si-W), Ti-Zr-(Si-W)-O (converted) and Ti-Zr-(Si-W) (not converted) coating systems exhibited varying degrees of coating deterioration when exposed at reduced air pressures for 1 hour periods at 3400-3500°F.

11. Pre-oxidation of the coating systems (including conversion of the Ti-Zr-(Si-W) coating) results in moderate to severe deterioration of the coatings during exposure at reduced (air) pressures of 1 mm

Hg or lower at temperatures of 3400-3500°F.

12. Both coating systems exhibited good resistance to erosion under high velocity air flows at reduced pressures (16-20 mm Hg) at heat fluxes between 180 and 325 BTU/ft^2/sec. Estimated temperatures corresponding to these heat fluxes were 2900°F (180 BTU/ft^2/sec) and 3400°F (325 BTU/ft^2/sec).

13. Tensile properties of coated arc cast tungsten sheet and coated powder product tungsten sheet are similar for comparable coating and base metal conditions.

14. Tensile properties of coated tungsten (arc cast or powder product sheet) are not significantly affected by the presence of coating layers but are affected by heat treatments necessary to apply the coating. Heat treatments necessary to apply the (Si-W) and Ti-Zr-(Si-W) coatings to arc cast sheet cause recrystallization of this material. Coated arc cast sheet has the same tensile properties as uncoated but recrystallized sheet.

15. A low creep rate is exhibited by coated arc cast tungsten sheet at 3350°F in air under loads approximating 20 percent of the coated base metal yield strength. The protective nature of the coating is not affected under load at this stress level.

16. Application of the (Si-W) or the Ti-Zr-(Si-W) protective coating to tungsten hardware has been made on a laboratory scale basis. Application of protective and uniform (2.0-2.5 mils) (Si-W) coatings has been made to tungsten hardware using the 7 1/2 inch diameter x 18 inch coating retort. Tungsten components up to 7 inch diameter x 12 inches long can be accommodated in this retort.

The work conducted under this and the preceding programs advanced the state of the art of tungsten coating technology. Tungsten hardware can be coated and protected in air to temperatures of 3600°F. Coating capabilities in excess of 3600°F in air are desirable and necessary if tungsten is to be effectively utilized as structural material in the aerospace industry. It is not unreasonable to think that coatings, protective to tungsten in air at temperatures of 4000°F and higher, can be developed. Such systems would undoubtedly combine the best aspects of current coating technology with new developments in refractory compounds.