

AD634402

STUDY OF DUCTILE COATINGS FOR THE OXIDATION PROTECTION OF COLUMBIUM AND MOLYBDENUM ALLOYS

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND
TECHNICAL INFORMATION

Hardcopy	Microfiche	
\$2.00	\$.50	45 pp as

ARCHIVE COPY

MAY, 1966

Final Report

Covering Period 1 March 1965 through 28 February 1966

PREPARED UNDER BUREAU OF NAVAL WEAPONS
CONTRACT NOW 65-0340-f

By E. H. Girard, J. F. Clarke and H. Breit

Qualified requesters may obtain copies of this report
direct from the Defense Documentation Center,
Cameron Station, Alexandria, Virginia



METALS & CONTROLS INC.
34 FOREST ST. • ATTLEBORO, MASS., U.S.A.
A CORPORATE DIVISION OF
TEXAS INSTRUMENTS
INCORPORATED

DISTRIBUTION OF THIS DOCUMENT
IS RESTRICTED

DD FORM 1
JUN 29 1966
RECEIVED

DISTRIBUTION OF THIS DOCUMENT
IS RESTRICTED

X

STUDY OF DUCTILE COATINGS FOR THE OXIDATION PROTECTION
OF COLUMBIUM AND MOLYBDENUM ALLOYS

MAY 1966

Prepared under Bureau of Naval Weapons
Contract N0w 65-0340-f

Final Report
Covering period 1 March 1965 through 28 February 1966

By E. H. Girard, J. F. Clarke and H. Breit

METALS & CONTROLS INC.
Attleboro, Massachusetts, U.S.A.
a corporate division of
TEXAS INSTRUMENTS INCORPORATED

FOREWORD

This report was prepared by Metals & Controls Inc., a Corporate Division of Texas Instruments Incorporated, under Bureau of Naval Weapons Contract NOw 65-0340-f. The acting contract monitor was Mr. Irving Machlin.

The authors wish to acknowledge the assistance of Joyce Kaltsas (Metallographic Technician), Stanley Ryng (Technician) and Sheldon White (Engineer) during the course of this program.

ABSTRACT

Nine materials were examined as potential barriers to the degrading diffusion of elements from FS-85 and TZM substrate through platinum coatings. One metal, hafnium, and one binary combination, iridium clad tungsten, were particularly effective as diffusion barriers. However, the increase in coating life produced through usage of these metals was no more than would be expected with a similar increase in coating thickness. Coating lives of up to 66 hours were obtained at 2550°F in flowing air.

It appears that when formed under the proper conditions, platinum-molybdenum and platinum-columbium intermetallic compounds may act as barriers to coating-substrate interdiffusion. Their usefulness in extending coating life should be explored further.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. MATERIALS	2
A. Substrate Materials	2
B. Coating Materials	2
C. Diffusion Barrier Materials	2
III. DIFFUSION BARRIER INVESTIGATION	4
A. Diffusion Barrier Materials	4
B. Preparation of Test Samples for Evaluation as Diffusion Barriers	8
C. Testing and Evaluation	14
IV. RESULTS AND DISCUSSION	17
V. CONCLUSIONS	19
REFERENCES	20
APPENDIX	22

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. MELTING POINTS AND THERMAL EXPANSIONS OF THE COATING, SUBSTRATES AND MATERIALS EVALUATED AS DIFFUSION BARRIERS.	5
II. SAMPLES EVALUATED FOR DIFFUSION BARRIER STUDIES	18

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1.	Graphite Clamp for Hot Press Bonding	11
2.	Diffusion Barrier Test Sample	13
3.	Hot Pressing Setup for Applying Upper Picture Frame and Completing the Sealing of a Diffusion Barrier Test Sample.	15
4.	Oxidation Test Furnace	16
5.	Cummulative Weight Losses as a Function of Time for Unalloyed Platinum, Platinum/TZM and Platinum/FS-85 Samples Tested in a 240 ipm Air Flow at 2550°F	23
6.	Changes in Concentration Gradient With Time (t) Which Would Be Expected in a Pt/Mo Diffusion Couple if These Elements Were Mutually Soluble.	24
7.	Electron Beam Microanalysis Data on Pt Clad TZM Tested for 7 hours at 2550°F in a 240 ipm Air Flow.	25
8.	Electron Beam Microanalysis Data on Pt Clad FS-85 Tested for 16 Hours at 2550°F in a 240 ipm Air Flow.	26
9.	Effect of Time on Thickness of Intermetallic Region.	28
10.	Effect of Solute Penetration on Hardness	29
11.	Pt (0.003 inch) Clad FS-85 Tested at 2550°F for 7 Hours in a 240 ipm Air Flow	31
12.	Concentration of Oxygen and Columbium (From FS-85) in a Coating at Failure	32
13.	Pt (0.003 inch) Clad FS-85 Tested for 16 Hours at 2550°F in a 240 ipm Air Flow.	33
14.	Pt (0.003inch) Clad FS-85 Tested for 16 Hours at 2550°F in a 240 ipm Air Flow.	34
15.	A Typical Void Area Formed at Failure of a Pt/TZM Sample Heated at 2550°F in a 240 ipm Air Flow.	35

I. INTRODUCTION

This program was initiated to investigate ductile coatings which might be used to protect columbium and molybdenum alloys from high temperature oxidation. It was suggested that the ability of such coatings to undergo significant deformation without fracture would enable them to withstand thermal and mechanical fatigue and shock far better than the brittle coating systems which have received wide attention. Specifically, a ductile coating has been sought which would be capable of providing 100 hours of protection to columbium and molybdenum alloys at temperatures up to 3000°F without causing significant degradation of the substrate metal. The current contract is a continuation of the work of an earlier one-year contract (1) with no change in program objectives.

Protective coatings for refractory metals are commonly limited to a thickness of 0.002 to 0.003 inches. There are several reasons why significantly thicker coatings are usually undesirable. For example, the poor mechanical properties of the coatings result in decreased strength-to-weight ratios. With increased thickness they are less easily deformed promoting the build up of thermally induced stresses that can cause interfacial fracture. Platinum and platinum-rhodium alloys were initially suggested as the most logical coating materials to supply the properties desired in these thicknesses. An extensive literature search has evidenced no better candidates. Both published and additional experimental data obtained during the first year's work have confirmed that platinum and platinum-rhodium alloys are sufficiently oxidation resistant to meet the specified coating objectives. However, it was found that diffusion of elements from the substrates into these coating metals would lead to significant oxidation and deterioration of the composites after about 15 hours at 2550°F. Near the end of first year of the program an investigation was undertaken to find a material or materials which could be interposed between the coating and substrate to reduce diffusion, thereby increasing the effective lifetime of the coating. One material, zirconia, showed promise as a diffusion barrier.

In the second year of work, which is the main concern of this Final Report, the investigative efforts were principally directed towards continued examination of potential diffusion barriers. Nine were tested. No barrier/platinum combinations proved better than a comparable thickness of platinum alone. Most were poorer and actually appeared to accelerate the failure process.

The mechanism of coating failure also received additional attention in the second year of the program and some further knowledge of the subject has been obtained.

II. MATERIALS

A. Substrate Materials

One molybdenum and one columbium alloy were selected for the program. They were, respectively, TZM(Mo-0.5Ti-0.1Zr) and FS-85 (Cb-28Ta-10W-1Zr). These were considered to be two of the more promising refractory metal alloys, and had been recommended for further development by the Refractory Metal Sheet Rolling Panel of the Materials Advisory Board⁽²⁾. Chemical analyses have been performed on the samples of these alloys employed in these studies. The quantities of alloying and impurity elements in each fell well within the prescribed limits.^(3,4)

The FS-85 and TZM were used as substrates for most of the coating tests. The exceptions were several tests involving unalloyed columbium and molybdenum substrates of better than 99.9 percent purity.

B. Coating Materials

While both platinum and platinum-rhodium alloys have been shown to have the necessary oxidation resistance, the first year's investigations evidenced no significant difference in their ability to protect columbium and molybdenum alloys. Therefore, the studies during the second year of the program were limited to the simpler case, pure platinum.

As investigations indicated that very small quantities of impurities could greatly reduce the effectiveness of platinum as a coating, 99.99 percent pure platinum was used for all but a few early exploratory experiments.

C. Diffusion Barrier Materials

The potential diffusion-barrier-forming materials examined in the first year's work included rhenium, gold (to form a refractory intermetallic), aluminum (to form a refractory intermetallic), boron nitride, alumina and zirconia. Only zirconia appeared to reduce diffusion. Two, gold and boron nitride, were eliminated from further consideration. Because of the poor quality of the layers applied, the non-oxidizing test conditions and the limited number of samples tested, further confirmation testing was deemed necessary for the remaining materials. All but aluminum were included in the second year's work. It was omitted in favor of materials which seemed more promising. The materials and material combinations investigated were:

- | | |
|---|---------------------|
| (1) Tungsten | (6) Silicon Carbide |
| (2) W-25 ^a /oRe-30 ^a /oMc Alloy | (7) Zirconia |
| (3) Rhenium | (8) Alumina |
| (4) Hafnium | (9) Magnesia |
| (5) Iridium Clad to Tungsten | |

The tungsten, rhenium, iridium, silicon carbide, alumina and magnesia used were greater than 99.5 percent pure. According to General Electric Company, the impurity level of their W-25^a/oRe-30^a/o alloy, was very low(5). The major impurity in the hafnium was two percent zirconium with other impurities amounting to less than 0.2 percent. The zirconia contained about 1 1/2 percent hafnia and under 1 percent additional oxide impurities.

III. DIFFUSION BARRIER INVESTIGATION

A. Diffusion Barrier Materials

The selection of materials for evaluation as diffusion barriers has been based upon:

- (1) Past studies indicating their effectiveness in retarding diffusion in systems similar to those under consideration
- (2) Chemical inertness
- (3) Refractoriness

The data available in conjunction with the first two criteria are mostly qualitative, but the substances may be easily compared in terms of the third criterion on the basis of melting point.

Two additional physical properties of the materials in question, ductility and coefficient of expansion, may also be considered. Decreasing ductility and increasing differences in expansion between the coating, barrier and substrate materials increase the likelihood of fracture within the layers or at the interface. Potential barriers have not been judged on the basis of either of these criteria, however, because it appeared that proper processing control might yield deposits which could undergo some deformation and still be capable of reducing diffusion. The importance of these properties, then, has been in sample preparation.

The materials and material combinations which were evaluated are presented in Table I. They are divided into two groups with substantially different bonding and ductility, (1) metallic elements and alloys and (2) nonmetals. Melting point and thermal expansion data are given and the coating and substrate metals have been included so that all the components of each coating/barrier/substrate combination may be compared. These materials and the basis of their selection for evaluation are considered in greater detail in the following paragraphs.

1. Metallic Elements and Alloys

Information of a general nature concerning the interactions of various high melting point metals, including those of which the substrate and coating are composed, has been obtained from phase diagrams (6-8) and from the reports of Passmore, et al. (9) on investigations of diffusion barriers for refractory metals. From these it was found that one of the most valuable assets of metals as barriers, ductility, is lost for any metals which might be considered. Brittle intermetallics are formed with either coating or substrate metals.

TAELE I

MELTING POINTS (10-13) AND THERMAL EXPANSIONS (11-14) OF THE COATING,
SUBSTRATES AND MATERIALS EVALUATED AS DIFFUSION BARRIERS

<u>Material</u>	<u>Melting Point °F</u>	<u>Linear Thermal Expansion from 60-1830°F %</u>
<u>Coating Metal</u>		
Platinum	3220	1.02
<u>Substrate Alloys</u>		
FS-85	4700	0.86
TZM	4730	0.61
<u>Diffusion Barriers</u>		
Metallic		
Tungsten	6110	0.47
W-25 ^a /oRe-30 ^a /oMo Alloy	5000	---
Rhenium	5760	0.67
Hafnium	4030	0.58
Iridium Clad to Tungsten	4450-6110	0.77-0.47
Nonmetallic		
Silicon Carbide	4890*	0.50
Zirconia	4910	0.57**
Alumina	3700	0.83
Magnesia	5070	1.33

* Dissociates

** Rapid change at 2200°F because of phase change

The broad coverage which Passmore, et al, gave to high melting point metal-metal systems in their reports proved very useful in selection of metals for evaluation as diffusion barriers. Other pertinent information has been found in the literature. However, it has been concerned with only a few specific metal combinations.

The metals which were selected for the diffusion barrier studies conducted in this program and the factors upon which each choice was based are discussed separately:

a. Tungsten

Tungsten is the most refractory of the metals, with a melting point of 6110°F. None of its binary combinations with the coating or primary substrate alloying elements has a solidus temperature below the melting point of the platinum coating 3220°F⁽⁷⁾. From their studies, Passmore, et al, ⁽⁹⁾ concluded that tungsten would be one of the optimum barriers for diffusion of molybdenum or columbium, the main constituents of the substrate alloys. However, they showed platinum to be a relatively poor barrier to tungsten diffusion when compared with other high melting point metals. It is known that as little as two percent of tungsten alloyed with platinum will lead to internal oxidation⁽¹⁵⁾.

b. W-25^a/oRe-30^a/oMo Alloy

There was no reason to expect that any tungsten alloy would be a better barrier than tungsten itself. However, the W-25^a/oRe-30^a/oMo alloy was attractive because it retains both the high degree of refractoriness expected of good barrier (melting point above 5000°F) and sufficient ductility (even after recrystallization) to allow easy sample preparation through cold roll bonding techniques.⁽¹⁶⁾

c. Rhenium

The melting point of rhenium, 5760°F, is second only to tungsten among the metals. The lowest solidus temperature in binary combinations with the coating and primary substrate alloying elements is above the melting point of platinum. As for tungsten, Passmore, et al, ⁽⁹⁾ specified rhenium as one of the optimum barriers for columbium and molybdenum. Rhenium is used as an effective barrier between platinum coatings and molybdenum as electron tube grids operating as high as 2200°F.⁽¹⁷⁾

d. Hafnium

Hafnium with its relatively high melting point of 4030°F

received no recommendation in the reported investigations of Passmore, et al,⁽⁹⁾ because its interdiffusion with the refractory metals was more extensive than many other combinations. Its potential usefulness in the systems under consideration lies in its gettering ability. This could slow oxygen diffusion through the platinum by forming a barrier of refractory hafnium oxide.

No phase diagrams or information on platinum-hafnium alloys have been found. Therefore, it is impossible to make any prediction as to how and to what extent this metal may interact with platinum to affect the composites.

e. Iridium-Tungsten

As has been pointed out, tungsten has been found to be a potentially excellent barrier to diffusion of columbium or molybdenum but may diffuse too rapidly through platinum. Therefore, iridium was selected as an additional barrier material for this system, to be placed between the tungsten and platinum. It was conjectured that this metal might afford significant improvement by acting as a barrier to tungsten-platinum interdiffusion. Passmore, et al,⁽⁹⁾ suggested it as one of the better barriers to tungsten diffusion. While no information was found concerning the rate of its interdiffusion with platinum, iridium alloys are known to be very oxidation resistant at the temperature in question (though not as good as platinum, rhodium or platinum rhodium alloys). The alloys formed may, however, be less effective in retarding diffusion of tungsten.

2. Nonmetallic Refractory Compounds

Many nonmetallic refractory compounds are noted for stability in contact with metals and should, therefore, be among the best barriers to metallic diffusion. It was anticipated, however, that considerable difficulties might be encountered in use of these materials. They are generally so brittle that their inclusion in coating/barrier/substrate combinations might be expected to produce composites of limited flexibility. Such minimal ductility could easily lead to failure. Nonmetallic refractory compounds are difficult to bond to metals making interfacial fractures also likely. It was assumed that problems from these sources could be reduced to acceptable limits through development of appropriate application techniques. The following nonmetallic materials were evaluated in this second year's work.

a. Silicon Carbide

Silicon carbide was chosen as a potential.

diffusion barrier because of its refractoriness and the easy availability of a proven good technique for its deposition. It decomposes at approximately 4530°F without melting.

b. Zirconia

The selection of zirconia was based primarily on its refractoriness. Its melting point is very high, 4910°F, and it is considered to be the best crucible material for platinum (18). In the first year's contract on this program the initial tests indicated that this material would be effective in preventing platinum-TZM interdiffusion at 2500°F.

c. Alumina

Alumina material was chosen because of its high melting point (3700°F) and its stability in contact with metals at high temperatures. Further, Rhys found it an effective barrier to platinum-molybdenum interdiffusion at 2200°F. (19)

d. Magnesia

Magnesia was also selected because of its high melting point (5070°F) and its stability in contact with molten metals.

B. Preparation of Test Samples for Evaluation of Diffusion Barriers

In the first year's contract a screening test was used in the evaluation of diffusion barriers. It was not necessary to pre-bond the materials together (although this was sometimes done) since they were held in a clamp during testing. Also, the samples were heated in vacuum and were not, therefore, required to be hermetically sealed within the coating. The effectiveness of the barriers was judged on the basis of the extent of diffusion observed across the interfaces. While such a test certainly has some merit, it does not take into account how small concentrations of the barrier in the coating or interaction of atmospheric gases with the barrier as it diffuses through the coating may affect the resistance of the coating to oxidation. Because of these inadequacies, the testing in the second year's work has been performed in air on hermetic samples.

Prior to describing the complete test sample configuration that has been used in the second year's work it is important to first consider the methods used for applying the barriers to the substrates and the coating to the barrier/substrate combinations.

1. Application of Coating and Barrier Layers

As noted earlier in this report, coatings much in excess of

0.002 to 0.003 inches are undesirable. The potential diffusion barrier layers being examined should probably not exceed this thickness and would preferably be much thinner. One reason for this is that their thermal expansions (as given in Table I) differ greatly from the coating and substrates and, hence, large degrading thermal stresses would be produced during heating or cooling. Also, the nonmetals become less flexible and more susceptible to fracture with increasing thickness. Therefore, application techniques were selected which could apply very thin layers of coating and barrier materials.

Four application techniques have been used. They are roll bonding, hot press bonding, chemical vapor deposition and physical vapor deposition via electron beam evaporation. Each test sample was prepared using the process or processes from among those specified, which was best suited to the particular combination of materials. Process development itself received attention only to ascertain the adaptations necessary to preparation of the selected combinations. The four techniques used are discussed more extensively below with reference to the combinations prepared.

a. Roll Bonding

With proper surface conditioning, coherent strongly bonded layers of almost any two ductile materials may be produced through roll bonding. If complete coherency is not required in both layers only one of the materials need be ductile, the other may be rolled onto and embedded in the surface of the other as a slightly porous layer of powder.

While pore free barriers were preferred, so that any reduction of diffusion by the substances being examined would be maximized, roll bonding of powders was used as a second technique for preparing some test samples with the oxides. Its main advantages over the other techniques available were:

- (1) An application procedure was known which required no more specialized equipment than a rolling mill.
- (2) No variation in composition could occur during application.
- (3) The lack of coherency in the layers obtained made the build up of thermally induced stresses unlikely.

Roll bonding was used to bond W-25^a/oRe-50^a/oMo alloy and hafnium foil and powders of zirconium oxide and aluminum oxide to the substrate alloys. Attempts to bond tungsten and rhenium foil to the substrates by this method failed.

The tungsten was not sufficiently ductile and the rhenium lost its ductility too rapidly through work hardening during the rolling.

b. Hot Press Bonding

This method has proved useful for joining together a wide variety of flat layer materials. The applied stresses help to increase and maintain the interfacial contact required for bonding. Since these stresses are essentially compressive, there was little likelihood that fracture would occur in application of any of the brittle substances under consideration as potential barriers. The heating promotes bonding by accelerating diffusion. If the temperature attained is sufficiently high, a small amount of plastic flow may occur producing some additional increase in interfacial contact.

The device used for hot press bonding in this work is essentially a simple graphite clamp, as shown in Fig. 1. It holds the pieces being bonded together in rigid contact while they are heated in a vacuum furnace. Since refractory oxide spacers in the clamp and the materials to be joined have higher thermal expansion coefficients than graphite, considerable pressure is created during heating.

In the studies of the second year's portion of this program, hot press bonding was used to bond tungsten and rhenium foils to the substrate metals, iridium foil to tungsten and to apply the coating metal to all of the barrier/substrate combinations prepared. A temperature of about 3000°F was used in bonding tungsten and rhenium to substrate metal, 2200°F for bonding the iridium to the tungsten, and less than 2000°F was required for applying the platinum coating metal.

c. Chemical Vapor Deposition

With this method deposition is accomplished through the decomposition of a compound at a heated substrate. Excellent deposits may be formed. However, special compounds are required and the deposition parameters may vary considerably from substance to substance.

Texas Instruments had previously developed capabilities for applying a number of materials by this method. One such material, boron nitride, was evaluated as a diffusion barrier and found inadequate in the first year of this program. Another which appeared of potential interest because of its extreme refractoriness was silicon carbide. Chemical vapor deposits of it have been prepared and evaluated

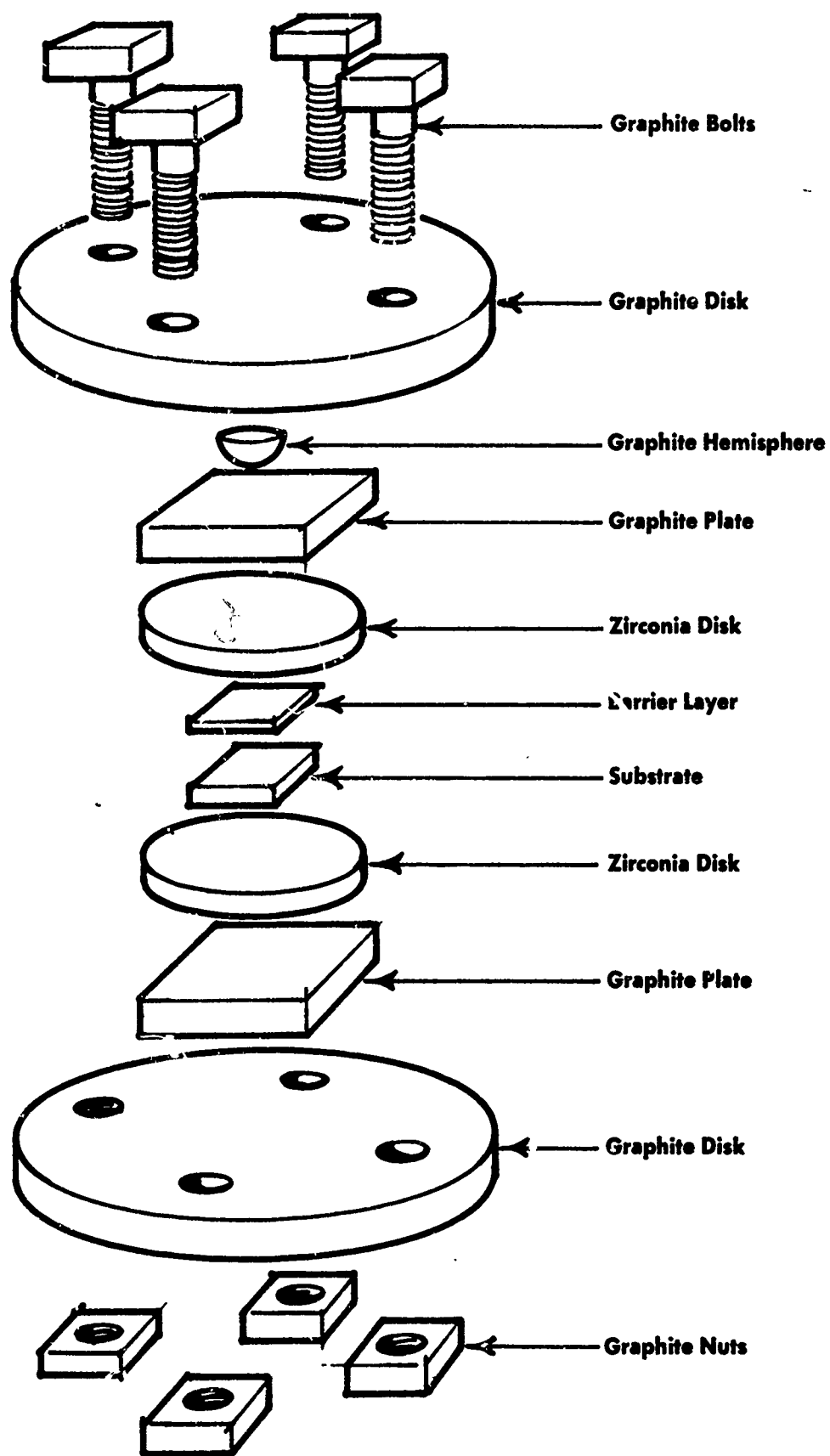


FIGURE 1
Graphite Clamp for Hot Press Bondings

in this second year's contract.

d. Physical Vapor Deposition Through Electron Beam Evaporarion

A focused high energy electron beam may be used to vaporize any known material. Subsequently the vapor may be condensed on a substrate to produce a coating. This technique was used for deposition of the refractory oxides under consideration in this program because no other application technique was available which appeared capable of forming the desired pore-free layers of these materials. Only one of the six refractory oxide/substrate combinations (ZrO_2 , MgO , and Al_2O_3 on TZM and FS-85 alloys) could not be prepared by this method - Al_2O_3 /TZM

Several attempts were made to apply this oxide to the TZM substrate, but in each case the deposits obtained were not adherent. It is likely that with further work a good layer could have been produced. However, due to time limitations additional efforts with this method were not justified.

2. Encasement in Platinum

A sample type was desired which could be used for all barrier-substrate combinations without influencing test results. The configuration designed is shown in Fig. 2 and consists of the following:

- (1) the substrate coated on one side with a layer of material to be evaluated as a diffusion barrier;
- (2) a platinum picture frame (lower picture frame in Fig.1) which holds and protects the edges of the barrier/substrate combination.
- (3) a 0.003 inch thick platinum coating (upper cover plate in Fig. 1) to be bonded onto the barrier layer;
- (4) a second outer picture frame (upper picture frame in Fig.1) with a smaller inside diameter to be placed over the 0.003 inch coating to afford more complete protection where shearing may have taken place in bonding and/or diffusion may be proceeding up from the edges; and
- (5) a thick layer of platinum bonded across the substrate to provide long time protection to the face where no barrier deposit is present.

All of the sample components except the outer picture frame are initially bonded together by hot pressing (at 2000°F) in the graphite clamp of Fig. 1. To assure complete sealing of the sample and apply the outer picture frame it is reheated in an induction coil to about 1400°F in air while pressure (approx-

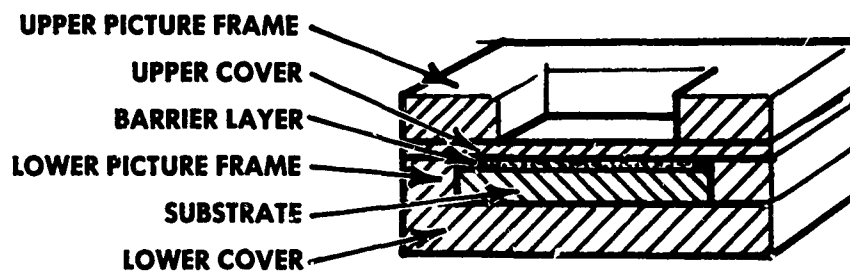
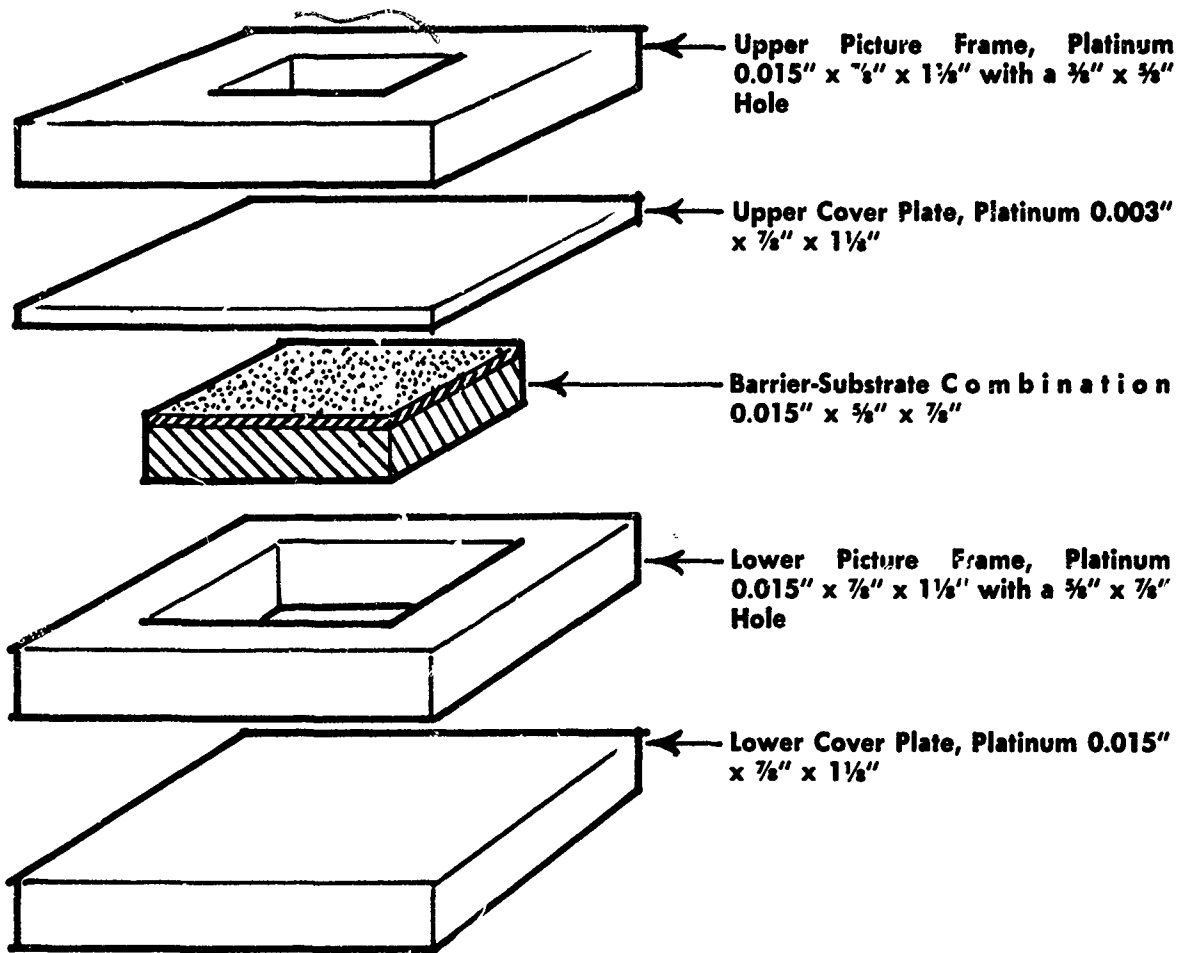
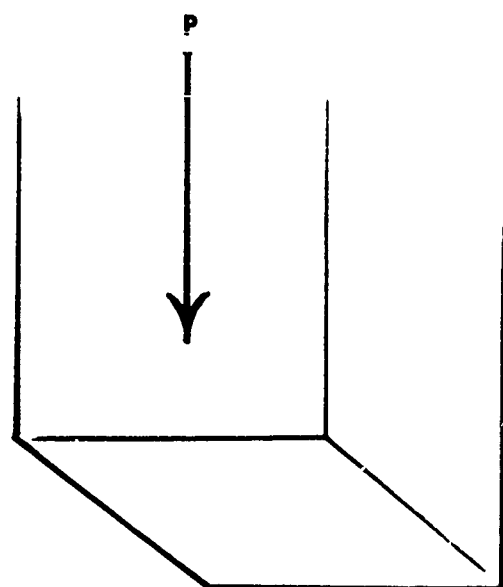


FIGURE 2
Diffusion Barrier Test Sample

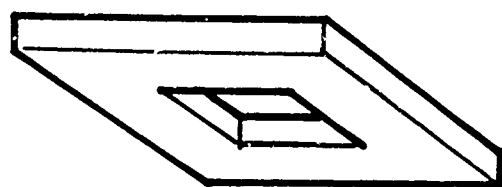
imately 2000 psi) is applied from a hydraulic press. This setup is pictured in Fig. 3.

C. Testing and Evaluation

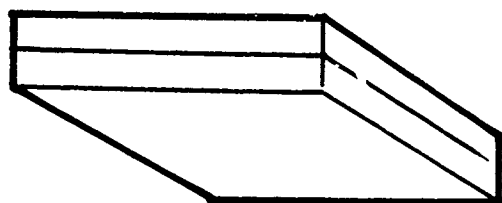
All tests were conducted in a horizontal tube furnace (Fig. 4) at 2550°F with air flowing at 240 inches per minute. The samples were removed from the furnace every few hours and examined at room temperature for change in surface appearance and weight. Any fracture noted in the coating or weight change differing significantly from that expected of the exposed surface of platinum were considered as denoting coating failure. Samples were sectioned after failure and observed metallographically for any pertinent interfacial reactions.



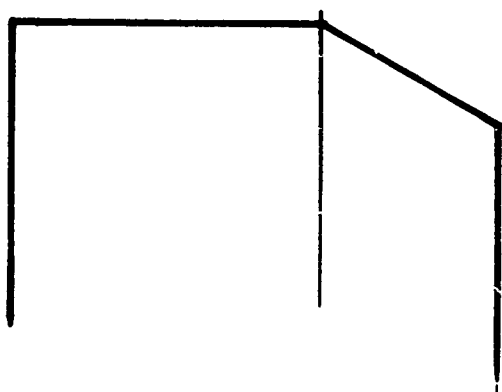
Upper Die, Inconel



Upper Picture Frame, Platinum



Remainder of Picture Frame Sample; Platinum, Substrate Alloy and Diffusion Barrier



Bottom Die, Inconel

FIGURE 3
Hot Pressing Setup for Applying Upper Picture Frame and
Completing the Sealing of a Diffusion Barrier Test Sample

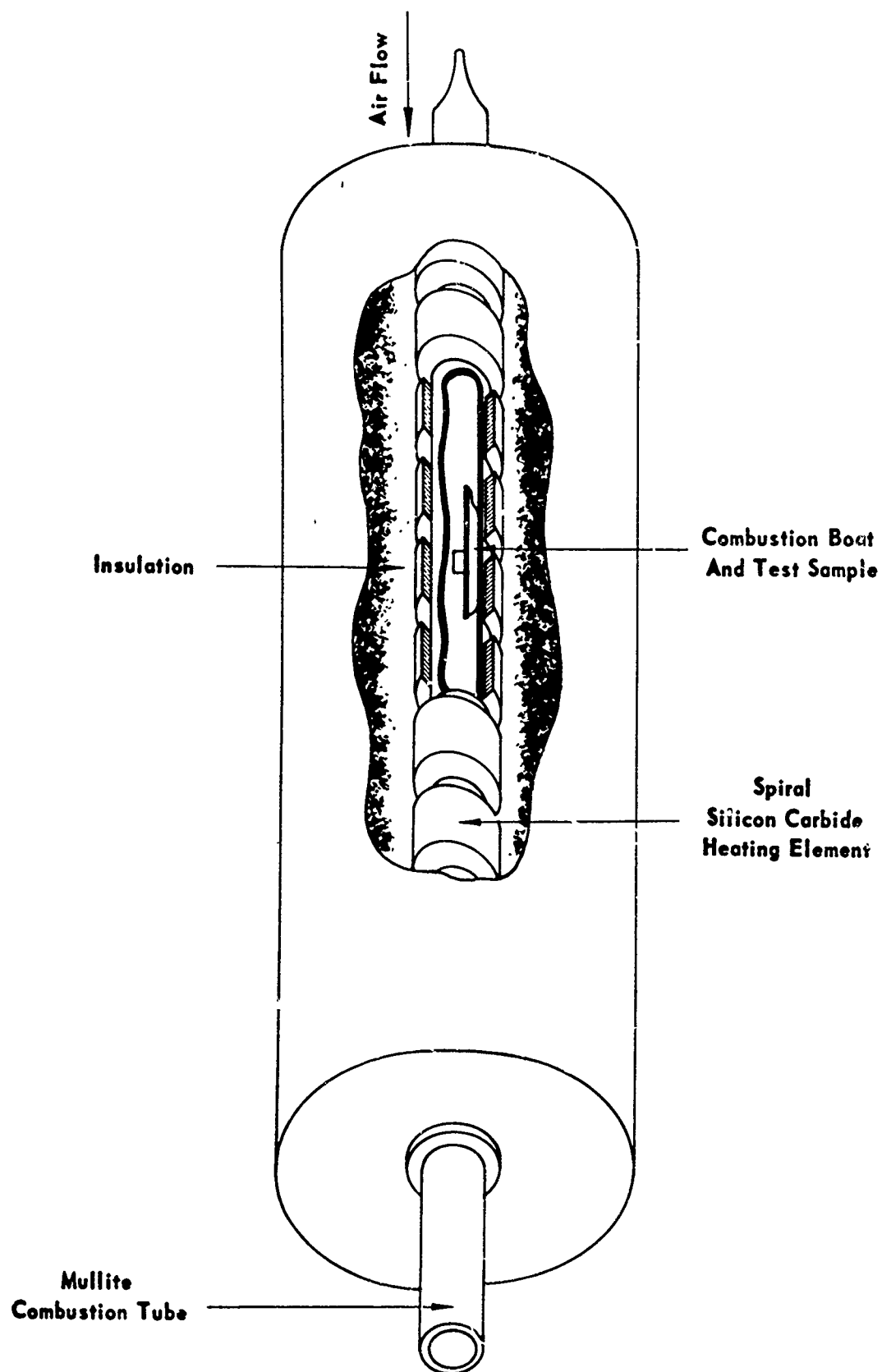


FIGURE 4
Oxidation Test Furnace

IV. RESULTS AND DISCUSSION

The results obtained for all barriers tested are given in Table II. Also included are test results on two additional types of samples from which useful comparisons may be drawn:

- (1) Samples which have the same configuration but contain no diffusion barrier.
- (2) Samples for which the diffusion barrier is replaced by an additional 0.002 inch thickness of platinum. (0.005 inches total coating thickness.)

The results obtained with 0.003 inches thick coatings and no diffusion barrier show that at 2550°F in air flowing at 240 ipm, coating life expectancy is approximately 16 hours. Such findings are similar to the life expectancy under similar operating conditions as determined on roll bonded samples in the first year of this program. Use of hafnium as a barrier essentially doubled coating life time and the iridium-tungsten barrier nearly tripled it. The 0.005 inch platinum coating offers similar protection.

The other materials evaluated as barriers either afforded no improvement to the basic sample configuration or actually degraded the coatings' effectiveness. It was particularly surprising that zirconia did not provide any barrier action since the work of the first contract indicated that it should (on TZM alloy). The second year's tests on zirconia were initially performed with vapor deposited material. Layers of compounds produced in this manner may often be non-stoichiometric and the inability of the zirconia deposit to reduce diffusion was first attributed to formation of such a defect structure. However, as indicated in Table II, a sample with roll bonded coating of zirconia was also evaluated and found ineffective. It is not evident why this substance appeared to prevent diffusion when tested in the first year of the program. Silicon carbide was seen to react with platinum during sample encapsulation and could not be tested. The samples containing hafnium failed through extensive rupture of the coating.

Following testing, all other sample combinations were sectioned for metallographic examination. No particularly unusual interfacial reactions were observed. The oxides being evaluated could no longer be visually found. Metallic appearing layers were noted at the interfaces of the samples in which metals were evaluated as barriers. Whether these were the original metals and/or newly formed intermetallic compounds was not established because of the complexity of the interface. To gain a better understanding of the diffusion-induced failure an extensive analysis of simpler systems containing no barrier was undertaken as discussed in the Appendix.

TABLE II

SAMPLES EVALUATED FOR DIFFUSION BARRIER STUDIES

<u>Coating/Barrier/Substrate</u>	<u>Method of Barrier Application</u>	<u>Barrier Thickness (Mils)</u>	<u>Time to Coating Failure (Hours)</u>
Samples which contained no potential diffusion barriers			
Pt/ - /FS-85			16
Pt/ - /TZM			16
Pt/Pt/FS-85	2 mils of platinum was substituted for the barrier		50
Pt/Pt/TZM	2 mils of platinum was substituted for the barrier		66
Samples containing materials evaluated as diffusion barriers			
Combinations in which metals were evaluated			
Pt/W/FS-85	Hot Press Bonding	1.5	18
Pt/W/TZM	Hot Press Bonding	1.5	18
Pt/W-25a/oRe-30a/oMo/FS-85	Roll Bonding	1.1	2
Pt/W-25a/oRe-30a/oMo/TZM	Roll Bonding	1.1	2
Pt/Re/FS-85	Hot Press Bonding	2.0	17
Pt/Re/TZM	Hot Press Bonding	2.0	13
Pt/Hf/FS-85	Roll Bonding	1.5	34
Pt/Hf/TZM	Roll Bonding	1.5	25
Pt/Ir+W/FS-85	Hot Press Bonding	1.5 + 1.5	66
Pt/Ir+W/TZM	Hot Press Bonding	1.5 + 1.5	63
Combination in which non-metals were evaluated			
Pt/SiC/FS-85	Chemical Vapor Deposition	0.02	0
Pt/SiC/TZM	Chemical Vapor Deposition	0.02	0
Pt/ZrO ₂ /FS-85	Physical Vapor Deposition	0.2	20
Pt/ZrO ₂ /TZM	Physical Vapor Deposition	0.2	17
Pt/ZrO ₂ /TZM	Roll Bonding	0.4	13
Pt/Al ₂ O ₃ /FS-85	Physical Vapor Deposition	0.2	16
Pt/Al ₂ O ₃ /TZM	Roll Bonding	0.2	16
Pt/MgO/FS-85	Physical Vapor Deposition	0.04	9
Pt/MgO/TZM	Physical Vapor Deposition	0.2	5

V. CONCLUSIONS

1. The placement of layers of tungsten, rhenium, W-25^a/oRe-30^a/oMo alloy, silicon carbide, zirconia, alumina or magnesia between platinum coating and TZM or FS-85 substrates will not significantly reduce the degrading interdiffusion of these binary combinations at 2550°F.
2. Hafnium and iridium clad tungsten layers interposed between platinum coating and FS-85 or TZM substrate will decrease the rate of degrading interdiffusion at 2550°F somewhat, but are no more effective at increasing coating life than would be a similar addition of coating metal.
3. After rapid initial formation the intermetallics produced between the coating and the substrate alloys appear to act as a barrier to additional diffusion from the substrates.
4. It is likely that coating life may be extended considerably if the formation of platinum-substrate alloy intermetallics is properly controlled.

Henry F. Breit
H. Breit

John F. Clarke
J. F. Clarke

Edward H. Girard
E. H. Girard

APPROVED BY: T. S. Burkhalter
Dr. T. S. Burkhalter
Director of Research and Development
Materials and Controls Division

REFERENCES

1. J. J. Buchinski and E. H. Girard. Study of Ductile Coatings for the Oxidation Protection of Columbium and Molybdenum Alloys. Final Report prepared under Bureau of Naval Weapons Contract NOW 63-0706-c. October 1964.
2. Evaluation Procedures for Screening Coated Refractory Metal Sheet. Report MAB-189-M. National Academy of Sciences, National Research Council, Washington, D. C. February 1963.
3. Developmental Data, Climelt TZM. Climax Molybdenum Company of Michigan, New York, N.Y. January 1962.
4. Fansteel 85 Metal, Technical Data Bulletin TD823C. Fansteel Metallurgical Corporation, North Chicago, Illinois.
5. Tarr, C. O. Personal Communication. General Electric Company. Nuclear Materials Propulsion Operation. Cincinnati, Ohio. 1965.
6. J. J. English. Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten. DMIC Report 183. February 1963.
7. J. J. English. Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten. DMIC Report 152. April 1961. pp. 26, 53, 90.
8. M. Hansen. Constitution of Binary Alloys. McGraw-Hill Company Inc., New York, N. Y. 1958. p. 1136.
9. E. M. Passmore, J. E. Boyd, and B. S. Lement. Investigation of Diffusion Barriers for Refractory Metals. ASD TDR 62-432. July 1962.
10. R. F. Vines. The Platinum Metals and Their Alloys. The International Nickel Company, Inc., New York, N. Y. 1941 p. 71.
11. F. F. Schmidt and H. R. Ogden. The Engineering Properties of Columbium and Columbium Alloys. DMIC Report 188. September 1963. p. A-79.
12. F. F. Schmidt and H. R. Ogden. The Engineering Properties of Molybdenum and Molybdenum Alloys. DMIC Report 190. September 1963. p. A-122.
13. A. Goldsmith, T. E. Waterman, and H. J. Hirschorn. Thermophysical Properties of Solid Materials. Volumes I and III. WADC Technical Report 58-476. AD 247193. August 1960.
14. O. H. Krikorian. Thermal Expansion of High Temperature Materials. UCRL 6132. September 1960.

15. W. Betteridge and D. W. Rhys. The High Temperature Oxidation of the Platinum Metals and Their Alloys. First International Congress on Metallic Corrosion 1961. L. Kenworth, Editor. Butterworths, Inc. London. 1962. pp. 186-192.
16. Fourth Annual Report - High Temperature Materials and Reactor Component Development Programs. Volume I - Materials. General Electric Company. Cincinnati, Ohio. February 26, 1965.
17. M. Deak. A New Method of Suppressing Thermionic Emission from the Grids of Transmitting Tubes. The Brown Boveri Review. Vol. 48, No. 7, July 1961. pp. 394-403.
18. Zirconium Oxides and High Temperature Materials. Product Bulletin No. 8. Zirconium Corporation of America., Cleveland, Ohio. Sept. 1962.
19. D. W. Rhys. Laboratory Studies on Processes Using Platinum for the Protection of Molybdenum Against Oxidation at High Temperatures. Compte rendm du Symposium sur la Fusion du Verre. Brussels. 1958. pp. 677-684.

APPENDIX

A. Diffusion Studies

Results of a preliminary examination of the failure mechanism in simple coating/substrate alloy samples were included in the reports for the first year of this program. They revealed that platinum protected the substrates from oxidation during the initial stages of testing but that deterioration of either substrate material followed after an incubation period. The deterioration was accounted for on the basis of columbium or molybdenum diffusing through the platinum coating. Molybdenic oxide was postulated to form and volatilize directly at the surface of TZM while columbium changed the solubility of oxygen in the platinum, allowing oxygen to rapidly diffuse to the FS-85 substrate and attack it. The purpose of investigating the diffusion barriers was to determine which materials would stop or slow down the movement of substrate atoms through the platinum cladding. As noted in earlier discussion the materials evaluated as barriers were no more effective than an equal thickness of platinum. In order to gain a more thorough knowledge of the failure mechanism and a better feeling for the choice of barriers, a study was made using the basic materials under examination. The following sections of this report are a result of this analysis.

1. Diffusion of Substrate Elements

A weight change versus time at temperature plot for both platinum and composite materials appears in Fig. 5. Since all surfaces of test specimens which are exposed to the atmosphere are platinum, the initial weight losses of all three materials are due to the oxidation of platinum. However, the weight change of pure platinum remains essentially linear with time while those of the clad materials do not. Changes in curve slopes are an indication of failure. As already noted diffusion has a profound effect on these slope changes.

Diffusion rates are initially very high when composite materials are heated to the testing temperature. If a metal was continuously soluble in platinum the condition represented in Fig. 6 would be met. As the substrate metal diffuses into the platinum lattice, the thickness of the alloyed layer designated "X" increases. The basic difference between such a system and those under examination is the presence of intermetallic compounds. Metallographic examination clearly reveals the existence of a number of intermetallics of different composition at the interface. The total thickness of the intermetallic layers increases with time but not at a uniform rate. Metallographic data shows that they grow at a very high initial rate followed by a much slower rate.

Microprobe analyses were run on two specimens which had failed. The data are represented in Figs. 7 and 8. Even though the original platinum coating thicknesses for each specimen did not exceed

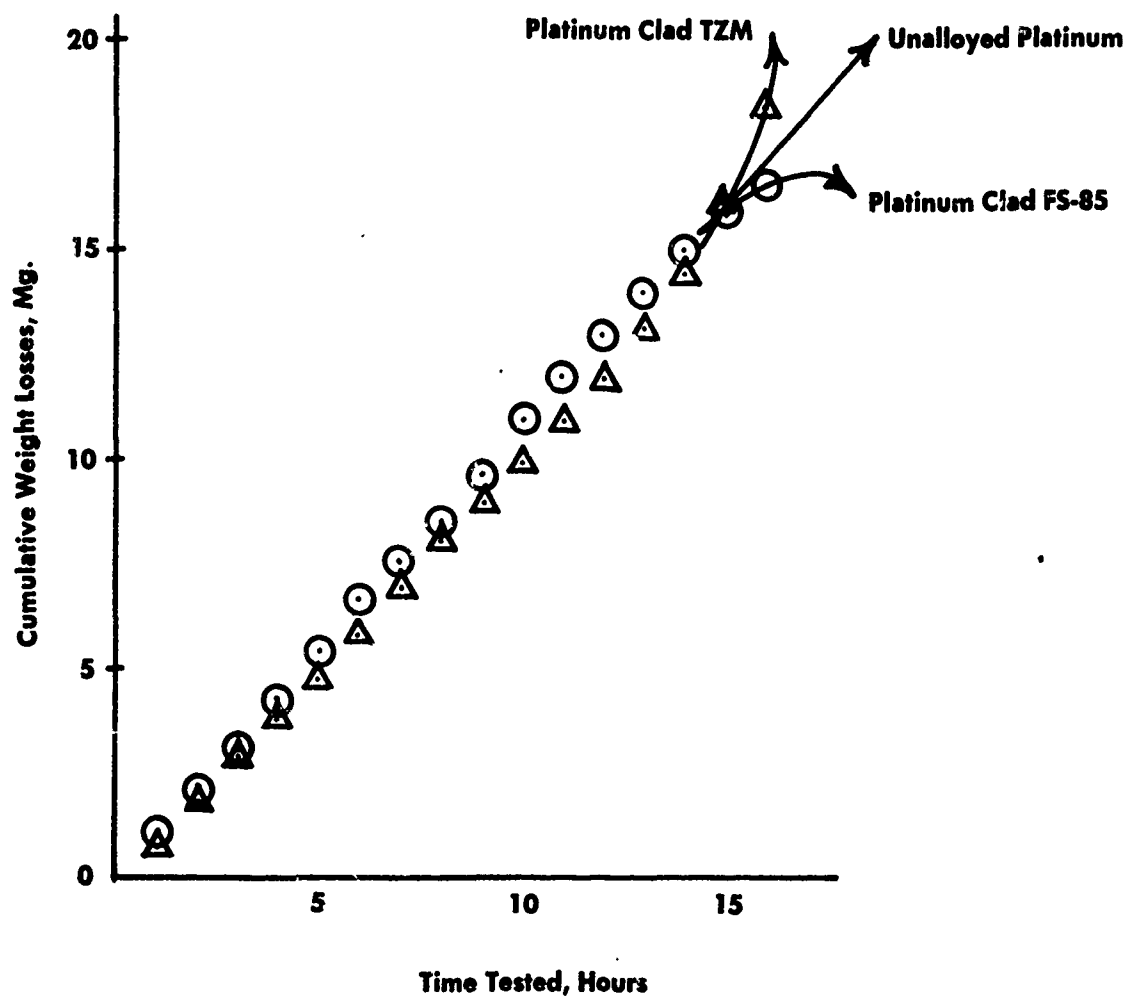


FIGURE 5

Cumulative Weight Losses as a Function of Time for Unalloyed Platinum, Platinum/TZM and Platinum/FS-85 Samples Tested in a 240 ipm Air Flow at 2550 °F

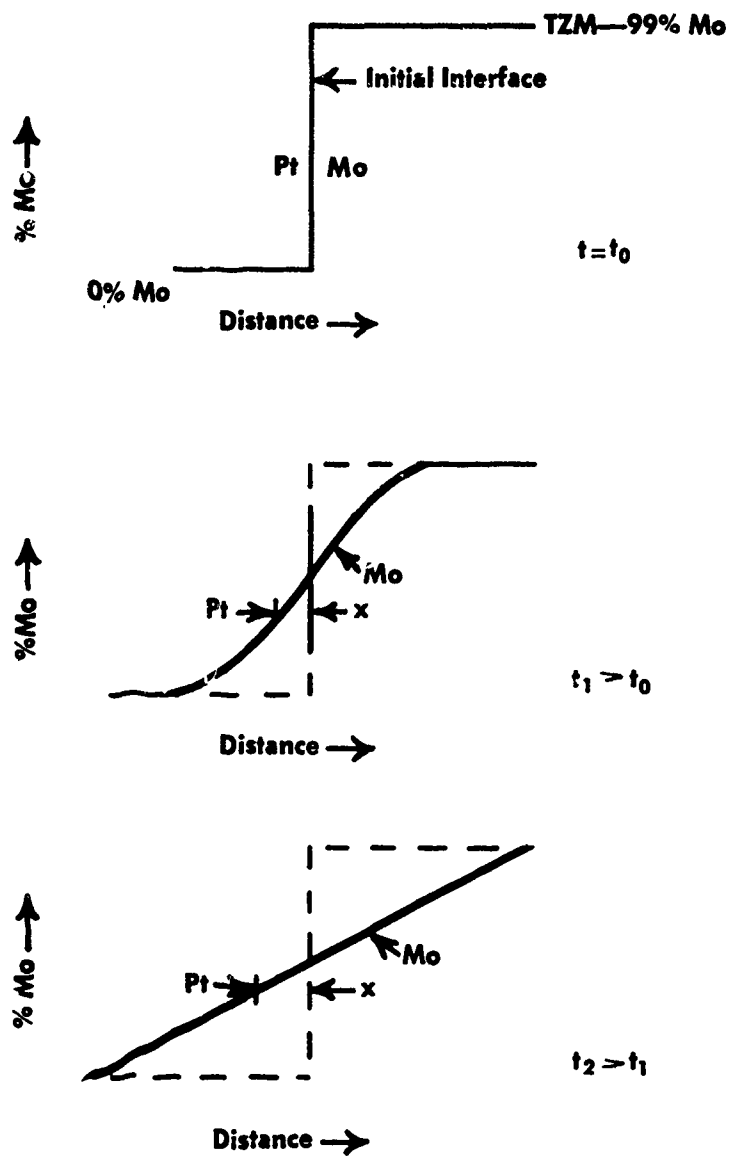


FIGURE 6

Changes in Concentration Gradient with Time (t) Which Would be Expected in a Pt/Mo Diffusion Couple if These Elements Were Mutually Soluble

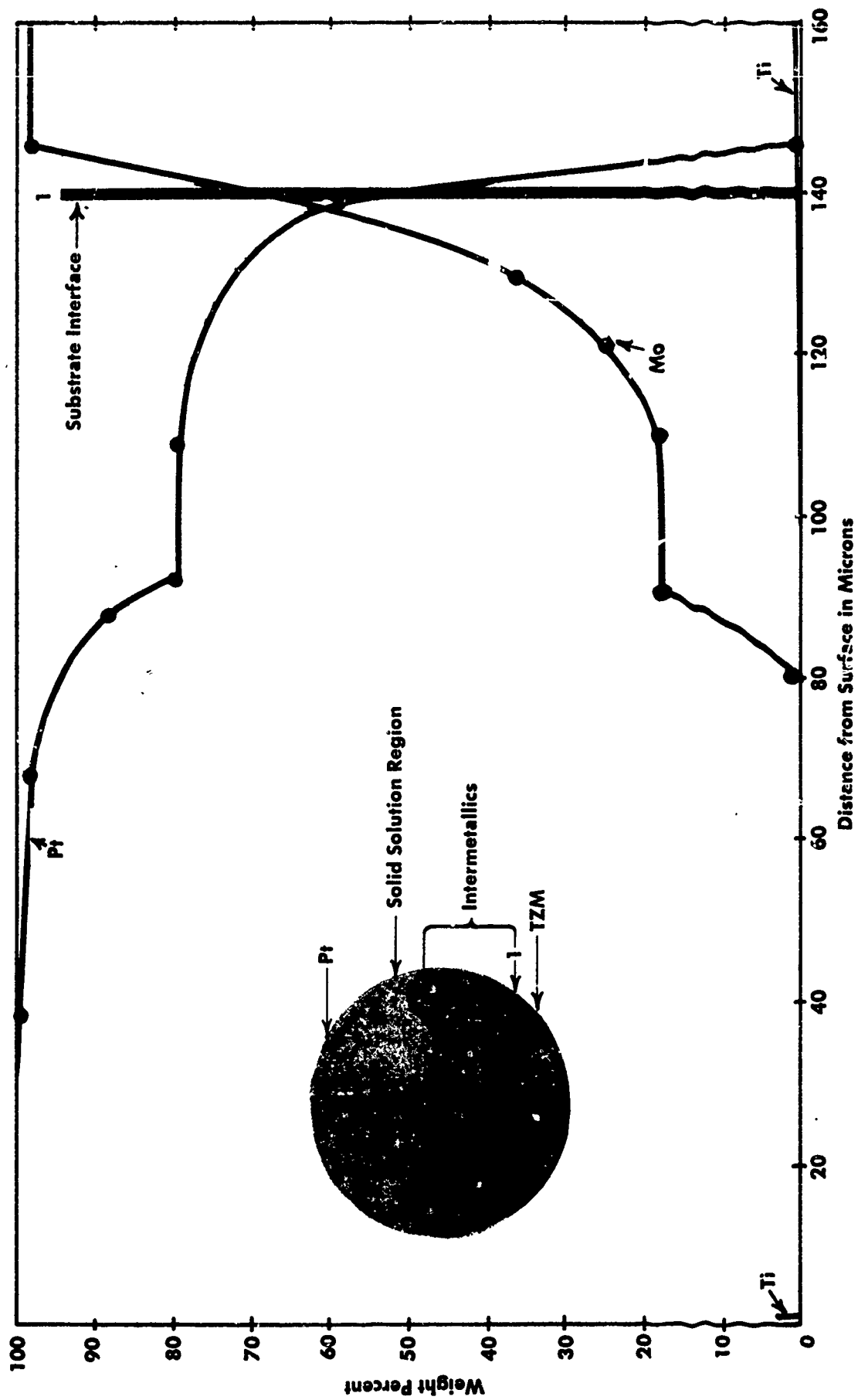


FIGURE 7
 Electron Beam Microanalysis Data on Pt Clad TZM Tested for
 7 hrs. at 2550 °F in a 240 ipm Air Flow

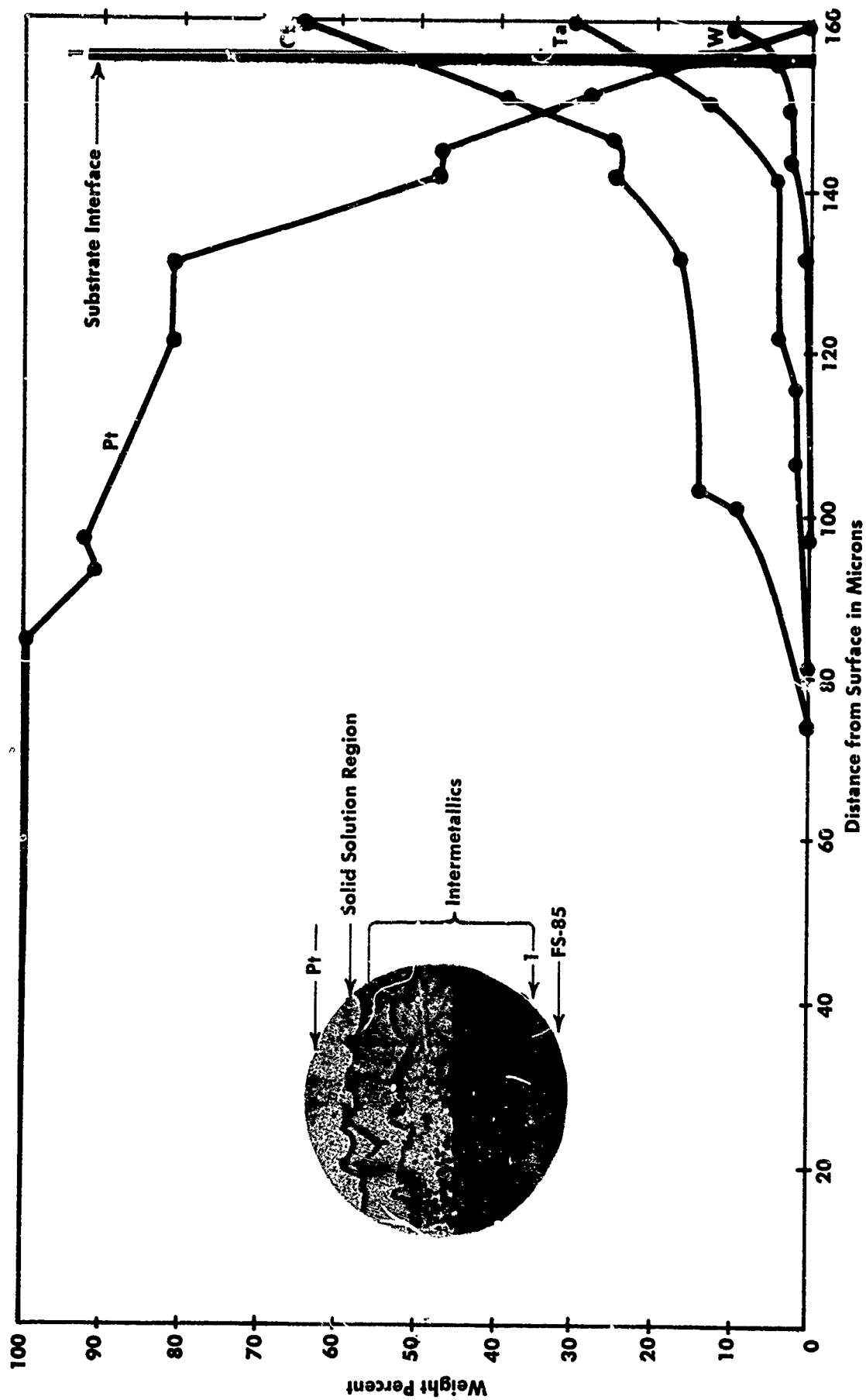


FIGURE 8
Electron Beam Microanalysis Data on Pt Clad FS-85 Tested
for 16 hrs. at 2550 °F in a 240 ipm Air Flow

0.003 inch, the analyses indicate that the substrate atoms (solute) have not reached the surface. However, these solute elements might exist in the platinum lattice at sufficiently low concentrations such that detection by microprobe analysis is difficult. Indeed, solute presence near the surface was indicated since both specimens had failed. Each of the concentration plots can be divided into two portions: (1) the intermetallic layers; and (2) the solid solution region.

Because of the low concentration gradients associated with the intermetallics, the diffusion mechanism should be hindered allowing less solute to diffuse toward the surface. However, the solute does diffuse rapidly into the platinum during early stages of testing before sufficient concentrations have been established to form intermetallic layers. This portion of solute is believed to be the main cause of failure in both the columbium FS-85 and molybdenum TZM base composites since it encounters only a platinum lattice which is low enough in solute to be receptive to further diffusion.

In order to investigate the growth of the solid solution and intermetallic layer regions a specimen was clad with 0.015 inches of platinum and tested at 2550°F. The purposes of the test were to have enough platinum to prevent substrate atoms from reaching the surface and to compare the growth of intermetallic layers with that of specimens having thinner platinum claddings. The changes in thickness of the intermetallic layers with time are presented in Fig. 9. The initial rate of growth is very high, followed by a significantly slower rate. The rapid increase in intermetallic layer thickness might be even higher than indicated if more data points were taken at shorter times. Of course, only the portion of the solid solution region at high concentrations can be observed by this technique while that at low concentrations cannot be. To obtain an estimate of the solute penetration into the platinum, microhardness traverses were run. The results are plotted in Fig. 10. Although the thickness of the intermetallic layers had not increased appreciably with time, the extent of the solid solution region had increased. Note that the approximately 20 micron solid solution region in Fig. 7 had increased to about 0.0045 inches in thickness. It is reasonable to expect that the far greater sensitivity of the microprobe analysis would indicate even further penetration. With the 0.015 inches thickness of platinum, the life of the specimen was 275 hours at 2550°F, indicating that the extent of the solid solution region has a profound affect on the failure mechanism.

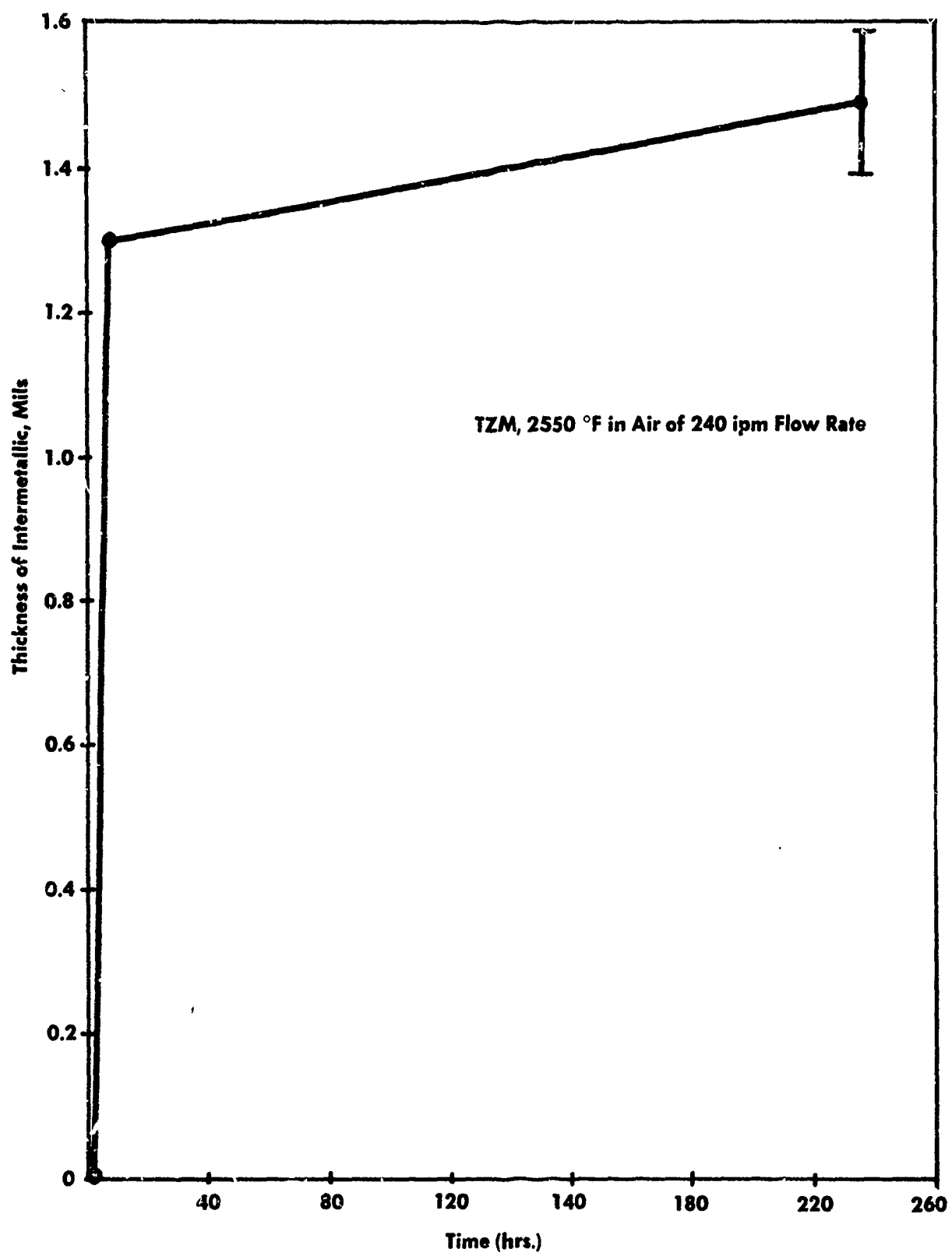


FIGURE 9
Effect of Time on Thickness of Intermetallic Region

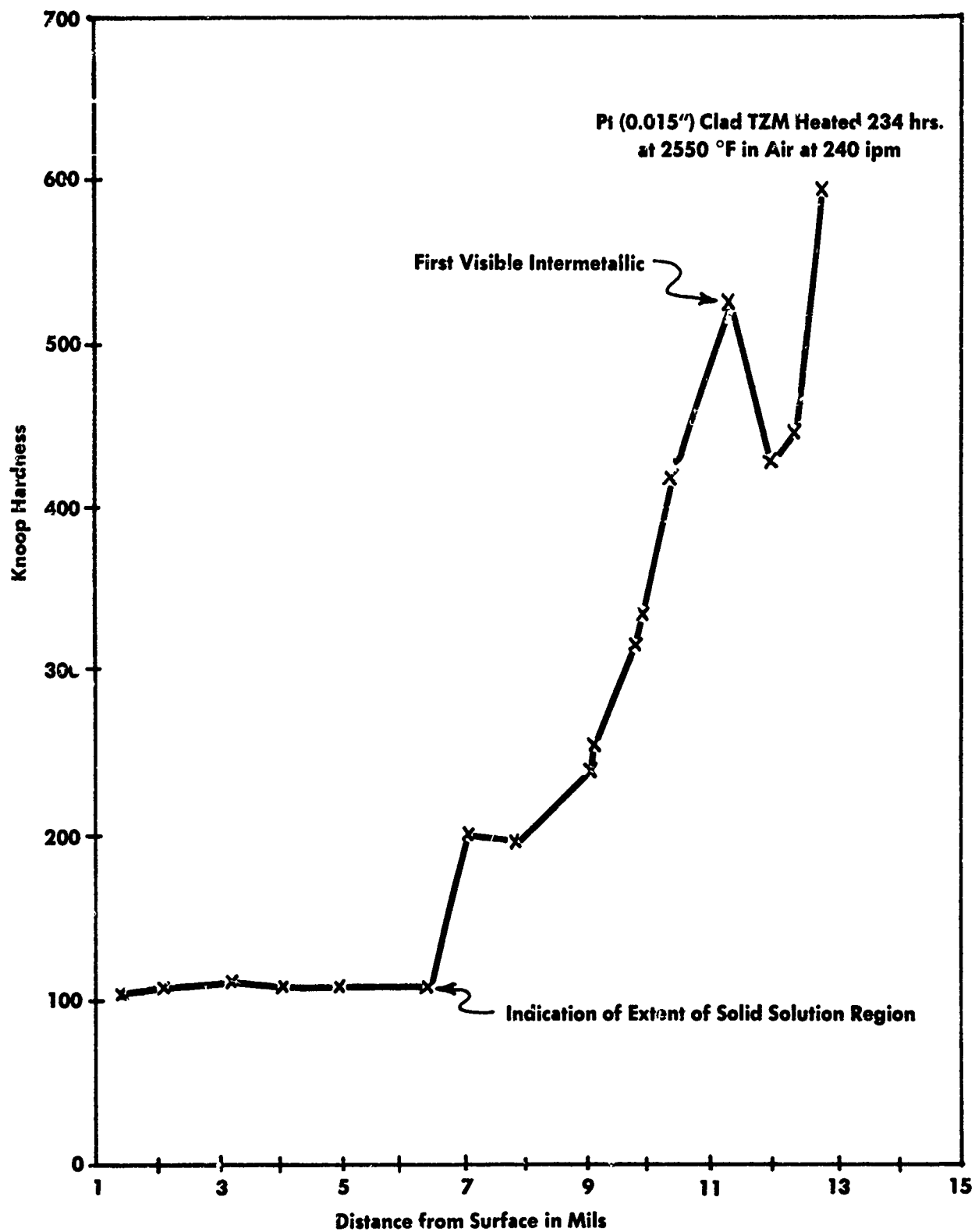


FIGURE 10
Effect of Solute Penetration on Hardness

2. Differences in Failure Mechanisms

a. Platinum Clad Columbium FS-85

Non-uniform growth of the intermetallic layers was frequently observed in platinum clad columbium FS-85. For example, some parts of the outermost intermetallic layer in Fig. 11 are much closer to the surface of the composite than others. Therefore the solid solution portion of the composition/distance curve was also closer to the surface and failure would most probably occur in these areas. When columbium was present in high enough concentrations near the platinum surface, the solubility of oxygen in the platinum increased. Oxygen could then move more easily toward the higher columbium concentrations. These conditions are presented in Fig. 12. The oxygen diffusing initially met such low concentrations of columbium that internal oxidation did not occur. At higher columbium concentrations internal oxidation occurred. This is shown in Fig. 13. As columbium oxide continued to form, the lattice became depleted of columbium thus, further driving force for the diffusion of columbium from the substrate to these depleted areas was created. Specifically, columbium was forced to diffuse from the intermetallic compound to the area of lower concentration. Such diffusion can be observed where the boundaries of an intermetallic layer receded to the substrate. However, the intermetallic layer was still of sufficient thickness to retard the movement of columbium to the region of lower concentration. With further time at temperature, columbium continued to internally oxidize at a rate dictated by the established oxygen concentration gradient.

If the above mechanism had continued, the weight loss versus time curves would have maintained their nearly constant slope. But, the curves eventually changed slope abruptly. This may be related to the fact that, with further internal oxidation, the lattice was strained. The straining present in the area of a grain boundary is indicated in Fig. 14. The strains were of such magnitude that the grain boundary was separated and oxygen was given easier access to the substrate, allowing blisters to form. The increased rate of oxidation i.e. the weight change, can be accounted for on the basis of a change in diffusion mechanism. The mechanism may be one of surface diffusion along the opened boundary, or merely direct contact with the atmosphere. Eventually the mechanism is not dissimilar to placing FS-85 in air in these isolated regions.

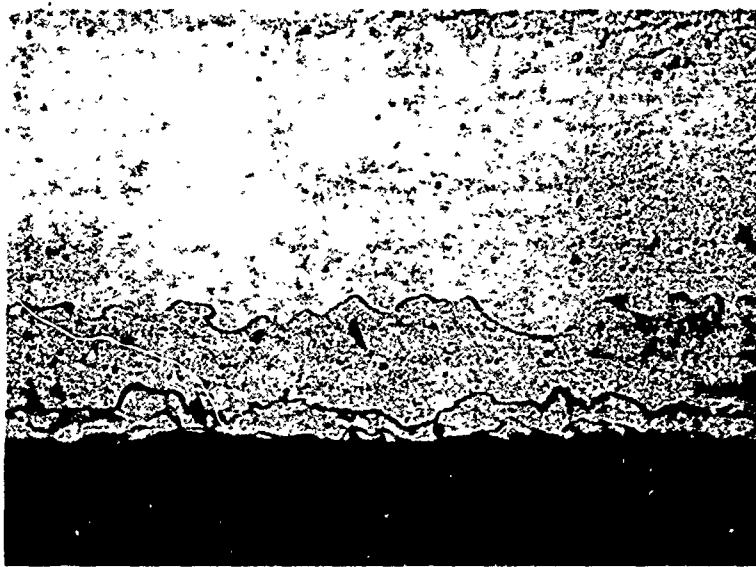


FIGURE 11

**Pt (0.003") Clad FS-85 Tested at 2550 °F for 7 hrs. in a 240
ipm Air Flow**

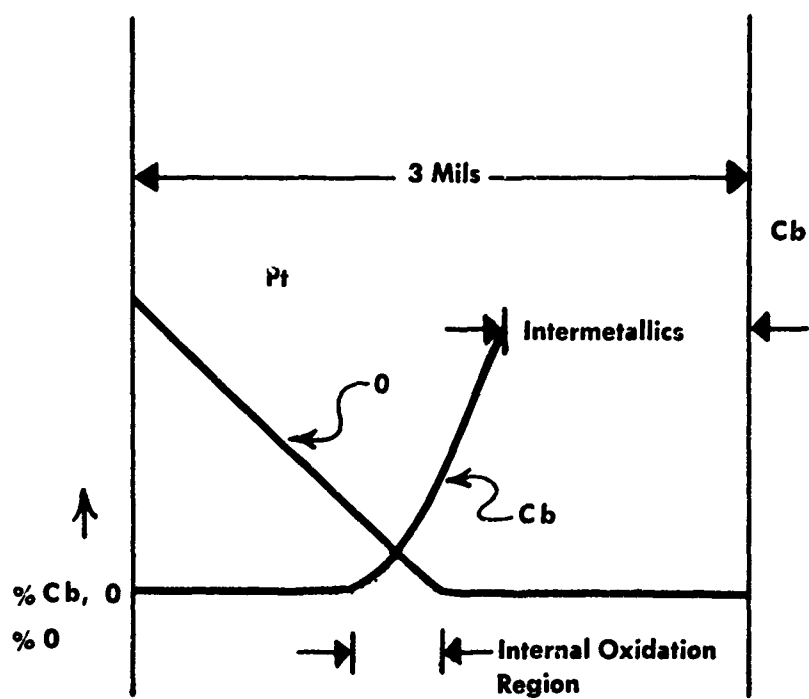


FIGURE 12
Concentration of Oxygen and Columbium (from FS-85) in a Coating at Failure

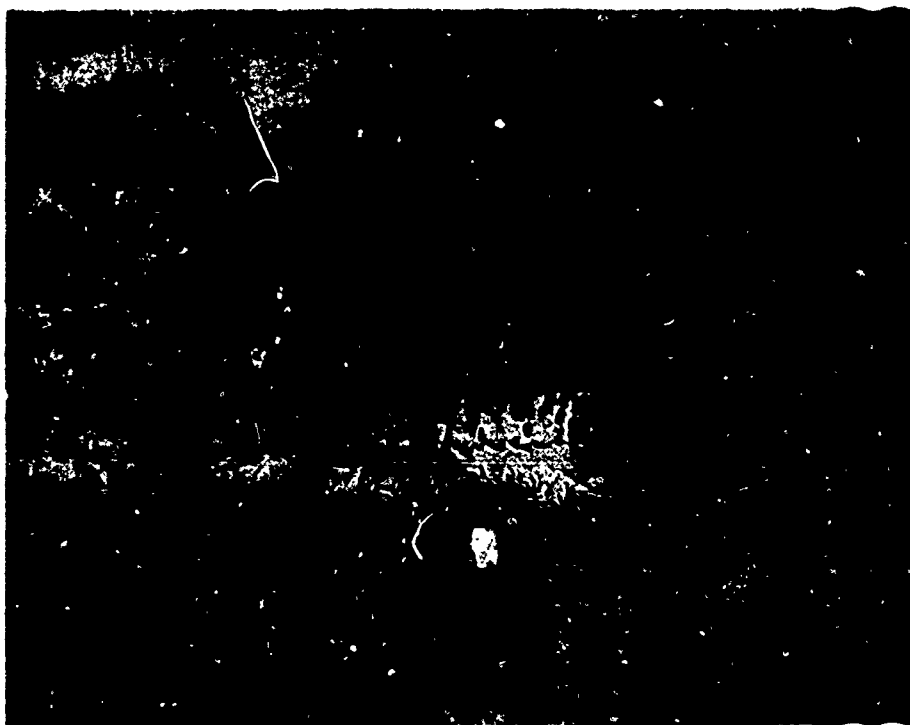
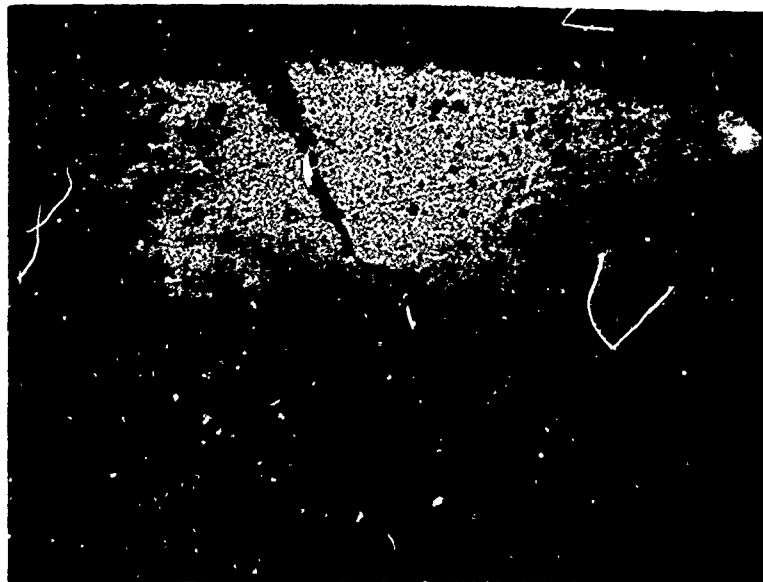


FIGURE 13

**Pt. (0.003") Clad FS-45 Tested for 16 hrs. at 2550 °F in a
240 ipm Air Flow**



1500X



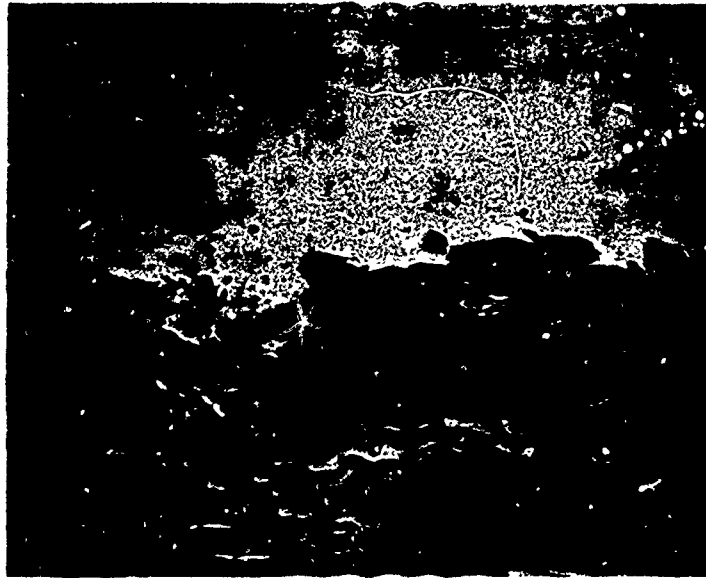
500X



1500X

FIGURE 14

**Pt. (0.003") Clad FS-85 Tested for 16 hrs. at 2550 °F in a
240 ipm Air Flow**



400X

FIGURE 15

**A Typical Void Area Formed at Failure of a Platinum Clad
TZM Sample Heated at 2550 °F in a 240 ipm Air Flow**

b. Platinum Clad Molybdenum TZM

The occurrence of nonuniform intermetallic compound formation along the platinum substrate interface was also common to molybdenum TZM. Although failure was expected in those areas where the intermetallic compound was closer to the surface, the mechanism of failure was markedly different from that of columbium FS-85. In fact, molybdenum TZM did not fail by blister formation. When solute reached the surface of the composite, oxide formed and vaporized. The net result was that the specimen continued to lose weight.

Since the rate at which molybdenum approached the surface is diffusion dependent, an abrupt change in slope of the curve should not have been observed; that is, molybdenum should have continued to diffuse to the surface. However, molybdenum also has difficulty in diffusing through an intermetallic compound layer. Also, voids formed at the platinum-intermetallic interface such as shown in Fig.15 and continued to grow as more molybdenum diffused to the surface.

It is believed that the mechanism which transferred molybdenum from one side of a void to the platinum cladding was highly dependent on void formation. Because of the high temperatures and the presence of a free surface, diffusion on the void surface should have played a role. However, it is not believed to have been the predominant mode of transfer. When the coating ruptured the presence of a blue-black oxide was observed on void surfaces. MoO_2 or Mo_2O_3 are characterized by such a blue-black oxide. The presence of such oxide indicates that oxygen was also diffusing from the surface to the substrate and forming these oxides. At the testing temperatures, the oxides have a high vapor pressure. This leads to the assumption that molybdenum is diffusing by means of molybdenum oxide vapor transport.

3. Influence of Substrate Alloying Elements

Certain elements in sufficient concentration can promote greater solubility of oxygen in platinum. This behavior was expected of the alloying additions in both molybdenum TZM and columbium FS-85. To determine the extent to which this influenced the results of the present experiments, both pure columbium and molybdenum were clad and tested. Results indicated that the failure time was not appreciably altered, indicating that alloying additions were not enhancing the penetration of oxygen. On the basis of the microprobe data represented in Fig.7 and 8 only very low concentrations of both

molybdenum and columbium are needed near the surface.

4. Diffusion Mode

In order to investigate the total contribution of diffusion through grain boundaries as opposed to bulk diffusion, three 0.001 inch layers of platinum were hot pressed onto a molybdenum TZM substrate instead of the standard 0.003 inch layer. This was done to minimize grain growth by restricting the grain growth to each of the three layers, thus offering a more tortuous path to the diffusing solute. No significant change in life was observed indicating that lattice (bulk) diffusion accounted for most of the transported material.

B. Summary of Observations

1. The failure of Pt-clad FS-85 and TZM is strongly dependent upon the substrate atoms which initially diffuse into the platinum before intermetallic compounds form near the Pt-FS-85 interface.
2. The growth rate of the intermetallic layers is very high initially but slows down with time at temperature.
3. The total penetration of the substrate atoms into the platinum is dependent upon movement of the substrate atoms in the platinum solid solution.
4. The intermetallic layers hinder the movement of substrate atoms into the platinum.
5. Columbium must be depleted from the intermetallic layers before oxygen can react directly with the substrate.

C. Suggestions for Future Work

It has been shown that the life of a composite can be prolonged by using increasing thicknesses of platinum. However, the additional expense and thermal expansion differences cannot be tolerated. A more logical approach would be to utilize the intermetallic layers which form between platinum and molybdenum or columbium. The data presented in this report show that the layers are excellent diffusion barriers, since enough solute cannot be pumped through them to compensate for material which has oxidized. Approaches such as forming thin layers of intermetallics on the substrate followed by the hot pressing of an additional platinum layer are recommended for further investigation.

B. Summary of Observations

1. The failure of Pt-clad FS-85 and TZM is strongly dependent upon the substrate atoms which initially diffuse into the platinum before intermetallic compounds form near the Pt-FS-85 interface.
2. The growth rate of the intermetallic layers is very high initially but slows down with time at temperature.
3. The total penetration of the substrate atoms into the platinum is dependent upon movement of the substrate atoms in the platinum solid solution.
4. The intermetallic layers hinder the movement of substrate atoms into the platinum.
5. Columbium must be depleted from the intermetallic layers before oxygen can react directly with the substrate.

C. Suggestions for Future Work

It has been shown that the life of a composite can be prolonged by using increasing thicknesses of platinum. However, the additional expense and thermal expansion differences cannot be tolerated. A more logical approach would be to utilize the intermetallic layers which form between platinum and molybdenum or columbium. The data presented in this report show that the layers are excellent diffusion barriers, since enough solute cannot be pumped through them to compensate for material which has oxidized. Approaches such as forming thin layers of intermetallics on the substrate followed by the hot pressing of an additional platinum layer are recommended for further investigation.