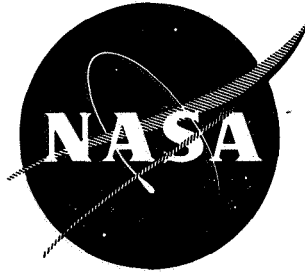


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COATINGS FOR ADVANCED THRUST CHAMBERS

by

W. J. Lewis

Final Report

Prepared for

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

NASA LEWIS RESEARCH CENTER

Contract NAS 3-11185

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THRUST CHAMBERS

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W. J. Lewis

AEROJET-GENERAL CORPORATION

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Charles F. Zalabak, Project Manager

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PREFACE

This report was prepared for NASA-LeRC under Contract NAS 3-7955. The NASA Technical Manager was Mr. C. F. Zalabak. The author wishes to acknowledge the contributions of J. A. Cunningham for the heat transfer analysis, E. W. Fraczek for the Stress Analysis, and D. Jassowski and C. M. Gracey for the HES evaluations.

The report was reviewed and approved by R. E. Anderson, Manager, Powder Metallurgy Section and A. V. Levy, Manager of the Materials and Technology department.

I. SUMMARY

Thermal barriers were developed to reduce the heat flux to the coolant for a regeneratively cooled engine operation with liquid O_2 and liquid H_2 propellant.

A thermal analysis and a propellant exhaust gas analysis were conducted to provide the thermal and chemical environments which were the basis for the selection of the material and thickness of the thermal barrier coatings. The thermal analysis was conducted for a typical thrust chamber to determine the range of coating thermal resistance required to maintain a maximum heat flux of 20 Btu/in.² sec. The design temperature for the coating-tube interface was 1600°F maximum with a coating surface temperature of 4000°F. The thermal resistance of the coating for these conditions was established at 200 in.²-sec-°F/Btu at the throat of the chamber.

The chemical environment at the throat of the chamber operating at 2000 psia with LO_2/LH_2 propellant at a mixture ratio of 6 was established as 70% H_2O , 24% H_2 , 3% OH , 2.5% H , 0.2% O_2 , 0.2% O . Materials Compatibility with these exhaust gases was evaluated for the refractory metals, oxides, and diborides with melting points above 4000°F. Compatibility between the respective materials in a composite was considered as well as compatibility with the exhaust stream gases. On the basis of the compatibility comparisons, the material systems selected for evaluation were tungsten-zirconia, molybdenum-zirconia, tungsten-hafnia, and molybdenum-hafnia.

Three coating concepts were evaluated in this program. They are: (1) the conventional concept of plasma arc spraying the thermal barrier on the ID surface of a conventionally fabricated thrust chamber; (2) the single tube concept in which the coating is plasma-arc sprayed on the crown of individual tubes and then the coated tubes are fabricated into a thrust chamber; and (3) the tile concept in which thermal barrier tiles are fabricated, setup on a mandrel and a thrust chamber is electroformed on the thermal barrier.

I, Summary (cont.)

A thermal analysis and a stress analysis were made on the single tube coating and the conventional coating concepts. The thermal analysis showed that the thermal barrier is only required on the crown of the tube and not in the valleys between the tubes and that a slot, 0.010 inch wide, extending longitudinally along the valley between tubes, could be tolerated. Therefore, the single tube coating concept is realistic from a thermal standpoint. The stress analysis showed that the maximum stresses in the coating in the single tube concept was 21,560 compared to 30,560 psi in the coating of the conventional coating concept. Therefore, the single tube coating concept is realistic from both the stress and thermal standpoints.

The selected materials were plasma-arc sprayed on disk and five tube specimens and then evaluated by plasma-arc exposure. In these tests, the heat flux was maintained at 12 Btu/in.²-sec and the surface temperature was maintained at approximately 4000°F. The thermal resistance of the coating was measured in the plasma tests and an indication of oxidation and thermal shock resistance was obtained by specimen examination. It was established that the oxidation resistance of the $\text{ZrO}_2^{(a)}$ and HfO_2 coatings was better than the coatings containing Mo or W and that the Mo- ZrO_2 coating was better than the W- ZrO_2 mixtures.

The single tube concept was evaluated by plasma-arc spraying the crown of single tubes and joining these coated tubes by TIG welding on the backside to form specimens for plasma-arc testing. These specimens performed satisfactorily and were similar to that of the conventionally coated tube specimens.

The tile concept fabrication was evaluated by pressing the sintering ZrO_2 tile and by impregnating ZrO_2 cloth. The pressed and sintered tiles had extremely low thermal resistance and were necessarily very thin, therefore, they were extremely fragile. The tile fabricated from impregnated ZrO_2 cloth were tested in the plasma arc and there was no measurable oxidation. However, the thermal resistance of the impregnated ZrO_2 cloth was

(a) ZrO_2 stabilized with 5% CaO and HfO_2 stabilized with 5% Y_2O_3 .

I, Summary (cont.)

800 in.²-sec/Btu-°F rather than the required 200 in.²-sec/Btu-°F. On the basis of the material evaluation tests, the ZrO₂, HfO₂ and Mo-ZrO₂ coatings were selected for evaluation in the H₂/O₂ Hyperthermal Environmental System (HES) tester. The nominal conditions were: test durations - 15 sec, gas flame temperature - 6000°F, chamber pressure - 50 psia, heat flux - 25 Btu-in.²-sec. The results of the HES tests were comparable to the laboratory plasma tests. The ZrO₂ and HfO₂ coatings performed equally well with little or no regression. Regression was observed on the Mo-ZrO₂ coatings, in the range of 0.06 mil/sec.

II. INTRODUCTION

The cooling limits are often reached in regeneratively cooled liquid rocket thrust chambers and supplementary cooling methods are required to reduce the heat flux to the coolant. In conventional systems, the heat flux is reduced by small amounts of fuel film coolant. In high performance, high heat flux systems, excessive fuel would be required to provide the necessary film cooling, resulting in a significant loss in overall engine performance. A thermal barrier coating on the nozzle ID permits a higher inside wall temperature than can be achieved with the bare tubes and thereby reduces the heat flux to the coolant.

The objective of this program was to develop thermal barrier coatings which can be applied to the inner wall of a regeneratively cooled thrust chamber operating with LH_2/LO_2 propellant at chamber pressures of 2000 psia. The coating would provide sufficient thermal resistance (thickness/thermal conductivity) to reduce the heat flux to a value which would permit operation well within the limits of state-of-the-art cooling materials, and fabrication technology. For this purpose the upper limit of heat flux was 20 Btu/in.²-sec with a maximum tube wall temperature of 1600°F.

This report is organized to cover each of the major program tasks as follows:

- III Analysis of Chemical and Thermal Environments
- IV Material Selection
- V Analysis of Coating Concepts
- VI Experimental Procedures
- VII Thermal Barrier Evaluation
- VIII Conclusions and Recommendations

III. ANALYSIS OF CHEMICAL AND THERMAL ENVIRONMENTS

A. THERMAL ANALYSIS

The thermal analysis was conducted for a typical regeneratively cooled thrust chamber to establish the coating thermal resistance (coating thickness/coating thermal conductivity) required to reduce the heat flux to the coolant under the conditions; LO₂/LH₂ propellant, 2000 psia chamber pressure, LO₂/LH₂ mixture ratio of 6, coating hot gas surface temperature 4000°F, and tube interface temperature of 1600°F.

The gas-side convective film coefficient was calculated using the Bartz⁽¹⁾ correlation which is a modified form of a Nusselt-type equation in the following form:

$$h_g = \frac{0.026}{D^{0.2}} \left[\frac{C_p \mu^{0.2}}{Pr^{0.6}} \right]_{AM} \left[\frac{W_T}{A} \frac{T_{FS}}{T_{AM}} \frac{M_{AM}}{M_{FS}} \right]^{0.8}$$

where:

- h_g = gas-side film coefficient
- D = chamber diameter
- C_p = specific heat
- Pr = Prandtl number
- μ = viscosity
- W_T = propellant flow rate
- T_{FS} = freestream temperature
- M_{AM} = molecular weight at arithmetic mean temperature
- AM = arithmetic mean, 1/2 (recovery temp. + gas side wall temp.)
- A = cross-sectional flow area
- T_{AM} = arithmetic mean temperature
- M_{FS} = freestream molecular weight

The recovery temperature used as the driving temperature between the combustion gases and chamber wall was calculated from the following equation using a combustion efficiency of 95%.

$$T_r = \eta^2 \left[T_{FS} + Pr^{1/3} (T_o - T_{FS}) \right]$$

T_r = recovery temperature

η = combustion efficiency

T_{FS} = freestream temperature for $\eta = 100\%$

Pr = Prandtl number

T_o = stagnation temperature for $\eta = 100\%$

The calculated gas side film coefficient and recovery temperature are plotted as functions of chamber area ratio in Figure 1. The coolant-side film coefficient (h_L) was not calculated because it is a function of the coolant passage geometry and a nozzle was not designed.

The heat flux to the coolant, Q/A , at the throat was derived as follows:

$$Q/A = \frac{T_r - T_B}{\frac{1}{h_g} + t/k + \frac{1}{h_L}}$$

with the following conditions:

recovery temperature $T_r = 5380^\circ\text{F}$ (calculated),

coolant bulk temperature $T_B = -350^\circ\text{F}$ (assumed),

gas side film coefficient $h_g = 0.012 \text{ Btu/in.}^2\text{-sec-}^\circ\text{F}$ (calculated),

stainless steel tube wall thickness $t = 0.015 \text{ in.}$ (assumed),

stainless steel thermal conductivity $k = 0.00025 \text{ Btu/in.-sec-}^\circ\text{F}$,

and coolant heat transfer coefficient $h_L = 0.03 \text{ Btu/in.}^2\text{-sec-}^\circ\text{F}$ (assumed);

a heat flux to the coolant of $33 \text{ Btu/in.}^2\text{-sec}$ was derived for uncoated nozzles

For coated nozzles, a heat flux of $13 \text{ Btu/in.}^2\text{-sec}$ was selected because it provided a significant decrease to the coolant and because it could be evaluated conveniently in the laboratory. The thermal resistance, R , for a

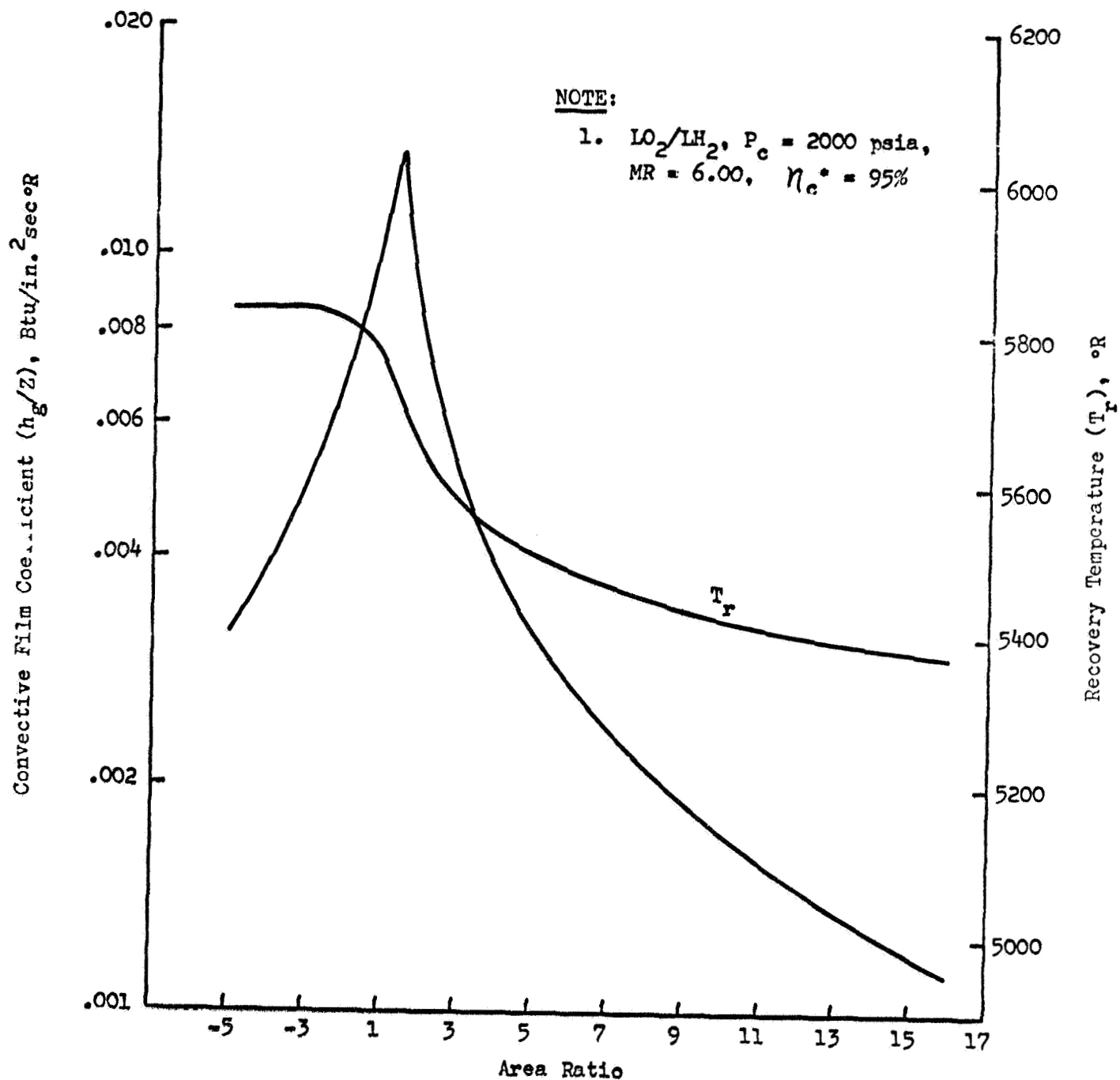


Figure 1. Convective Film Coefficient and Recovery Temperature

III, A, Thermal Analysis (cont.)

coating to provide a heat flux to the coolant of 13 Btu/in.²-sec was derived as follows:

$$Q/A = \frac{T_r - T_{MW}}{\frac{1}{h_g} + R}$$

where: stainless steel tube surface temperature $T_{MW} = 1600^\circ\text{F}$.

The thermal resistance for the coating was 200 in.²-sec/Btu. This value was used throughout the program for the design of the thermal barrier coatings.

B. CHEMICAL ENVIRONMENT

The combustion products or exhaust gas species were obtained from calculated chemical equilibrium equations. The quantity of each gas specie as a function of oxidizer/fuel mixture ratio is shown in Figure 2. The theoretical gas composition of the throat for a mixture ratio of 6 is:

70% H₂O, 24% H₂, 3% OH, 2.5% H, 0.2% O₂ and 0.2% O.

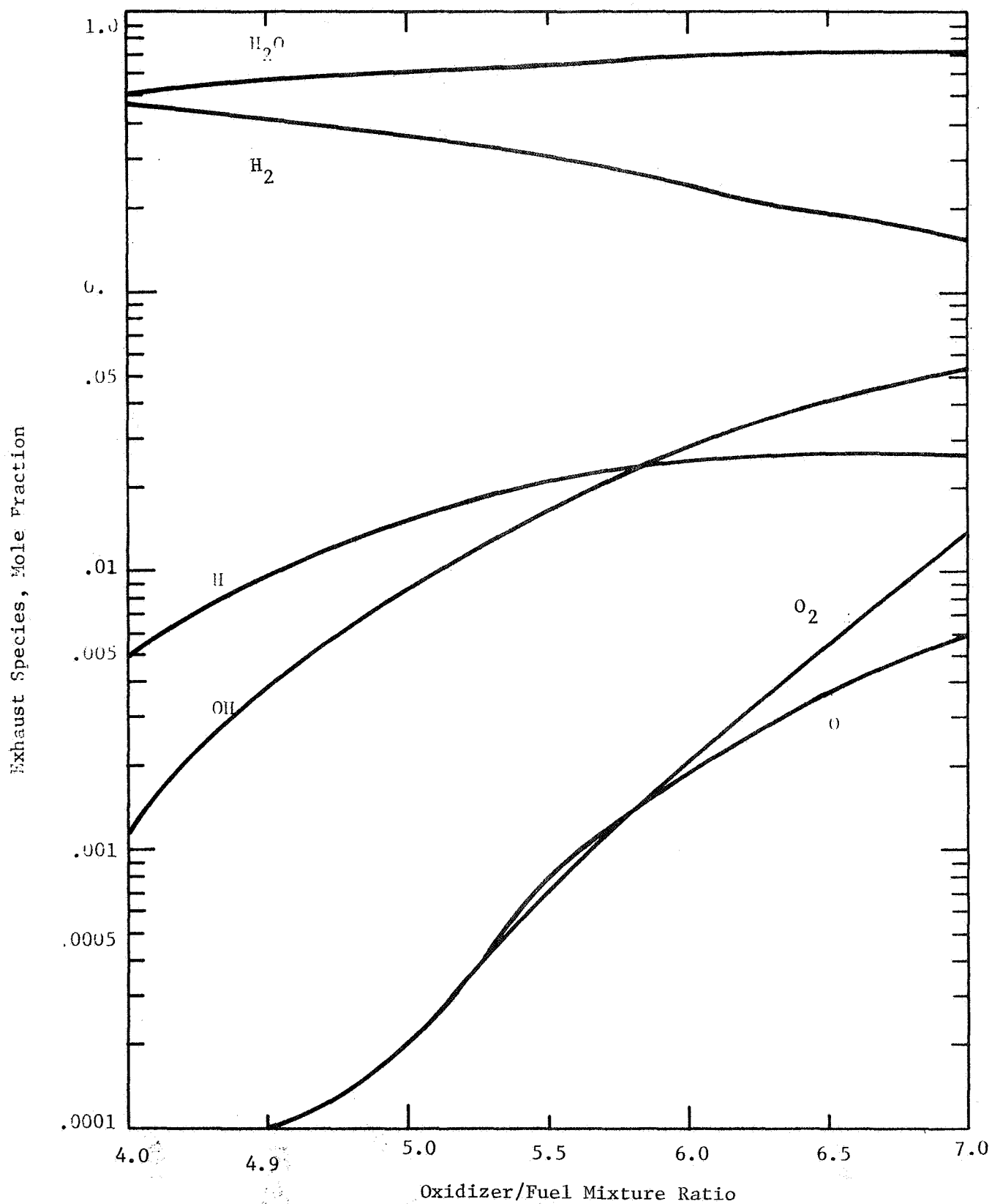


Figure 2. Exhaust Gas Species vs Mixture Ratio For H_2/O_2 Propellant at Throat with Chamber Pressure of 2000 psia

IV. MATERIAL SELECTION

The selection of the material for the thermal barrier is based on the melting point, thermal conductivity, density, costs, compatibility with the exhaust gases and capability of being sprayed.

The candidate materials for the thermal barrier coatings are W, Mo, ZrO_2 , Al_2O_3 , HfO_2 , MgO , ThO_2 , TiB_2 and ZrB_2 . The candidate materials and the propellant exhaust gas specie were examined on the criteria of the free-energy calculated from available data⁽²⁾⁽³⁾. The calculations were made for a pressure of 2000 psia and for temperatures of 3000, 4000, and 5000°F. The results of these calculations are shown in Table I; negative free-energy of reaction numbers indicate that the reaction will occur.

An examination of Table I shows that the candidate metals for the thermal barrier composites, tungsten and molybdenum have similar compatibility with the propellant gas species based on the free energy calculations; both are compatible with H_2O but not free oxygen or OH. The candidate oxide materials, ZrO_2 , HfO_2 , MgO , and ThO_2 , are compatible with the oxidizing gas species, but, both HfO_2 and MgO are not compatible with H. ZrO_2 is compatible with all the species at all temperatures. The candidate diborides, TiB_2 and ZrB_2 , do not have a compatibility advantage over the oxides. Both are expected to react with H, O, O_2 , and OH as shown in Table I.

Data^(4,5,6,7) are available on the compatibility of tungsten and molybdenum nozzle inserts with the exhaust of solid and liquid rocket test firings in which the only variable was the nozzle insert material. These data, Table II, show that the regression rate of both tungsten and molybdenum are comparable. However, with high flame temperature (5600°F) propellants, the regression rate of molybdenum increased because of surface melting. The regression rate of both metals increased with a decrease in density; the use of additives to the tungsten did not significantly lower the regression rate.

TABLE I
FREE ENERGY OF REACTION FOR MATERIALS EXPOSED TO EXHAUST OF HYDROGEN/OXYGEN AT 2000 PSIA

Wall Temperatures Gas Species:	Free Energy of Reaction, F, kcal/mole at 2000 psia																	
	3000°F						4000°F						5000°F					
	H ₂	H	H ₂	O	O ₂	OH	H ₂	H	H ₂	O	O ₂	OH	H ₂	H	H ₂	O	O ₂	OH
<u>Metals</u>																		
3W+9H ₂ O → W ₃ O ₉ +9H ₂	+54						+44	-					+33					
W+H → No Data																		
W+H ₂ → No Data																		
3W+9O → W ₃ O ₉					-618						-602					-550		
6W+9O ₂ → 2W ₃ O ₉					-673						-595					-555		
6W+18OH → 2W ₃ O ₉ +9H ₂						-717					-606						-550	
Mo+3H ₂ O → MoO ₃ +3H ₂	+32						+20					+10						
Mo+H → No Data																		
Mo+H ₂ → No Data																		
Mo+3O → MoO ₃					-217						-194					-172		
Mo+3O ₂ → 2MoO ₃					-195						-189					-178		
2Mo+6OH → 2MoO ₃ +3H ₂						-209					-192							-172
<u>Oxides</u>																		
ZrO ₂ +H ₂ O → No Data																		
ZrO ₂ +2H → Zr+H ₂ O		+9						+66						+65				
ZrO ₂ +2H ₂ → Zr+2H ₂ O			+109						+102						+95			
ZrO ₂ +O → No Data																		
ZrO ₂ +O ₂ → No Data																		
ZrO ₂ +OH → No Data																		
Al ₂ O ₃ +H ₂ O → No Reaction																		
Al ₂ O ₃ +6H → 2Al+3H ₂ O		-26						+9						+32				
Al ₂ O ₃ +3H ₂ → 2Al+3H ₂ O			+192						+185						+178			
Al ₂ O ₃ +O → No Data																		
Al ₂ O ₃ +O ₂ → No Data																		
Al ₂ O ₃ +OH → No Data																		

TABLE I (Cont.)

Wall Temperatures Gas Species:	Free Energy of Reaction, F, kcal/mole at 2000 psia											
	3000°F				4000°F				5000°F			
	H ₂ O	H	H ₂	O	H ₂ O	H	H ₂	O	H ₂ O	H	H ₂	O
HfO ₂ +H ₂ O → No Data	-				-				-			
HfO ₂ +4H → Hf+2H ₂ O		-32				-10				-6		
HfO ₂ +2H ₂ → Hf+2H ₂ O			+124				+138				+133	
HfO ₂ +O → No Data				-				-				-
HfO ₂ +O ₂ → No Data								-				-
HfO ₂ +OH → No Data									-			-
MgO+H ₂ O → No Data	-				-				-			
MgO+2H → Mg+H ₂ O		-45				-50				-50		
MgO+H ₂ → Mg+H ₂ O			+45				+30				+10	
MgO+O → No Data				-				-				-
MgO+O ₂ → No Data												-
MgO+OH → No Data												-
<u>Borides</u>												
TiB ₂ +H ₂ O → No Data	-				-				-			
TiB ₂ +6H → B ₂ H ₆ +Ti		-90				-50				-20		
TiB ₂ +3H ₂ → B ₂ H ₆ +Ti			+120				+130				+145	
TiB ₂ +3O → B ₂ O ₃ +Ti			-275				-260				-245	
TiB ₂ +2O → TiO+2B			-40				-65				-40	
TiB ₂ +3/2 O ₂ → B ₂ O ₃ +Ti				-150				-135				-135
TiB ₂ +O ₂ → TiO ₂ +2B				-100				-95				-85
TiB ₂ +4(OH) → B ₂ (OH) ₄ +Ti					-155			-125				-65
ZrB ₂ +H ₂ O → No Data	-				-				-			
ZrB ₂ +6H → B ₂ H ₆ +Zr		-95				-45				-5		
ZrB ₂ +3H ₂ → B ₂ H ₆ +Zr			+130				+140				+180	
ZrB ₂ +2O → ZrO ₂ +2B			-225				-180				-160	
ZrB ₂ +3O → B ₂ O ₃ +Zr			-260				-230				-210	
ZrB ₂ +O ₂ → ZrO ₂ +2B				-145				-110				-90
ZrB ₂ +3/2 O ₂ → B ₂ O ₃ +Zr				-140				-130				-125
ZrB ₂ +OH → No Hydroxide Formed					-				-			-

TABLE II
REGRESSION RATE OF TUNGSTEN AND MOLYBDENUM INSERTS IN ROCKET TEST FIRINGS

Material	Arcite 368 (Highly Oxidizing, Flame Temperature 4700°F)					N ₂ O/A-50 (Highly Oxidizing, Flame Temperature 5600°F)					Arcogel 113 (Mildly Oxidizing, Flame Temperature 6470°F)					HDEM (Mildly Oxidizing, Flame Temperature 6400°F)					Arcite 373 (Neutral, Flame Temperature 5600°F)							
	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec	No. of Tests	dia, in.	Duration, sec	Regression Rate, mils/sec
Pressed and Sintered Molybdenum	---	---	---	---	2 (12)	1.2	43 & 96	0.18, 0.88																				
Arc Cast Molybdenum	1 (10)	0.289	30	0	1 (12)	1.2	6	0.75									1 (10)	0.289	30	2.2	1 (10)	0.289	30	0				
Pressed and Sintered Tungsten																												
65% Dense	1 (10)	0.289	30	5.4													1 (10)	0.289	30	23.8 (cracked)	1 (10)	0.289	30	0				
75% Dense	1 (10)	0.289	30	4.0													1	0.289	30	16.4 (cracked)	1 (10)	0.289	30	0				
95% Dense	---	---	---	---	1 (12)	1.2	81	0.68	3 (9)	0.53 to 0.55	40 to 48	0.0, 0.14																
Plasma Sprayed Tungsten (Wire Reinforced)	---	---	---	---					1 (9)	0.557	60	0.89																
Arc Cast Tungsten	2 (10)	0.289	30	0.2 to 1.1					3 (9)	0.530	31 to 33	0.16, 0.30, 0.52	1 (10)	0.289	30	0	1 (10)	0.289	30	0	1 (10)	0.289	30	0				
Forged Tungsten	1 (10)	0.289	30	0	2 (12)	0.65	89 & 101	0.36, 0.96									1 (10)	0.289	30	0	1 (10)	0.289	30	0				
Extruded Tungsten									3 (9)	0.530	33 to 49	0.06, 0.24, 0.29																
W-3% Mo	---	---	---	---	---	---	---	---	7 (9)	0.528 to 0.544	36 to 52	0.01, 0.02, 0.03, 0.18, 0.21, 0.41																
W-15% Mo					6 (9)	0.530	47 to 51	0.11, 0.12, 0.12, 0.12, 0.21, 0.37																				
W-3% Re					2 (9)	0.530	47 to 55	0.15, 0.19																				
W-9% Re					1 (9)	0.530	52	0.92																				

IV, Material Selection (cont.)

Little data are available on the performance of oxides in rocket test firings because the very high thermal shock sensitivity oxides precluded their use for nozzle insert materials. However, firings were made by Winters, et al⁽⁷⁾, with highly oxidizing propellant (N_2O_4 /AeroZINE 50) using inserts of ZrO_2-SiO_2 , 85 BeO - 15 SiC, Al_2O_3 , and BeO. The regression rates were very low (0.0 to 0.43 mils/sec). These data show that the ceramic oxides are compatible with oxidizing environments which agrees with the free energy calculations.

A. REFRACTORY METALS SELECTION

The information on the refractory metals is summarized in Tables III and IV. On the basis of the data in these tables, molybdenum was selected for the prime metal addition in the thermal barrier coating. The use of initial additions are desirable to improve the thermal shock resistance of ceramic coatings. In addition, the density and cost of molybdenum, although secondary considerations, are also the lowest of the metals being considered. The thermal expansion of molybdenum is relatively low but is comparable with the other refractory metals.

Tungsten was selected as the second metal to be evaluated in the thermal barrier composite. The compatibility of tungsten at 4000°F with both the ceramic phase and the exhaust species is about the same as that of molybdenum. However, tungsten has almost twice the density and is more expensive than molybdenum. Iridium was not selected because of its excessively high cost and hafnium was not selected because of its relatively poor compatibility and high cost.

B. CERAMIC OXIDES

The information on the ceramic materials is summarized in Tables V and VI.

TABLE III
 PROPERTIES AND COST RATING OF CANDIDATE REFRACTORY METALS

Material	Melting Point, °F	Density, lb/ft ³	Thermal Conductivity, Btu/hr/ft-°F				Thermal Expansion % from Room Temperature to		Rating of Estimated Costs
			500°F	3000°F	4000°F	500°F	3000°F	4000°F	
			Refractory Metals						
Mo	4760	638	72	46	40	0.15	1.1	1.6	1
W	6170	1204	73	60	56	0.1	0.75	1.05	2
Ir	4429	1405	84	--	--	-.16	1.5	--	4
Hf	4032	817	12.2	--	--	0.15	0.55 (1800°F)	--	3

TABLE IV
COMPATIBILITY OF REFRACTORY METALS WITH OXIDIZING EXHAUST GAS SPECIES

<u>Metal</u>	<u>Compatibility at 4000°F and 2000 psia On the Basis of Free Energy Calculations</u>				<u>Estimated Compatibility in Rocket Test Firings</u>
	<u>H₂O</u>	<u>H₂</u>	<u>O₂</u>	<u>OH</u>	
Mo	NR	NR	R	R	2
W	NR	NR	R	R	2
Ir	NR ^(a)	NR ^(a)	NR ^(a)	NR ^(a)	1
Hf	NR ^(a)	R ^(a)	R ^(a)	R ^(a)	3

Note: NR indicates no reaction predicted
R indicates reaction is possible

^(a) Estimated (Free Energy Data Not Available).

TABLE V
PROPERTIES OF CANDIDATE OXIDES AND BORIDES

Material	Melting Point, °F	Density, lb/ft ³	Thermal Conductivity, Btu/hr/ft-°F			Thermal Expansion % from Room Temperature to		
			500°F	3000°F	4000°F	500°F	3000°F	4000°F
			<u>Oxides</u>					
BeO	4540	188	125	10	15	0.3	1.8	2.5
HfO ₂	5260	604	0.95	0.8	--	0.25	1.3	--
				(1500°F)				
MgO	5070	223	12	2.5	4.0	0.25	2.4	3
ThO ₂	5910	624	5	1.0	--	0.25	1.6	--
ZrO ₂	4700	360	0.9	1	1	0.25	1.7	--
<u>Borides</u>								
TiB ₂	5320	281	--	23	28	0.2	1.2	1.3
ZrB ₂	5500	380	24	12	17	0.2	0.9	1.3

TABLE VI
COMPATIBILITY OF CERAMIC OXIDES AND BORIDES
WITH AN OXIDIZING EXHAUST GAS

<u>Material</u>	<u>Compatibility at 4000°F and 2000 psia on the Basis of Free Energy Calculations</u>				<u>Estimated Compatibility in Rocket^(b) Test Firings</u>
	<u>H₂O</u>	<u>H₂</u>	<u>O₂</u>	<u>OH</u>	
	<u>Oxides</u>				
BeO	R	NR ^(a)	NR	R ^(a)	2
HfO ₂	NR	NR	NR	NR	1
MgO	NR	NR	NR	NR	3
ThO ₂	NR	NR	NR	NR	1
ZrO ₂	NR	NR	NR	NR	1
	<u>Borides</u>				
TiB ₂	-	R	R	R	3
ZrB ₂	-	R	R	R	3

^(a) Estimated

^(b) Lowest No. Indicates Most Compatible

IV, B, Ceramic Oxides (cont.)

Zirconia and hafnia were selected as the prime ceramic materials for thermal barriers in this program. Zirconia melts at 4700°F and has the lowest thermal conductivity of all the common oxides. Zirconia is stable in vacuum, hydrogen, and is compatible with the oxidizing species in a O_2/H_2 exhaust. Zirconia undergoes a transition from the normal monoclinic form at room temperature, inverting to a tetragonal form at above 2160°F. This would be a disadvantage because the transition is accompanied with a large volume change and expansion of about 10%, but the transition can be minimized by the addition of about 3% CaO to form a solid solution of cubic structure.

Hafnia has similar properties to zirconia except that it melts at a higher temperature, 5260°F. Hafnia undergoes the same transition as zirconia. The inversion occurs at about 2700 to 3300°F but is not accompanied with a large volume change or expansion as with zirconia. Hafnia is stabilized into the cubic form the same as zirconia and is readily sprayed similar to zirconia.

Magnesia has a very high vapor pressure at temperature above 3000°F. Vaporization occurs by dissociation into the elements rather than as MgO molecules. As a result, magnesia is plasma-sprayed with difficulty. In addition, magnesia shows a tendency to hydrate in the dense condition.

The diborides are of interest because of their refractory properties. Oxidation of the borides occurs by formation of an oxide of the metal. Such oxide products on the diborides may have a tendency to spall at the high-pressure rocket conditions. The thermal conductivity of the borides is higher than the oxides which would require thicker thermal barriers than those made with the ceramic oxides, and the porosity of the conversion layer would permit continued oxidation of sublayers.

IV, Material Selection (cont.)

C. CERMET MIXTURE

The key considerations in the selections of materials for cermet coatings are the compatibility of the metal and ceramic at the operating temperatures, and the thermal resistance provided by the mixture so that the coating thickness may be determined.

1. Compatibility of Refractory Metals and Ceramics

Resnick, et al.⁽⁹⁾ studied the interdiffusion of tungsten and selected oxides by placing the oxide on tungsten foil and heating in an inert gas to temperatures as high as 5400°F for 1 to 5 minutes. His results are summarized as follows:

- W + ThO₂ - no reaction at 5400°F for 3 minutes
- W + ZrO₂ - no reaction at 5400°F for 1 minute
- W + HfO₂ - slight reaction at 5150°F for 2 minutes, no new phases distinguishable after 5400°F for 1 minute

Manning, et al.⁽¹⁰⁾ studied the diffusion of ThO₂, stabilized HfO₂ and ZrO₂ in vacuum and found no reactions with W, Mo, or Re at the highest temperature they evaluated (4260°F). On the basis of this information, the ceramic and W or Mo metal mixture would be stable at the 4000°F gas-side surface temperature.

2. Thermal Resistance

The thermal resistance (thickness/thermal conductivity) as a function of composition and coating thickness for the candidate materials is presented in Figures 3 and 4. The thermal conductivities of the mixtures were

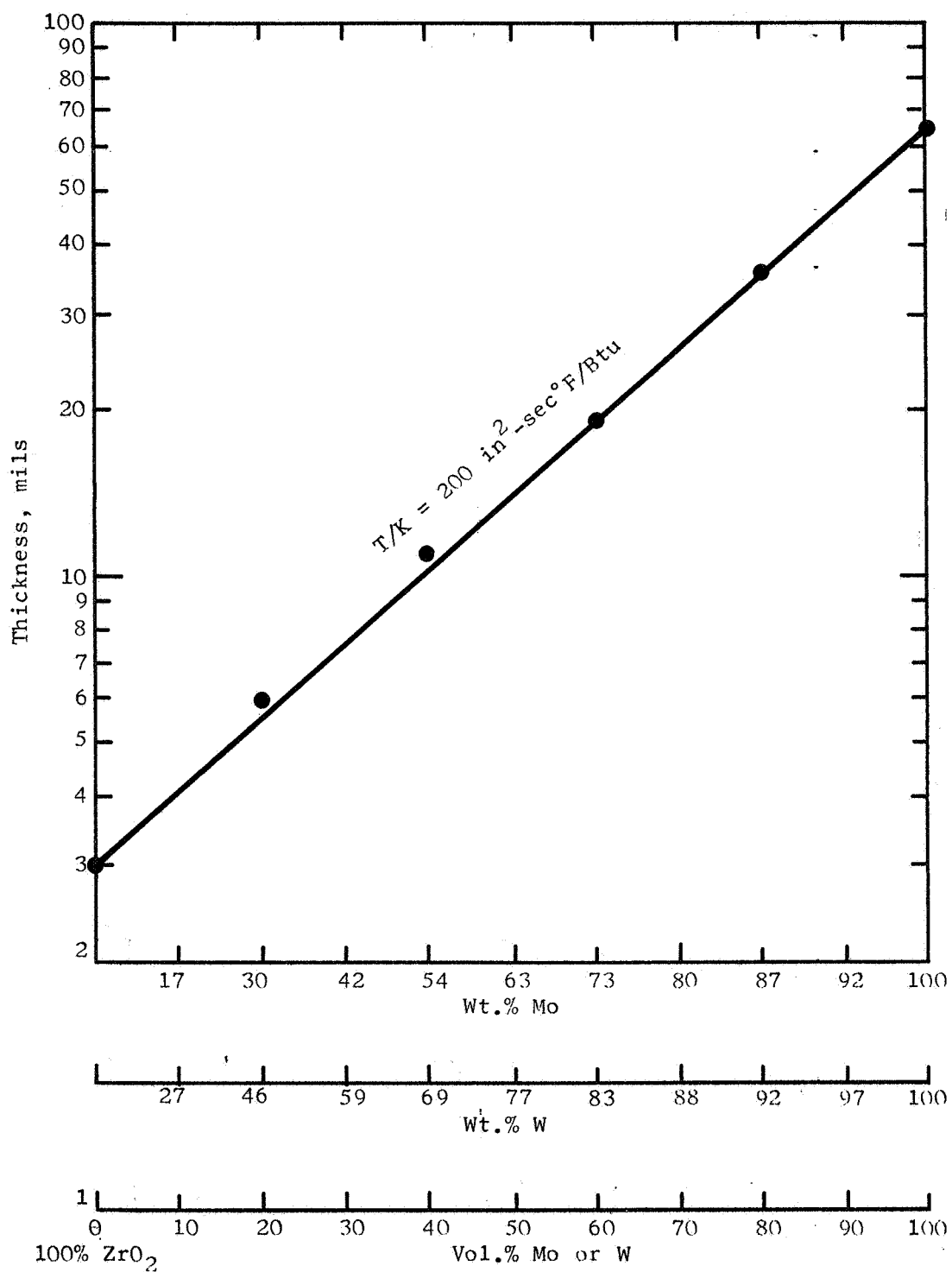


Figure 3. Thermal Resistance as a Function of Coating Thickness and Coating Composition - Mo or W and ZrO₂.

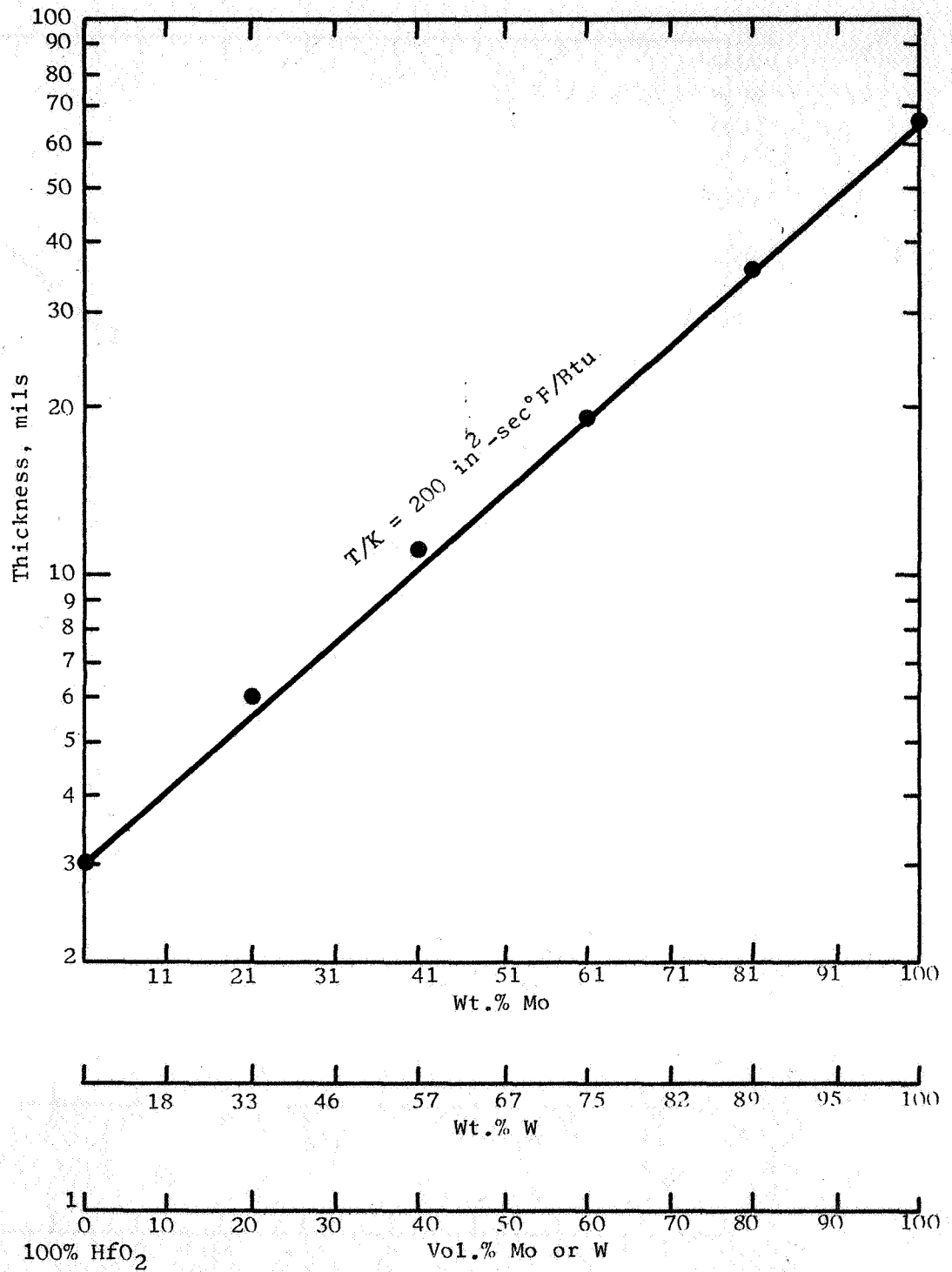


Figure 4. Thermal Resistance as a Function of Coating Thickness and Coating Composition - Mo or W and HfO₂

IV, C, Cermet Mixture (cont.)

obtained from a previous program⁽¹¹⁾. In that program, the thermal conductivities of the plasma-sprayed deposits were generally 40% of handbook values. The thermal resistance data presented in Figures 3 and 4 provided the basis for the thickness and composition selection.

D. PLASMA-SPRAYED THERMAL BARRIERS

The techniques generally used to promote bonding of the plasma-sprayed thermal barrier to the stainless-steel substrate were used in this program. These include grit blasting the substrate to obtain a rough surface (250 to 300 microin.); shielding the plasma flame with an inert gas to minimize oxidation of the metal powders; and spraying a metal primer coat. Primers of nichrome, nickel alumide, or molybdenum-2% titanium have improved room temperature shear strength^(12,13,14,15) of thermal barrier coatings. These primers were selected for evaluation in shear bond tests for this program.

V. ANALYSIS OF COATING CONCEPTS

A. CONCEPTS

Three concepts, shown schematically in Figure 5, were evaluated in this program. Concept 1, the single tube concept, consists of coating the individual tubes prior to nozzle fabrication. Concept 2, the tile concept, consists of fabricating individual tiles and electroforming the regeneratively cooled nozzle on the tiles. Concept 3, the conventional concept, consists of coating the ID of a conventional brazed tube bundle, the regeneratively cooled thrust chamber.

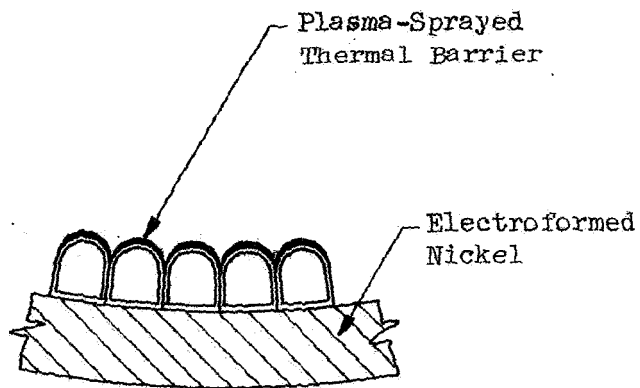
1. Single Tube Concept

In the single tube concept, the thermal barrier is applied to each individual tube prior to assembly. The success of this concept is based on the fact that the valley region between adjacent tubes experiences only a static hot-gas boundary layer and is not subject to any significant heat flux.

The advantages of applying the thermal barrier to individual tubes are:

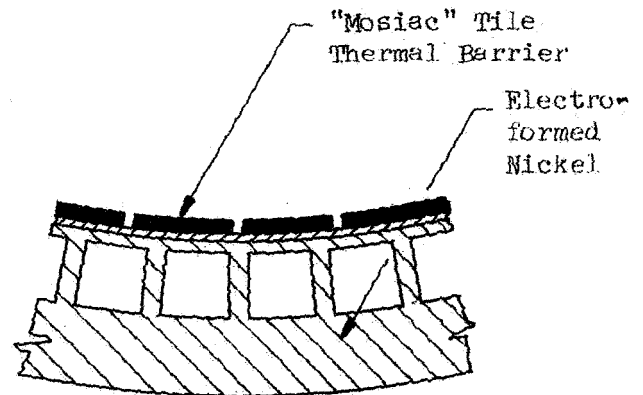
a. A natural expansion joint is built into the thermal barrier coating at the tube valley, eliminating a possible mode of failure; i.e., buckling due to expansion of the gas-side wall which is restrained by the coolant side wall. In addition to buckling of the coating as a shell, failure has been known to occur because of the thermal stress between the hot crown and the relatively cool stagnant area in the tube valleys. The elimination of coating in the tube valleys will reduce the temperature differential and again provide space for expansion without buckling.

CONCEPT 1



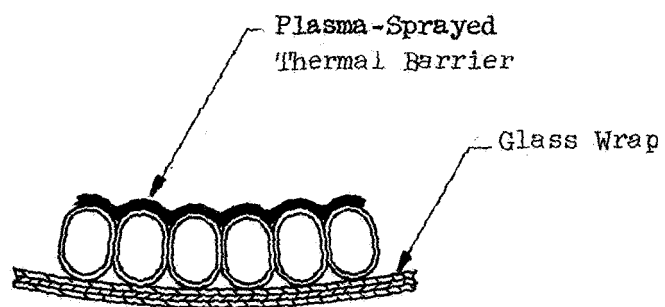
Single Tube Concept

CONCEPT 2



Tile Concept

CONCEPT 3



Conventional Brazed Tube Bundle

Figure 5. Basic Design Concepts

V, A, Concepts (cont.)

b. Large or small regeneratively cooled chambers can be fabricated without extensive tooling and equipment. The tooling and equipment required to plasma-arc spray individual tubes are simple compared to the handling fixtures and drive mechanism necessary to rotate a large thrust chamber. Also, the available plasma-arc torches are not capable of passing through a 3.0-in.-dia throat and maintaining the proper standoff distance. Spraying individual tubes permits coating of small thrust chambers without a splice at the throat that might reduce the coating quality.

The individually coated tubes permit design flexibility and adaptation to potential cost saving fabrication of the thrust chamber, e.g., electroformed structural jacket over the tubes laid up on a mandrel.

The individually coated tubes can be joined by tungsten inert gas welding (TIG) and electroforming but not by furnace-brazing because of the difference in thermal expansion of the coating and tube.

2. Tile Concept

This concept consists of a thrust-chamber structure in which the coolant passages are electroformed nickel, formed in place over a previously placed thermal barrier. The thermal barrier is 1/4- to 1/2-in. tiles with a gap. The gap is intended to provide thermal stress relief between tiles of approximately 0.005 in. thus eliminating certain restrictions. The tile thermal barrier is pressed and sintered refractory-ceramic mixtures on the thermal barrier imposed by the plasma-spraying process.

3. Conventional Concept

In this concept, the thermal barrier coating is applied to the ID of a conventional brazed thrust chamber by plasma-arc spraying.

V, Analysis of Coating Concepts (cont.)

B. THERMAL ANALYSIS

1. Single Tube Concept

a. One-Dimensional Analysis

The thermal analysis of the single tube concept depended on establishing the gas-side boundary conditions in the gaps between tubes where there is no coating. It was expected that lower gas velocities existed in the gaps between coated tubes than on the crowns, and the hot gas-side heat transfer coefficient would be lower than at the crown resulting in a reduction of the heat flux in the valley.

The gap between the tubes is a rectangular-shaped cavity bounded on two sides by the coating and on the third side by the metal coolant channel wall with the top open to the hot gas flow. The gap is aligned with the gas flow direction.

Heat transfer and friction coefficients with air in square, triangular and rectangular (aspect ratio 5:1) channels for a range of Reynolds numbers of 1000 to 330,000 were measured by Lowdermilk, Weiland, and Livingood⁽¹⁶⁾. An average Nusselt number correlation was developed which could be used for all three geometries investigated. Eckert and Low⁽¹⁷⁾ calculated local film coefficients for triangular and rectangular heat exchanger passages with turbulent flow by assuming the similarity between the velocity and temperature fields. The calculations indicated that the corner region film coefficient varied with included angle and distance from the corner, and that the reduction of film coefficient was confined to the immediate vicinity of the corner with rectangular geometries. Deissler and Taylor⁽¹⁸⁾ extended the analytical work of Lowdermilk⁽¹⁶⁾, et al., to higher Reynolds numbers and considered the effect of Prandtl number.

V, B, Thermal Analysis (cont.)

A number of analytical investigations such as Han⁽¹⁹⁾ were concerned with laminar channel flow. The experimental data of Steinback^(20,21) were obtained for supersonic corner flow, but these data could not be used because the slot configuration was not duplicated. Some other rectangular channel flow data obtained by Gambill⁽²²⁾ were available, but did not apply to the longitudinal gap problem.

The data obtained from these studies cannot be used directly to establish the film coefficient variations and wall temperature distribution in the longitudinal gap region of the single coated tube because the viscous shear interface between the slot gas and the main gas flow occurring near the open top of the slot was not taken into account. This interface will probably produce a flow field and film coefficient variation in the slot that is totally different than that which might occur in channel flow. In addition, the effect of varying the main gas stream angle of attack in the longitudinal direction on the slot film coefficient was not considered and the angle of attack does vary in the convergent and divergent portions of a thrust chamber.

However, there is enough similarity between the conditions in the references and the longitudinal slot situation to provide some insight into the effect of mainstream gas flow on the slot region heat transfer coefficients. It is expected that the reduction of the film coefficient and heat flux in the corner region, that were predicted analytically by Eckert⁽¹⁷⁾ and Deissler⁽¹⁸⁾ and verified experimentally by Lowdermilk⁽¹⁶⁾, indicates that the reduction of the base region film coefficient will vary with mainstream Reynolds number and slot depth. Eckert⁽¹⁷⁾ indicates that a slot region geometry with an included angle less than 90° , which would occur at the base of a triangular slot, is expected to produce a different film coefficient variation and probably a lower average slot region Nusselt number than a rectangular geometry.

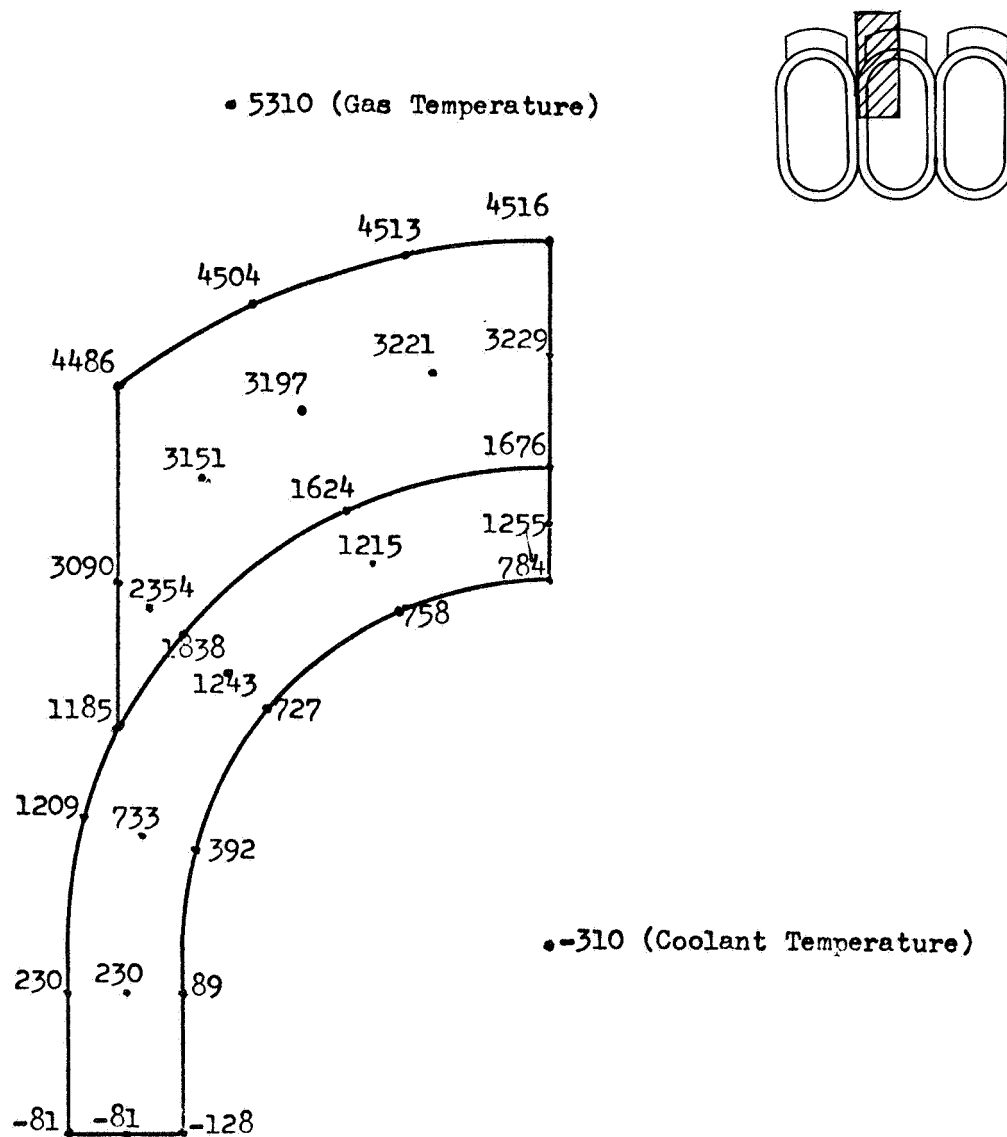
V, B, Thermal Analysis (cont.)

The results of the referenced studies indicated that it would be possible to develop a coating with longitudinal slots between tubes while maintaining reasonable coating and coolant channel temperatures. The narrowest slot should be employed with either a deep rectangular slot or a triangular slot with a small base angle. Data were not available which compared the best flux in the slot to that of flat surfaces; however, because the heat flux in the corners of the slot are reported to approach zero, it was estimated that the heat flux in the slot would be significantly less than at the surfaces. For the purposes of a two-dimensional conduction analysis, a heat transfer coefficient in a gap or slot was assumed to be 25% of the tube crown value.

b. Two-Dimensional Temperature Distribution

A two-dimensional conduction analysis was performed for the single coated tube concept assuming a coated thermal resistance of $200 \text{ in.}^2\text{-sec-}^\circ\text{F/Btu}$ and a 347 stainless-steel tube wall thickness of 0.015 in. The boundary conditions were established assuming LO_2/LH_2 propellants at 2000 psia chamber pressure. The results shown in Figure 6 indicate a maximum coating temperature of 4516°F on the crown and a maximum tube wall temperature in the slot of 1209°F . For comparison purposes, a conventional coated tube, i.e., where the tubes are coated after tube bundle assembly, is shown in Figure 7. The maximum coating temperature was 4473°F on the crown.

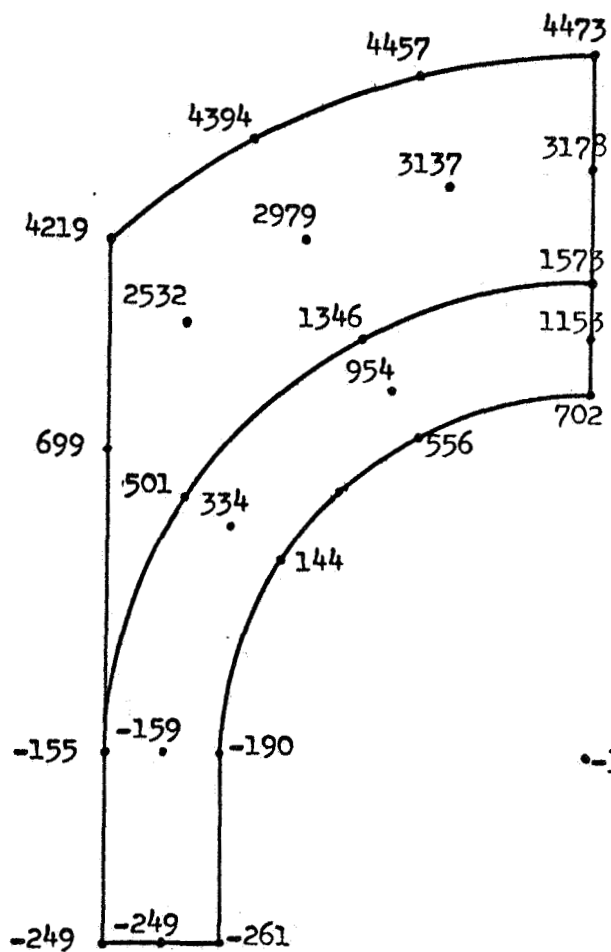
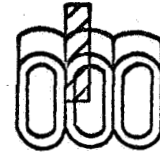
As shown in Figure 6, the predicted channel temperatures near the base of the slot are excessively high for a steel channel. Since these results are based on conservative assumptions of the film coefficient in the slot, the excessive temperature was not considered a problem.



- NOTE: All Temperatures in °F
1. Tube: 317 Stainless Steel
0.015-in. thick
 2. Coolant: Hydrogen
 3. Coating $t/k = 200 \text{ in}^2 \text{ sec } ^\circ\text{F/Btu}$

Figure 6. Temperature Distribution for Coating in Single Tube Concept

• 5310 (Gas Temperature)



• -310 (Coolant Temperature)

NOTE: All temperatures in °F

1. Tube: 347 Stainless Steel
0.015-in. thick

2. Coolant: Hydrogen

3. Coating $t/k = 200 \text{ in.}^2 \text{ sec } ^\circ\text{F/Btu}$

Figure 7. Temperature Distribution for a Conventional Coated Tube

V, B, Thermal Analysis (cont.)

2. Tile Concept

The tile concept consists of 1/4-to 1/2-in. square coating tiles which are bonded to the ID of a regeneratively cooled chamber. The tiles provide natural circumferential and longitudinal expansion gaps through the thermal barriers. Information is available on theoretical and experimental efforts on the heat transfer and flow characteristics in rectangular cavities transverse to the direction of gas flow.

The experimental work of Nestler⁽²³⁾ and Fox⁽²⁴⁾ with cylindrical and rectangular cavities indicates that the cavity base heat fluxes will be less than 10% of the plane (vertical) wall flux for a cavity whose depth to width ratio is 4:1. Using this data in analyses similar to that for the single tube concept, a gap width of 0.010 in. would be estimated to be adequate to maintain reasonable wall temperature in the gap.

C. STRESS ANALYSIS

A stress analysis was conducted to compare the stresses obtained in the coating of the single tube concept with the stresses obtained in the conventionally coated concept. In conducting the analysis, the following criteria were used for both concepts: (1) 5.6 in. inside throat diameter, (2) 180 oblong-shaped 347 stainless-steel tubes, (3) 0.015 in. tube wall thickness, and (4) design safety factor of one for the thermal stress that is based on the yield strength at a given temperature. The main difference in the analysis was the gap in the coating in the single tube concept of 0.010 in. at the valley of the tubes. The difference in thermal condition in the coatings was established in the heat transfer analysis (Figures 6 and 7 and was used in the stress analysis.

V, B, Thermal Analysis (cont.)

Physical and mechanical properties of materials used are shown in Figures 8 and 9.

The analysis was conducted using the Finite Element Computer Program E11401. The finite element method is applied to the determination of displacements and stresses within plane or axisymmetric solids with linear and nonlinear material properties. The continuous body is replaced by a system of elements with triangular or quadrilateral cross sections. Since the elements are of arbitrary shapes and material properties, the procedure may be applied to structures composed of many different materials of practically any symmetrical geometry.

In the finite element approximation of solids, the continuous structure is replaced by a system of elements which is interconnected at joints or nodal points. Equilibrium equations, in terms of unknown nodal point displacements, are developed at each nodal point. A solution of this set of equations constitutes a solution to the system.

The advantages of the finite element system are (1) it is completely general with respect to geometry and material properties, (2) complex bodies made up of many different materials are easily represented, and (3) filament structures are easily handled.

The stress analysis showed that the coating layer is above the elastic range locally in both concepts but higher stresses and strains are developed in the conventional coating, principally because of the hoop restraint as a result of the continuous coating. The magnitude of the stresses at the nodal points for each concept is shown in Figure 10 and 11. The analysis showed that the maximum stresses in the thermal barrier coating in the single tube concept is 20,560 psi compared to 30,560 psi in the

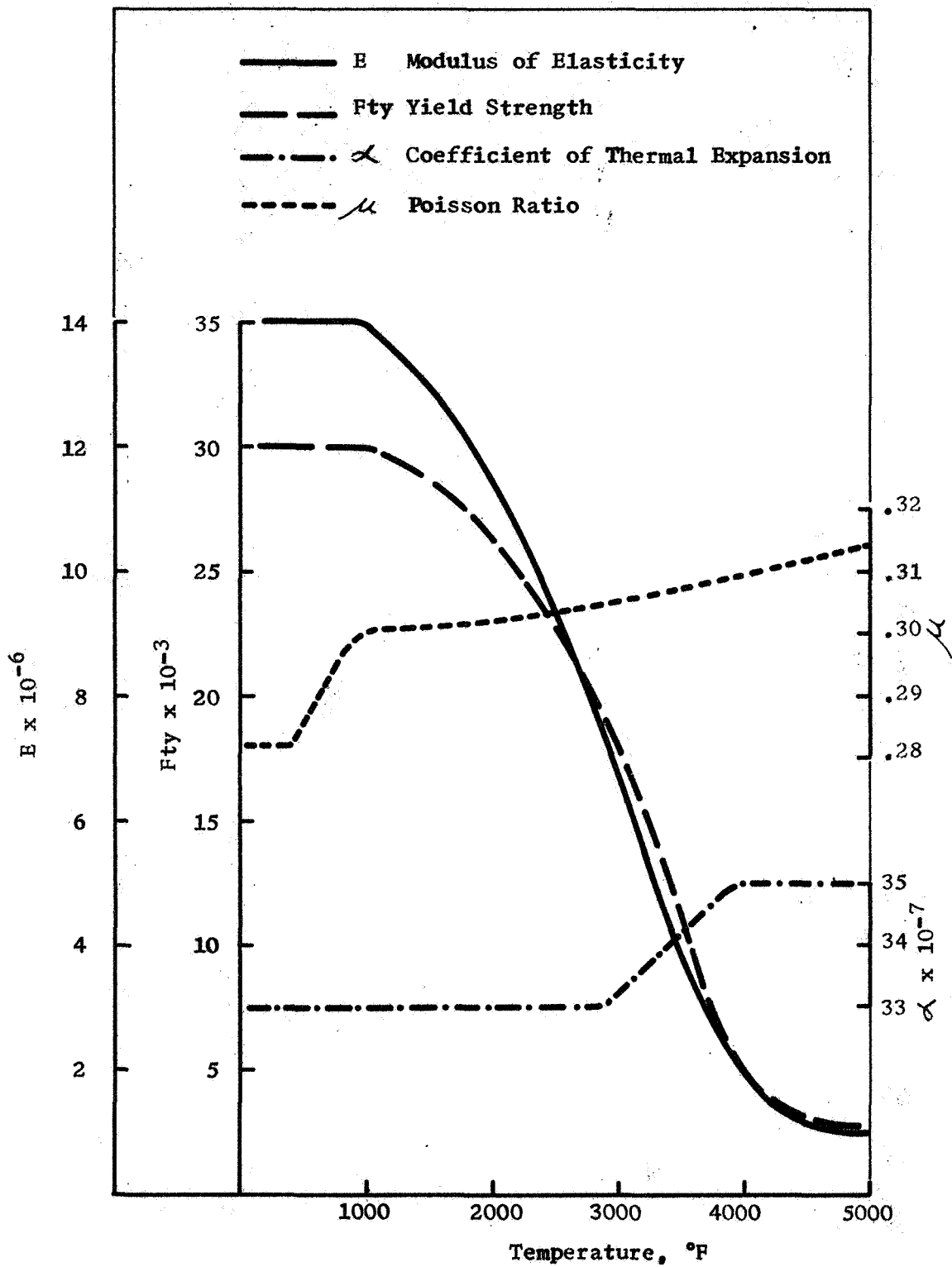


Figure 8. Properties of Thermal Barrier 85%W - 15%ZrO₂ used in Stress Analysis

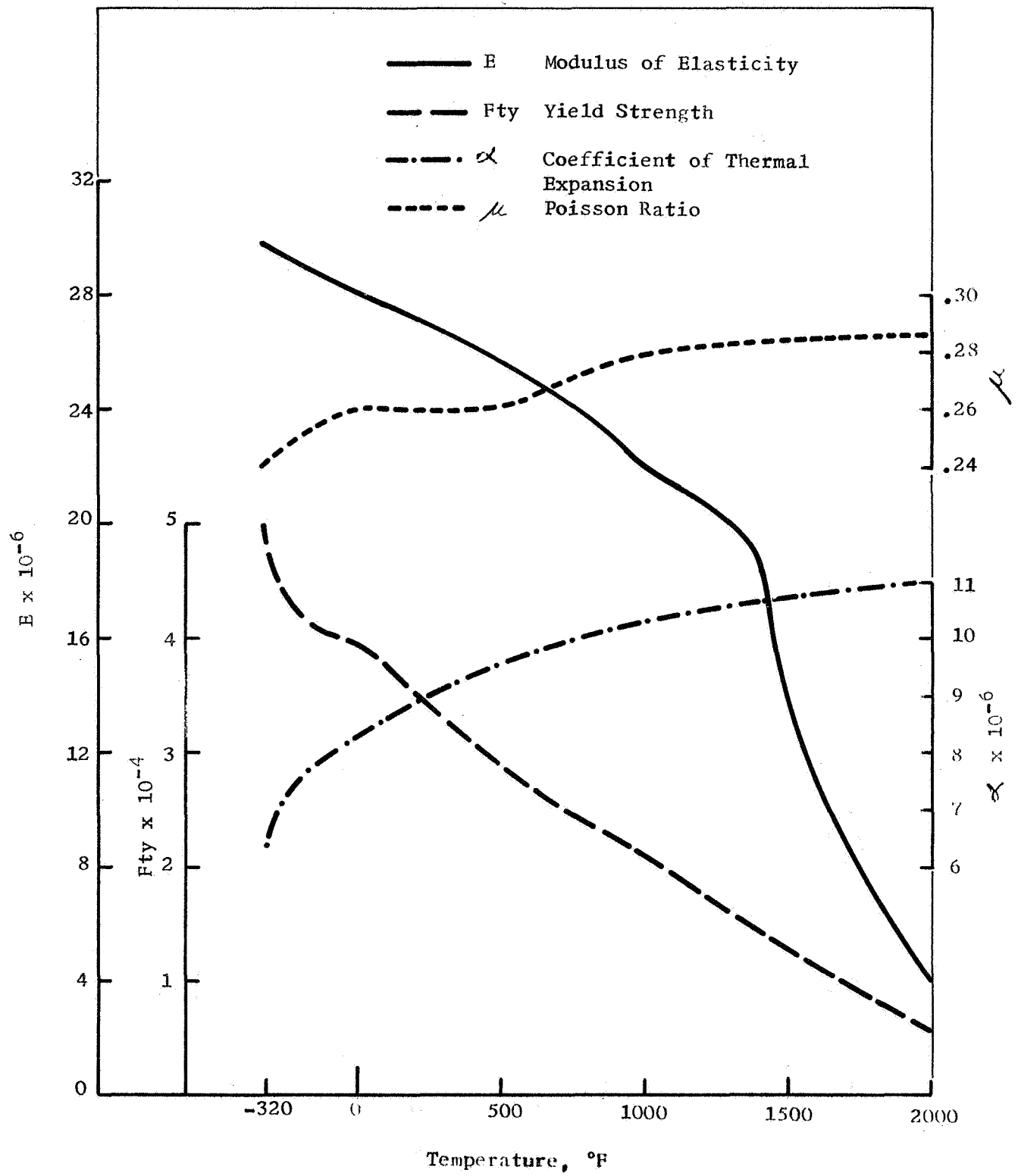


Figure 9. Properties of Stainless Steel 347 used In Stress Analysis

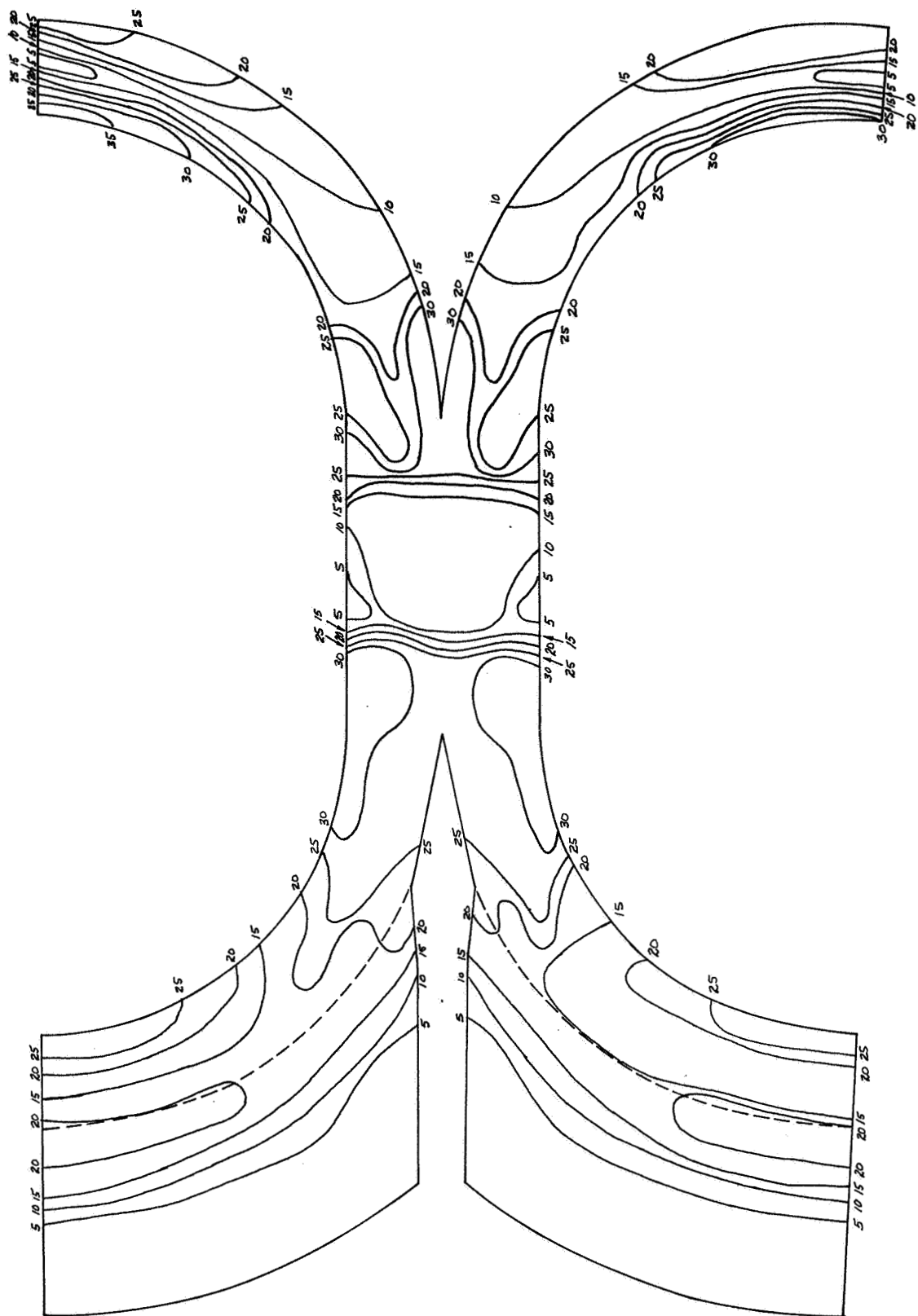


Figure 10. Chamber Tube Stress Map - Single Tube Concept

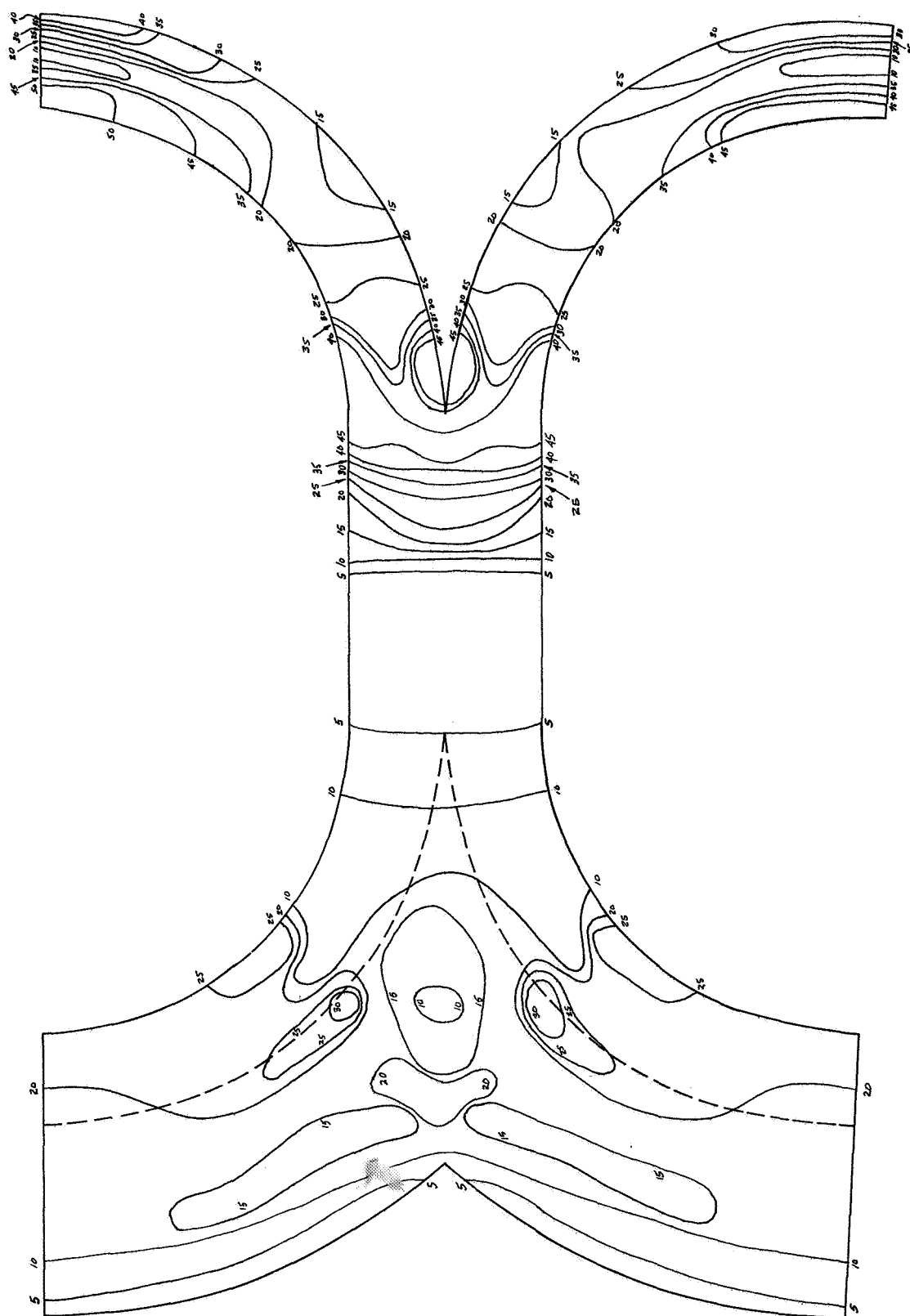


Figure 11. Chamber Tube Stress Map of the Conventional Tube Concept

V, B, Thermal Analysis (cont.)

conventional coating. The difference in stress is due to the gap extending down the valley. The stress pattern in the single coated concept is such that the maximum stresses in the stainless-steel tube occur near the flame surface. The reverse is true in the conventional cooling concept. The maximum stress is on the cold side of the tubes. The shift results in effective stresses of only 36,100 psi in tubes of the single tube concept compared to 50,850 psi in the conventional concept.

The analysis confirmed the prediction of lower stress in the coating in the single tube concept compared to the conventional coated concept.

VI. EXPERIMENTAL PROCEDURES

A. SPECIMEN PREPARATION

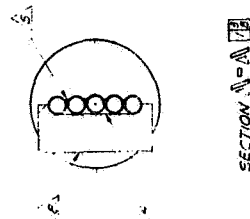
Two types of specimens were used in the testing of the thermal barrier - a disk coupon and a five tube internally cooled specimen shown in Figure 12. The disk specimen was used to obtain thermal resistance of the coating and as a thermal shock test for the coatings. The five-tube specimen was used to simulate the tube bundle in a rocket nozzle and to obtain an indication of thermal shock properties of the coating.

The disk specimen was prepared by plasma torch spraying a candidate coating on a stainless-steel disk (0.025 in. thick x 3.25 in. dia). The disk and tube specimen were first grit blasted on one surface using 24 mesh silicon carbide grit to produce a 250-300 rms microinch surface roughness. After grit blasting the specimens were plasma-spray coated using a 35kw plasma torch, a power feeder, and specimen-positioning fixture.

The plasma torch was mounted horizontally on a screw-driven traversing head to permit lateral traverse across the specimen face at a programmed speed of 12 in./min. A shield of argon gas was maintained around the spray cone and spray impingement area to exclude air from the test specimen hot surface.

The disk test specimen and 5-tube specimen were held in a frame that was mechanically oscillated vertically in front of the torch at a specimen surface speed of 300 in./min. The plasma torch traveled horizontally with respect to the specimen at a speed of 12 in./min. During deposition, cooling water was pumped through the specimen holder (disk specimen) or specimen tubes. The deposition rate of the plasma sprayed coatings was about 2 mils/pass.

1. REMOVE ALL BURRS AND SHARP EDGES.
2. INITIAL DRAWING PER STANDARDS PRESCRIBED IN 4-1-0-70327.
3. SURFACE REFINISHED 125/ UNLESS OTHERWISE NOTE.
4. BRAZE - 1 TO 3 TIMES USING .002 COPPER FILL.
5. BRAZING CO- PER BRAZE POWDER.
6. BRAZE CYCLE 5 HOURS AT 2 MINUTES AT 2025°F. ± 25°F IN HYDROGEN.
7. POST WITH ETON 320 PER MANUFACTURERS INSTRUCTIONS.
8. MARK PER AGO 52185 WITH 1130447 AND APPLICABLE DASH NO.
9. CLEAN WHEELS PER AGO-46350, LEVEL W. PRESERVE AND PACKAGE PER AGO-46387.
10. CLAMP 1.



SECTION 11-13

VI, A, Specimen Preparation (cont.)

Single tube specimens were made by plasma spraying in individual tubes 3/16-in. dia by 9-in. long masked to provide a coating area about 1/8 in. wide on the OD surface of the tube. Each tube was sprayed at the same travel speed as the conventionally coated specimens. In preparing the tubes for spraying, the grit blasting pressure had to be reduced from 80 to 30 psia. This was done to minimize warpage caused by the compressive stress in the tubes and resulted in less surface roughness.

B. LABORATORY DISK AND 5-TUBE PLASMA TESTS

The plasma torch used for thermal shock testing of thermal barrier coatings on disk specimens and on 5-tube specimens was similar to that used for spraying. A specially designed test bench was provided for cycling specimens in the plasma torch flame under controlled heat flux conditions. Test specimens were mounted on the side of the calorimeter on a rotating head with hot surfaces at the same distance from the nozzle. Manual rotation of the holding fixture presented the test specimen or the calorimeter in turn to the plasma torch flame.

The torch generated heat flux was measured with a water-cooled circular foil calorimeter and the specimen flame surface temperature was continuously measured with a recording pyrometer. The measured temperature was corrected using handbook spectral emissivity for the sprayed material. The distance of the plasma torch nozzle from the specimens or calorimeter was adjusted to obtain the required heat flux. The plasma flame carrier gas was nitrogen with argon gas introduced just downstream of the nozzle to provide an inert gas shield over the flame impingement area.

The condition of the coatings was observed during flame exposure to detect melting, cracking, or spalling. Following thermal shock testing,

VI, B, Laboratory Disk and 5-Tube Plasma Tests (cont.)

the coatings were examined under 40X magnification to detect cracks or spalled conditions.

The thermal resistance of the coatings was calculated by using the gas-side surface temperature and the heat flux measurement from the water-cooled calorimeter. A water side temperature of 350°F, the saturation temperature for 150 psi pressure water, was used. The calculations were based on the equation:

$$Q/A \text{ (heat flux)} = \frac{T_1 \text{ (gas-side temperature)} - T_2 \text{ (water-side temperature)}}{t/k \text{ (stainless steel)} + t/k \text{ (coating)}}$$

where: t = thickness and k - thermal conductivity

The thermal conductivities data obtained from these tests were considered qualitative because of the possible inaccuracies in measuring heat flux and surface temperature. The accuracy of this method was ascertained by comparing the thermal flash method of determining thermal conductivity⁽¹¹⁾. The data obtained from both methods were comparable as shown in Figure 13.

C. HYPERTHERMAL ENVIRONMENTAL SIMULATOR (HES) TESTING

The HES test was designed to establish the compatibility of the thermal barrier coatings with the thermal and chemical environment of a H_2/O_2 engine. The HES unit is a high pressure one-megawatt plasma generator developed to provide a controlled rocket motor combustion environment for heat transfer and material studies. The HES unit operates at pressures up to 550 psig, and at gas temperatures to 10,000°F. A mix chamber on the HES torch permits simulation of the exhaust gas environment of most liquid and solid propellant rockets.

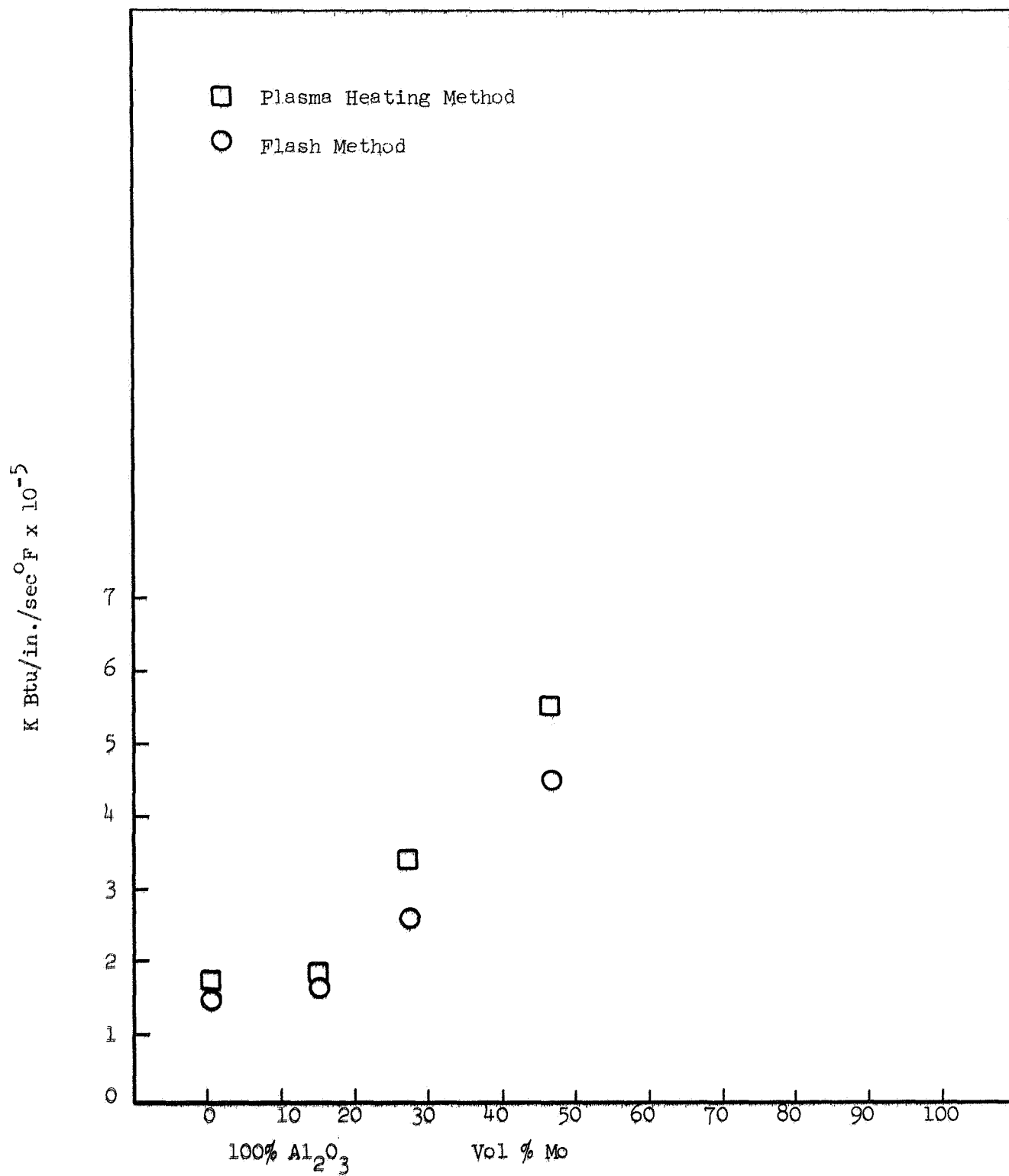


Figure 13. Comparison of Thermal Conductivity of Mo-Al₂O₃ Mixtures As Determined by the Plasma Heating Method and Flash Method

VI, C, Hyperthermal Environmental Simulator (HES) Testing (cont.)

A schematic diagram of the HES system is shown in Figure 14. The specimens evaluated were 5-tube coated specimens. The specimens were mounted on an inserter arm in the high-pressure chamber and exposed to the combustion products from the HES. During exposure the surface temperature of the tube specimen was measured optically.

Under ideal conditions where the specimen performed without water leakage, the following environmental HES chamber conditions were achieved:

Gas enthalpy	2600 to 3800 Btu/lb
Temperature	5900 to 6100°F
Mix chamber pressure	80 to 60 psia
Specimen chamber pressure	60 to 45 psia
(Mach number)	0.5 to 0.8

The exposure of the material specimens to these conditions achieved as close as possible the actual thermodynamic test conditions that might be encountered at or near the nozzle throat of most liquid rocket engines.

1. Determination of HES Thermodynamic Test Environment

The HES gas enthalpy was determined through an energy balance of the plasma-arc chamber as defined by the following equations:

$$E_{in} = VI - w_g (H_g)_a$$

$$E_{out} = w_w C_{p_w} \Delta t_w + w_g (H_g)_p$$

At steady state conditions the balance becomes

$$E_{in} = E_{out} \text{ and}$$

To 1.2 megawatt power supply

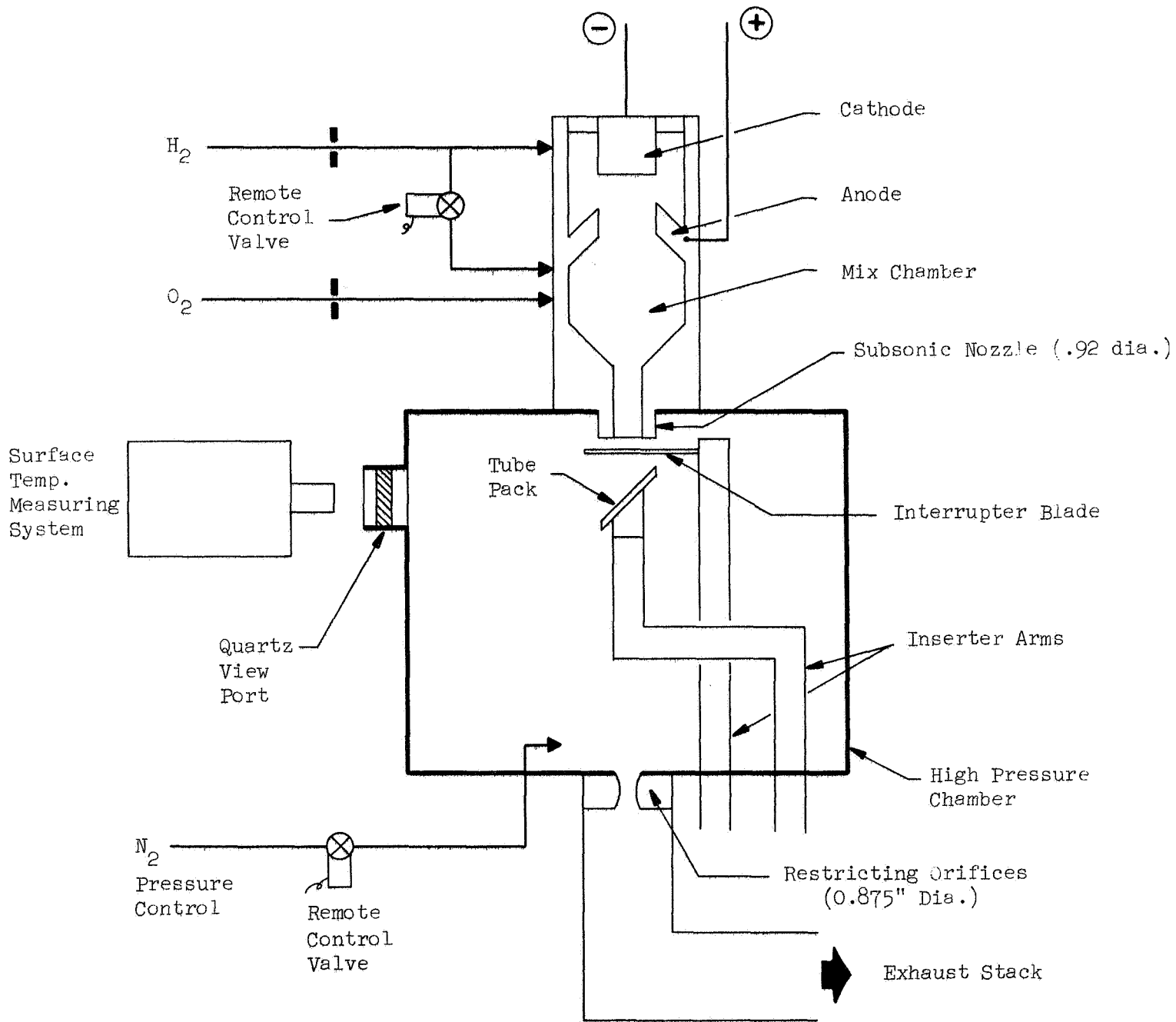


Figure 14. Schematic of HES Setup For $H_2 - O_2$ Tube Pack Tests

VI, C, Hyperthermal Environmental Simulator (HES) Testing (cont.)

$$(H_g)_p = \frac{VI - w_g (H_g)_a - w_w C_{p_w} \Delta t_w}{w_g}$$

where,

E = energy
V = plasma arc voltage
I = plasma arc current
w = weight flow
H = enthalpy
C_p = specific heat
Δ_t = temperature rise

Subscripts:

g = gas
a = ambient
w = water
p = plasma

Measurement of the plasma arc voltage and current, water flow rate and respective temperature rise, and total gas flow rate was made during the entire test run. The enthalpy of the plasma gas was calculated by a special computer data reduction program⁽²⁵⁾ developed to allow averaging of steady-state energy balance parameters. In addition, the program calculates gas temperature, Mach number, and specimen heat flux. Generally, ten steady-state reading sets of data from the HES digital data system were input for computer reduction of average conditions. Such conditions were determined before the material specimen entered the gas stream and during its later five seconds of exposure to direct gas impingement.

Theoretical temperature-pressure-enthalpy data for a 6 to 1 oxygen/hydrogen combustion mixture were used to derive the gas temperature.

VI, C, Hyperthermal Environmental Simulator (HES) Testing (cont.)

The Mach number was calculated from the adiabatic compressible flow equation using computed average mix chamber pressure and specimen chamber pressure by the following relationship:

$$M = \frac{U_t}{a} = \sqrt{\frac{2}{\gamma-1} \left[(P_a/P_c)^{\gamma-1/\gamma} - 1 \right]}$$

where, γ = isentropic exponent
 u = velocity
 a = velocity of sound
 P = pressure
 R = gas constant

subscripts: t = plasma nozzle throat
 g = gas
 c = chamber
 a = arc

Heat flux to the material specimen was determined from measured energy inputs to the specimen arm before and after insertion into the plasma gas flow field. Assuming that the heat input to the specimen arm and holder was approximately the same regardless of specimen position in the HES chamber, subtraction of heat inputs while in and outside the plasma gas flow field produces the specimen heat input during exposure. The following equations described this energy calculation:

$$Q_{igf} = (w_w C_{p_w} \Delta t_w)_{igf}$$

$$Q_{ogf} = (w_w C_{p_w} \Delta t_w)_{ogf}$$

$$Q_s = Q_{igf} - Q_{ogf}$$

VI, C, Hyperthermal Environmental Simulator (HES) Testing (cont.)

Assuming an elliptical shape heat transfer area which includes the 45° position of the specimen and its five cooling tubes, the area can be estimated from

$$\begin{aligned} A_{es} &\sim \frac{\pi}{4} (D_{gj}/\cos 45^\circ) (5 \pi D_{tu}/2) \\ &= \pi^2 D_{gj} D_{tu} / 1.6 \cos 45^\circ \end{aligned}$$

thus heat flux becomes

$$q = Q_s / A_{es}$$

where,

Q = heat input
w = weight flow
Cp = specific heat
 Δt = temperature rise
A = area
q = heat flux

Subscripts:

ifg = in gas field
ogf = out of gas field
s = specimen
w = water
es = exposed specimen
gj = gas jet
tu = tube

The gas jet diameter was selected to be equal to the plasma arc nozzle throat diameter, 0.920 in.

VI, C, Hyperthermal Environmental Simulator (HES) Testing (cont.)

2. Specimen Surface Temperature Measurement Technique

A system was designed which would measure, indirectly, the true surface temperature in the presence of arc radiation. The radiation from the hot sample was measured with and without the interrupter blade in place. With an independent calibration of the arc radiation it is then possible to determine both true surface temperature and emissivity of the hot sample surface. The theory and operation of the temperature measurement apparatus are described in the Appendix.

VII. THERMAL BARRIER EVALUATION

The thermal barrier evaluation consisted of testing coated disk and 5-tube specimens in the plasma flame in the laboratory with final evaluation in a plasma flame simulating the exhaust of a H_2/O_2 engine.

A. LABORATORY EVALUATION

1. Coating Adherence

Prior to the evaluation of coatings, the use of three different plasma-sprayed primer materials was evaluated for improving coating adherence. As described in the specimen preparation section, the substrate was grit blasted to a 250 microin. surface finish before plasma spraying. The primers evaluated were nichrome, nickel aluminide, and Mo-2% Ti. The test apparatus use to conduct the bond shear tests was patterned after that used by Grisaffe⁽¹⁴⁾. The results of the shear tests are found in Table VII. The highest strengths were obtained with nichrome and it was selected as the primer for the coatings applied in the program.

2. Disk Coupons

The disk coupon tests were conducted to measure the thermal resistance of the coating, and to obtain a qualitative evaluation of the thermal shock resistance and oxidation resistance of the coating. These tests were made with a nitrogen plasma flame. The test heat flux was 12 Btu/in.²-sec. The test conditions consisted of a heating cycle of 20 sec and nine heating cycles of 10 sec with cooling cycles of 5 to 10 sec.

The first series of specimens consisted of ZrO_2 and HfO_2 with additions of W and Mo. The results of these tests are shown in Table VIII. All of the specimens withstood the 10 cycles without cracking or separating

TABLE VII
RESULTS OF SHEAR BOND ADHERENCE TESTS

<u>Specimen</u>	<u>Primer</u>	<u>Coating Composition wt%</u>	<u>Coating Thickness, mils</u>	<u>Shear Strength, psi</u>
S-1	Nichrome	73% Mo-27% ZrO ₂	21	2730
S-2	Nichrome	27% Mo-73% ZrO ₂	21	1830
S-3	Nichrome	69% W-31% ZrO ₂	22	1300*
S-4	Nichrome	41% W-59% ZrO ₂	22	1260*
S-5	Nickel-Aluminide	73% Mo-27% ZrO ₂	20	2190
S-6	Nickel-Aluminide	27% Mo-73% ZrO ₂	20	1540
S-7	Nickel-Aluminide	69% W-31% ZrO ₂	20	1540
S-8	Nickel-Aluminide	41% W-59% ZrO ₂	20	1450
S-9	Mo-2% Ti	73% Mo-27% ZrO ₂	20	2170
S-10	Mo-2% Ti	27% Mo-73% ZrO ₂	20	1480
S-11	Mo-2% Ti	69% W-31% ZrO ₂	21	2110
S-12	Mo-2% Ti	41% W-59% ZrO ₂	21	790*

*Questionable data. Base of specimen was not flat.

TABLE VIII
DISK COATING EVALUATION - FIRST SERIES

Specimen Number	Composition, wt%	Thickness, mils	Gas Side Surface, Temp, °F	Thermal Resistance in.² sec/Btu	Thermal Conductivity, Btu/in.² sec °F	Regression Rate, mils/sec
1	100% HfO ₂	3	4160	223	1.35 x 10 ⁻⁵	0.009
2	100% ZrO ₂	2	4000	211	1 x 10 ⁻⁵	0.009
3	27% Mo-73% ZrO ₂	5	3515	140	3.57 x 10 ⁻⁵	0.0182
4	41% W-59% ZrO ₂	5	4160	224	2.23 x 10 ⁻⁵	0.0318
5	27% Mo-73% HfO ₂	5	4655	265	1.89 x 10 ⁻⁵	0.0182
6	41% W-59% HfO ₂	5	5240	324	1.54 x 10 ⁻⁵	0.0182
7	54% W-46% ZrO ₂	10	4050	214	4.67 x 10 ⁻⁵	0.0455
8	69% W-31% ZrO ₂	10	4110	220	4.54 x 10 ⁻⁵	0.0546
9	54% Mo-46% HfO ₂	15	4625	262	5.72 x 10 ⁻⁵	0.1095
10	77% W-23% HfO ₂	15	3790	193	7.77 x 10 ⁻⁵	0.0954
11	83% W-17% ZrO ₂	21	3925	204	10.3 x 10 ⁻⁵	0.100
12	83% W-17% HfO ₂	21	3835	196	10.7 x 10 ⁻⁵	0.1365
13	73% Mo-27% ZrO ₂	21	3880	200	10.5 x 10 ⁻⁵	0.0728
14	73% Mo-27% HfO ₂	21	4340	238	8.83 x 10 ⁻⁵	0.1045

VII, A, Laboratory Evaluation (cont.)

from the disks. However, melting occurred in all of the coatings containing metal additions and appeared to increase with increased metal content. The lowest regression rates were obtained with the coatings that did not contain metal additions. The regression of the ceramic-metal mixture increased with an increase in metal content. The regression rates were excessive for Mo-ceramic mixtures containing Mo additions above 27 wt% and for W-ceramic mixtures containing W additions above 41 wt%.

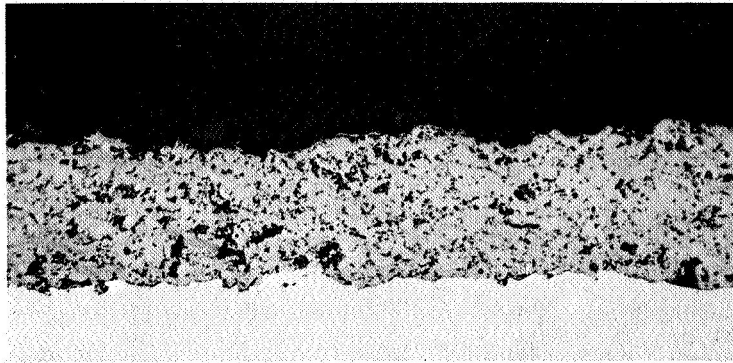
A second series of tests was conducted using Si and Cu additions to the coating in attempts to improve regression resistance. The results of these tests are shown in Table IX. The regression resistance was not significantly improved with the Si or Cu additions in the Mo - ZrO₂ coatings. The use of Si and Cu in W base composites was not effective in improving regression resistance and was eliminated from further evaluations in this program.

A third series of tests were made on stabilized ZrO₂ and HfO₂ coatings plasma-sprayed by Union Carbide and Aerojet. The Union Carbide coatings are sprayed with a proprietary procedure without grit blasting or use of a primer. A cross section of the Union Carbide coated specimen is shown in Figure 15. For comparison, a cross section of the Aerojet coatings made with and without a primer and with the conventional plasma process is also shown. The Union Carbide coatings appeared denser than the Aerojet coating but the conductivities were not significantly different. The regression rate of all the coatings was nil as shown in Table X.

The regression rate of the HfO₂ coating was similar to the ZrO₂. The HfO₂ coating at 4 mils thick also withstood the thermal cycling without melting because of the high HfO₂ melting temperature. Because of this, the coating thickness tolerance for HfO₂ coatings could be less stringent than the ZrO₂ coatings.

TABLE IX
DISK COATING EVALUATION AND SECOND SERIES

Specimen	Composition, wt%	Thickness, mils	Gas Side Surface Temperature, °F	Thermal Resistance, in. ² sec/Btu	Thermal Conductivity, Btu/in. ² sec °F	Regression Rate, mil/sec
C-13a	97% (27% Mo-73% ZrO ₂)-3% Si	6	4480	251	2.4 x 10 ⁻⁵	0.033
C-32a	94% (27% Mo-73% ZrO ₂)-6% Si	7	4490	220	3.2 x 10 ⁻⁵	0.017
C-33a	90% (27% Mo-73% ZrO ₂)-10% Si	6	4430	247	2.4 x 10 ⁻⁵	0.033
C-34a	85% (27% Mo-73% ZrO ₂)-15% Si	6	4160	225	2.7 x 10 ⁻⁵	0.017
C-35a	97% (85% W-12% ZrO ₂ -3% Si)-3% Cu	22	4130	221	10 x 10 ⁻⁵	0.15
C-36a	95% (85% W-12% ZrO ₂ -3% Si)-5% Cu	21	4000	212	10 x 10 ⁻⁵	0.15
C-37a	90% (85% W-12% ZrO ₂ -3% Si)-10% Cu	24	3900	203	12 x 10 ⁻⁵	0.17



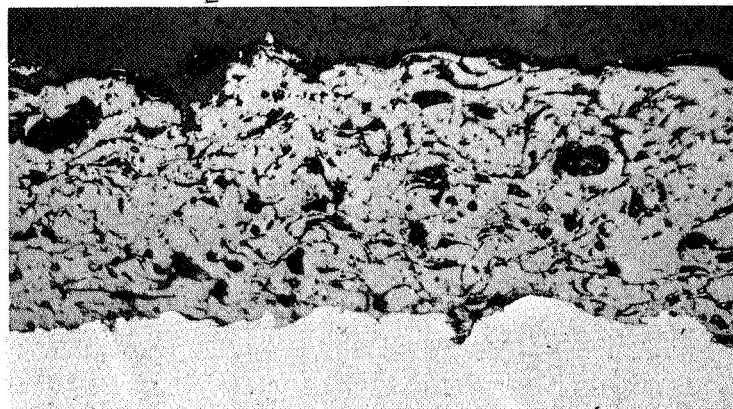
ZrO₂ Coating

Stainless Steel
Substrate

250X

Neg. 18820

Union Carbide Plasma Sprayed
ZrO₂ Without a Primer



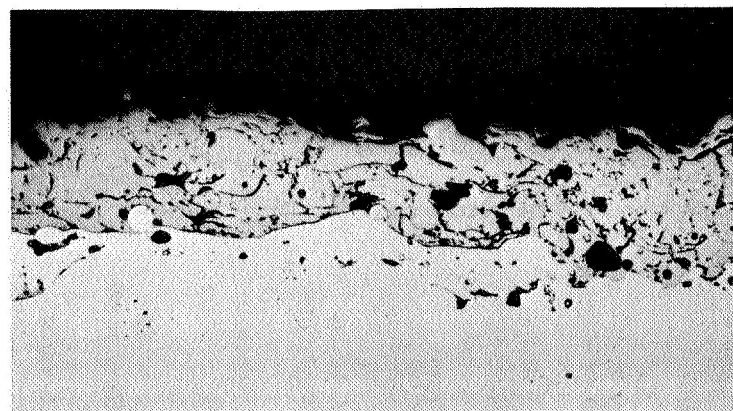
ZrO₂ Coating

Stainless Steel
Substrate

250X

Neg. 18817

Aerojet Plasma Sprayed ZrO₂
Without a Primer



ZrO₂ Coating

Nichrome Primer

Stainless Steel
Substrate

250X

Neg. 18818

Aerojet Plasma Sprayed Coatings
With a Nichrome Primer

Figure 15. Comparison of ZrO₂ Coatings Sprayed With and Without Nichrome Primer

TABLE X
EVALUATION OF ZrO₂ AND HfO₂ COATINGS

Specimen (1)	Primer	Coating	Thickness, mils	Gas Side Temperature, °F	Thermal Resistance, in. ² sec/Btu	Thermal Conductivity Btu/in. ² sec °F	Regression Rates, mils/sec
Union Carbide No. 1	None	ZrO ₂	2	3300	160	1.3 x 10 ⁻⁵	0
C-58	None	ZrO ₂	2	3800	205	0.98 x 10 ⁻⁵	0
C-61	2 mils Nichrome	ZrO ₂	2	4000	214	0.94 x 10 ⁻⁵	0
C-64	3 mils Nichrome	HfO ₂	2	3800°F	194	1.03 x 10 ⁻⁵	0
Union Carbide No. 3	None	ZrO ₂	4	Coating Melted			
C-62	2 mils Nichrome	ZrO ₂	4	Coating Melted			
C-65	3 mils Nichrome	HfO ₂	4	4300°F	240	1.66 x 10 ⁻⁵	0
C-66	3 mils Nichrome	HfO ₂	7	5100°F	Melted after 5th cycle		
C-56	2 mils Nichrome	ZrO ₂	2	3950°F	180	1.1 x 10 ⁻⁵	0.009

(1) Substrate for specimen C-56 was electroformed Ni-84 mils thick. Substrate for all other specimens was stainless steel - 26 mils thick.

VII, A, Laboratory Evaluation (cont.)

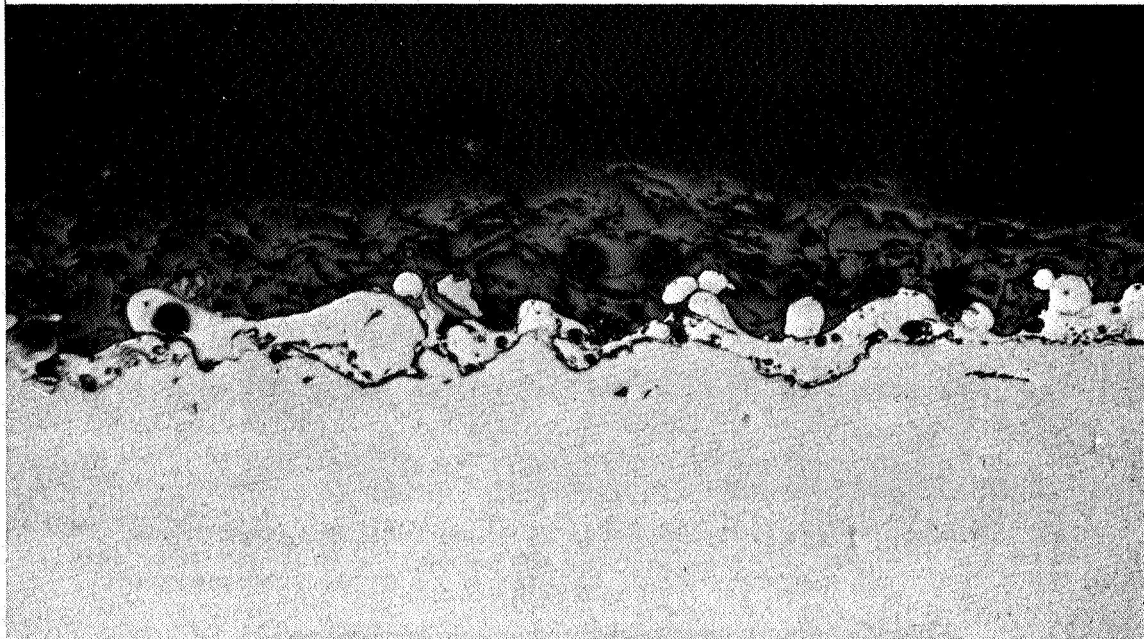
One coating was evaluated in which an electroformed nickel substrate was used instead of the stainless-steel substrate shown in Figure 16. The thickness of the nickel substrate was made to provide the same thermal resistance as the stainless-steel substrate. The plasma-sprayed coating on the nickel substrate had comparable thermal properties and performed similar to comparable coatings on stainless-steel substrate.

3. Disk Tile Specimens

Disk specimens fabricated with tiles instead of a continuous coating were fabricated for laboratory evaluation. As an expediency, attempts were made to fabricate dense tiles of ZrO_2 by pressing and sintering blocks and cutting and grinding the tiles to 3 to 5 mils thick. The fabricated tiles were so fragile that they fractured in handling and studies with the pressed and sintered tile were stopped.

In the next experiment, tiles were made from Zirconia cloth impregnated with ZrO_2 . The impregnated cloth consisted of three components: the cloth, a fine ZrO_2 powder, and a proprietary liquid cement. The cement when cured consists of little or no phosphates or silicates. The impregnated cloth was about 15 mils thick and about 50% dense. A solid piece of the impregnated cloth was attached to a stainless-steel disk with double backing tape. Tiles (1/4 in. square) were cut in the attached cloth. In a similar specimen, the tiles were cut to 1/4 in. square and then placed on the tape individually. On both specimens, a conductive coating of AgNO_3 was applied to the ZrO_2 surface and a nickel disk was electroformed on the ZrO_2 tiles. After electroforming, the stainless-steel bonded disk was removed exposing the tiles shown in Figure 17. The bond between the electroformed nickel and ZrO_2 tiles along with the gap region are shown in Figure 18.

The tile specimen was tested in the plasma similar to the standard disk specimens. The thermal resistance for the ZrO_2 impregnated



ZrO₂

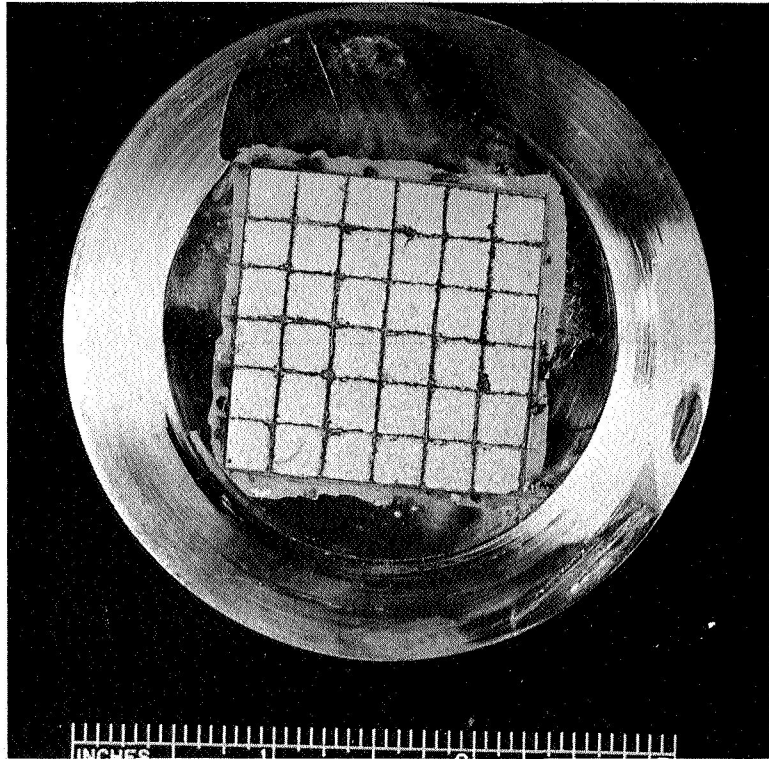
Nichrome
Primer

Nickel
Substrate

Mag 280X

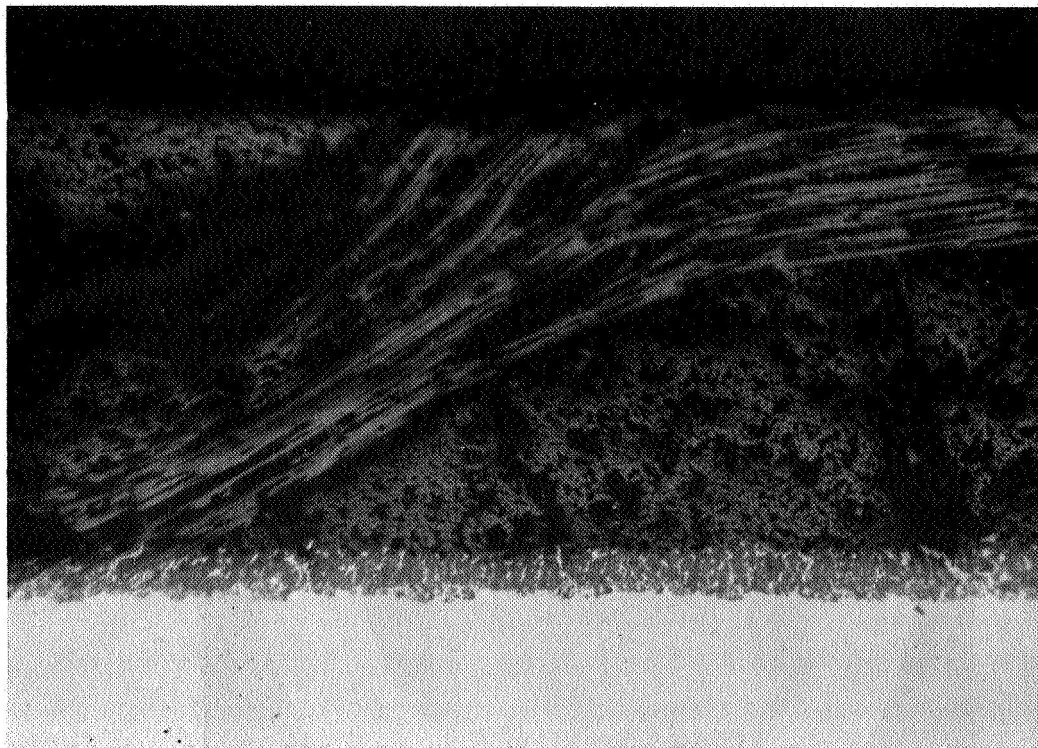
Neg 19416

Figure 16. Postfired Specimen Consisting of ZrO₂ Coating Deposited on a Nickel Substrate



Neg. 18593

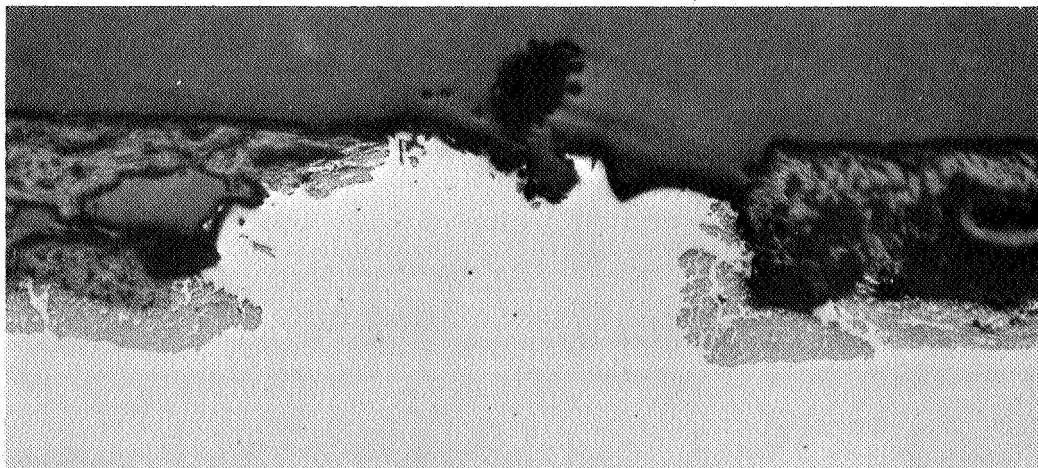
Figure 17. Nickel Disk Electroformed to Impregnated ZrO_2 Tiles



250X

Neg 19421

Bond between electroformed Nickel and
ZrO₂ tiles



100X

19419

Gap region between tiles showing penetration
of Electroformed Ni

Figure 18. Bond Between Electroformed Nickel and ZrO₂ Tiles

VII, A, Laboratory Evaluation (cont.)

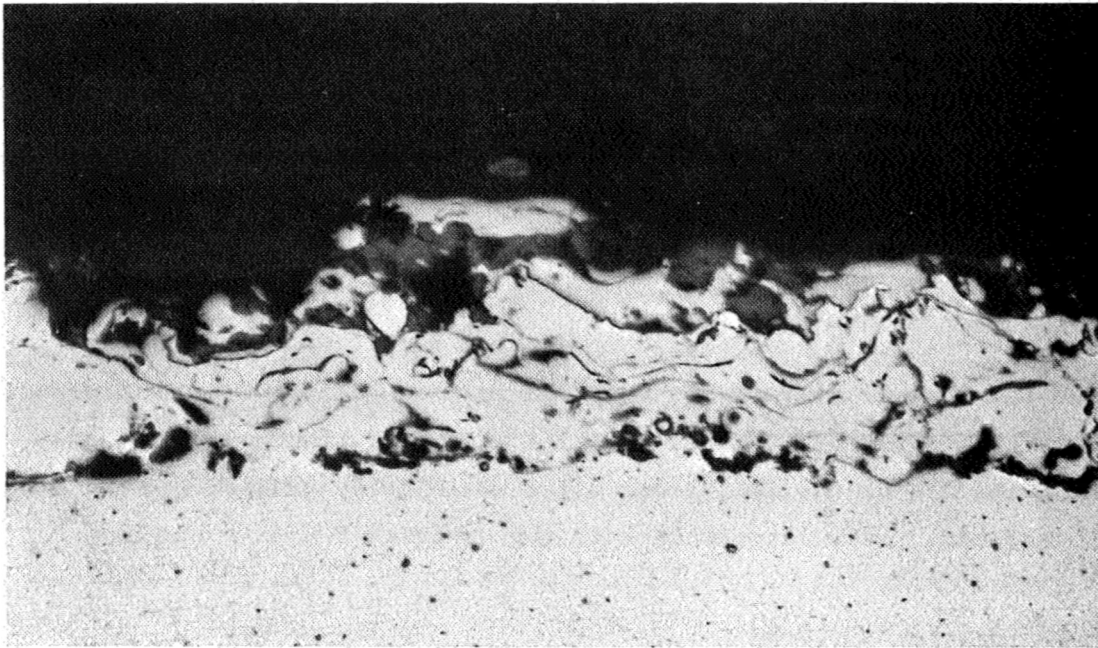
cloth was not known so that a low heat flux of 3.8 Btu/in. sec was used. Surface temperatures of 3800°F were obtained and the heat flux was adjusted to 4.3 Btu/in. sec. At this heat flux, the surface temperature of the ZrO_2 was 4000°F and the thermal resistances were 800 in.²-sec/Btu. The performances of the tiles were satisfactory without evidence of degradation. On the basis of these tests, the use of the ZrO_2 cloth tiles would be beneficial for applications requiring thermal resistance in the range of 800 in.²-sec/Btu.

4. 5-Tube Specimens

Coatings were evaluated on the conventional water cooled 5-tube specimens using the same procedure used for the disk tests. The test conditions were: a heat flux of 12 Btu/in.²-sec, a continuous 60 sec per test in an area on one end of the specimen and 15 thermal cycles on the opposite end of the specimen consisting of 10 sec heating and 5 sec cooling.

Specimens coated with ZrO_2 , HfO_2 , 27% Mo-73% ZrO_2 and 85% (27% Mo-73% ZrO_2) + 15% Si were evaluated. All of the coatings withstood the tests with no evidence of transverse cracking or longitudinal cracking in the valleys between the tubes. The material loss on the ZrO_2 , HfO_2 and 27% Mo-73% ZrO_2 was only 0.008 mils/sec compared to 0.02 mils/sec on the 85% (27% Mo-73% ZrO_2) + 15% Si coating. A comparison of the prefired and postfired condition of tube coated with the 27% Mo-73% ZrO_2 mixture is shown in Figure 19. The relatively high regression was attributed to the melting of the SiO_2 (3100°F M.P.).

Single-tube pack specimens were also evaluated with the same procedures as the conventional coated tube specimens. In the single tube specimens the coating was applied to the crown of the tube and then the coated tubes were joined by TIG welding the tubes together on the backside of the specimen.



Mo-ZrO₂

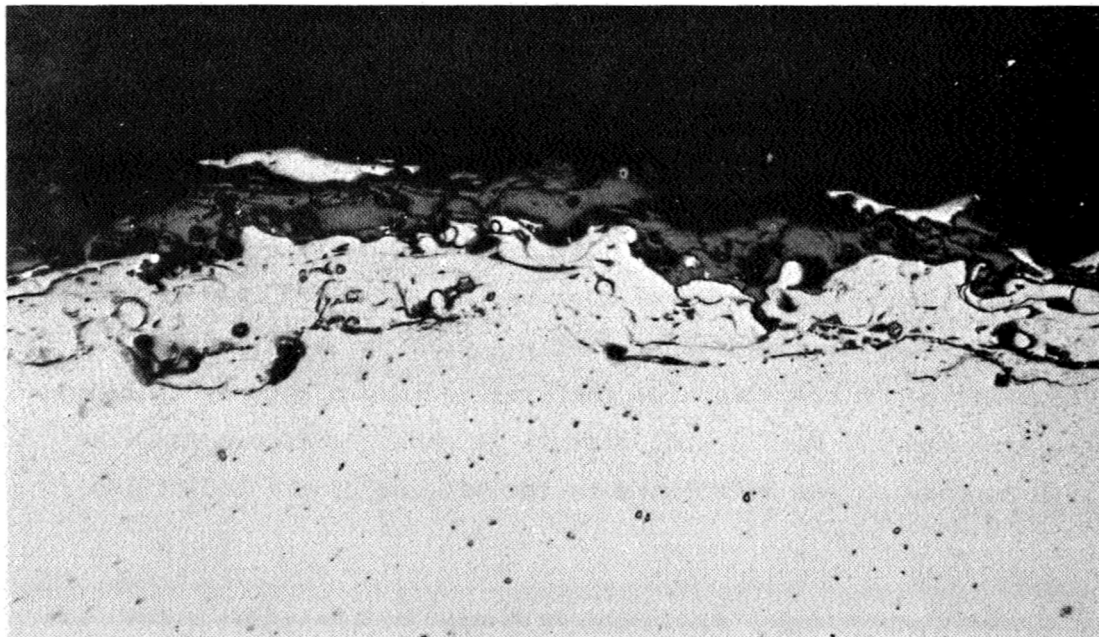
Primer

Tube
Wall

250X

Neg. 19413

Prefired



Mo-ZrO₂
Coating
Nichrome

Tube
Wall

250X

Neg. 19415

Postfired

(15 thermal cycles of 10 sec. heating and 5 sec cooling)

Figure 19. Comparison of Prefired and Postfired Coatings
Consisting of 27% Mo - 73% ZrO₂

VII, A, Laboratory Evaluation (cont.)

Both ZrO_2 and 27% Mo-73% ZrO_2 coatings were evaluated. Both coatings had low regression 0.008 mils/sec, the same as the conventional coating, along with good performance through the test. The Mo- ZrO_2 spalled on the fifteenth cycle in the cyclic thermal tests similar to the performance of this coating in the disk coupon evaluation.

VII, Thermal Barrier Evaluation (cont.)

B. HES TESTS

The HES test conditions are summarized in Table XI. The desired operating conditions (limited to protect associated hardware) were obtained in Tests U-5, U-7 and U-10. On Test U-6, because of an operator error, the HES chamber gas restricting orifice was not installed. The increase in orifice diameter from the normal value of 0.875 to 2.000 in. gave a large Mach number.

1. Specimen Surface Temperature and Performance Data

Temperature data obtained from the coated specimens when exposed to direct impingement of the plasma gas are summarized in Table XII. The temperatures reported were calculated using handbook value of tungsten reflectance and handbook value for the emissivity of tungsten. The corrected temperatures shown in Table XI in parenthesis were calculated using the reflectance measurement from the tungsten specimen in U-14 and the corrected emissivity of the coating material. A sketch of the typical strip chart data is shown in Figure 20. The region identified H-30 indicates the signal for the sample in place in the arc stream. When the shield comes in, the signal drops to the level which is contributed by the emission from the sample itself. The horizontal dashed lines represent the estimated average levels used in the calculations. The data in the area I_{sc} are questionable because the specimen surface would be cooled to ambient conditions, during that time. In order to provide accurate data, a fast response strutter system would be required. The noise on the signal is due to the erratic behavior of the plasma arc. HES Tests U-6 and U-7 yielded successful attempts to measure the specimen surface temperature. In Test U-5, the temperature measuring apparatus was aligned properly in the crown of the center tube before the test but was found to be aligned on a valley after the test. In Test U-10, a leak occurred

TABLE XI

HES THERMODYNAMIC ENVIRONMENTAL TEST DATA

HES Test	Specimen	Coating (1)	Gas Enthalpy, Btu/lb	Gas Temp, °F	Mixer Chamber Press, psia	Specimen Chamber Press, psia	Specimen Arm Heat Input, Btu/sec	Gas Flow Rate, lb/sec	Mach Number	Specimen Heat Flux, Btu/sq in. sec	AV Coolant (2) Temperature Rise, °F
U-5	H-20	Zirconia	3132	5887	72	55	18.03	0.125	0.66	-	-
Remarks - Sample out of Gas Stream											
U-5	H-20	Zirconia	3333	5960	80	58	58.06	0.125	0.73	26	65
Remarks - Sample in Gas Stream											
U-6	H-22	Hafnia	3860	5965	67	20	18.40	0.126	1.00	-	-
Remarks - Sample out of Gas Stream											
U-6	H-22	Hafnia	3815	5945	65	23	57.54	0.127	1.00	26	65
Remarks - Sample in Gas Stream											
U-7	H-25	27 Mo-Zirconia	4047	6091	84	59	17.75	0.126	0.74	-	-
Remarks - Sample out of Gas Stream											
U-7	H-25	27 Mo-Zirconia	3823	6054	83	61	54.57	0.127	0.72	25	63
Remarks - Sample in Gas Stream											
U-10	H-23	Hafnia	3737	5917	62	48	16.40	0.128	0.63	-	-
Remarks - Sample out of Gas Stream											
U-10	H-23	Hafnia	2579	5758	62	50	52.51	0.128	0.58	24	63
Remarks - Sample in Gas Stream											
U-13	H-30	Zirconia	3487	5901	65	55	18.58	0.128	0.51	-	-
Remarks - Sample out of Gas Stream											
U-13	H-30	Zirconia	3370	6035	93	83	48.63	0.130	0.42	20	60
Remarks - Sample in Gas Stream											
U-14	H-31	Tungsten	3407	6012	87	76	18.00	0.131	0.46	-	-
Remarks - Sample out of Gas Stream											
U-14	H-31	Tungsten	3724	6294	152	85	33.83	0.132	0.99	11	45
Remarks - Sample in Gas Stream											

(1) As fabricated thermal resistance 200 in.²-sec-°F/Btu

(2) Coolant inlet pressure 450 to 500 psia and exit pressure 100 to 150 psia

TABLE XII

SPECIMEN SURFACE TEMPERATURE AND PERFORMANCE DATA

<u>HES Test</u>	<u>Specimen</u>	<u>Specimen Description</u>	<u>Specimen Surface Temp, °F</u>	<u>Specimen Surface Emissivity</u>
U-6	H-22	Hafnia	4060 (3940)*	(0.639)*
U-7	H-25	27% Mo- Zirconia	3510 (3430)*	(0.571)*
U-14	H-31	Tungsten**		

*Quantities in parenthesis use reflectance measurement from Test U-14 after correcting for change in calibration and emissivity of the coating. The other values were obtained by using the emissivity of tungsten.

**Surface temperature for tungsten was not reported because it was deliberately kept cool so as to measure only the reflective contribution.

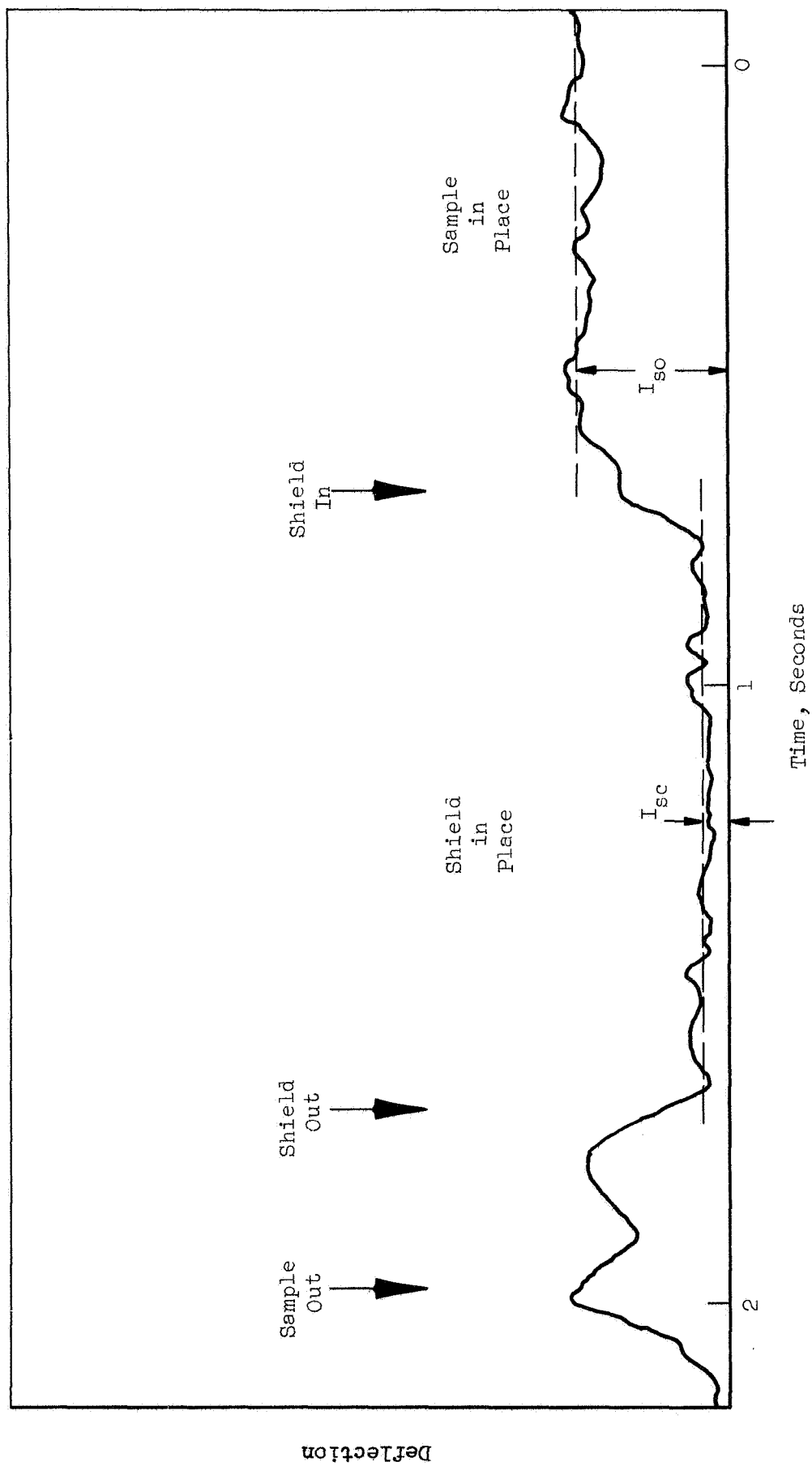


Figure 20. Typical Strip Chart Data for Coated Tube Specimens

VII, B, HES Tests (cont.)

in the braze at the end of the specimen, and in Test U-13, the specimen tube ruptured, and as expected the optical signals were distorted. No values of emitted radiation with the shutter closed were obtained in these latter tests and corrected values could not be calculated for these tests.

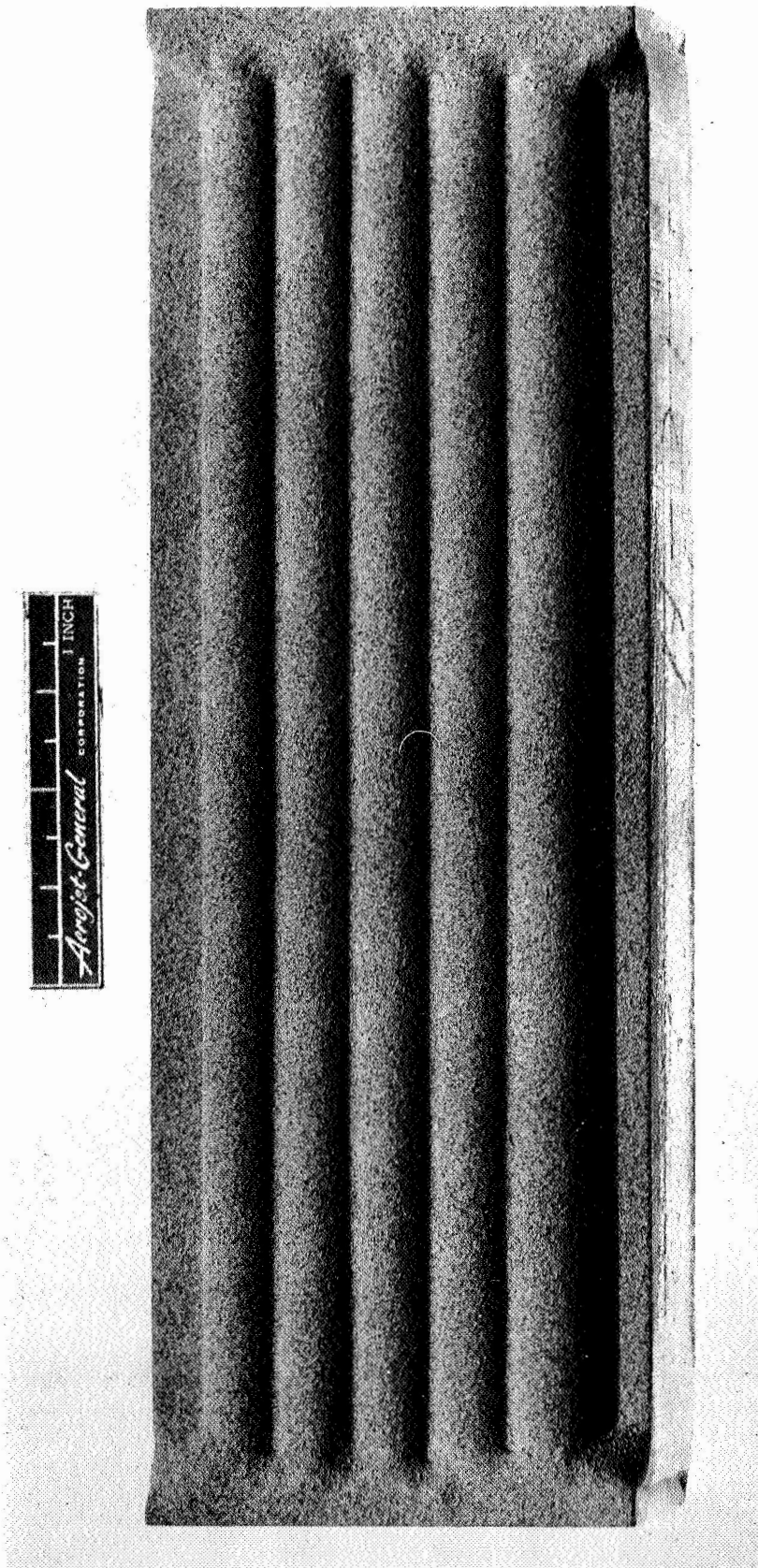
2. Coating Performance

The coated specimens evaluated in the HES tests were 5-tube specimens similar to those evaluated in the plasma test. Four of the 5-tube specimens (H-20, H-22, H-23, H-25) were of the standard tube brazed construction shown in Figure 21. Specimen H-30 was a single tube specimen which was fabricated by first coating the individual tubes, welding water manifolds on each end of the tube and then joining the backside of the tubes together with electroformed nickel (Figure 22). The electroforming operation joined the tubes satisfactorily.

All of the specimens including the single tubes were grit blasted prior to plasma-spraying and were primed with 2 mils of Nichrome. The plasma liner was applied to provide a thermal resistance of $200 \text{ in.}^2\text{-sec-}^\circ\text{F/Btu}$. The specimens were fabricated by brazing the tubes to a stainless steel backup and then machining holes through stainless steel backup into the tube as shown in Figure 23. A hole restrictor was used to force the water flow to the end of the specimen and swirlers were used to increase the water velocities at the tube surface. The backside of the specimens were machined to fit O-ring seals in the HES arm holder.

a. Specimen H-20

The flame liner on this specimen consisted of 2 mils of ZrO_2 . After exposure to the 15-sec HES test, visual examination revealed that the coating was in excellent condition with no cracking or ruptures as shown



Neg. 369 SP 268

Figure 21. Plasma Sprayed 5-Tube Specimen Prior to Testing

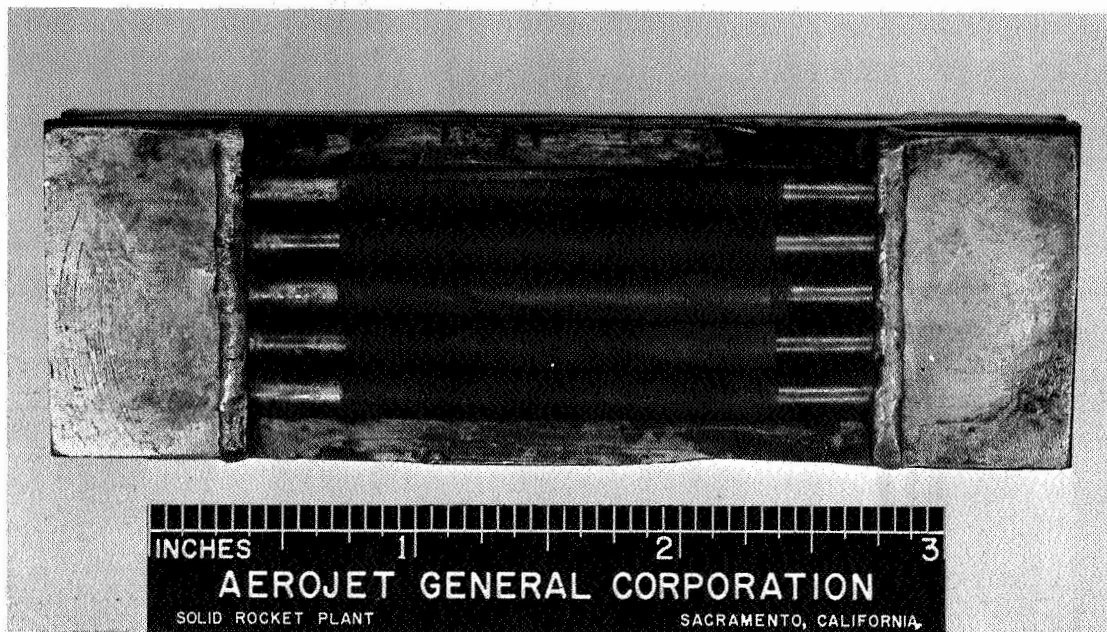


Figure 22. Plasma Spray Single Tube Specimen Prior to Testing

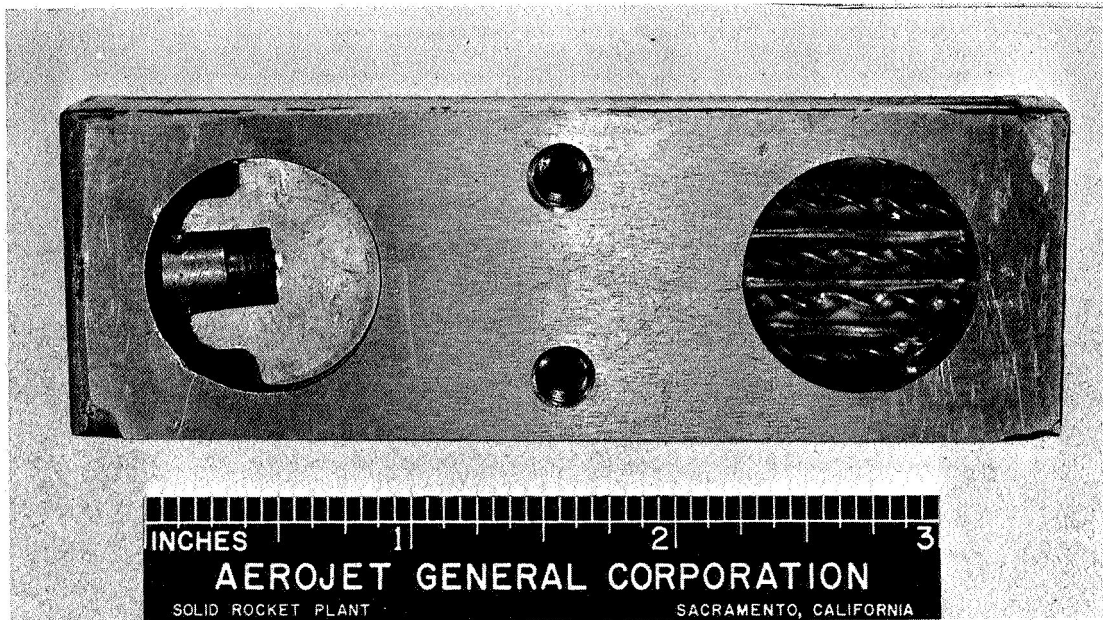


Figure 23. Backside of Test Specimen

VII, B, HES Tests (cont.)

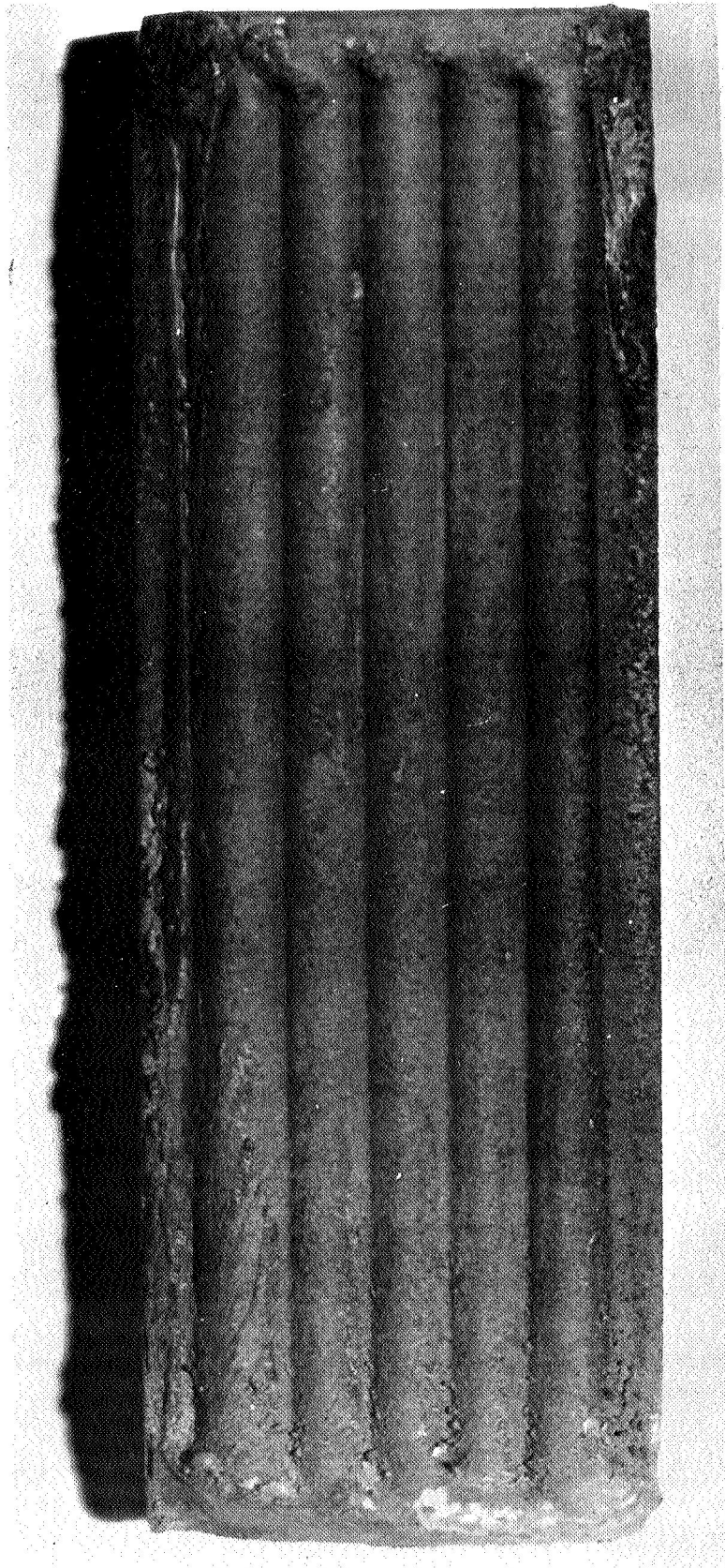
in Figure 24. Melting did occur on the outer edges of the stainless-steel backup to which the tubes were brazed. Micrometer measurements and metallographic examinations made after the test indicated no material loss. A cross section of the as-tested center tube and the coating is shown in Figure 25. Metallographic examination revealed no evidence of cracks.

b. Specimen H-22

This specimen had a flame liner consisting of 2 mils of HfO_2 . The sides and end of the backup of the specimen were melted and are shown in Figure 26, but the coating was satisfactory with no indication of ruptures or cracking. Micrometer measurements indicated no material loss but metallographic examination revealed that some coating regression occurred. The irregularity of the coating undercoat prevents accurate measurement of the regression but the best estimated material loss was about 1/2 mil in comparing with the untested section of the specimen. The cross section is shown in Figure 27.

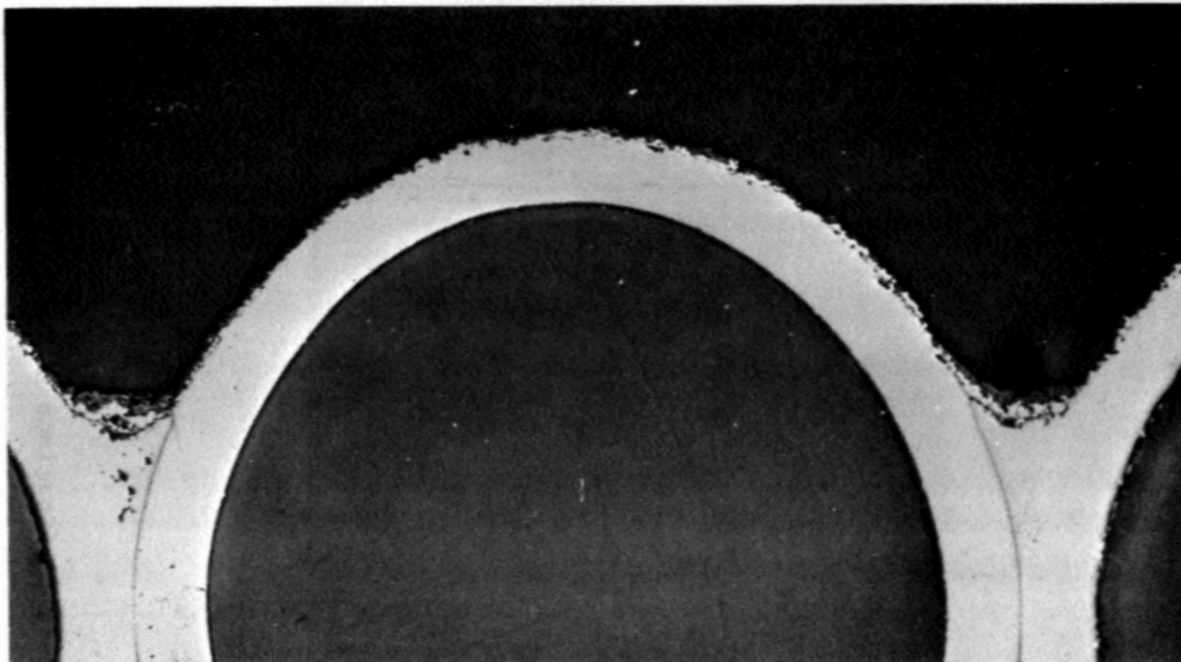
c. Specimen H-23

This specimen was similar to H-22. During the test, a leak occurred in a tube on the outside edge near the end of the specimen shown in Figure 28. This was outside the main impingement area of the gas stream. Melting occurred along the outside of the specimen along this tube and at the end of the specimen near the rupture indicating a lack of water cooling in this area. In the plasma gas impingement area of the specimen, the coating was satisfactory with no cracking or material loss as evidenced by micrometer measurements and metallographic examinations.



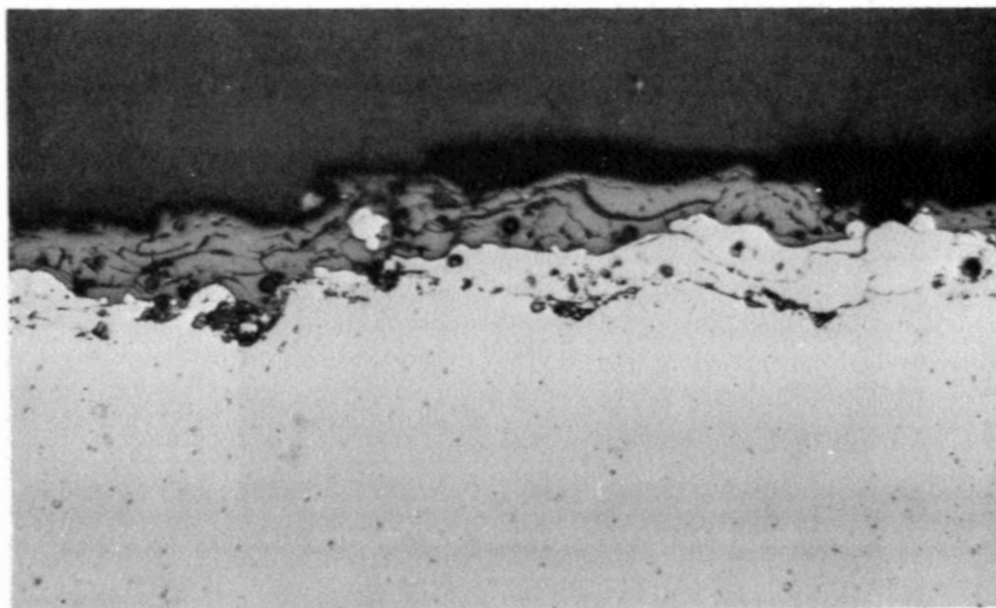
SP 864

Figure 24. As-Fired Condition of ZrO_2 Coating (Specimen H-20)



Mag: 24X

Neg. 18430



ZrO₂ Thermal
Barrier

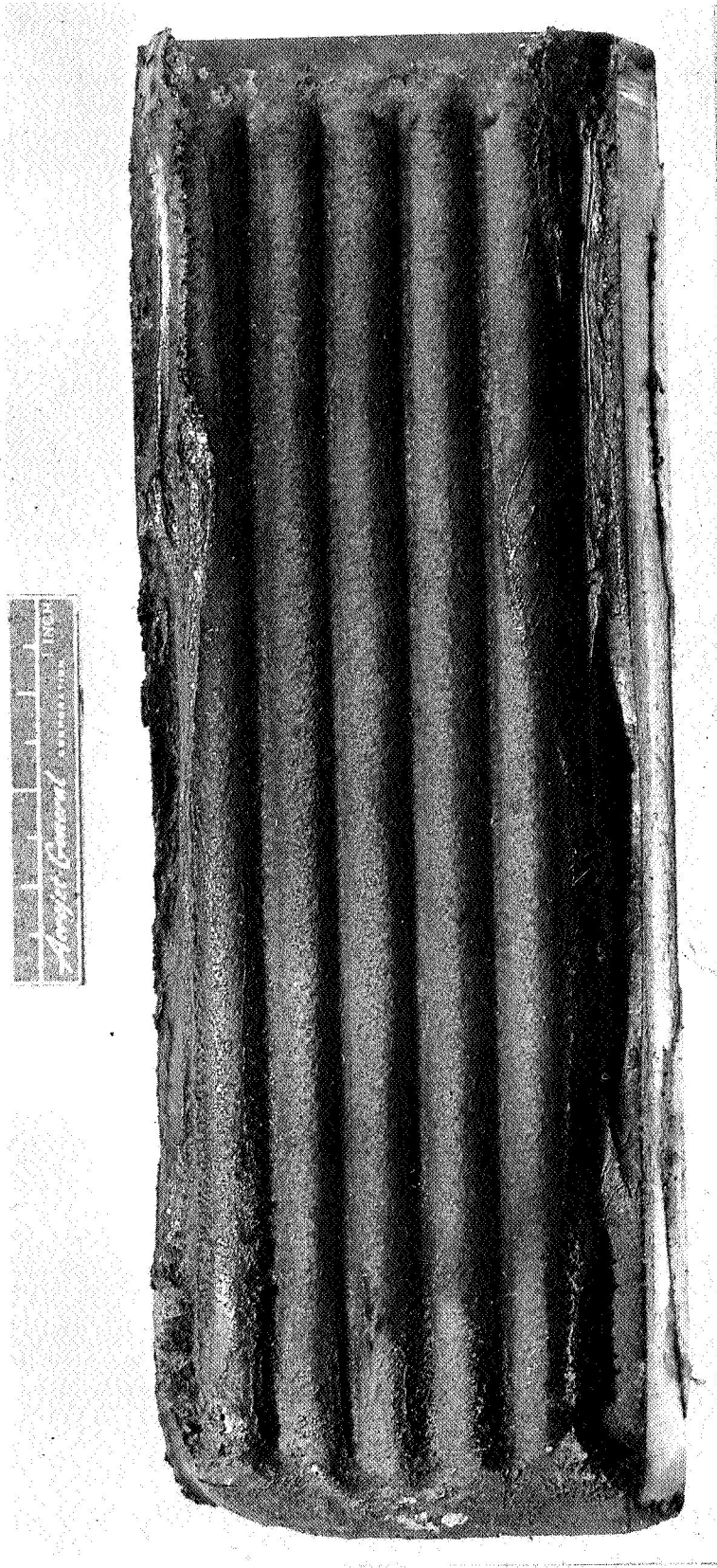
Nichrome Primer

Stainless Steel
Substrate

Mag: 250X

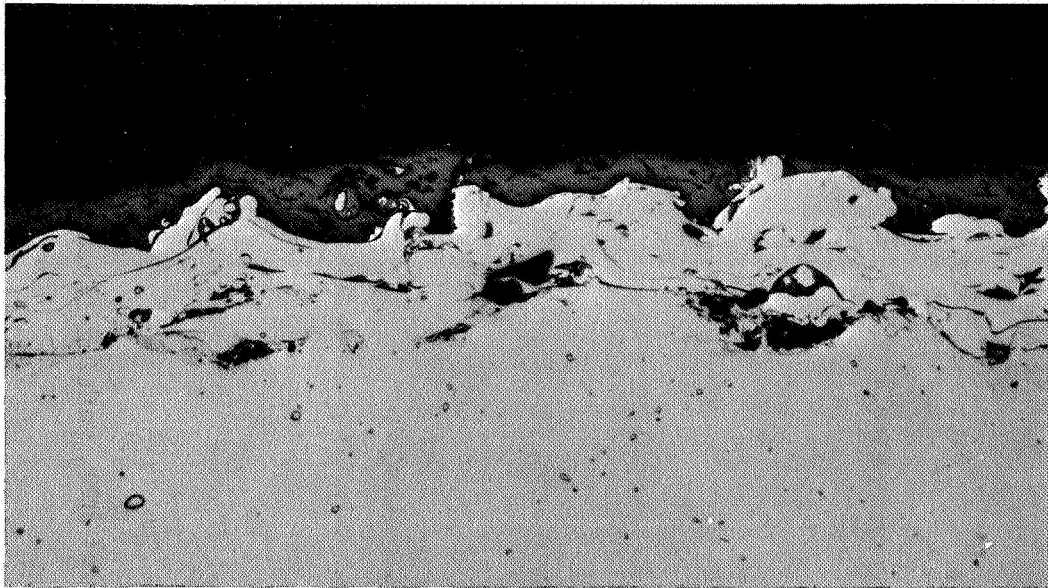
Neg 18437

Figure 25. Postfired Coated Specimen Consisting of ZrO₂
(Specimen H-20)



Neg. 369 SP 265

Figure 26. As-Fired Condition of HfO_2 Coating (Specimen H-22)



HfO_2 Thermal
Barrier

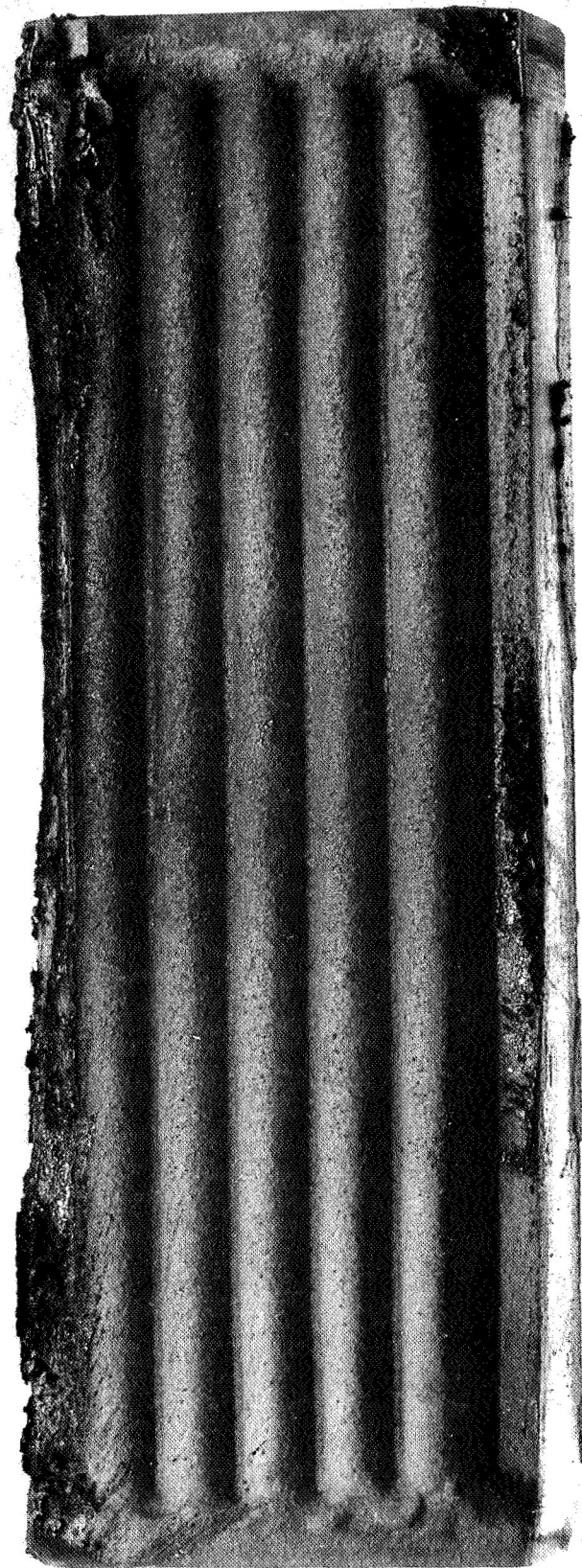
Nichrome Primer

Stainless Steel
Substrate

Mag: 250X

Neg. 18439

Figure 27. Postfired Coated Specimen Consisting of HfO_2 (Specimen H-22)



369 SP269

Figure 28. As-Fired Condition of HfO_2 Coating (Specimen H-23)

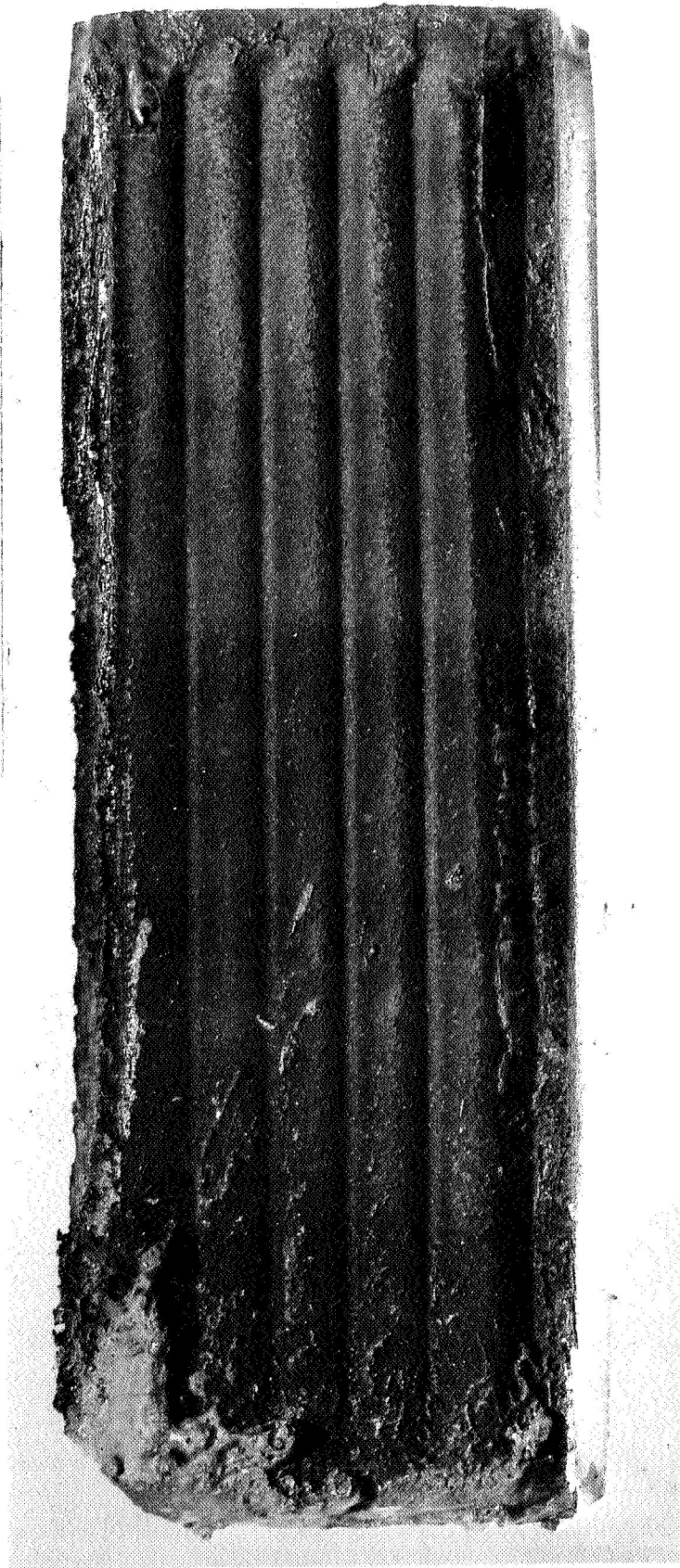
VII, B, HES Tests (cont.)

d. Specimen H-25

This specimen had a flame liner consisting of 3 mils of 27% Mo + 73% ZrO₂. Considerable melting occurred on the stainless-steel backup along the sides of the specimens shown in Figure 29, and also along the end of the specimen. The coating performed satisfactory with no evidence of cracking or coating ruptures. Micrometer measurements indicated no material loss but metallographic examination indicated that regression occurred and best estimates indicate about 1 mil regression occurred.

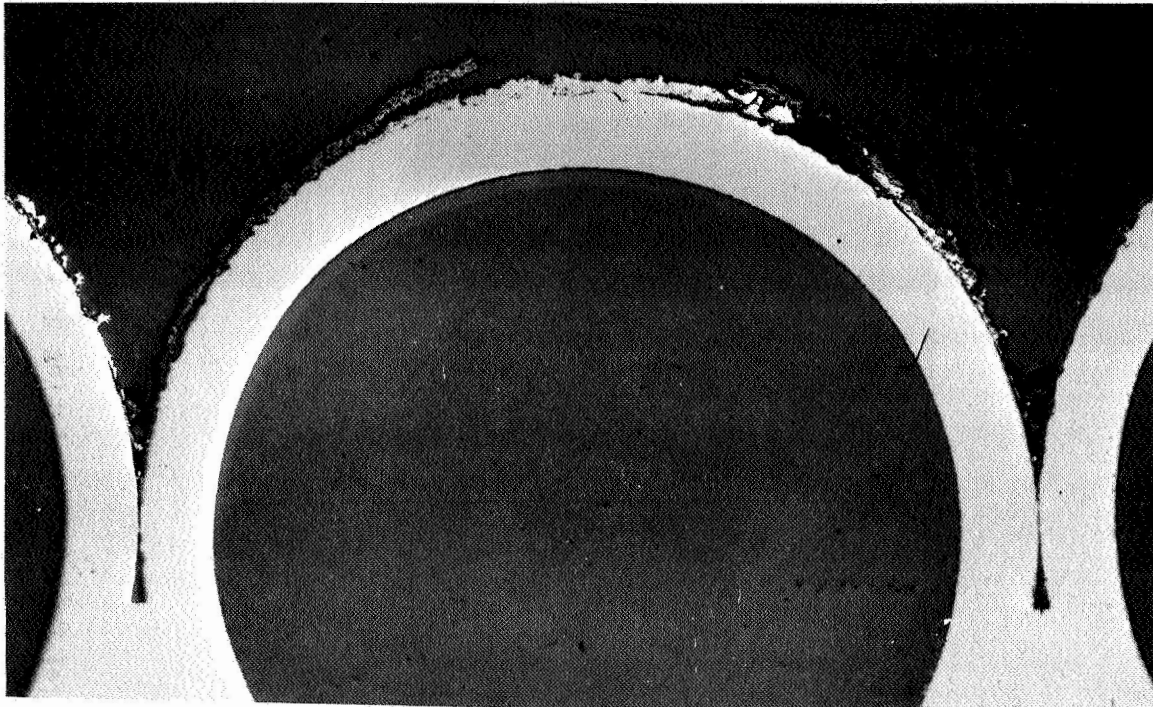
e. Specimen H-30

This was a single tube specimen in which each tube was coated individually and then joined by electroforming. The flame liner on the tube was 2 mils of ZrO₂ similar to specimen H-20. The coating in the impingement area ruptured during the test. Metallographic examination revealed that the coating and primer lifted away from the tube in the area of the rupture as shown in Figure 30. It appeared that poor bonding occurred in the areas between the primer and the substrate. In preparing the single tube for spraying, severe distortion occurred along the tube surface during grit blasting. To minimize distortion the blast pressure was lowered from the standard 80-lb pressure to 30 lb. The lower pressure resulted in a smooth substrate surface and poor bond adherence.



Neg. 369 SP 267

Figure 29. As-Fired Condition of Coating Consisting of 27% Mo + 73% ZrO_2 (Specimen H-25)



Mag: 24X

Neg. 18436

Figure 30. Coating Failure on Single Tube Specimen

VIII. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

1. A thermal analysis showed that a thermal barrier with a thermal resistance of $200 \text{ in.}^2\text{-sec/Btu-}^\circ\text{F}$ would be required to achieve a maximum heat flux of $20 \text{ Btu/in.}^2\text{-sec}$ for a LO_2/LH_2 engine operating at 2000 psi with gas-side surface temperature of 4000°F and a maximum tube wall temperature of 1600°F .

2. A thermochemical analysis showed that ZrO_2 and HfO_2 would withstand the highly oxidizing exhaust gases in the LO_2/LH_2 thrust chamber.

3. The important findings from tests of the coatings were:

a. The best coatings consisted of 100% ceramic either ZrO_2 or HfO_2 .

b. The addition of either Mo or W to the ceramic resulted in an increase in regression rates. The best cermet coating consisted of 27% Mo-73% ZrO_2 .

c. Use of either the conventional design concept or the single-tube concept worked equally well.

d. Use of the tile concept was satisfactory using impregnated ZrO_2 cloth cut into tiles and backed with electroformed nickel. Thin pressed and sintered ceramic tile was too brittle and fragile to be fabricated into test specimens.

e. The performance of the coating in the HES tests was similar to the performance in the laboratory plasma test.

VIII, Conclusions and Recommendations (cont.)

B. RECOMMENDATIONS

On the basis of laboratory and HES tests, the ZrO_2 and HfO_2 would be recommended for H_2/O_2 service. The coatings should be evaluated in H_2/O_2 rocket nozzle tests in which the coating is exposed to the exhaust gases that are obtained in the chambers at the throat in the exit areas of the nozzle. For these tests, it is recommended that a 2-dimensional nozzle system now being used for evaluating coating in fluorinated environments be used.

REFERENCES

1. Bartz, D. R., "A Simple Equation for Rapid Estimation of Rocket Nozzle Convective Heat Transfer Coefficients," *Jet Propulsion* 27, 1957, pp. 49-51.
2. JANAF Thermochemical Tables, The Thermal Research Laboratory, Dow Chemical Company.
3. Bechonski and Rossini; Thermochemistry of Chemical Substances, 1936.
4. A Study of Tungsten Alloys for Rockets, Atlantic Research Corporation, AFML-TR-65-101, Olcott, E.L. and Batchelor, J. P., April 1965.
5. Johnston, J.R., et al., "Performance of Rocket Nozzle Materials with Several Solid Propellants," NASA Technical Note TND 34228 C.1, May 1966.
6. Qualildo, S.P., "Phase Report on the Evaluation of Nozzle Materials," Thiokol Chemical Corporation, Contract DA-01-021-ORD-11919 Mod. 33.
7. Experimental Evaluation of Throat Inserts in a Storable-Propellant Rocket Engine, Report NASA TMX-1266, Winters, J. M., Plews, L. D., Johnston, J. R., October 1966.
8. Stability Characteristics of Refractory Material under High Velocity Atmospheric Flight Conditions, Progress Report 2, Kaufman, L., AF 33(615)-3859, December 1966.
9. Resnick, R. and Steinitz, R., "High Temperature Reaction Between Tungsten and Several Refractory Compounds," Fifth Meeting of the Refractory Composites Working Group, Dallas (8-10 August 1961).
10. Manning, C. R., Jr., and Stoops, R.F., "High Temperature Cermets" Journal of the American Ceramic Society, Vol 51, No. 8, pp. 411-414, August 21, 1968.
11. Coatings for Regenerative Engines, NASA Cr-72413, Lewis, W.J., Contract NAS 3-7955, 12 July 1968.
12. Thermal Barrier Liners for Regeneratively Cooled Combustion Chambers (U), BSD-TDR-135, Harrington, D. G. and Peterson, L.E., Contract AF04(694)-212 SA3, 20 November 1964 (C).
13. Development of Thermal Barrier Coatings for Regeneratively Cooled Rocket Engine Thrust Chambers (U), BSD-TDR-119, Harrington, D.G. and Adair, S.E., Contract AF 04(647)-652 SA4, 28 June 1963(C).

REFERENCES (cont.)

14. Grisaffe, S.J., "Analysis of Shear Bond Strength of Plasma Sprayed Alumina Coatings on Stainless Steel," NASA TND 3113, November 1965.
15. The Evaluation of Material Systems for High Temperature Aerospace Applications, Tech Report AFML-TR-65-339, Wurst, J.C., Cherry, T.A., Gerderman, D.A., and Hecht, N.L., Contract AF 33(615)-1312, July 1966.
16. Lowdermilk, W.H., Weiland, W.F., Jr., Livingood, J.N.B., "Measurement of Heat Transfer and Friction Coefficients for Flow of Air in Non-Circular Ducts at High Surface Temperatures," NACA RM E53J07, January 1954.
17. Temperature Distribution in Internally Heated Walls of Heat Exchangers Composed on Non-Circular Flow Passages, NACA Report No. 1022, 1951, Eckert, E.R.G. and Low, B.M.
18. Deissler, R.G. and Taylor, M.F., "Analysis of Turbulent Flow and Heat Transfer in Non-Circular Passages," NASA TR R-31, 1959.
19. Han, L.S., "Laminar Heat Transfer in Rectangular Channels," ASME Trans. 81C (J. of Heat Transfer) 2, 121, May 1959.
20. Stainback, P.C., "An Experimental Investigation at a Mach Number of 4.95 of Flow in the Vicinity of a 90° Interior Corner Aligned with the Freestream Velocity," NASA TN D-184 February 1960.
21. Stainbach, P.C., "Heat Transfer Measurements at a Mach Number of 8 in the Vicinity of a 90° Interior Corner Aligned with the Freestream Velocity," NASA TN D-2417, August 1964.
22. Gambill, W.R. and Bundy, R.D., Nucl. Sci. and Engrg. L8, No. 1, 80, 1965.
23. Nestler, D.W., "Laminar Heat Transfer to Cavities in Hypersonic Low Density Flow," Proc. of the Third International Heat Transfer Conference, Vol. II, pp. 251-261, August 1966.
24. Fox, J., "Heat Transfer and Air Flow in a Transverse Rectangular Notch," Int. J. Heat Mass Transfer, Vol. 8, pp. 269-279, February 1965.
25. AGC Computer Program, Job 166, Subject: A General Computer Program for Calculation of Rocket Engine Performance Parameters.

APPENDIX

SPECIMEN SURFACE TEMPERATURE MEASUREMENT TECHNIQUE

A description of the theory and operation of the spectroradiometer which was used for surface temperature measurements on the test specimens is presented in the following paragraphs. The measurements were made in the visible region of the spectrum to allow usage of standard optics and detectors.

With an arc, specimen and spectroradiometer arranged as shown in Figure 1A, the temperature of the surface at the point under observation was determined by sequential radiometric measurements of the spectral radiance at an angle θ to the surface normal, with and without the arc radiation imposed.

The heat specimen emits light of wavelength according to the equation

$$I_s(\lambda, T) = \epsilon_s(\lambda, T) I_b(\lambda, T) \quad (\text{Eq 1})$$

where I_s is the radiance of the specimen at temperature T and I_b is the radiance of a black body at the same temperature.

When the shutter is open, the radiance can be written

$$I_{so} = K_1 I_s + K_2 I_R \quad (\text{Eq 2})$$

Where I_R is the contribution due to the light reflected from the arc K_1 and K_2 are constants which include the geometrical properties of the system.

When the shutter is closed, the only light is that emitted by the specimen is

$$I_{sc} = K_1 I_s \quad (\text{Eq 3})$$

When the specimen is cold, the only light is the reflection of the arc. With a dummy specimen coated with W , the measured radiance is:

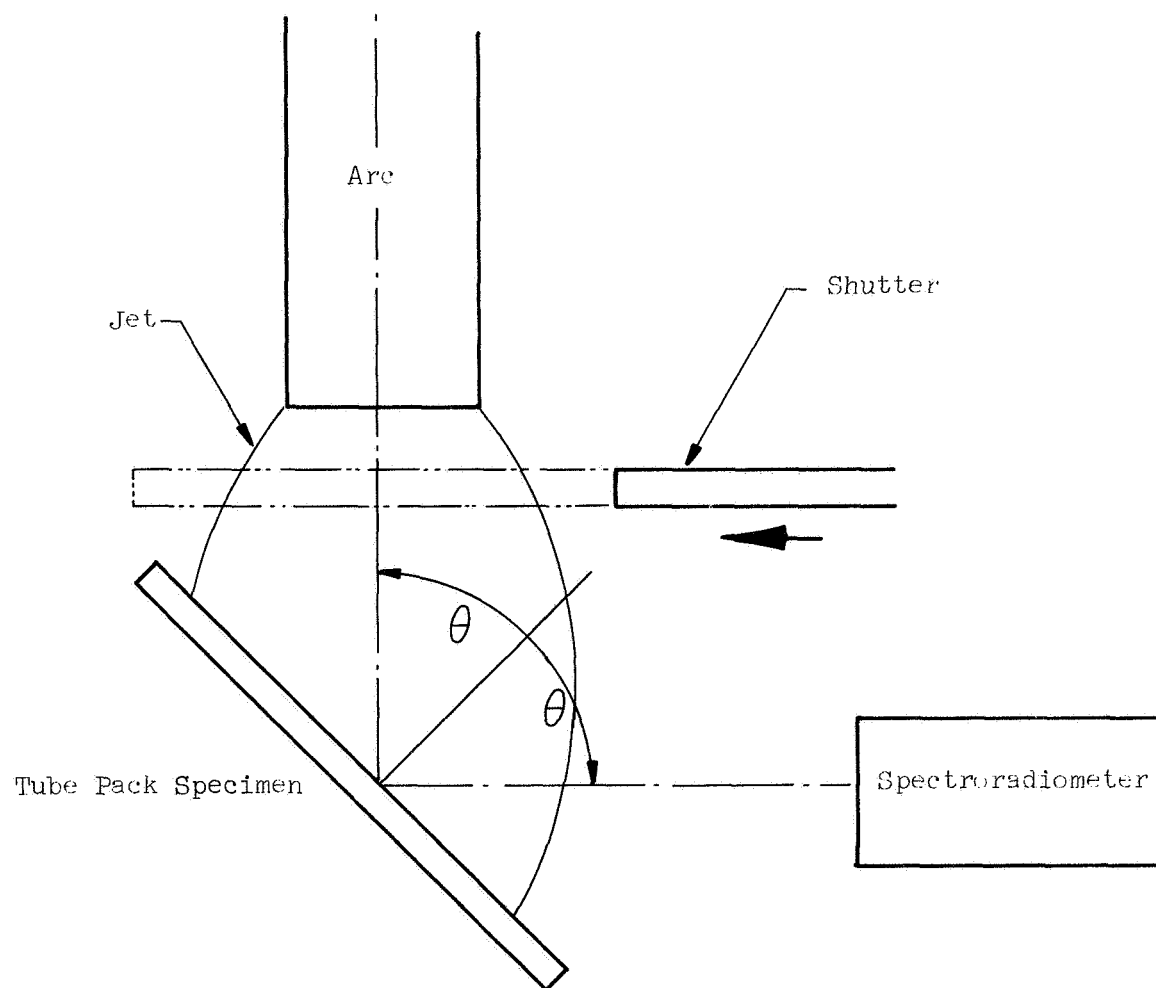


FIGURE 1A. EXPERIMENTAL ARRANGEMENT SCHEMATIC

$$I_{AR} = K_2 I_{RW} \quad (\text{Eq 4})$$

where I_{RW} is the arc reflection radiance from tungsten.

Radiance from a real material is expressed in terms of the radiance from a black body. The black body formula is

$$I_b(\lambda, T) = \frac{C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)} \quad (\text{Eq 5})$$

where $C_1 = 3.74 \times 10^4 \text{ watts cm}^{-2}$

and $C_2 = 1.438 \times 10^4 \text{ }^\circ\text{K}$

The reflected light can be written in terms of the arc radiance and the specimen reflectance, P_s

$$I_R = P_s \epsilon_A C_1 / \lambda^5 (e^{C_2/\lambda T_A} - 1) \quad (\text{Eq 6})$$

and for the tungsten coated specimen

$$I_{RW} = P_W \epsilon_A C_1 / \lambda^5 (e^{C_2/\lambda T_A} - 1) \quad (\text{Eq 7})$$

where the subscripts A denote properties of the arc.

From equations 6 and 7,

$$I_R/P_s = I_{RW}/P_W \quad (\text{Eq 8})$$

Reflectance and emittance are related by

$$P = 1 - \epsilon \quad (\text{Eq 9})$$

Therefore Equation 8 becomes

$$I_R (1 - \epsilon_W) = I_{RW} (1 - \epsilon_s) \quad (\text{Eq 10})$$

Substituting Equation 10 into Equation 2 yields

$$I_{so} = K_1 I_s + K_2 I_{RW} \frac{(1 - \epsilon_s)}{(1 - \epsilon_W)} \quad (\text{Eq 11})$$

Using Equations 3 and 4, Equation 11 becomes

$$I_{so} = I_{sc} + I_{AR} \frac{(1 - \epsilon_s)}{(1 - \epsilon_W)} \quad (\text{Eq 12})$$

Solving for ϵ_s :

$$\epsilon_s = 1 - \left(\frac{I_{so} - I_{sc}}{I_{AR}} \right) (1 - \epsilon_W) \quad (\text{Eq 13})$$

ϵ_W is known as a function of T and λ . The now known ϵ_s can be used with Equation 1:

$$C_1 \epsilon_s / \lambda^5 (e^{C_2 / \lambda T} - 1) = C_1 / \lambda^5 (e^{C_2 / \lambda T_b} - 1)$$

or

$$T = C_2 / \lambda \ln \left[1 + \epsilon_s (\lambda, T) (e^{C_2 / \lambda T_b} - 1) \right] \quad (\text{Eq 14})$$

Equation 13 is solved as described in the next section. The black body at temperature T_b which produces the measured radiance I_{sc} is obtained by calibrating the system with a tungsten ribbon filament lamp and an optical pyrometer.

The solution procedure of Equations 12 and 13 is outlined in the following chart:

Conversion of Photometer
readings to equivalent
calibration lamp current

Conversion of equivalent
calibration lamp current
to black body temperature

Conversion of b.b. temp to
radiance I_{so} , I_{sc} , I_{AR}

Find ϵ_s ($\epsilon_w = \text{Constant}$)

Find T from Equation 14.

Output T and ϵ_s

Optical Temperature Measurement Apparatus

A schematic representation of the optical assembly is shown in Figure 2A. The collimating lens is positioned so that the emitting source (calibration lamp or tube pack) is at the focal point (20 in.).

The detector components consist of a monochromator to transmit only a narrow band of wavelengths, a photomultiplier tube to convert the incident light into an electrical signal proportional to the light intensity, and a photometer to measure this output current.

To be able to interpret the readings from the photometer, an accurate calibration of the system was required. This included calibration of the monochromator and the photometer. The latter required a calibrated lamp. Since no primary standard was available, a tungsten lamp was used for this purpose. These calibrations are described in detail below.

Calibration of the Monochromator

A wavelength vs setting on the micrometer dial calibration was supplied by the manufacturer. It was necessary to check this to ensure operation of the photometer at $\lambda = 0.55 \mu$. A Hg lamp was chosen for this purpose. The 0.57696μ line and the 0.5460μ line bracketed the wavelength of interest and the peaks of these lines were measured. The 0.57696μ line corresponded to a micrometer setting of 5.128 and the 0.5460μ line to a setting of 4.951. Therefore 0.550μ occurs at 5.10. Figure 3A shows the manufacturer's calibration data and Figure 4A the measured response.

The slit width in the monochromator was chosen to be 0.1 mm. This corresponds to a wavelength interval of $\Delta\lambda = 7m\mu$ at $\lambda = 0.55\mu$. A narrower width and hence a better resolution was impractical because of the extreme sensitivity and loss of signal of the (nonlinear) adjustment at high resolutions.

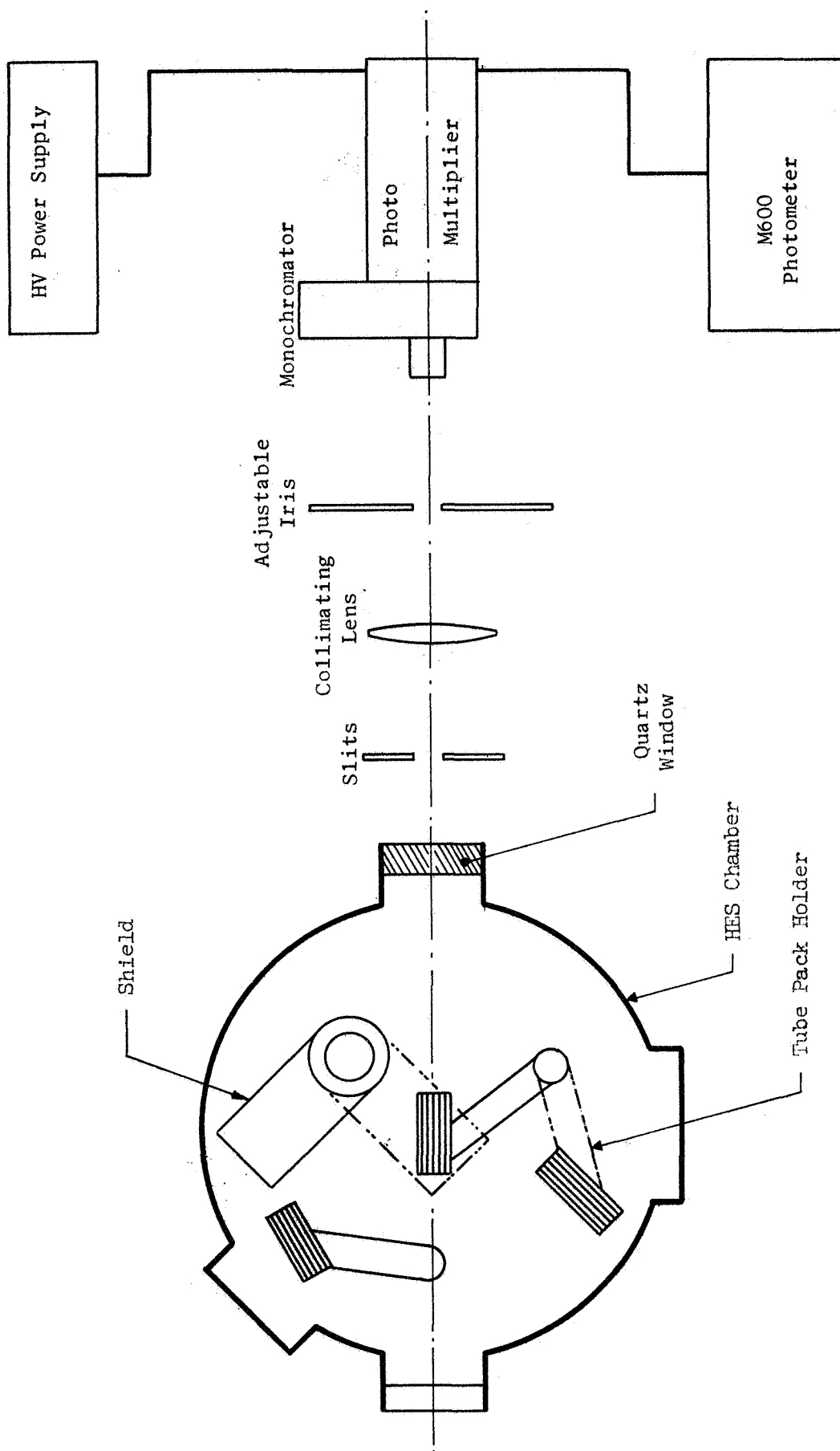


FIGURE 2A. INSTRUMENTATION LAY OUT

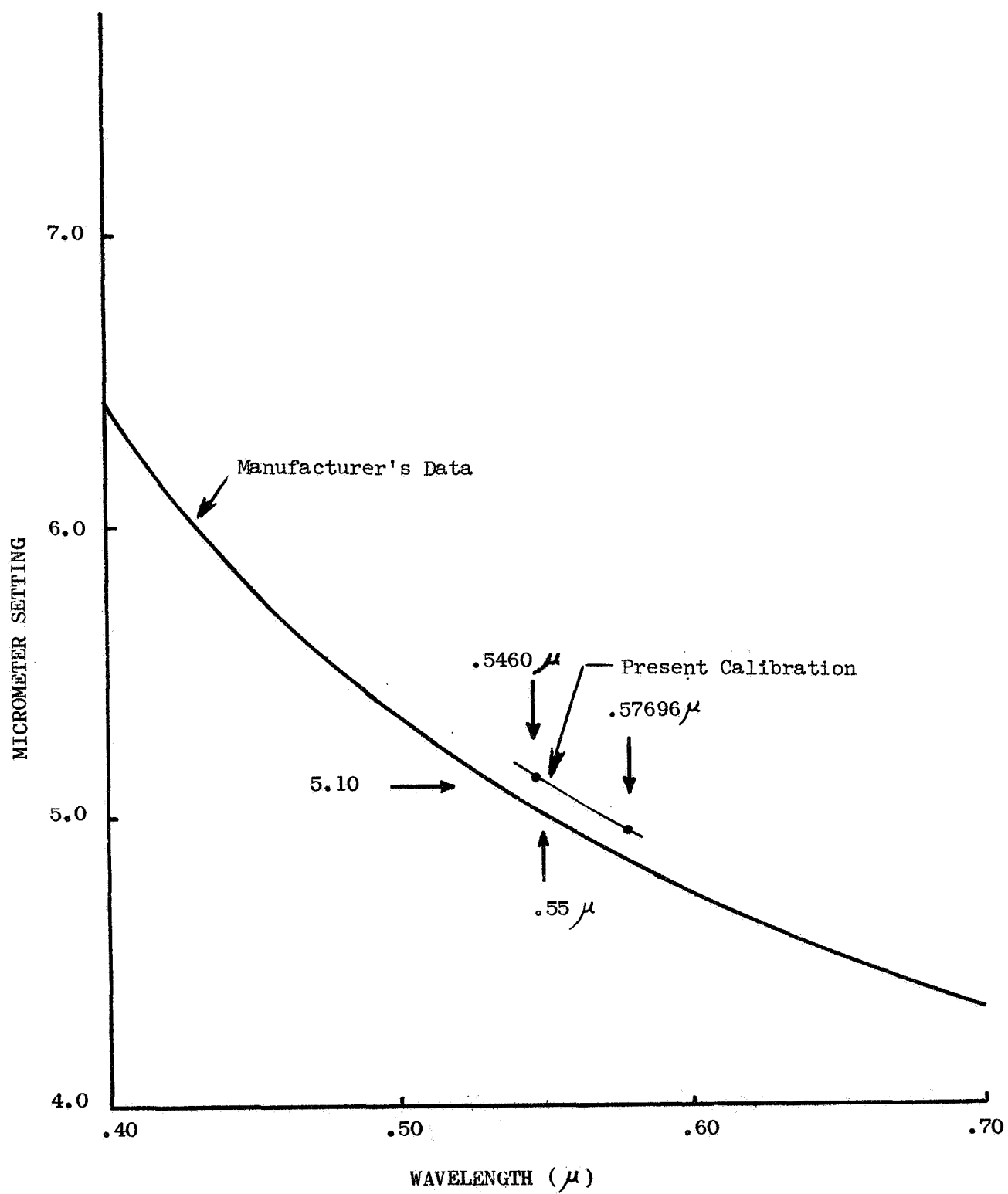


Figure 3A. Wavelength Calibration of the Monochromator

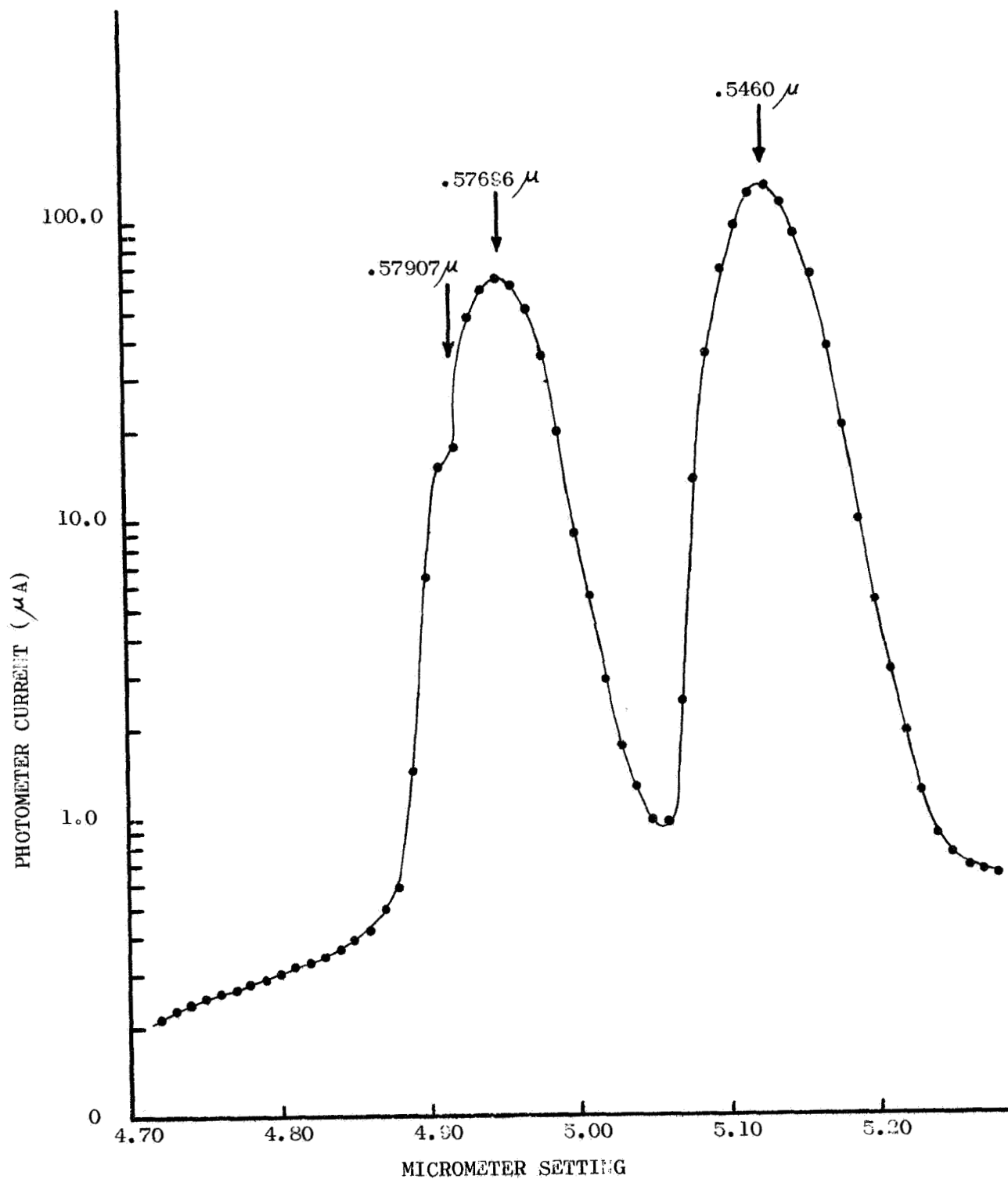


Figure 4A. Data for the Light Curve used in the Temperature Measurements

Calibration of the Tungsten Lamp

A GH 18A/T10/2P-6V tungsten ribbon filament lamp was calibrated using an accurate optical pyrometer which itself has been accurately calibrated in the Measurement Standards Laboratory. The filament current required to produce a radiance equivalent to that from a black body at the temperature indicated by the optical pyrometer was thus obtained. These data appear in Figure 5A. The current range was swept six times in order to obtain a large number of points. The calibration curve was fit by a second order polynomial by the method of least squares using AGC computer program H62203. These results are represented by the solid line in Figure 22.

The optical pyrometer measured the light at 0.65μ whereas the monochromator was set at 0.55μ . The difference in the emissivity at these two wavelengths is small, so no significant error was introduced.

Calibration of the Photometer

The calibrated tungsten ribbon filament lamp was placed in the HES chamber at the target location with due care that the region of the filament used was that sighted on with the optical pyro. The adjustable slits (with their slit opening crossed at 90° to make a net rectangular opening) were narrowed until the filament more than covered the entire field of view. The monochromator was set to $\lambda = 0.55\mu$. The photometer was zeroed out and compensation for the photomultiplier dark current was introduced with the lamp out and all stray light eliminated. The component arrangement is shown in Figure 19 with the lamp substituted for the tube pack during the calibration.

The lamp was operated at several filament currents and the photometer current readings noted. From the known lamp current-temperature relation, the temperature vs photometer reading calibration was completed. This calibration was done twice; one at the beginning of the experiment and once

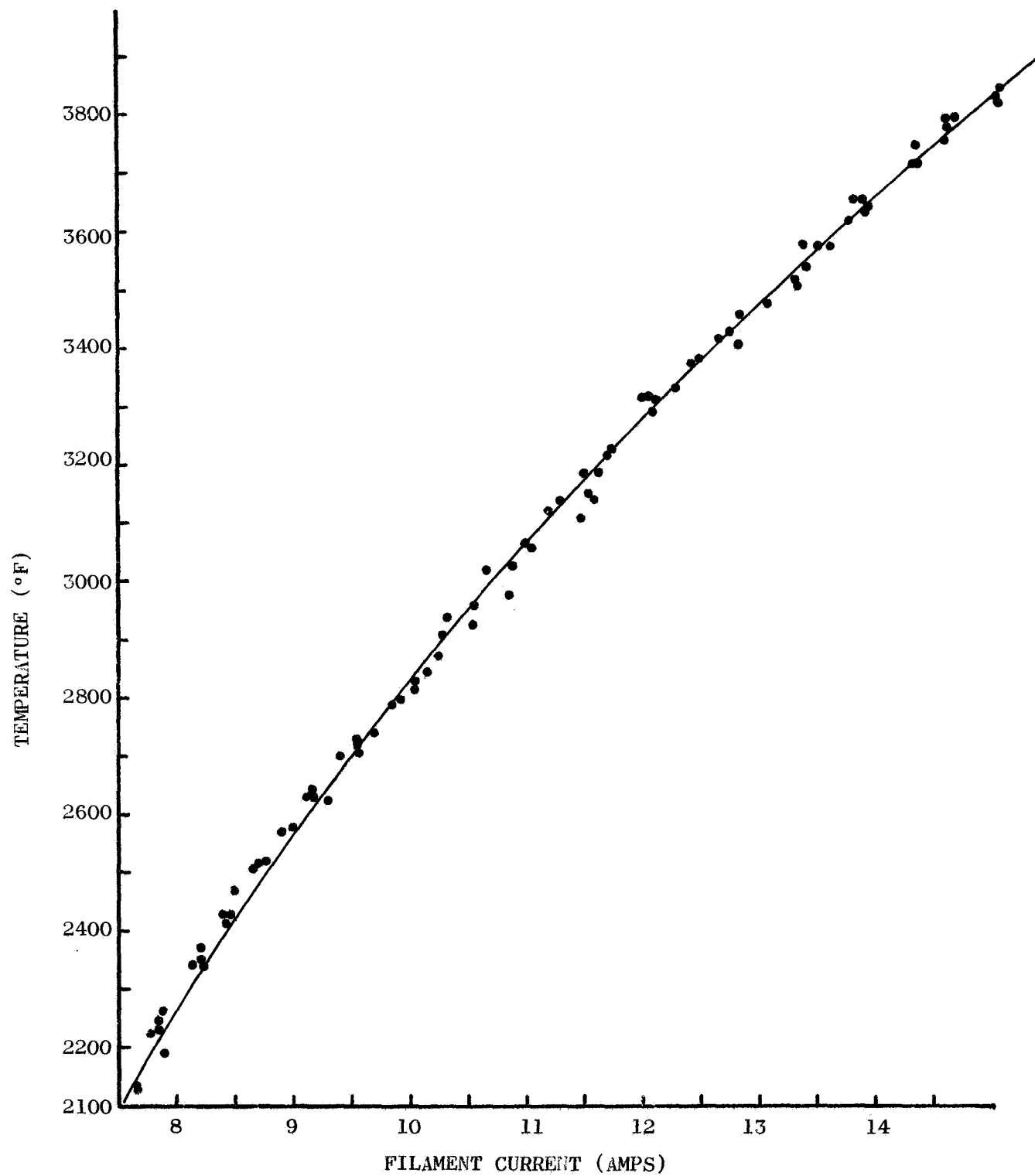


Figure 5A. Calibration Curve for the
Ribbon Filament Tungsten Lamp

more just before Run U-11. The second calibration was required because of misalignment of the apparatus. The calibration curves are shown in Figure 6A. The solid lines are least square polynomial fits to the data points as obtained from the computer program. The difference in the results of these calibrations occurred because the apparatus was not repositioned in the exact original position.

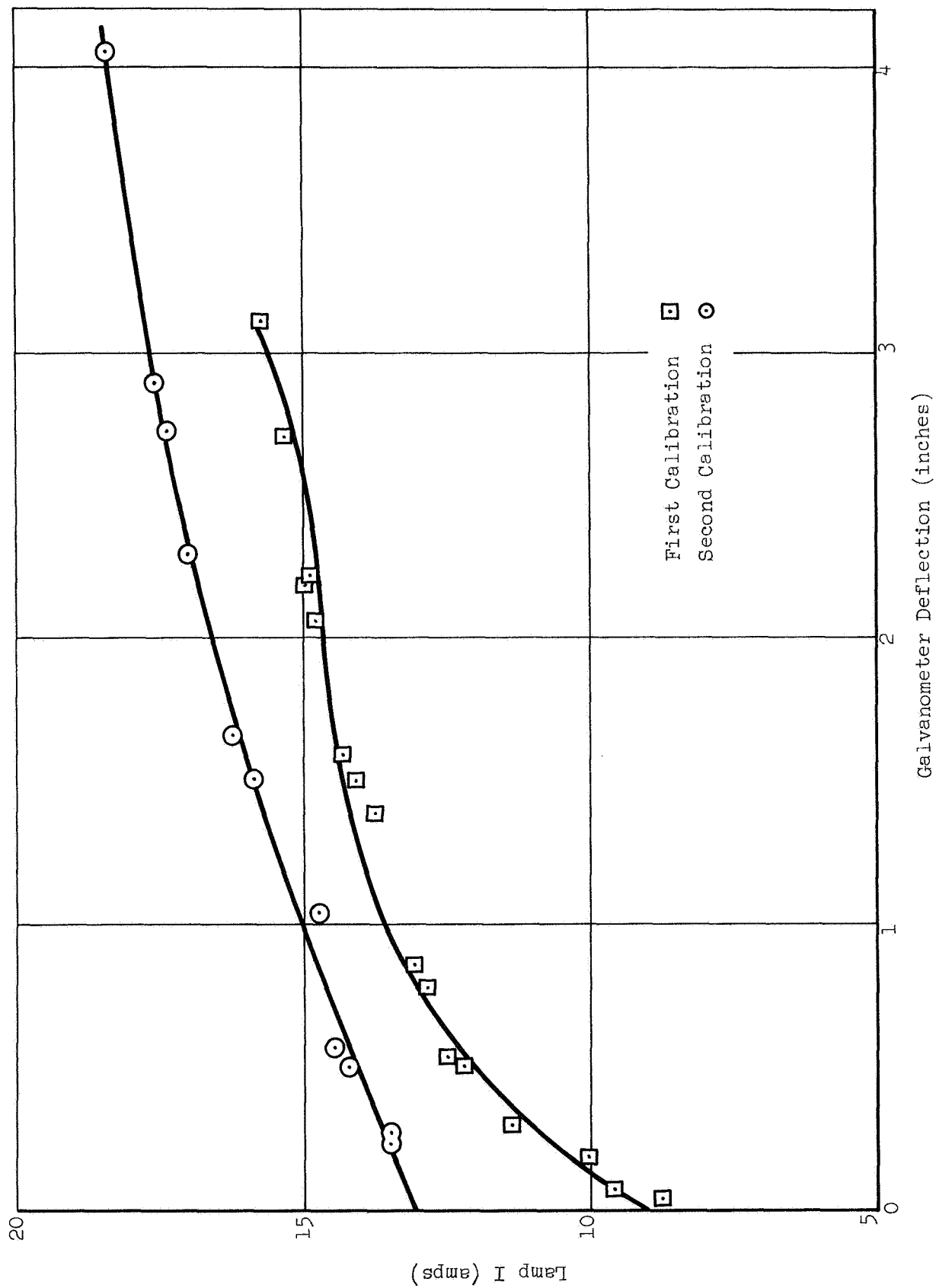


FIGURE 6A. M600 PHOTOMETER CALIBRATION CURVES

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