THE ROLE OF EMITTANCE IN REFRACTORY METAL COATING PERFORMANCE

PART I – REVIEW AND ANALYSIS

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FOREWORD

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ABSTRACT

The role of emittance in refractory metal coating performance was reviewed and analyzed for the purpose of orienting the planning of a comprehensive program to provide accurate and proper emittance data for thermal calculations needed in the design of advanced aerospace vehicles and engines. The following was found: Coated refractory metals are used and are planned for future use on reentry and hypersonic cruise vehicles which are cooled almost solely by the radiation of heat to space. Space engine nozzles and extensions fabricated of coated refractory metals may be cooled to advantage by radiation. Emittance values have a profound effect on the rate of heat rejection, and thereby, on the metal-coating system temperature which, in turn, controls coating life and metal strength. The emittance of a coated refractory metal is a function of its environment which includes temperature, time, partial pressures of the atmospheric constituents, and the free-stream velocity of the atmosphere under extreme temperature conditions. Total hemispherical emittance values are needed for thermal calculations involving exterior vehicle and engine surfaces that radiate to space, but for calculations between surfaces, the use of spectral emittance values is indicated if emittance varies appreciably with wavelength. Most emittance data in the literature are total normal data which do not necessarily equal total hemispherical data unless the coatings radiate diffusely. The extent to which refractory metal coatings display diffuse radiation is not known.

As an aid in planning the comprehensive program, a number of preliminary emittance experiments were performed. Heating as-received silicide-coated columbium and molybdenum alloys and one tin-aluminide-coated tantalum alloy to 2000°F in air caused a marked increase in emittance which, for the silicide coatings, was associated with oxide formation. The total normal emittance of these coatings measured at 2000°F was found to equal the total normal emittance calculated by integrating the spectral curve (as a function of a 2000°F graybody) inferred from room temperature reflectance data. This indicates that the shape of the spectral curve at 2000°F is not a strong function of temperature.

A comprehensive emittance program is presented for possible future action. It covers the effect of cyclic environmental exposure on emittance, including exposure in a hypersonic tunnel; the relationship of coating process control parameters to emittance; the significance of various types of emittance properties in thermal calculations; and recommendations concerning the determination of special emittance properties such as angular emittance.

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ρ_W	Wall material density	lb/ft^3
c_{pw}	Wall material specific heat	$Btu/lb_m \; °F$
b_W	Wall or skin thickness	ft
T_W	Wall temperature	
t	Time	sec
h	Convective heat-transfer coefficient	$Btu/ft^2 \; sec \; °F$
T_{Aw}	Adiabatic wall temperature	$°R$
ϵ_H	Total hemispherical emittance	-
σ	Stefan-Boltzmann constant	$Btu/sec \; ft^2 \; °R^4$
α_S	Solar absorptance	
G_S	Solar irradiation	$Btu/ft^2 \; sec$
H	Heat-transfer coefficient based on enthalpy difference	$lb_m/ft^2 \; sec$
i_{Aw}	Adiabatic wall enthalpy	Btu
ρ_λ	Monochromatic reflectivity	-
α_λ	Monochromatic absorptance	-
λ	Wavelength	Microns
θ	Polar angle from the normal	-
ϕ	Azimuth angle	-
Δ	Fractional error in either h or ϵ_H	-
T	Temperature at time, "t"	$°R$
T_i	Initial temperature	$°R$
i_w	Enthalpy at wall surface	Btu

T_{wB}	Wall temperature based on previous calculation	-
E	Radiative flux	$Btu/ft^2\ sec$
ϵ_N	Total normal emittance	-
ϵ_{SN}	Spectral normal emittance	-

Section I

INTRODUCTION

Refractory metals such as alloys of molybdenum, columbium, tantalum, and tungsten are suitable for use as hot structure for lifting reentry and hypersonic vehicles, and as engine components. Unfortunately, while these metals possess usable strength properties up to 3000°F and greater, they are rapidly attacked in an oxidizing atmosphere unless protected by a refractory coating. Coating failure then leads to rapid destruction of the refractory metal itself. Coating life falls rapidly above 2000°F and, therefore, it is important to keep the metal-coating system at as low a temperature as possible. A coating that may survive 10 to 20 hours at 2700°F may fail in an hour or less at 3000°F. A variation of as little as +50°F from a given temperature could produce a significant change. Reliable performance of such coatings above 2000°F is dependent upon the exact environment encountered, pre-exposure factors which may degrade the coatings, and control of the processing conditions during coating application.

One approach to keeping cool metal-coating systems used as exterior vehicle surfaces is to select a coating with a high thermal emittance and one which retains this high emittance during use. For example, the relationship between thermal emittance and turbulent equilibrium temperature at a 140,000-foot altitude for a flat plate parallel to flow one foot from the leading edge at an angle of attack of 0 degrees at Mach 20 is as follows:

Hemispherical Total Emittance	Approximate Temperature (°F)
0.9	2100
0.7	2250
0.6	2350
0.5	2500

It can be seen that, as the emittance goes up, the temperature goes down. In actual hypersonic design, thin insulated skins are often used and the actual metal temperature follows these values closely. At angles of attack greater than 0 degrees, the temperatures would be greater. As an example, for angles of attack slightly greater than 0 degrees, skin temperatures for one typical reentry vehicle could be between 2500°F to 2800°F for an 8-minute period with an emittance of 0.6.

The need of a high-emittance coating for the exterior surfaces of such vehicles has been recognized for some time. Considerable work has been done on the use of a high-emittance overlay for the basic oxidation protective coating in conjunction with refractory metals for the X-20 (Reference 1). Likewise, work has been done on the development of single coatings which will both impart oxidation resistance and high emittance (Reference 2).

For some materials, the emittance rises with temperature, and for some, it drops (Reference 3). Various reasons exist for this situation:

1. If the material is a coating, it may become "transparent" with an increase in temperature and cause the emittance of the base metal to contribute to the system.

2. The material may simply display a different total emittance due to phase changes or chemical changes such as oxide formation associated with an increased temperature.

3. The basic spectral emittance curve of a material may not be flat. It may vary significantly with wavelength due to the chemical nature of the substance. Since the peak wavelength of thermal energy emitted by a surface moves to a shorter wavelength as the temperature rises in accordance with Wien's Displacement Law, one finds the total emittance of such materials will often vary greatly with temperature.

For design calculations, the thermodynamicist finds that accurate values for total hemispherical emittance are needed to determine vehicle exterior surface temperatures when the vehicle is radiating to space. Unfortunately, there is a lack of adequate information in the literature for emittance values at elevated temperatures for refractory metal coatings. The literature contains little spectral emittance data, which is especially needed in calculating the radiant exchange of heat within enclosures, typically, that between front spars and leading edges of hypersonic vehicles. This lack of spectral data and the consequent conventional use of the graybody assumption in such calculations can lead to large errors in heat-transfer rates.

Much of the data are not reliable, the samples are not well-identified, and some of the measurement methods that were used are questionable.

Further, the data that exist do not necessarily include the effect of flight service environments on emittance stability. A typical service cycle might include cool-down to -70°F for 1/2 hour, heating to 1500°F for 1/2 hour, exposure to a space vacuum for several days, and heating to 2800°F for 1/2 hour at 0.01 to 0.1 atmospheres. At these high temperatures and oxidizing conditions, any oxide forming on the surface of the coating might be subject to shear forces tending to remove it and to expose fresh surfaces

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for further oxidation. This situation has the potentiality for a changing emittance. It is not known at this time what would happen to a particular coating system. Under similar circumstances, the shear forces may not be large and the oxide may be tenacious. Testing in a hypersonic tunnel would appear indicated, although the measurement of emittance under these circumstances would certainly be difficult above, 2500°F. Optical pyrometery would be required, which is dependent upon knowing the emittance of the surface. In addition, no tunnel simulates all conditions properly.

Most coatings are applied by pack processes which do not always yield completely reproducible results. Some compositional variations exist as well as thickness and smoothness differences. Effort has been expended in controlling the factors that affect oxidation protection, but no specific effort has been put forth to identify and control the factors that may affect emittance of coatings of current interest.

In summary, it may be stated that a knowledge of coating emittance is essential for predicting metal-coating system performance and heat transfer; the available emittance data are inadequate; emittance measurement methods are not always reliable; service environments can have a profound effect upon emittance and its attempted simulation in the laboratory; and, lastly, little is known of the factors in coatings that must be controlled to ensure reproducible emittance.

The purpose of the present study is to devise a plan which, when implemented, will give designers reliable emittance values of refractory metal coatings upon which to base heat-transfer calculations.

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Section II

PROGRAM OBJECTIVES

OVERALL PROGRAM

This report, subtitled "Review and Analysis," covers Phase I of a four-phase, 2-year program concerned with the role of emittance in refractory metal coating performance. The four phases of this program are:

Phase I - Review and Analysis
Phase II - Measurement Capability Advancement
Phase III - Emittance Measurements
Phase IV - Correlation of Emittance Data

OBJECTIVES OF PHASE I EFFORT, "REVIEW AND ANALYSIS"

The objectives of this Phase I study are:

1. To explain the role of emittance in refractory metal coating performance.

2. To define the dynamic environments in which emittance properties of coatings are significant.

3. To define the environmental and other factors which affect emittance including the interdependence of such factors.

4. To show the relationship between emittance and coating composition and other properties, including the effect of variations in such composition and properties as are found in normal coating application practice. This information, especially spectral emittance data, should be of assistance in the design of coatings with known and reproducible emittance properties.

5. To determine which emittance properties should be measured in order to permit the accurate calculation of temperatures of refractory metal-coating systems and heat-transfer data involving such systems for vehicles and engines in dynamic-use environments.

6. To plan a comprehensive emittance measurement program which will result in accurate emittance data for design calculations and which recognizes the effect of environment, composition, and other factors on emittance.

The Phase I effort includes limited experimental measurements of emittance, composition, and physical structure. It is not expected that the comprehensive program will be completed in the subsequent three phases of this program. However, Phases II, III, and IV are to be substantial contributions toward the implementation of the complete program. In particular, dynamic environment simulation via hypersonic tunnels is reserved for future programs, as also is statistical sampling of coating suppliers.

Section III

EFFECT OF EMITTANCE IN CONTROLLING OVERALL COATING/METAL PERFORMANCE

BACKGROUND

At the present time, the most important refractory metals and alloys for use in high-temperature applications are molybdenum, columbium, tantalum, and tungsten. These metals possess appreciable strength at elevated temperatures, but all oxidize severely at high temperature unless suitably protected with coatings. The emittance of the coating, or more properly of the coating/substrate system, becomes of considerable importance for applications in which radiation cooling is an important mechanism in controlling temperature. Figure 1 illustrates the rather significant role played by the emittance in establishing the temperature of a radiatively cooled surface. The radiant heat flux, E, exhibited in the figure was determined in terms of the remaining parameters by employing the expression

$$E = \epsilon_H \, \sigma \, T^4 \tag{1}$$

with ϵ_H the surface emittance and σ the Stefan-Boltzmann constant. Clearly, at a specified thermal flux, significant changes in the effective emittance of the surface can alter surface temperature appreciably.

Application of this emittance relationship is concerned with the use of coated refractory metals as exterior surfaces of reentry and hypersonic vehicles. Such vehicles will be subjected to extreme temperatures and associated high Mach numbers in level flight or in reentry. Figures 2 and 3 show the relationship between emittance and temperature for an insulated thin aerodynamic skin at Mach 10 to 20. (The derivation of this relationship for aerodynamic surfaces is explained in Section V.) It thus can be seen from figure 2 that at Mach 20 and 140,000 feet, if the total hemispherical emittance is 0.7, the temperature one foot from the leading edge would be 2250°F; but, if the emittance were 0.55, the temperature would be 2400°F. Coating life is dependent upon temperature, as is illustrated by the coating-life curves, figure 4. It can be seen from these curves that the following situation exists:

Material	Range of Life at Temperatures, Hours	
	2250°F	2400°F
Sn-Al Coat on Ta 10%W	60 to 460	40 to 310
MoSi$_2$ on Mo	60 to 2250	25 to 1350
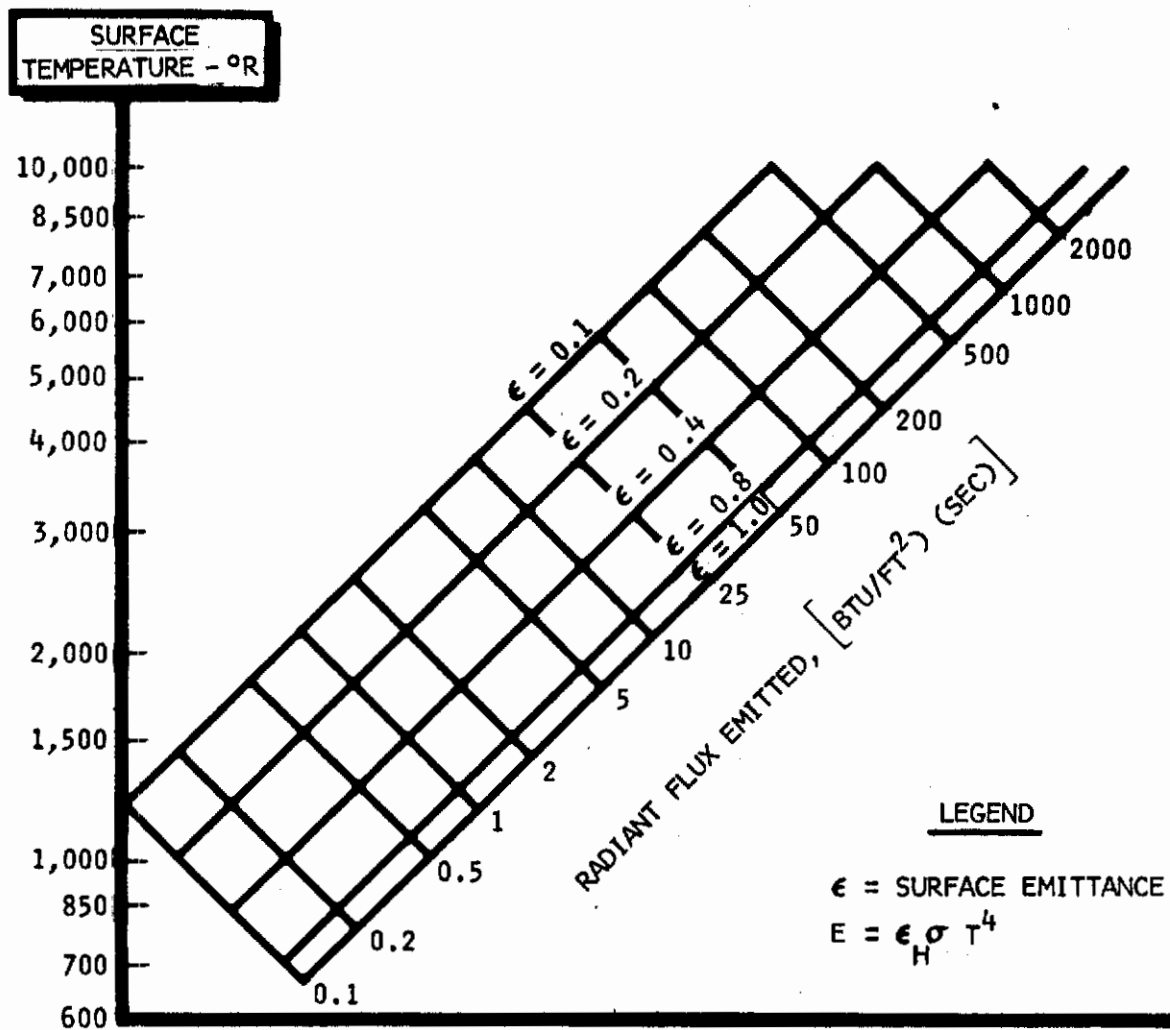
Figure 1. Thermal Radiation Heat Flux Rate as a Function of Surface Temperature and Emittance

CURVES BASED ON:

TURBULENT BOUNDARY LAYER
FLAT PLATE FLOW ANGLE OF
ATTACK 0 DEG

$0.08 \times 10^6 < N_{RE} < 0.8 \times 10^6$

WHERE N_{RE} = REYNOLD'S NUMBER
BASED ON FREE-STREAM
CONDITIONS

(FROM REFERENCE 4)
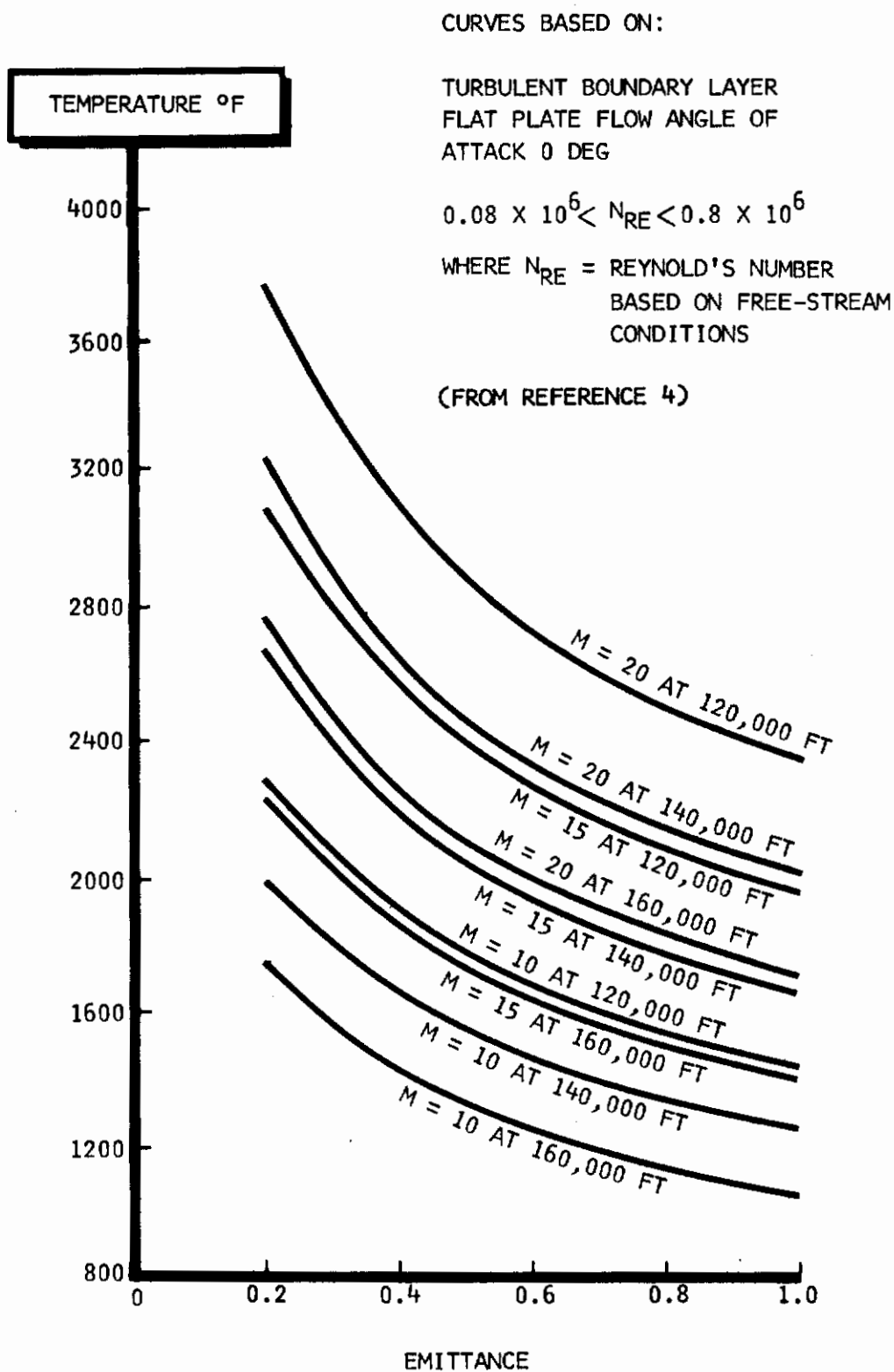
Figure 2.   Insulated Radiation Equilibrium Temperatures
One Foot From Leading Edge

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CURVES BASED ON:

TURBULENT BOUNDARY LAYER
FLAT PLATE FLOW ANGLE OF
ATTACK 0

$0.8 \times 10^6 < N_{RE} < 8 \times 10^6$

WHERE N_{RE} = REYNOLDS NUMBER
BASED ON FREE-
STREAM CONDITIONS

(FROM REFERENCE 4)

TEMPERATURE °F

3600
3200
2800
2400
2000
1600
1200
800

0   0.2   0.4   0.6   0.8   1.0

M = 20 AT 120,000 FT
M = 20 AT 140,000 FT
M = 15 AT 120,000 FT
M = 20 AT 160,000 FT
M = 15 AT 140,000 FT
M = 10 AT 120,000 FT
M = 15 AT 160,000 FT
M = 10 AT 140,000 FT
M = 10 AT 160,000 FT

EMITTANCE

Figure 3.   Insulated Radiation Equilibrium Temperatures
10 Feet From Leading Edge
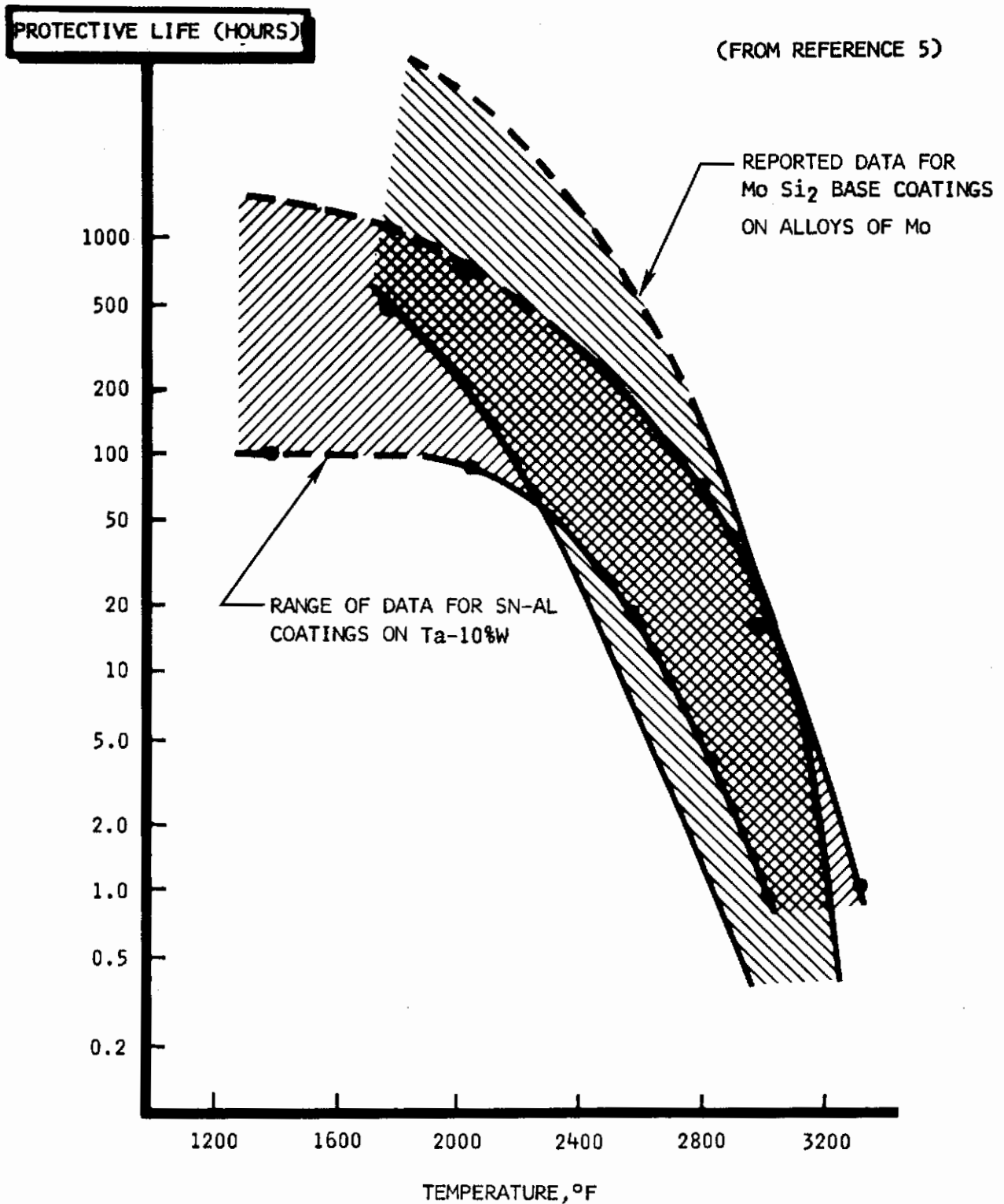
Figure 4. Ranges of Protective Lifetimes Observed for Sn-Al Coating for
Tantalum and Silicide Coatings for Molybdenum

While it is obvious that the coating lives are quite variable, the 150°F temperature difference could change the life of coatings 30 percent to 60 percent, with the greatest effect being shown by marginal coatings. The data cited are for atmospheric pressure.

OXIDATION MECHANISM

The chief function of the refractory metal coating is to afford oxidation protection. Failure of this protection occurs in quite varied ways. It has been well-established that an important mechanism through which oxidation of the coating/substrate system is impeded is the formation of an outer oxide layer. In the case of molybdenum alloys, which to date have received the greatest attention, the disilicide-based coating is of chief importance. The oxidation resistance of the coating is effected by the establishment of a layer of silica, in which the diffusion of oxygen and metal ions is relatively slow. Formation of this layer is believed to occur through the oxidation of $MoSi_2$, as follows:

$$5 \, MoSi_2 + 7 O_2 \longrightarrow Mo_5Si_3 + 7 \, SiO_2$$
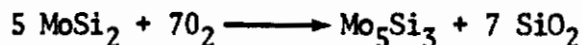
Raising the temperature will increase the diffusion rate, cause increasing amounts of silica to form, and thereby lead to oxidation of the base metal because of coating loss.

Figure 4 also presents data obtained on the protective lifetime for Sn-Al coatings on Ta-10W. This is a particularly interesting system in that it employs containment of liquid phases beneath an oxide film to provide a reservoir of the stable oxide-forming constituent. In this manner, a high self-healing capability is achieved (Reference 5). More particularly, it is believed that after diffusion treatment at 1900°F during preparation, the coating consists essentially of $TaAl_3$ with enough unreacted Sn-Al to give the residual defect-healing liquid phase at elevated temperatures. On exposure at temperatures above 1900°F, the $TaAl_3$ interdiffuses with the substrate and quickly converts to lower aluminides. For protection against oxidation, it is essential that an oxide film be formed on the surface before this rapid interdiffusion occurs to the extent that most of the $TaAl_3$ phase is converted to Ta_2Al (Reference 6). Too high a temperature too soon could be disastrous.

DIFFUSION MECHANISM

Changes in temperature in the direction of an increase are most likely to be sources of coating degradation or failure, and diffusion plays a large part in this. The general results to be anticipated in the event of

this kind of change have been nicely summarized by Krier (Reference 6): "Generally speaking, the higher the temperature, the greater the potential is for different materials to react and interdiffuse; and the higher the temperature and the longer the time, the greater the extent to which reaction and diffusion occur. Chemical reaction and interdiffusion between coating and substrate can substantially reduce the thickness of the substrate, alter the mechanical properties on which the design of the structure was based, produce undesirable interface phases, and destroy the protective characteristics of the coating by changing the composition and the various properties originally designed into the coating."

Diffusion can degrade the system by means other than reduction of the oxidation protection afforded by the coating. Thus, it is possible for the coating materials to diffuse into the substrate. A consequence of this might be embrittlement of the substrate material with loss in strength of the system. On the other hand, diffusion of the substrate metal into the coating can cause a loss in substrate metal thickness. Mathauser (Reference 7) reports a decrease of approximately 17 percent in the total thickness of an 8.1-mil-thick coated molybdenum alloy sheet during an exposure to a temperature of 2500°F for 29 hours, and illustrates the variation of substrate loss with time. Krier cites numerous examples of equal or greater substrate loss as a result of diffusion (Reference 6). In the case where the coatings have negligible load-carrying capacity, the net result of either of these interdiffusional effects, or both in concert, is the loss in strength of the system.

THERMAL EXPANSION MISMATCH

An additional category of failure mechanisms is that associated with thermal-expansion mismatch, i.e., with differential expansion between coating and substrate resulting from differences in the respective thermal expansion coefficients. This leads to a condition in which at temperatures below the process temperatures (which is the no-stress condition), a higher-expansion coating will be in tension, while above the process temperature, it will be in compression. The substrate, on the other hand, will be in compression and tension, respectively, under these two conditions. If, at temperatures below the processing temperature the tensile strength of the coating is exceeded, cracks will develop in the coating. [Lack of surface continuity prior to coating deposition (i.e., sharp edges, corners, and notches) leads to uneven coating deposition which together with thermal-expansion mismatch increases the severity of cracking].

Emittance-temperature changes could possibly aggravate these problems in several ways. Merely driving the "exposure" temperature to a higher level might aggravate the stresses resulting from the mismatch condition and reduce protective life. This will be most pronounced in cyclic

applications. Moreover, a change in emittance, in addition to affecting the final equilibrium temperature of the coating/substrate system, will alter the path on a temperature versus time plot by which that temperature is reached. For example, a low-emittance system with a specified heat input effecting cooling by radiation would experience a sharper rate of temperature rise. Even though the equilibrium operating temperature after change in coating emittance may be acceptable, the thermal fatigue characteristics might be found to be less satisfactory.

REDUCTION OF BASE METAL PROPERTIES

Raising the temperature of a refractory metal from, say, 2500°F to 2600°F can have a marked effect upon strength properties. Taking creep as a typical and important representative of the strength properties, it has been postulated that molybdenum- and tantalum-based alloys and tungsten will probably encounter creep problems at temperatures above 2500°F. Mathauser (Reference 7) presents data to indicate that many of the currently available columbium alloys have low strength at high temperatures and will show little resistance to creep deformation. This data is presented in figure 5, which shows typical tensile stresses, one-hour rupture stresses, and stresses producing 0.2 percent creep strain in one hour in the temperature range from 2000°F to 3000°F for some representative alloys which were developed during or shortly before 1963. The specific alloys included in these tests are not identified.

From the figure, it is seen that, typically for this category of alloys, a stress of 1000 psi (one ksi) will produce 0.2 percent creep strain in one hour at about 2500°F. At 2600°F, the creep strain load would be 825 psi. The difference represents a 17 percent loss in strength. Thus, a small decrease in the emittance of a coated, radiation-cooled, columbium structural member could result in a 17 percent increase in weight for equal performance. Similar statements can be made about the other refractory metals under only slightly changed conditions.

OPTIMUM SERVICE TEMPERATURE

Thus far in the discussion, little emphasis has been placed upon the influence of a lowered system temperature. The importance of change in this direction would relate primarily to the observation that some coating-composition substrate combinations exhibit shorter life at lower temperatures than they do in the moderately high range. Thus, several aluminide-base coatings on tantalum have been found to afford shorter-lived protection at temperatures in the vicinity of 1400°F than at higher temperatures. Similar results have been observed for aluminide-based coatings on columbium.

(FROM REFERENCE 7)

STRESS KSI

100

ULTIMATE STRENGTH

10

CREEP RUPTURE, 1 HR

1

0.2 PERCENT CREEP
STRAIN, 1 HR

0.1

2000   2200   2400   2600   2800   3000
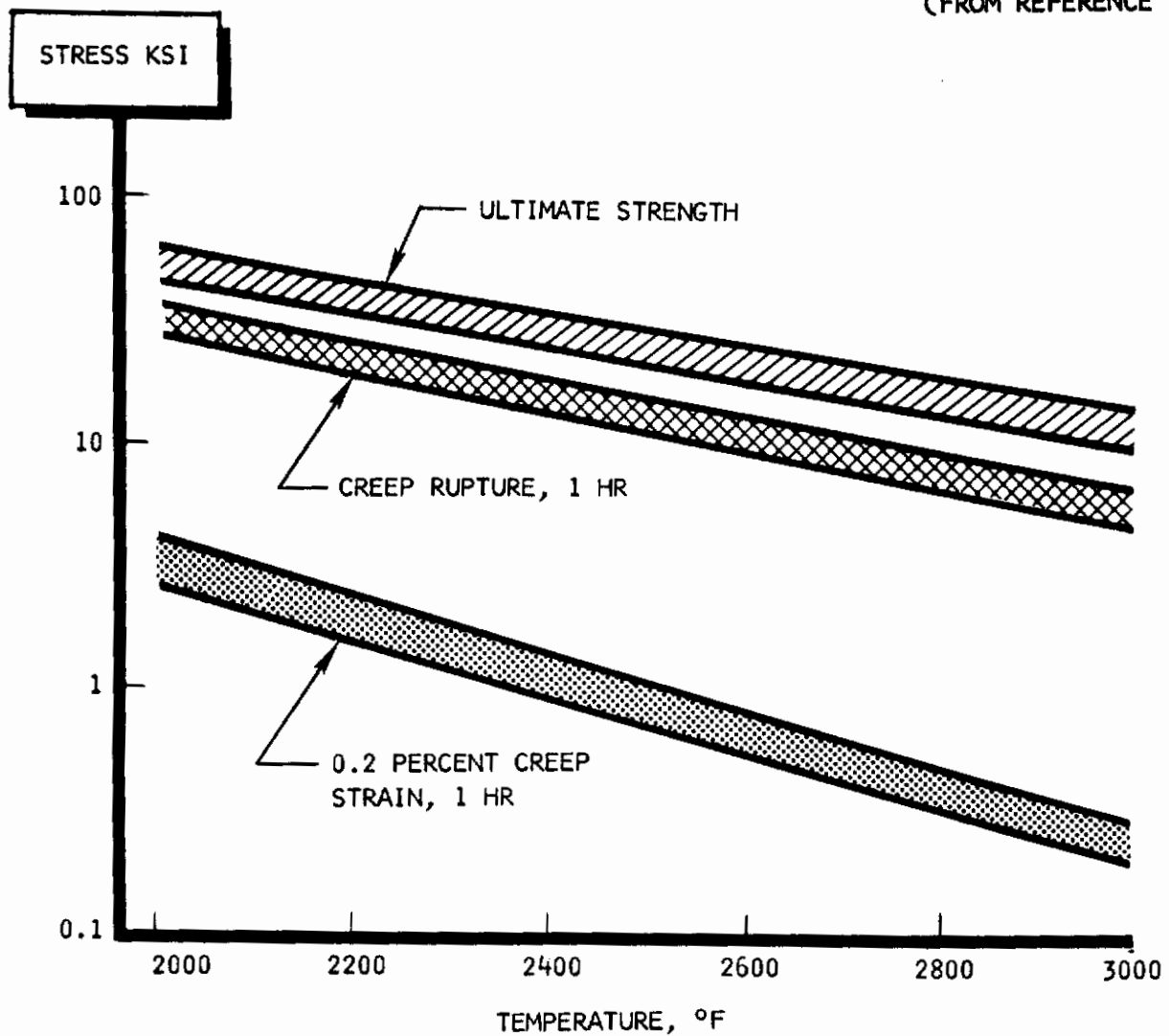
TEMPERATURE, °F

NOTE: DATA ARE FOR TYPICAL COLUMBIUM ALLOYS
        DEVELOPED DURING OR SHORTLY PRIOR TO 1963.
        THE SPECIFIC ALLOYS INCLUDED IN THE DATA
        ARE NOT REPORTED IN REFERENCE 7.

Figure 5.   Elevated Temperature Characteristics of Typical Columbium Alloys

VEHICLE TEMPERATURE

In practical vehicle design to minimize skin weight, it is always important to keep the temperature as low as possible, regardless of the coating/metal life. Fuel heating and environmental control problems for personnel and instrumentation, control systems, etc, are minimized by as low a vehicle temperature as possible.

SUMMARY

The effects upon oxidation-resistant coated refractory metals due to changes in emittance have been considered. The change in the emittance property, specifically, can affect the coating only by producing a temperature change; consequently, significant effects can ensue only if radiative transfer of heat is of considerable importance in the overall heat balance.

Section IV

RADIATIVE PROPERTIES OF SURFACES

TOTAL EMITTANCE

In the usual practical calculation of the exterior surface temperature of a hypersonic vehicle, the Stefan-Boltzmann expression $\epsilon_H \sigma T_w^4$ is employed. In this expression ϵ_H, is the total hemispherical emittance. This value is temperature dependent for a given material and may be defined as: "The total hemispherical emittance of a material is the summation of the energy over all wavelengths radiated per unit surface area of the material into a hemisphere, divided by the energy of a blackbody derived from identical physical conditions at the same exact temperature as the material."

For metals, this value is often measured directly at temperatures below 2000°F, by electrically heating a strip inside a chamber having black walls kept at a low temperature. The temperature of the strip is determined with thermocouples, and the electrical energy required to keep the strip at a constant temperature is measured. This approach is called the "heat loss method" and is reasonably successful up to 2500°F. Above this temperature, serious thermocouple problems arise. This method is most successful in vacuum. In air convective cooling, currents introduce an error which becomes increasingly significant as the temperature rises above 1000°F.

Regarding the errors inherent in emittance measurements, Seiler (Reference 8) states: "The measurement of sample temperature whether absolutely or differentially is usually one of the major sources of error in emittance measurements. No generally satisfactory techniques have been perfected for the determination of the surface temperatures of ceramics, metals, and plastics without some perturbation of the sample temperature."

Many total emittance measurements reported in the literature are total normal values, because it is usually easier to carry out a total normal measurement than a hemispherical measurement. Energy emitted from a heated surface (the temperature is generally measured with thermocouples) is measured directly with a radiometer. A comparison is made directly with a blackbody of the same temperature. A sliding specimen technique for measuring total normal and spectral emittance does not involve the inherent thermocouple error described above and was used for total normal measurements in this investigation. (Refer to Section IX of this report.)

Total normal emittance may be defined as follows: "The summation of the energy over all wavelengths radiated per unit surface area of a specimen into a small solid angle perpendicular to the surface of the specimen, divided by

the energy radiated from a blackbody viewed under the identical physical conditions and at the same exact temperature as the specimen."

DIFFUSE RADIATION

For diffusely radiating surfaces, the total normal emittance value equals the total hemispherical value, as shown mathematically in Reference 9. Therefore, for such surfaces, the emittances determined by the total normal method may be used in equations where total hemispherical values are specified. A diffusely radiating surface is one which exhibits Lambertian radiation. To an observer viewing such a surface from various directions, the surface will appear equally bright, regardless of the view angle. Such a surface exhibits equal radiating flux density in all directions, i.e., Btu per square foot per steradian per second. To an observer sighting on the emitting area from the direction of the receiving area, the apparent emitting area is reduced by a cosine factor:

$$dA, \text{ to } dA \cos \theta$$

Surfaces that follow the cosine distribution by definition are diffuse. In practice, actual surfaces vary with respect to the cosine law depending on material composition and surface finish. Consequently, the degree of correlation between normal and hemispherical measurements depends upon the extent to which a given surface obeys the Cosine Law. Except for polished metals, it has been found that many materials follow the Cosine Law to a fairly high degree. Surfaces which are not smooth and appear to the eye to be equally bright from all angles may approximate the Cosine Law. It is pointed out in Section V, that such an assumption may be valid for many practical thermodynamic calculations considering the many uncertainties inherent in making such calculations for real systems.

SMOOTH SPECULAR SURFACES

Studies have also been made to determine the relationship betweem hemispherical and normal measurements for smooth specular surfaces. Emslie (Reference 10) has shown that the radiation properties of homogeneous materials with smooth surfaces such as metals and dielectrics can be evaluated if the optical properties are known. Specifically needed are the optical "constants," n and k, the components of the complex refractive index, as functions of wavelength and temperature. For the purpose of aiding in the estimation of hemispherical properties from values measured normal to the surface, Dunkle (Reference 11) has calculated the ratio of hemispherical emissivity to normal emissivity by integration of the Fresnel equations. The results, for a variation in values of the index of refracting, n, and the absorption index

k, are shown in figure 6. Clearly, wide latitude in the value of the emissivity ratio is possible, depending upon the optical properties of the emitter. It must be pointed out that these curves are for monochromatic radiation and the absorption index and refractive index are wavelength dependent. Thus application of these curves for estimating total hemispherical radiation from normal values would require a knowledge of how the optical "constants," n and k, vary with wavelength.

It should be obvious from this discussion that if an accurate value for hemispherical emittance is desired, a direct measurement of it is needed and that an inference of the correct value from normal measurements is only proper if an approximate value is needed. As previously pointed out, however, the direct measurement of hemispherical emittance is often difficult, especially at temperatures greater than 2500°F. An extension of the total normal technique to angles other than 90 degrees would appear to offer promise. Such a goniometric approach would permit the angular emittance to be measured from 0 to 90 degrees and a determination to be made of the deviation from the Cosine Law. Integration of the values would yield total hemispherical emittance. Attention would, of course, have to be given to any anisotropy in the specimen.

SURFACE ROUGHNESS

The radiant properties of any specimen are dependent on both the intrinsic properties of the material and its physical surface characteristics. The separation of the two effects is difficult and often impossible in practical systems. The difficulty in establishing the quantitative effects of surface roughness stems from many reasons. Exact theory has not been developed to handle gross surface roughness. The empirical approach has been hampered by inability to properly characterize the surface. The effects of surface roughness have only been characterized in a semiquantitative manner in the form of trends.

Surface roughness effects are generally separated into two regions for theoretical treatment, the diffraction region and the geometric optical region. When the ratio of surface roughness, G, to wavelength, λ, is much less than unity, surface roughness is a diffraction problem. Good agreement has been obtained between theory and experimental specular reflectance measurements for G/λ ratios up to 0.15 (Reference 12). The theory is based on the assumption that no change in total reflectance occurs with surface roughness of this magnitude. Only a change in the specular component is predicted. Since no change in total energy occurs, slight surface roughness will not affect the emittance of a specimen. At a wavelength of 1μ, the surface roughness must be somewhat greater than 6μ in order to have an effect.
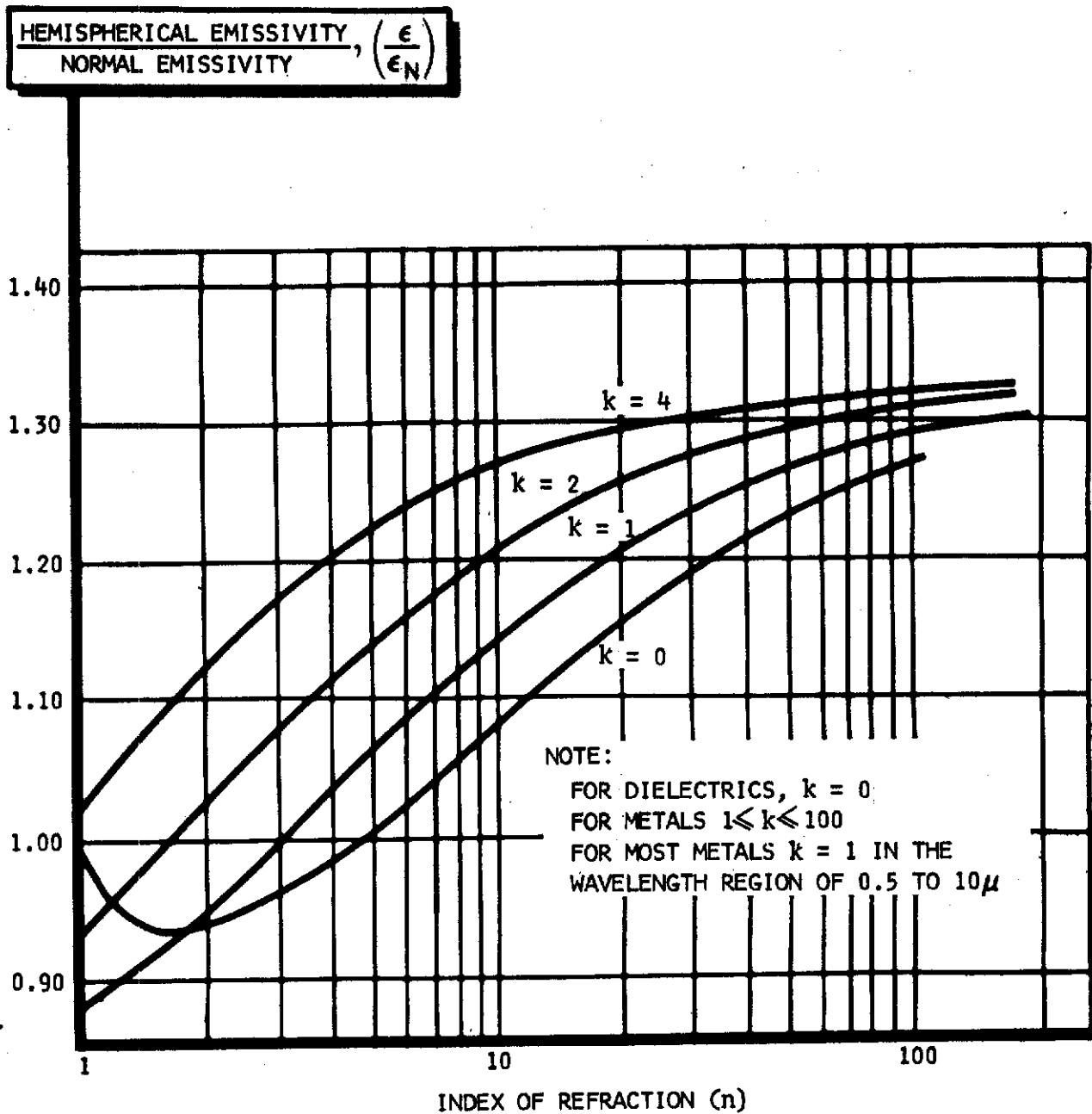
Figure 6. Ratio of Hemispherical to Normal Emissivity as a Function of Index of Refraction, n, and Absorption Index, k

The other extreme of surface roughness, that of gross roughness, has not been given the necessary theoretical treatment to enable prediction, of emittance for real surfaces. The theory has been developed for single cavities, Reference 13, and the emittance of a cavity can be predicted if the properties of the material and geometry of the cavity are known. Figure 7 shows the emittance predicted for V-groove and conical cavities as a function of opening angle θ and emittance of the wall material. As can be seen from this figure, the cavity effect is less at a given angle θ for highly emitting materials. Surface roughness will, therefore, have less effect on coatings composed of materials with high emittance.

If the material is semitransparent, surface roughness will have little effect on the emittance of the specimen, depending on the mean free path of a photon in the material. Experiments with alumina have shown that surface roughness ranging from 10 to 200 microinches produced no effect on emittance.

A translucent coating on an opaque substrate, such as obtained by the oxidation of a protective coating, may produce different effects, depending on the relative roughness of the oxide and opaque coating material and the optical properties and thickness of the oxide layer. If the oxide is thin, uniform in thickness, and follows the surface roughness of opaque coating material, interference effects such as reported by Schatz, et al (Reference 2), can occur, but the roughness effects are dependent on the opaque material. If the oxide layer is thick, compared to the mean free path of a photon, the surface roughness of the opaque coating material will have little effect on the overall emittance. An oxide of intermediate thickness presents a different situation. The roughness of the unoxidized coating material may be important, since the energy emitted from this surface may contribute a significant portion of the energy emitted from the coating system.

The roughness of the coating-substrate interface is not expected to influence the emittance of a coated specimen. The silicide coatings are opaque at a thickness of 2 mils (References 2 and 14).

Surface roughness produces several other effects which should be mentioned. Certain wavelengths may be affected more than others, since the G/λ ratio changes as a function of wavelength. The angular emission will become more Lambertian as roughness increases. The hemispherical emittance will, therefore, become more nearly equal to the normal emittance.

SPECTRAL EMITTANCE

So far, this consideration of emittance values has been concerned with total emittance. Any consideration of emittance must recognize that energy is spectrally radiated from surfaces and that the total values are the

ϵ_C = EFFECTIVE EMITTANCE OF CAVITY
α_C = EFFECTIVE ABSORPTANCE OF CAVITY
ϵ_W = WALL MATERIAL EMITTANCE
α_W = WALL MATERIAL ABSORPTANCE

(REFERENCE 13)
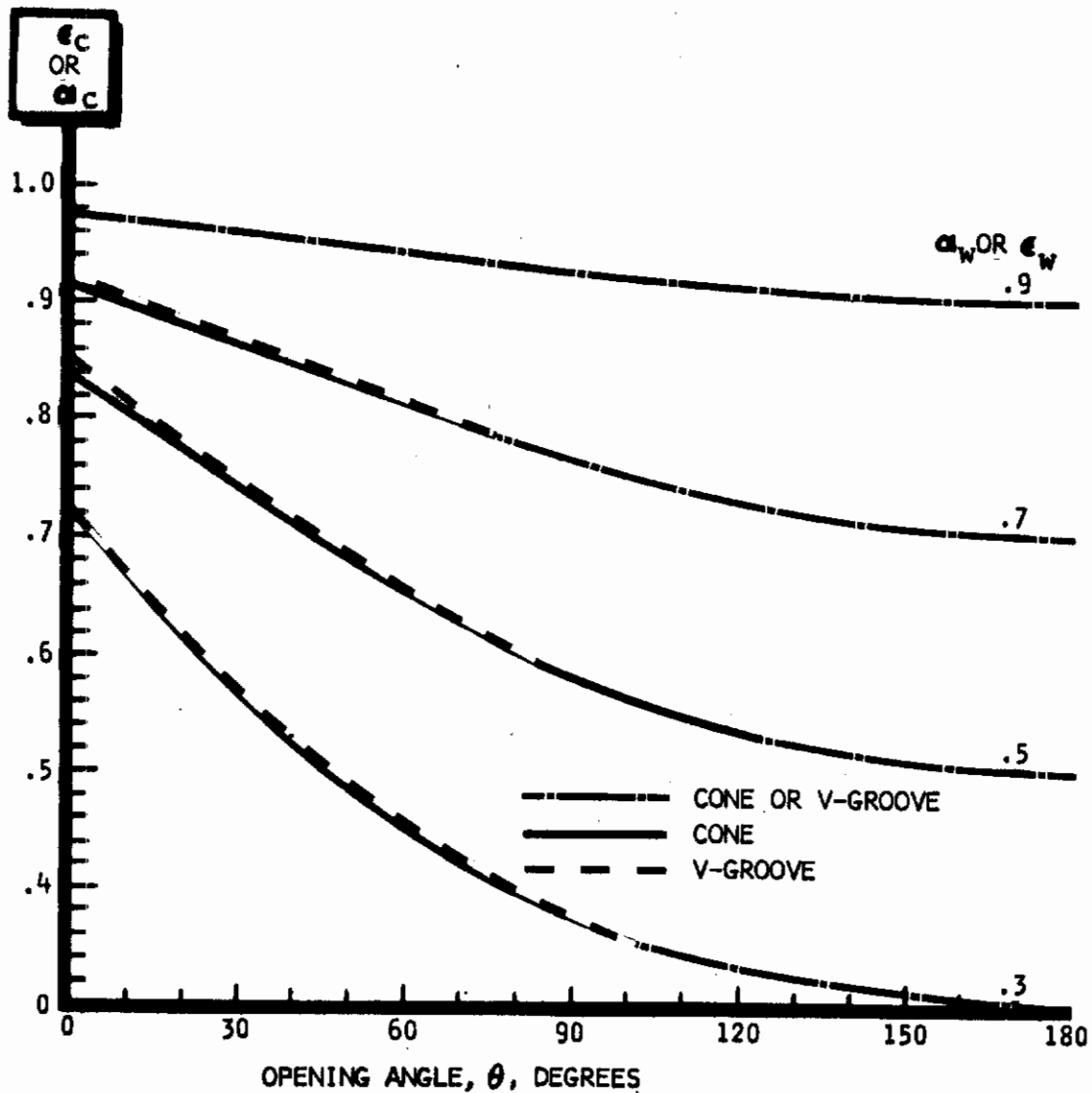
Figure 7. Radiation Properties of Diffusely Emitting and Reflecting
V-groove and Conical Cavities

integral of the spectral energy increments. The mathematical relationships involved, while fairly simple in concept, can become very involved in actual use.

Both spectral hemispherical and normal emittance are of concern and they may be defined as follows: "Spectral hemispherical emittance is similar to hemispherical emittance except that the emissive power is restricted to the wavelength interval (λ to $\lambda + \Delta\lambda$). Spectral normal emittance is similar to total normal emittance except that the emissive power is restricted to wavelength interval λ to $\lambda + \Delta\lambda$." In these definitions, $\Delta\lambda$ refers to the spectral slit width of the measuring instrument.

The basic relationship concerned with emission from a point surrounded by a receiving hemisphere is of concern.

The amount of spectral radiant energy within the wavelength interval emitted by an infinitesimal area element, dA, during time, dt, within a "pencil of radiation" characterized by the solid angle, dW, making an angle, θ, measured from the normal to dA, is

$$dQ_\lambda = I_\lambda \cos\theta \, dA \, d\lambda \, dW \, dt \tag{2}$$

This expression may be written as

$$I_\lambda = \frac{dQ_\lambda}{\cos\theta \, dA \, d\lambda \, dW \, dt} \tag{3}$$

The spectral intensity of I_λ of radiation, defined by Equation 3, therefore, has the dimensions of $Btu/sec\text{-}ft^2\text{-}micron\text{-}steradian$, in engineering units. Equation 3 implies that radiant energy transfer is a function of time. The $\cos\theta \, dA$ term implies that it depends on the orientation of the area in question with respect to all other area elements of the communicating surroundings. This dependence involves the geometry of the radiating system and its surrounding. For the restricted case of diffuse radiation (i.e., radiation that follows Lambert's Cosine law), this geometrical dependence is accounted for by the simple expedient of defining and evaluating a "geometric configuration factor" of the individual system and communicating surroundings. For systems in which the emittance of all surfaces is unity, such evaluations are not very difficult.

For systems in which the emission of radiation is not diffuse, thermal radiation predictions are considerably complicated. As a rule, such directional variations are frequently ignored. Thus, emittance measurements of surfaces are often found to be given as hemispherical emittance or normal emittance. The former is limited since it can be used to predict the emission to an entire half-space or hemisphere, but not necessarily to any

individual surface elements subtending a solid angle smaller than 2π steradians. In consequence, its use in radiation heat-transfer calculations involving complex geometry is open to some question in the absence of supporting evidence of diffuseness. Normal emittance is measured on a line-of-sight normal to the emitting surface. Consequently, it is subject to questionability similar to that of hemispherical emittance in its applicability to radiative heat transfer to specified surface elements. It is particularly true in the case of radiation systems of the type presently under consideration that measurements made upon a sample are affected by geometry, emission characteristics, chemical composition, and surface condition.

The dW term in Equation 3 implies that radiation intensity is a function of direction due not only to geometric effects, but also to a departure from diffuse emission. Under some circumstances, this consideration becomes important. The wavelength dependence explicit in Equation 2 further complicates matters, making it clear that the emission and absorption of real (nongray) surfaces or volumes should be analyzed spectrally, with the spectral effects then integrated over all frequencies. It should be mentioned that the resulting spectral hemispherical emittance is only valid for the view angle defined by the measuring instrument. With nongray or specular surfaces, the angular distribution of the radiated energy must be known before a total hemispherical emittance value can be calculated. The total absorption of a surface or volume is dependent then, not only on the properties of the receiving body itself, but also on temperature and frequency distribution of the surroundings.

Section V

THERMODYNAMIC CALCULATIONS

BACKGROUND

In the calculation of the temperature profile of the external surfaces of an aerospace vehicle, it is recognized that heat is generated by the passage of the vehicle through the atmosphere. This phenomenon is called aerodynamic heating. Solar radiation is an additional source of heat. Heat is lost from the vehicle surfaces by radiation to space at absolute zero and in a terrestrial environment to the earth as well. The temperature of the vehicle skin at any given instant can be obtained by dividing the amount of heat energy present in a thin outer layer of the vehicle by the mass of the material affected times its specific heat. In the case of an engine, the heat is generated by the combustion process. Heat is lost from the engine by radiation and by the discharge of hot combustion gases. Obviously, in addition, the same considerations regarding aerodynamic heating for the vehicle would also apply to the engine. The temperature of a vital part of an engine such as a combustion chamber at any given time is dependent upon the amount of heat present in the material, divided by the specific heat, times the mass of material present.

Fortunately for some real vehicles and engine situations thermal equilibrium is quickly attained because the mass of material affected is small and the rate of heat input to the system then equals the rate of loss. Once equilibrium is attained, the rate of heat loss by radiation may be directly found by the application of the Stefan-Boltzmann radiation law thus:

$$E = \epsilon_H \sigma T_W^4 \tag{4}$$

The heat is considered to be rejected to space at absolute zero, hence the receiving term equals zero and does not appear in the relationship.

In actual practice, the thermodynamicist makes such calculations of heat exchange for vehicles and engines by methods ranging from simple slide rule manipulations to large computer programs. The approach taken is dependent upon the accuracy required, the accuracy possible, and, of course, the funds available.

Many current programs are in support of parametric studies of hypersonic vehicles and engines. Exact temperature data are usually not needed; rather, approximate temperatures are required to determine the kinds of materials needed, the possible trajectories, etc. Once the go-ahead is given for a specific vehicle design, calculations are performed which

include the use of exact vehicle geometry, skin thicknesses, carefully specified aerodynamic conditions, etc.

Even when an effort is made to calculate the exact temperatures of real vehicles and engines, such difficulties are encountered as transient temperature effects across complex geometry, variable heat-transfer rates across mechanically fastened joints, convective coefficients that vary with shifting aerodynamic conditions, etc. Such problems, therefore, not only introduce uncertainty into the answers, but they also tend to force the use of simplified approximate methods in order to keep the calculations manageable.

The advent of the computer has in recent years tended to bring more exact mathematical methods (which are also more complex) into use and, therefore, there is an increasing need for more exact constants such as metal emittance, convective coefficients, specific heat variation with temperature, etc. Nevertheless, there probably will always be some uncertainty in such calculations since aerodynamic conditions cannot always be carefully controlled. For example, under certain conditions either laminar or turbulent flow may exist for the same values of Reynolds Number.

EXTERIOR SURFACES

The simplest and most frequently used calculation of thermal environment in hypersonic vehicles design is the calculation of equilibrium surface temperature of the vehicle exterior assuming that each surface element "sees" only space. As a prelude to more sophisticated calculations, and because this simple calculation does show clearly the first-order role of coating emittance on structure temperature, it is appropriate to review this simplest calculation first. (Refer to List of Symbols.) It is assumed that each element of the surface is insulated from the remaining structure, and that each element receives heat from the fluid streaming by on the exposed side and exchanges heat by radiation with a relatively cold external environment. A simple heat balance gives:

$$\rho_w c_{pw} b_w \frac{dT_w}{dt} = h(T_{Aw} - T_w) - \epsilon_H \sigma T_w^4 + \alpha_S G_S \tag{5}$$

(where $\alpha_S G_S$ is the heat gained by the surface from solar radiation)

If a thin, high conducting, honeycomb heat shield is subjected to a step change in fluid temperature, the billet equation gives the temperature response as:

$$\frac{T_W - T}{T_W - T_i} = \exp\left[-\frac{ht}{\rho_w c_{pw} b_w}\right] \tag{6}$$

The time constant $\rho_w c_{pw} b_w / h$ is the time in seconds for the temperature difference to be reduced to $1/e$ of its initial value.

If the mission profile, or trajectory, is such that the time for an appreciable change in h and T_{Aw} is long with respect to the element time constant $\rho_w c_{pw} b_w / h$ then the wall temperature at each time will follow closely the wall temperature given by the steady-state equation:

$$0 = h\,(T_{Aw} - T_w) - \epsilon_H \sigma T_w^4 + \alpha_S G_S \tag{7}$$

During hypersonic flight within the sensible atmosphere, the solar heat flux absorbed ($\alpha_S G_S$) is usually much smaller than either the aerodynamic heating term, $h(T_{Aw}-T_w)$ or the emission term $\epsilon_H \sigma T_w^4$, and is very often neglected. The resulting simplified Equation 7 forms the basis for the charts of Reference 4 and for figures 2 and 3 of this report.

or,

$$0 = h\,(T_{Aw} - T_w) - \epsilon_H \sigma T_w^4$$

$$\frac{h}{\epsilon_H} = \frac{\sigma T_w^4}{(T_{Aw}-T_w)} \tag{8}$$

Figures 2 and 3 show the insulated radiation equilibrium surface temperature for turbulent boundary-layer flow one foot and 10 feet from the leading edge of a flat plate. These figures display the obvious first-order role of coating emittance in establishing an insulated surface temperature. The Mach numbers vary from 10 to 20 and the altitudes vary from 120,000 to 160,000 feet. In this Mach number and altitude range, there exist uncertainties in the type of boundary-layer flow and in the heat flux due to uncertainties in h and in T_{Aw} in Equation 5 (or uncertainties in H and in i_{Aw} if the enthalpy difference ($i_{Aw}-i_w$) is used as the driving potential). The curves of figures 2 and 3 may be shifted vertically by more exact analyses, measurements, and correlations. The effects of improvements in the determination of h and ϵ_H can be discussed easily because these parameters appear in ratio form (h/ϵ_H) in Equation 8.

If T_{wB} is the wall temperature given by a basic determination of h, T_{Aw} and ϵ_H; and if Δ is a plus fractional change in h or a minus fractional change in ϵ_H; and if $T_w \ll T_{Aw}$; then

$$T_w = T_{wB}\,(1+\Delta)^{1/4} \tag{9}$$

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Assuming $\Delta < 1$, and using the binominal expansion, there results:

$$T_W = T_{WB} \left(1 + \frac{\Delta}{4} - \frac{3}{32}\Delta^2 + \frac{7}{128}\Delta^3 - - - -\right) \tag{10}$$

In this case a 12 percent increase in h or a 12 percent decrease in ϵ_H gives a 3 percent increase in T_W. When T_W is less than, but of the order of T_{Aw} the effects of changes in h, ϵ_H and T_{Aw} on T_W are more involved and will not be discussed here. In any case, the effect of emittance on the temperature of an insulated surface is of major importance as shown by figures 2 and 3.

In the insulated structure concept, and when the primary load-carrying structure is separated from the hot outside heat cover, or shingle, by an insulating layer, the outer metallic heat shield usually follows very closely this insulated thin-skin radiation equilibrium.

INTERIOR SURFACES

From this simplest, and most frequently used, calculation of the thermal environment in hypersonic vehicle design, thermal calculations branch off in several directions depending upon the specific mission, the specific structural concept and design, and the required refinement and accuracy of the computed temperatures. This branching of thermal calculations might be visualized as shown in figure 8. The total hemispherical emittance ϵ_H suffices in most geometrical situations for the calculation of the insulated equilibrium surface temperatures, and for the gray-wall diffuse (Reference 15) calculation of radiant exchange within enclosures inside the structure. Wherever a box called radiant exchange appears in figure 8, an engineer will ask about the spectral and directional characteristics of the surface coatings. When the reflectivity ρ_λ or the absorptance a_λ vary appreciably with either wavelength, λ, or with direction θ or ϕ, more refined analyses of radiant exchange must be considered.

The gray-wall, diffuse calculations of radiant exchange within an enclosure most frequently follow Reference 15. The configuration factor program of Reference 16 and the radiosity network solution of Reference 17 have proved most useful in these calculations. An example of an engineering use of the tools of References 16 and 17 is presented, and the results compared with an exact solution in Reference 18. Various geometries and various combinations of perfectly diffuse, or perfectly specular walls are discussed in References 13, 19, 20, and 21. Complications that are introduced by spectral and directional characteristics are explored in References 22, 23, 24, 25, and 26.
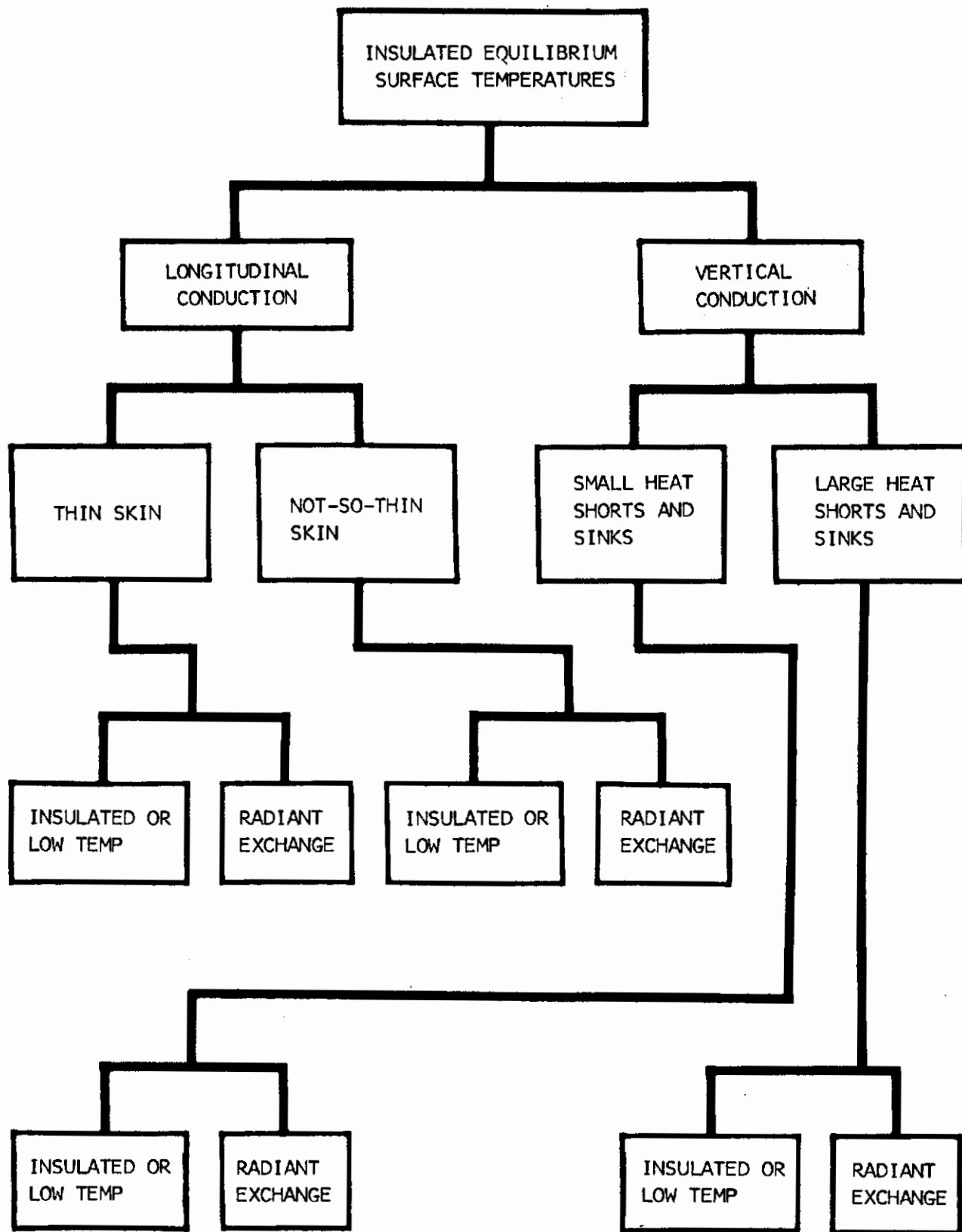
Figure 8. Branching of Thermal Calculations

A list of simplifying assumptions commonly made in engineering calculations of internal radiant interchange and of structure temperatures is presented in Reference 23. That list can be rearranged and shortened as follows:

1. Fractions of energy absorbed, reflected, and transmitted are independent of wavelength. The coatings are not wavelength selective radiators. This is the gray-wall assumption.

2. The walls emit and reflect in a perfectly diffuse manner. The θ directional variations of the coating properties are neglected (Lambertian assumption).

3. Fractions of energy absorbed, reflected, and transmitted are independent of the directions of the irradiation. The ϕ directional variations of the coating properties are neglected, i.e., there are no striations in the surface. At a given θ angle from the surface, if the surface is rotated through 360 degrees about the normal, there will be no change in the thermophysical surface properties (isotropic surface assumption).

4. Radiosity of a finite surface element is independent of position on the element. Since the radiosity includes the sum of the emitted and reflected radiation, this assumption requires that each surface element be at constant temperature and be uniformly irradiated.

Typical nonmetallic coatings have a directional emittance that drops off as θ approaches 50 to 90 degrees from the normal. As a result, the total hemispherical emittance is usually less than the total normal emittance. (Refer to page 380 of Reference 27 and page 86 of Reference 28.) This difference, however, is generally less than 5 to 10 percent. A frequently used engineering procedure for ceramic coatings consists of measuring the total normal emittance and reducing the measured value by 5 percent to give a value of the total hemispherical emittance, ϵ_H, required in radiant exchange calculations. When two surfaces of an enclosure exchange radiation strongly, a check of the geometry and angles is indicated to find whether the drop in emittance in the range of θ from 50 degrees to 90 degrees will alter the radiosity distribution within the enclosure significantly. As emphasized in Reference 23, the engineer should be alert for those conditions leading to errors from neglecting the spectral and directional selectivity of the material. The calculation required when either or both spectral and directional properties of the surfaces are included are described in References 24 and 26. Calculations of this nature have not, apparently, found widespread engineering use as yet.

An engineer will usually take a pragmatic view of the role of surface emittance, and will not include second-order complications. As a first example, the gray-wall assumption will be retained and spectral variations

will be neglected as long as available property data and engineering judgment indicate that the resulting errors in computed temperatures do not force a change of materials. As a second example, directional properties of surface coatings will be neglected as long as the geometry is such that the probable errors in computed temperature do not force a change of materials. The only way that the validity of these assumptions can be checked is by, first, measuring the detailed surface coating properties and, second, carrying through the original radiation and temperature calculations in a more exact manner, and by comparing results.

Performance of the final hardware is, of course, the ultimate check, but includes factors other than emittance.

APPLICATION OF SPECTRAL PROPERTIES

As previously pointed out, the spectral properties of surfaces and gases (e.g., combustion gas containing carbon dioxide) may in some cases be extremely important in calculating the radiant energy exchange within an enclosure. The customary gray radiation assumption has been shown to lead to serious errors in some cases. Regarding this situation Bevans and Dunkle (Reference 29) have said:

"The approximation (gray radiation) is based upon the assumption of frequency independent radiation characteristics of the surfaces and the gases involved. This assumption is the result of inadequate knowledge of the spectral behavior of these characteristics and is a necessity born from ignorance."

However, it is not universally true that the spectral properties of surfaces and gases are important in practical calculations, and it is only when all the following conditions prevail that spectral properties should be incorporated into the calculation:

1. The emittance of the radiating surface, or the absorptance* of the receiving surface, must vary significantly with wavelength.

2. Significant energy must be present in the wavelength interval over which the radiating and absorbing surfaces vary.

The spectral properties of many oxidized metallic surfaces and some refractory metal coatings are known to vary greatly with wavelength. It is not known, however, how the spectral emittance values of refractory metal

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*For opaque surfaces absorption equals emittance.

coatings vary spectrally from 2000°F to 3000°F, since above 2500°F the top layers of the coatings may become transparent and the emittance properties of the metal underneath could become a factor.

Bevans and Dunkle (Reference 30) compare three approaches to solving radiant exchange problems within enclosures:

1. The integrated monochromatic or exact solution

2. Energy band approximation

3. Graybody approximation

Goodman (Reference 31) also compares the graybody approximation with the monochromatic solution. Table I, which is based on figure 9, obtained from Reference 30, and figure 10, obtained from Reference 31, presents examples of the heat-transfer rates computed by these methods for parallel plates of several metals. It can be seen that the graybody approach can be seriously in error. The errors shown vary from 2 to 30 percent. Most of the errors shown are in the negative direction, but one large error is positive, 29 percent.

Several additional examples were prepared to illustrate solutions to thermodynamic problems which are typical of service conditions expected for future aerospace vehicles. These solutions show the inaccuracies involved in using the graybody approximation as opposed to using an integrated mono-chromatic solution. Three hypothetical materials were selected with spectral variations of their surfaces as shown in figure 11. In an actual service situation, perhaps only one of these materials would be a coated refractory metal, while the other materials might be metals with oxidized surfaces. All these surfaces are idealizations of surfaces tested by or for NAA. The idealizations were made to simplify the calculations for this particular example. Figure 31 shows an emittance curve for an actual refractory metal coating which generally follows the shape selected for material C. Although the curve shown in figure 11 is more extreme than the actual curve shown in figure 31, this difference would only reduce the large error in calculated temperature resulting from the use of graybody approximation. It would not eliminate the error. The three materials shown in figure 11 are used in all possible pairs in the example problems.

Table I

COMPARISON OF SOLUTIONS FOR RADIANT EXCHANGE BETWEEN PARALLEL PLATES

Surface and Temperature	HEAT TRANSFER RATES Btu/Hr-Ft^2			
	Monochromatic or Exact Solution	Energy Band Approx	Graybody Approx	Graybody Compared to Exact Solution
*Titanium at 800°F to titanium at 200°F	2004	1977	1400	-30%
*Titanium at 800°F to anodized aluminum at 200°F	1646	1626	2120	+29%
**Aluminum at 752°F to aluminum at 572°F	97	-	95	- 2%
**Aluminum at 1112°F to aluminum at 932°F	311	-	259	-17%
**Inconel at 1832°F to Inconel at 1652°F	7660	-	6780	-12%
**Inconel at 1472°F to Inconel at 572°F	11,090	-	7820	-29%

* Reference 30

** Reference 31

See figures 9 and 10 for spectral curves.

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MONOCHROMATIC REFLECTANCE

(FROM REFERENCE 30)
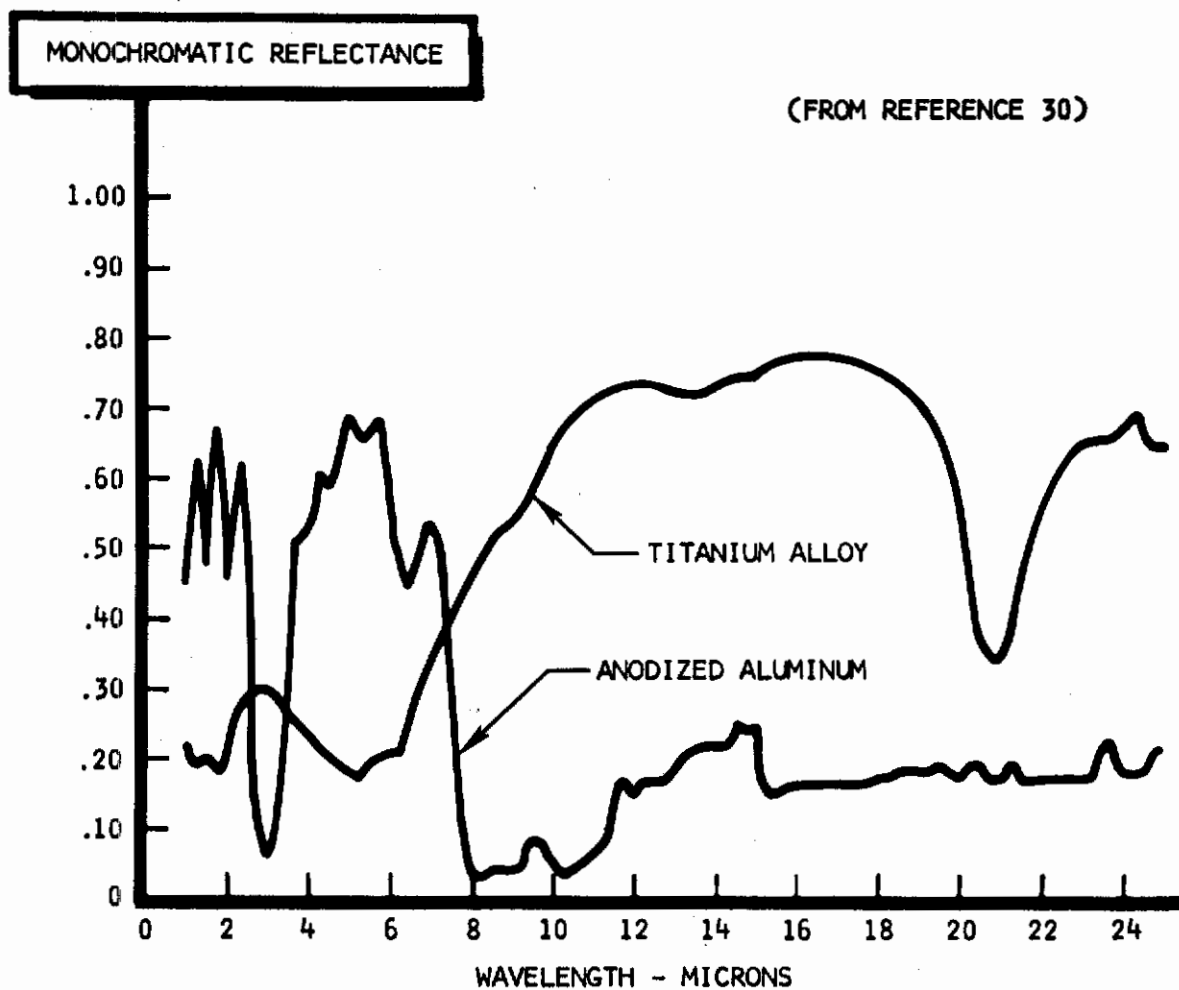
Figure 9. Spectral Reflectance of Oxidized Titanium Alloy C-110
and Anodized Aluminum
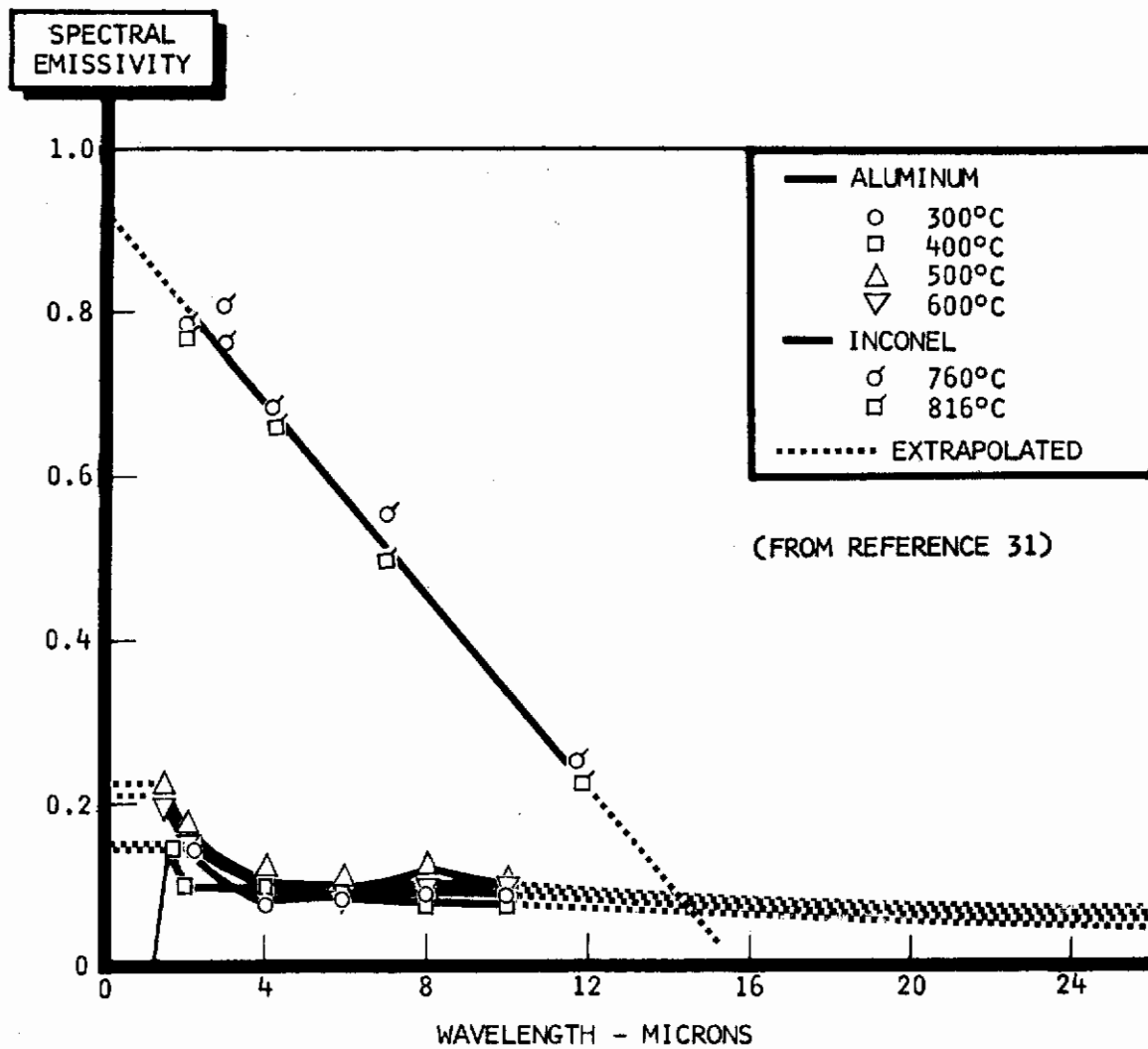
Figure 10.   Spectral Normal Emissivities of Polished
Aluminum and As-rolled Inconel
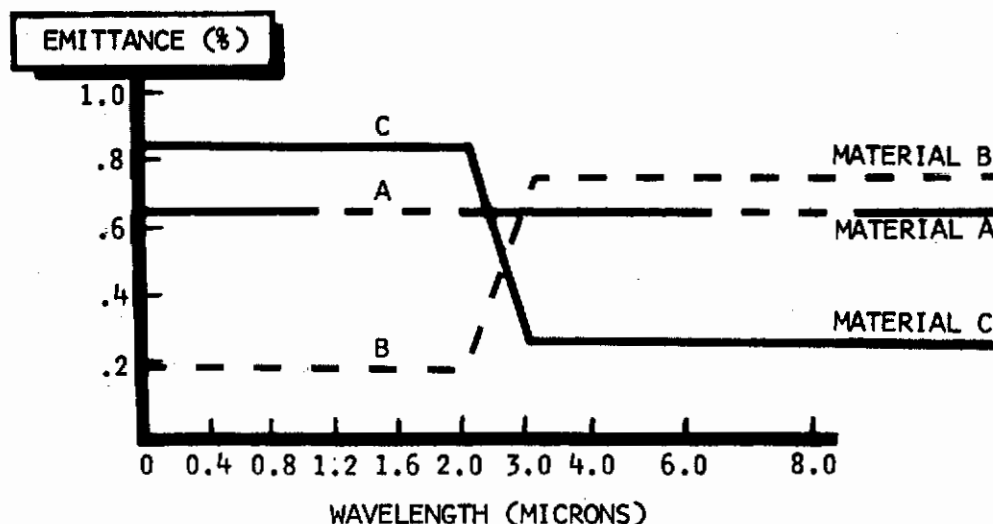
Figure 11. Emittance of Hypothetical Materials Used in Sample Calculations

In the first example the radiative heat exchange is determined between two surfaces. One surface is at 2500°F, the other at 3000°F (figure 12). For simplicity, interreflections are ignored. In this example, the total radiation is divided into two wavelength bands (i.e., one above and one below 2 microns). This was done to provide an equation which would entail as few computations as possible when applied to the materials shown in figure 11. The equation fulfills this intention because the emittances of all three of these materials remain constant over both the wavelength range below 2 microns and the range above 2 microns, although a considerable change occurs in the emittance values of two of these materials at approximately 2 microns.
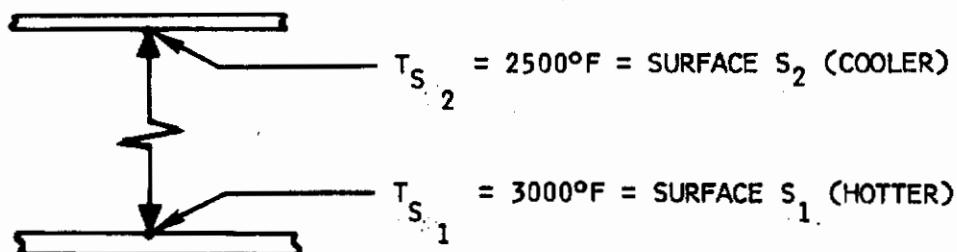
Figure 12. Net Radiative Heat Exchange Between Two Surfaces

The equation for the net radiative heat exchange for the energy band approximation is:

$$E = \sigma T_{S_1}^4 \left[\alpha_{Sa} \epsilon_{Ea} \eta_E + \alpha_{Sb} \epsilon_{Eb} (1 - \eta_E) \right] - \sigma T_{S_2}^4 \left[\alpha_{Sa} \epsilon_{Ea} \eta_S + \alpha_{Sb} \epsilon_{Eb} (1 - \eta_S) \right] \tag{11}$$

where

α_{Sa} and ϵ_{Ea} = the absorptance of surface S and the emittance of surface E, respectively, below 2μ wavelength

α_{Sb} and ϵ_{Eb} = the absorptance of surface S and the emittance of surface E, respectively, above 2μ wavelength

η_S = the percentage of radiation emitted below 2μ at temperature T_{S_2}

η_E = the percentage of radiation emitted below 2μ at temperature T_{S_1}

The equation for the graybody approximation is:

$$E_g = \epsilon_{ET} \alpha_{ST} \sigma (T_{S_1}^4 - T_{S_2}^4) \tag{12}$$

where

ϵ_{ET} = total emittance of surface S_1 at temperature T_E.

α_{ST} = total absorptance of surface S_2 at temperature T_S.

E_g = Graybody radiative flux (Btu/ft^2 sec)

Table II shows the results of the computations.

Table II

COMPARISON OF SOLUTIONS FOR RADIANT EXCHANGE USING ENERGY BAND
APPROXIMATION AND GRAYBODY APPROXIMATION

Case No.	Material of 2500°F Surface	Material of 3000°F Surface	Energy Band Approx (E) (Btu/Hr-Ft^2)	Graybody Approx (E_g) (Btu/Hr-Ft^2)	Error Due to Using Graybody Approx (%)
1	A	A	5.5×10^4	5.5×10^4	0
2	A	B	12.0×10^4	3.9×10^4	-68
3	A	C	4.9×10^4	4.2×10^4	-14
4	B	A	10.1×10^4	4.4×10^4	-57
5	B	B	3.8×10^4	3.1×10^4	-18
6	B	C	10.3×10^4	3.3×10^4	-71
7	C	A	4.9×10^4	3.5×10^4	-29
8	C	B	10.3×10^4	2.4×10^4	-77
9	C	C	10.4×10^4	2.6×10^4	-75

The second example consists of determining the temperature of skin surfaces facing an engine (figure 13). The aircraft is assumed to be flying at Mach 6.3 and 100,000 feet. The adiabatic wall temperature will be 2500°F and the convective coefficient will be 4.0 Btu/hr ft^2°F. The engine surface temperature is 3000°F.

In solving for the skin temperature, T_S, the following equation was used to obtain the energy band approximation. This solution is based on the same assumptions and considerations as Equation 11.

$$T_S = T_{Aw} + \frac{\sigma}{h} \left\{ T_E^4 \left[\eta_E (\epsilon_{1a}\epsilon_{2a} - \epsilon_{1b}\epsilon_{2b}) + \epsilon_{1b}\epsilon_{2b} \right] \right.$$

$$\left. - T_S^4 \left[\eta_S (\epsilon_{1a} + \epsilon_{1a}\epsilon_{2a} - {}^\epsilon_b - \epsilon_b\epsilon_{2b}) + \epsilon_{1b} (1 + \epsilon_{2b}) \right] \right\} \qquad (13)$$
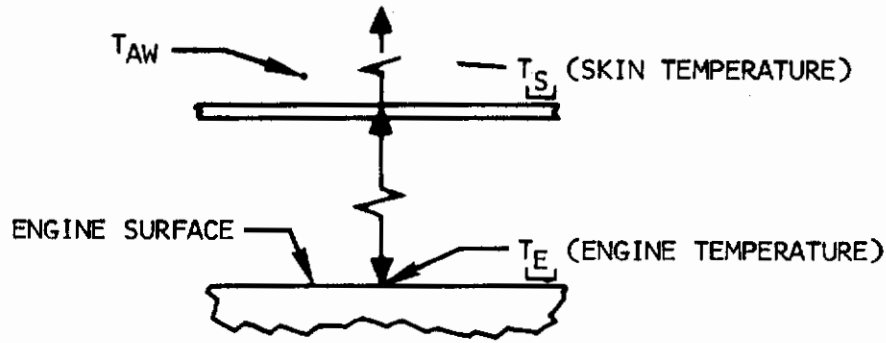
Figure 13. Skin Temperature Around an Engine

where

T_S = skin temperature to be solved for

T_{Aw} = adiabatic wall temperature

h = convective coefficient

ϵ_a and ϵ_{2a} = emittances of the skin and engine surfaces, respectively, below 2 μ wavelength

ϵ_{1b} and ϵ_{2b} = emittances of the skin and engine surfaces, respectively, above 2 μ wavelength

η_S = the percentage of energy emitted below 2 μ at temperature T_S

η_E = the percentage of energy emitted below 2 μ at temperature T_E

T_E = engine surface temperature

For the graybody approximation:

$$T_S = T_{Aw} - \frac{\sigma}{h} \; \epsilon_{Sm} \left[T_S^4 \; (1 + \epsilon_{Em}) - \epsilon_{Em} T_E^4 \right] \tag{14}$$

where ϵ_{Sm} and ϵ_{Em} are the total emittance at temperatures T_S and T_E, respectively. Values can be obtained from figure 3.

All other variables are as defined above. The results are shown in table III.

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Table III

COMPARISON OF SOLUTIONS FOR SKIN TEMPERATURE, USING ENERGY BAND
APPROXIMATION AND GRAYBODY APPROXIMATION

Case No.	Skin Surface Material	Engine Surface Material	Skin Temperature ($^\circ$F)		Graybody Compared to Energy Band (%)
			Energy Band Approx	Graybody Approx	
1	A	A	2316	2316	0
2	A	B	2477	2152	-13
3	A	C	2091	2180	+ 4
4	B	A	2169	2318	+ 7
5	B	B	2382	2168	- 9
6	B	C	1715	2194	+27
7	C	A	2115	2320	+10
8	C	B	2149	2175	+ 1
9	C	C	1786	2200	+23

It will be noted that considerable error occurs in the calculated temperatures by using the graybody approximation. This error is generally on the high side, in which case structural designs based on the data will make the air vehicle unnecessarily heavy, expensive, and impractical.

Total emittance can always be computed from spectral data, but the converse is not true. There is no way to get spectral data from the total. If the spectral is needed, as indicated by these two sample problems, it must be measured in the laboratory.

SPECULAR EMITTANCE

Variation of emittance as a function of angle (i.e., "specular emittance") is important, but it is difficult to use in practical calculations. Engineers frequently avoid this difficulty by assuming the surface to be

diffuse. For many materials, this is an acceptable assumption. For others, the assumption may produce a substantial error in the calculated results. Bevans and Edwards (Reference 24) have shown an extreme case in which the actual heat transfer is five times the value that would be computed by assuming a diffuse surface.

Section VI

USE AND ENVIRONMENT FOR REFRACTORY METAL COATINGS

GENERAL

It is appropriate to review the current and projected uses of refractory metals and coatings in order to arrive at a definition of the environmental conditions that could affect emittance values. An examination of projected flight profiles for vehicles and engine operating conditions is helpful in defining environment in terms of temperature, time, pressure, and other pertinent conditions.

Reference 32 is a recent review of refractory metal coating technology. Current use of coated refractory metals is quite small on flyable hardware. Most parts that are being coated are for laboratory test programs. Several notable exceptions exist. Disilicide-coated, molybdenum alloy, heat-shield panels were flight-tested on ASSET vehicles, as well as various columbium hardware items which were coated with the LB-2 aluminide system. Cr-Ti-Si coated columbium parts also were included in the ASSET hardware. Some 25 Apollo services module skirt extensions for rocket engines fabricated of columbium alloy (approximately 5-foot major diameter by 5 feet high) have been coated with the North American aluminide coating No. NAA-85. Also, Sn-Al coated tantalum alloy thrust chambers are used as orbital adjust engines on Agena, and W-Si coated molybdenum is used for attitude control thrusters on Saturn S-IVB.

A review of actual existing hardware items is by no means indicative of refractory metal use potential. Hypersonic and lifting reentry vehicles and high-performance engines and power devices that would require the use of refractory metals are mainly in the proposal and study phase. J. Elbaum and N. Geyer (Reference 33) reviewed refractory metals and coatings and categorized their current and potential use. (Refer to table IV.)

The largest projected use of refractory metals that is obvious as presented in table IV concerns structures and engines. Principal applications in these areas are discussed in the ensuing paragraphs.

LIFTING REENTRY VEHICLES

Leading edges and heat shields for lifting reentry vehicles are important applications of coated refractory metal sheet in aerospace structures. These vehicles essentially are spacecraft, which utilize the forces

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Table IV

SUMMARY OF USES FOR REFRACTORY METAL-COATING SYSTEMS

Affiliation	Hardware Requirement
Structures	
Lifting reentry and Hypersonic vehicle	Leading edges, heat shields, structure
Propulsion	
Rockets	Nozzles, chambers, skirts
Chemical - air-breathing	
Turbojet	Combustion liners, etc
Ramjet	Structure, tubing
Electric	Miscellaneous
Auxiliary power	
Nuclear Magnetohydrodynamic Thermionic Solar	Miscellaneous

of aerodynamic lift during reentry. This results in relatively low rates of heating compared with ballistic reentry, and generates surface temperatures which can be accommodated by refractory metal structures.

The vehicle undergoes aerodynamic heating during ascent, is subjected to a space vacuum during orbit, and undergoes aerodynamic heating during reentry. Perkins, et al. (Reference 34) have made a careful analytical study of such vehicles assuming a typical vehicle design for both an orbital trajectory and a superorbital trajectory. From ascent to orbit, the temperature typically at a leading edge stagnation line may go from zero °F to 1100°F in 1-3/4 minutes, and then to 250°F in 4 minutes as the atmosphere becomes less dense. The external pressure at the peak temperature during ascent would be about 25 mm Hg. Wing surface temperatures would be considerably lower than these leading edge

temperatures. A reentry velocity of 25,500 fps is assumed for the orbital trajectory, and a velocity of 36,000 fps for the superorbital trajectory. Figure 14 shows the time variation of temperature on the wing upper surface of the superorbital vehicle during reentry as influenced by boundary layer and flow conditions. The emittance is taken at 0.6. It is considered that the turbulent flow condition with the correction for oxygen dissociation is probably a realistic curve (Reference 34). The external pressure during the 45-minute reentry period shown is considered to vary from less than 0.01 mm Hg to 4 mm Hg.

HYPERSONIC VEHICLES

Hypersonic vehicles are considered to be vehicles that do not leave the sensible atmosphere of the earth and generally operate at a 100,000- to 200,000-foot altitude at Mach numbers to about 20. Some possess flight trajectories lasting only typically 10 to 15 minutes at high Mach numbers, while others designed for cruise conditions may possess trajectories lasting up to 2 hours at high Mach conditions. Such vehicles, from a materials point of view, present much the same problems as the lifting reentry bodies. Extreme temperatures are encountered at reduced pressures. Projected use of both classes of vehicle envisions many flights per vehicle. Potentially, the hypersonic cruise vehicle could be subject to hundreds of flight hours at extreme temperatures and reduced pressures throughout its life.

The use of refractory metals in such vehicles could be extensive. One tentative North American design of an X-15 delta wing configuration vehicle required approximately 3000 columbium alloy parts consisting of 2000 square feet of metal plus clips and fasteners. This included 670 shingles (0.060 x 7.5 x 0.9 inch) for leading edges and forward wing. Interior as well as exterior surfaces were to be constructed of coated columbium.

AIR-BREATHING ENGINES

So far the use of refractory metals in chemical air-breathing engines (turbojet and ramjet) has not been extensive. Engine efficiencies could be increased if operating temperatures could be raised, but material limitations have retarded this development. Current emphasis in the instance of turbojet engines has been on the development of refractory metal turbine blades, but this development has not yet progressed beyond rig testing of developmental coatings and alloys.

ROCKET ENGINES

A review of coating use in regeneratively cooled rocket engines indicates that the radiative properties of coatings are generally not of great significance in this application. Coatings of several different types (for
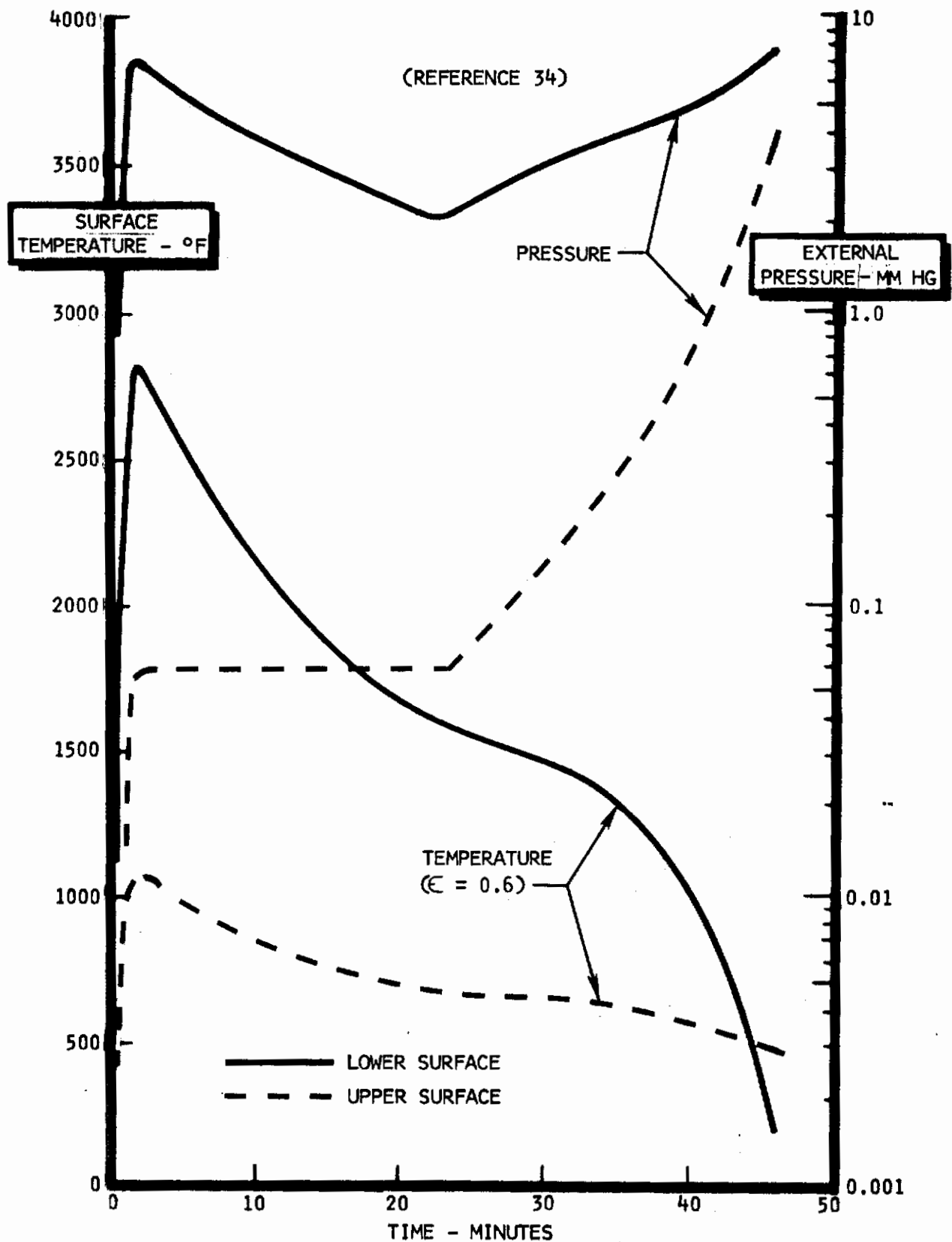
Figure 14. Time Variation of Temperature and Pressure on Upper and Lower
Surfaces of Wing During Reentry From Superorbital Velocity

example, Rokide 3 on Nichrome undercoat or, in graded layers, nickel-alumina laminations, zirconia-zirconium boride laminations, and graded Nichrome-alumina) have from time to time been applied to the Thor, Atlas, H-1, and J-2 thrust chambers. The purposes have usually been to provide a thermal barrier with which to afford maximum tube protection. The emittance properties of these coatings are not considered to be important in this role where convective heat-transfer dominates, unless strong emission bands are present within the flame. The presence of such bands is dependent upon the type of fuel and oxidizer used.

Similar considerations prevail with respect to solid-propellant and nuclear engine systems, in which provision of abrasion- and temperature-resistance has been the dominant role of coatings. In the former case, the presence of metal particles in the exhaust for purposes of ensuring stability of combustion makes the chamber and nozzle environment particularly severe and use of coatings particularly difficult. Other approaches to solving the problems of high-temperature and thermal shock have been followed, such as use of graphite and the impregnated nozzle concept (Reference 35). The nuclear rocket, using liquid hydrogen as propellant, represents in all present designs merely a variation of a regeneratively cooled rocket thrust chamber. The combination of very high heat fluxes and nonoxidizing atmosphere in the chamber points up the need for a thermal barrier while eliminating the oxidation-resistant aspect of any coating employed.

On the other hand, the use of coatings and the significance of their emittance stability becomes of extreme importance for the case, common among space engines, in which cooling of the chamber and/or nozzle extension is effected by direct radiation of heat. The attractiveness of this concept is apparent in its elimination of the complexity associated with the dynamics of chamber cooling methods requiring regulation. The high-temperature requirement necessitates use of high-temperature alloys or refractory metals. The latter, in turn, usually requires use of coatings for the purpose both of providing oxidation resistance and of increasing the emittance of the radiating chamber.

RADIATION-COOLED SPACE ENGINES

A radiatively cooled space engine may be used as the upper stage of a propulsion system designed for propelling a body into space or orbit. It also may be used in space for attitude control of a vehicle, to propel it further into space, or to push it into orbit for a reentry trajectory. Its duration of firing generally would be short, quick bursts for a few seconds up to 5 minutes. Its total use time probably would not exceed one hour for systems that might be built during the next 5 years.

Obviously oxidation preventive coatings, per se, have no function on the exterior surfaces during space use because of the lack of an oxidizing atmosphere. Internal surfaces may be subject to burning propellant-oxidizer mixtures that could be oxidizer-rich at a particular time during the combustion process. Some engines may also be subject to oxidizing conditions at high altitudes during some part of the blastoff or reentry. Additionally, terrestrial tests of engines cannot always be done under conditions of complete space simulation.

Two primary advantages exist for the radiation-cooled thrust chamber over the ablation-cooled concept:

1. Radiation-cooled chambers are generally more suitable for long storage in space, since they are relatively immune to losses of material by vaporization or to degradation of the materials by high-energy radiation (References 36 and 37).

2. A distinct weight advantage exists for long-duration firings. An example of this is presented graphically in figure 15, which compares the weights of equivalent radiation-cooled and ablation-cooled chambers as a function of the total firing time.
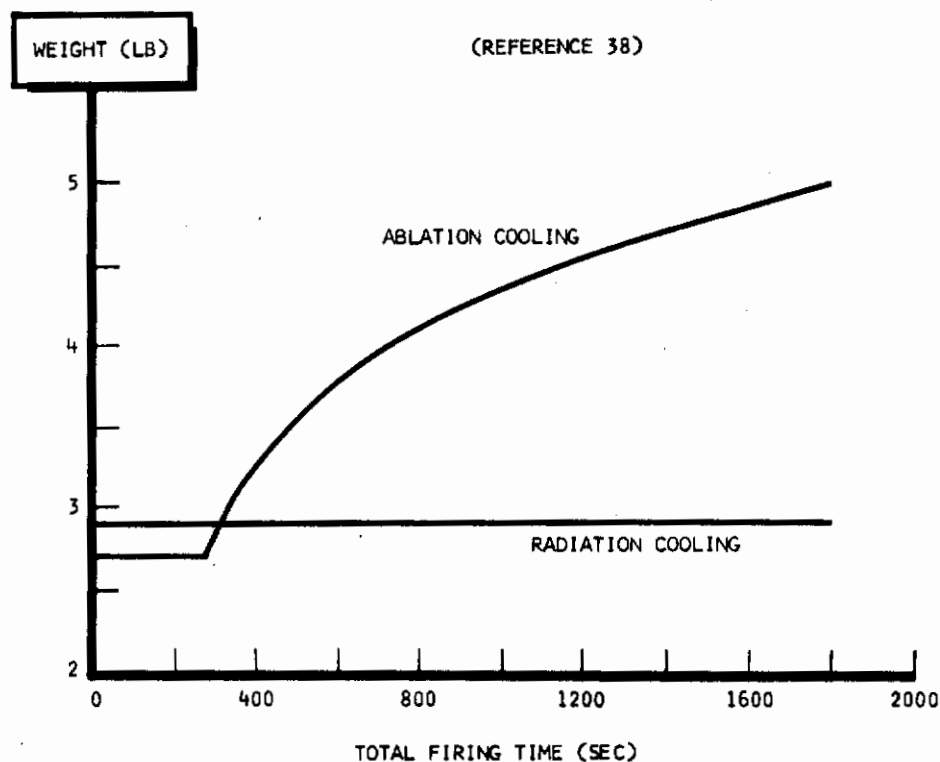
Figure 15. Weights of Ablation and Radiation-cooled Rockets With a Nozzle Exit Area Ratio of 70, Thrust of 25 Pounds, and Chamber Pressure of 40 Psia

Considerable analytical and experimental work relative to radiation-cooled chambers has been performed by NASA, JPL, Marquardt, Reaction Motors, Bell Aerosystems, Vickers, Aerojet-General, and others. Practicality of the use of refractory metals, protected against oxidation by means of suitable coatings, for an engine cooled solely by radiation has been demonstrated over a range of low chamber pressures. A maximum practical operating chamber pressure of about 50 psia is quoted in the open literature (Reference 38).

Romaine (Reference 38) cites two Bell Aerosystems operational, storable, hypergolic, bipropellant, radiation-cooled thrust chambers used in the Agena Rocket. A 16-pound thrust unit made of 90 tantalum/10 tungsten operates at an equilibrium wall temperature of 2300°F, and a 200-pound thrust unit employs Haynes 25 high-temperature steel and operates at a 1900°F equilibrium wall temperature. Both chambers employ an aluminide diffusion coating for oxidation protection, coupled with an outer high-emittance coating. These data indicate an ultra-low chamber pressure operation, possibly coupled with use of fuel-rich mixture ratios.

RADIATION-COOLED THRUST CHAMBER RESEARCH STUDY

The interrelationship of a large number of the factors affecting the radiation-cooling concept and its dependency upon coating properties has been presented in a fairly recent research study (Reference 39). Several refractory metal chambers were used in the study—spun molybdenum chambers and machined tantalum chambers.

The refractory metal thrust chambers were protected against oxidation with disilicide coatings, 0.003 inch thick, applied to both internal and external surfaces. One of the spun molybdenum thrust chambers was coated with a modified molybdenum disilicide coating, "Durak B," by the Chromizing Corporation. This is a pack cementation process. The second spun molybdenum chamber was dip-coated by a proprietary Atomics International process employing a molten sodium bath to carry the silicon. The 90 tantalum/10 tungsten chambers were both coated with the Chromizing Corporation "MGF" tantalum disilicide coating. It is believed that this involves a preliminary pack cementation deposition of manganese to form a diffusion barrier substrate for the subsequent formation of a tantalum disilicide main coating (also by the pack cementation process). Firing tests were run with these chambers. Figure 16 presents computed radiant fluxes at the various chamber stations for all firings made with the spun molybdenum thrust chambers. The failure flux line corresponds to a surface temperature of 3200°F.
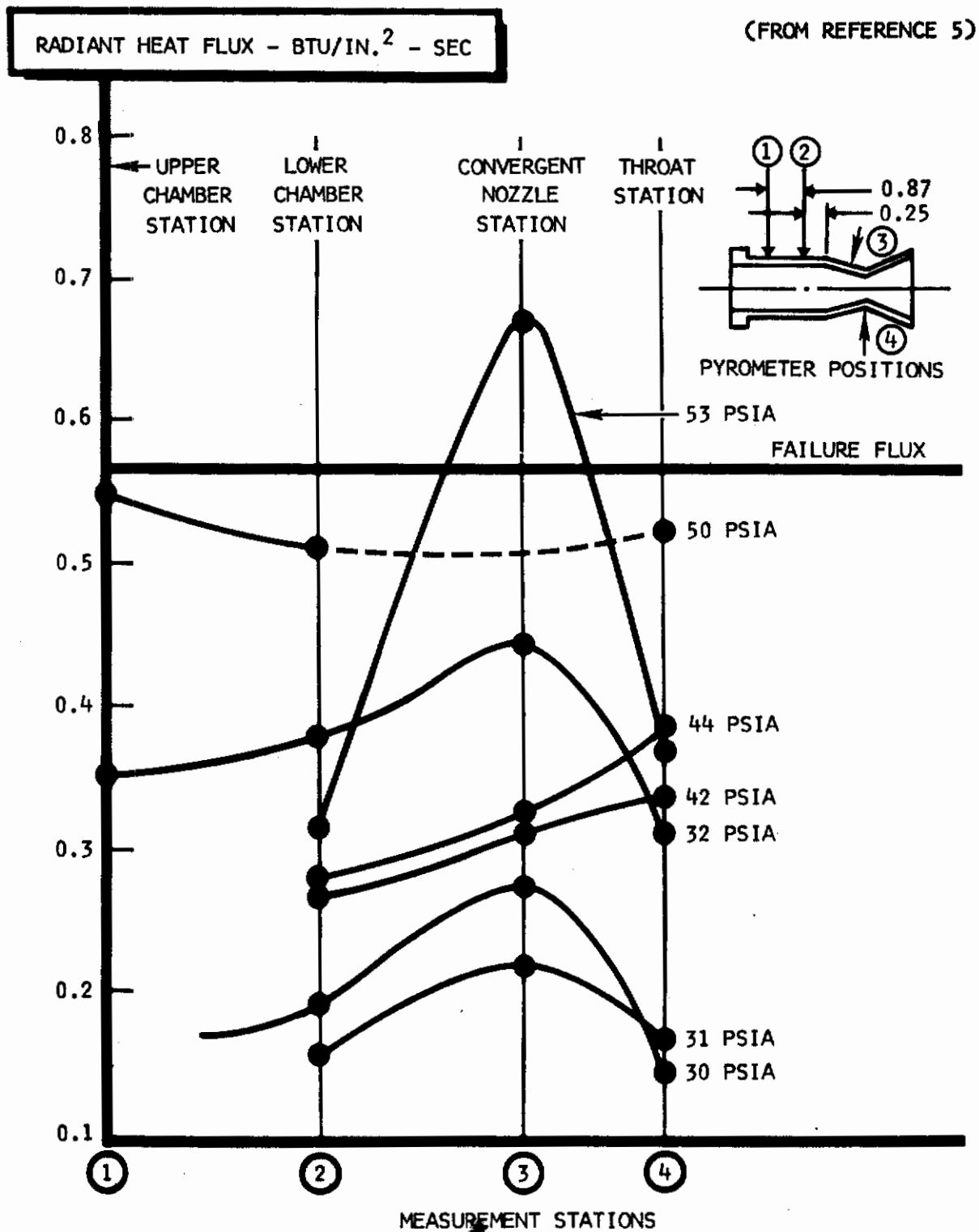
Figure 16.   Computed Radiant Heat Fluxes for Tests Performed With the Spun
Molybdenum, Molybdenum Disilicide Coated Thrust Chamber

Figure 1 shows a plot of surface temperature achieved at equilibrium as a function of emittance and radiant heat flux. A heat flux of 0.5 Btu/in.^{2}-sec (72 Btu/ft^2-sec on the scale of figure 1) then corresponds to an emittance of about 0.7. It is apparent from this chart that high emittance will permit high heat fluxes.

SUMMARY OF TYPICAL TEMPERATURE-PRESSURE-TIME CONDITIONS

Table V is a summary of typical temperature-pressure-time conditions for vehicles and engines previously discussed where emittance would be a significant factor in temperature control. A table of this nature is difficult to construct, since many projected vehicles and engines are possible. The designers' only limitations are those of materials and available power and, of course, money. This table should, therefore, be considered only typical of some situations that might be encountered. The column headed "Typical Number of Use Cycles or Flights" is an assumed number considering some degree of multiple use of vehicles and is projected to a value considered acceptable for vehicles in advanced development stage. Such values for radiation-cooled engines are difficult even to assume since many may be used actually only once as the last stage of a system for propelling a body into space. In addition, reliability requirements will require ground testing. The number of such test cycles would be difficult to predict and would depend upon the overall reliability of the engine system.

ENVIRONMENTAL PARAMETERS

The thermal emittance test program which is currently being conducted under Phases II, III, and IV fails to simulate exactly several environmental conditions which will be encountered in actual service. This program did not attempt exact simulation of the possible service environments because of the obvious complexity of such a program and the much higher testing costs that would have been necessary. However, in planning for emittance measurement programs which may be undertaken in the future, serious consideration should be given to simulating actual service conditions more closely wherever it appears to be technically and economically feasible. As is pointed out elsewhere in this report, the totality of factors affecting the properties of a coating for use in a lifting reentry vehicle include the following:

1. Total ambient pressure

2. Partial pressures of the various constituents of the atmosphere to which the coating is exposed (including both oxidizing and reducing components).

Table V

SOME TYPICAL TEMPERATURE-PRESSURE-TIME CONDITIONS FOR EXTERNAL[c] SURFACES

Use	Condition	Elapsed Time (Minutes)	External Pressure (mm Hg)	Temperature (°F)	Typical Number of Use Cycles or Flights
Lifting reentry vehicle	Ascent[a]	0 to 1.5	900 to 40	10 to 1050	50
		1.5 to 4.5	40 to .01	1050 to 250	
	Space	Hr to mo	10^{-7}[b]	100	50
	Reentry (Surfaces back of leading edge)	1 to 2	10^{-7}[b] to 7	100 to 2819	50
		2 to 13	7 to 3.4	2810 to 1980	
		13 to 28	3.4 to 2.8	1980 to 1500	
		28 to 46	2.8 to 7.8	1500 to 180	
Hypersonic vehicle	Cruise Mach 20	0 to 15	760 to 1.6	100 to 2300	200
	140,000 ft	15 to 90	1.6 to 1.6	2300 to 2300	
		90 to 120	1.6 to 760	2300 to 100	
Radiation-cooled engine	Space cruise	0 to 5	10^{-7}	2300	50[d]
	Space cruise	Hr to mo	10^{-7}	100	3
	Final stage	0 to 5	0.01	2300	1
	Test	0 to 5	760	2300	50[e]

a Condition of leading edge at stagnation line - Surfaces back of line are at lower temperatures and pressures.

b A pressure of 10^{-7} mm Hg is a practical value for laboratory space simulation.

c Interior surfaces for vehicles and engine parts may be at the same temperatures as exterior surfaces, depending on location. Pressure typically would be at a minimum static pressure corresponding to altitude.

d Includes ground tests.

e Ground test only.

3. Thermal shock and stresses

4. Dynamics of gas flow

5. Electromagnetic radiation

6. Corpuscular radiation

7. Meteoroid bombardment

The present experimental program has been designed to evaluate the coating properties under controlled environmental conditions which simulate several of the listed environmental factors. This test program simulates the environmental factors of total ambient pressure, partial pressures of the various constituents of the coating atmosphere, and thermal stress under stabilized service temperature for space/reentry vehicle components not exposed to rocket-engine exhaust gases. However, the limited size of this program does not permit tests to be conducted which simulate all of the anticipated conditions of the service environment. Several environmental factors which are considered likely to have a marked effect on the service performance of coated refractory metals, and which, therefore, should be considered for incorporation into any future expanded program for evaluating the emittance of refractory metal coatings, include the following:

1. High Mach number gas flow of both atmospheric air and rocket-engine exhaust products

2. Thermal shock

3. Electromagnetic radiation in the near ultraviolet range

Simulation of corpuscular radiation and meteoroid bombardment of coated refractory metals is not currently considered to be necessary in tests designed to measure emittance under service conditions. Simulation of these radiation and bombardment conditions would be extremely difficult to accomplish if it were considered to be necessary. Such simulation is considered to be unnecessary, however, because no evidence can be found which indicates that significant damage has occurred to the exterior surface finish of space vehicles during space flights in the past due to either corpuscular radiation or meteoroid bombardment. This conclusion is supported by Reference 34.

The effect of ultraviolet radiation on space environment coatings should be simulated in future testing. The chemical effects of this radiation on ceramic coatings is believed to be too slight to affect the coating's physical properties, although this opinion may be discovered to be

inaccurate due to the unknown effects of the other special experimental test conditions. However, it is considered likely that ultraviolet radiation may cause the coatings included in these tests to undergo significant changes in optical properties as a result of the formation of color centers. Sources of strong ultraviolet radiation are readily available, and, hence, no difficulties are expected in the experimental simulation of this condition.

One environmental condition which would appear to have a considerable effect on the physical properties of coatings during either lifting reentry into the atmosphere or very-high-altitude cruise is dynamic gas flow. During atmospheric reentry, velocities of between Mach 20 and Mach 25 can be expected, and during hypersonic flight, velocities of Mach 18 and higher can be expected. At such speeds various physical effects occur which could affect the exterior surface coating of the reentry vehicle. These physical effects include increased shear stress on the coating, which might either cause wear or plastic deformation; changes in the chemical composition of the boundary-layer gases, which could result in chemical alteration of the surface coating; and changes in the temperature (and enthalpy) of the boundary-layer gases, which could either soften the coating or increase its chemical reaction rate.

In view of the possibility that reentry and hypersonic flight airflow velocities could produce significant changes in the physical properties of surface coatings, it would be desirable to simulate the effects of such dynamic airflow in future test measurements of the emittance properties of coated refractory metals under service conditions. Exact duplication of the airflow velocities, air temperatures, and exposure times encountered during actual atmospheric reentry or hypersonic flight would require the use of a wind tunnel facility, capable of operating under typical service environment parameters. Therefore, an investigation was made of existing wind tunnel facilities in the United States, in an attempt to determine, which, if any, of these facilities are capable of duplicating atmospheric reentry conditions. The results of this investigation are summarized in table VI which describes the capabilities of existing hypersonic and hypervelocity test facilities in the United States.

The actual environmental conditions encountered during atmospheric reentry include simultaneous exposure for several minutes at a time to a velocity of approximately Mach 25 and a stagnation temperature of approximately 7000°R for lifting reentry vehicles (Reference 35). As the chart shows, none of the existing test facilities is capable of simultaneously duplicating both of these conditions for more than a fraction of a second. However, it can be seen that either the reentry velocity or reentry stagnation temperature condition can be separately produced as a test environment. It would be possible, therefore, to expose a coated refractory metal successively to each of the different environmental conditions that would

Table VI

AVAILABLE HYPERSONIC TEST FACILITIES IN THE UNITED STATES

Type of Test Facility	Maximum Operating Velocity	Maximum Running Time	Maximum Stagnation Temperature	Physical Location of a Typical Facility
Hypersonic wind tunnel	Mach 4 to Mach 18	Continuous	4500°R	FluiDyne Engineering Corp Minneapolis, Minn.
Impulse wind tunnel	Mach 25	Several milliseconds	8000°R to 20,000°R (for extremely short runs)	Cornell Aeronautical Lab, Inc, Buffalo, N.Y.
Arc-heated tunnel	Mach 10	Continuous	12,000°R	Purdue University, Lafayette, Ind.
Ballistic range (limited to very small free-flight models)	Mach 25	1/3 second	7000°R	Arnold Engineering Development Center, Tullahoma, Tenn.
Counterflow facilities (limited to very small free-flight models)	Mach 30	Several micro-seconds	7000°R	Ames Research Center, Moffett Field, Calif.
Magneto-hydrodynamic accelerators	Mach 25	Continuous	12,000°R	None operating as test facilities at the present time. (General Electric Co., Wright-Patterson Air Force Base, etc)

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be encountered during atmospheric reentry. However, it is unlikely that the effect of all environmental reentry conditions operating simultaneously could be accurately estimated from a knowledge of the individual conditions because these conditions are obviously highly interdependent. As an example, the eroding effects of high-velocity gas flow and the oxidizing effects of the atmospheric oxygen can both be expected to increase as the coated metal is heated from room temperature to reentry temperatures. Any test facility which is to be used to duplicate the lifting reentry environment must be capable of simultaneously producing Mach 25 airflow velocities and a 7000°R air stagnation temperature. Conversely, accurate duplication of the service environment is provided by any test facility which produces a Mach 25 airflow velocity and a 7000°R air stagnation temperature with the density of the freely flowing air equal to the density of air at the reentry altitude.

An examination of the operating parameters of the various types of wind tunnels listed in the preceding chart shows that the available tunnels can provide a continuous airflow environment at air velocities up to Mach 18. Since this airflow velocity approaches actual atmospheric reentry velocities of Mach 25, and is equal to the maximum airflow velocities expected for most hypersonic cruise flights, it would appear, on the basis of a casual analysis, that a good approximation of the reentry and hypersonic cruise environments could be obtained using existing operating wind tunnel test facilities. Unfortunately, however, this is not the case, because the physical operation of accelerating the air in a wind tunnel to the desired test speed is accomplished by expanding the air through a nozzle. This expansion causes a marked decrease in the air temperature. The maximum stagnation temperature of air in a wind tunnel is thermodynamically limited to the temperature of the air prior to acceleration through the expansion nozzle, unless this air is subjected to additional heating after expansion. This means that, in order to simultaneously duplicate atmospheric reentry or hypersonic cruise conditions of velocity and stagnation temperature in a wind tunnel, the temperature of the air just prior to expanding into the tunnel would have to be approximately 7000°R for duplication of lifting reentry or 14,500°R for duplication of the hypersonic cruise environment. These are the stagnation temperatures which would be encountered during a typical service mission. Although no practical method is known for heating air to these temperatures prior to its introduction into a wind tunnel, several procedures have been used successfully to heat air as high as 4500°R. These procedures consist of passing air over either a hot ceramic surface or electrically heated tungsten or Kanthal wire, or of using hot combustion gases as the tunnel atmosphere. However, none of these procedures is considered acceptable for use in test simulation of lifting reentry conditions. Air which is heated by flowing over extremely hot ceramic picks up small ceramic particles which might erode the exterior surface of a wind tunnel specimen. Only inert gases can be heated with tungsten or kanthol wire heaters due to the high susceptability of these

metals to oxidation. Such gases cannot be used to simulate the oxidizing characteristics of the air present in the actual reentry environment. Hot combustion gases are unsuitable for simulating the atmospheric environment for the same reason.

It would appear, however, that a magnetohydrodynamic test facility, with the operating characteristics shown in table VI could be used to accurately duplicate the lifting reentry environment. This type of facility consists essentially of an arc-heated (plasma) tunnel in which the gas flow is given additional acceleration by a magnetic field. At the present time, this type of facility is only in the advanced development stage. However, when, in the future, such facilities become available for use in testing, it is believed they will provide an excellent means for duplicating the lifting reentry environment. At that time, it is recommended that consideration be given to using such a facility in the study of the effect of reentry on the emittance properties of coatings applied to refractory metals.

The actual erosive or other possible deleterious effects of high Mach number airflow on protective coatings for refractory metals is not definitely known. Therefore, as has been previously pointed out, the effects of atmospheric reentry and orbital cruise on the thermal emittance properties of such protective coatings are uncertain and must be established if aerospace thermodynamicists are to have the reliable data they require for future design predictions. However, there is some available evidence which indicates that the effects of high-velocity airflow on refractory metal coatings are slight, and may be unimportant. It is considered that high airflow velocities do not significantly affect refractory metal coatings unless the coatings are heated to their softening temperature, in which case, the coating may flow under the aerodynamic loading. At the high altitudes where reentry velocities approach orbital speeds, the atmospheric density is relatively low. As a result, the shear stress imposed on the exterior surfaces of a reentry or orbital vehicle are low enough that they would not normally be expected to cause any mechanical damage to typical protective coatings for refractory metals. Calculations have been made at NAA to determine the approximate magnitude of typical reentry aerodynamic shear loading. As an example, calculations based on a service condition described in Reference 40, using a velocity of Mach 20 and an altitude of 140,000 feet, gives a shear load of 1.19 pounds per square foot.

Section VII

EMITTANCE OF REFRACTORY COATINGS FROM THE LITERATURE

BACKGROUND

A review of the literature revealed that many thousands of emittance measurements have been made of various refractory metal coatings mainly during the last 5 years. Reference 14, alone, contains at least 6000 separate measurements. Some of these measurements were made of coated alloys no longer of interest or of coatings not currently being considered for use. This situation is the natural result of the rapidly moving technology of refractory metals and the great need in this field for improvement. Unfortunately this also means that many of these measurements are of no immediate direct practical interest.

A number of researchers have reported that there is considerable variation in the data reported by various workers for the same or similar material (References 32 and 33). One of the main causes for this is that emittance is a function of temperature, pressure, and chemical environment in which the material is being tested. In addition, the history of the material, thickness of coating, surface roughness, and chemical composition variation affect it. Considering all the possible variations, it is no wonder that varying results can be obtained. Additionally, some of the measuring techniques which were employed may contribute to the problem. (Refer to Section IV regarding emittance measurements).

There appears to be a tendency to ascribe much of the data variation reported in the literature to inadequate measurement techniques and to varying compositions due to poor control in coating application. While these are problems, they are resolvable.

The major problem, however, is that the emittance of a coating is a function of its environment. Most coatings change rapidly in emittance upon being heated initially. (See figures 39 and 46.) Figure 17 shows that the emittance of Tapco-coated columbium is a function of pressure. The basic problem, therefore, is that coatings are not chemically stable throughout the range of environments they encounter. At least their surfaces are not chemically stable. Preconditioning coatings at the temperature and pressure of use would be an assist in this regard and lead to more consistancy in data.

O ALUMINIZED LB-2 COATED COLUMBIUM MEASURED IN AIR ATMOSPHERE (MC DONNELL)
□ TAPCO COATED COLUMBIUM (CB-752) MEASURED IN AIR
■ TAPCO COATED COLUMBIUM B-66 MEASURED IN AIR (11T RTD-TDR-63-4006, PART II)
▼ TAPCO COATED COLUMBIUM MEASURED AT REDUCED PRESSURES* (BOEING COMPANY)

  * NUMBERS IN PARENTHESES ARE IN MILLIMETERS OF HG
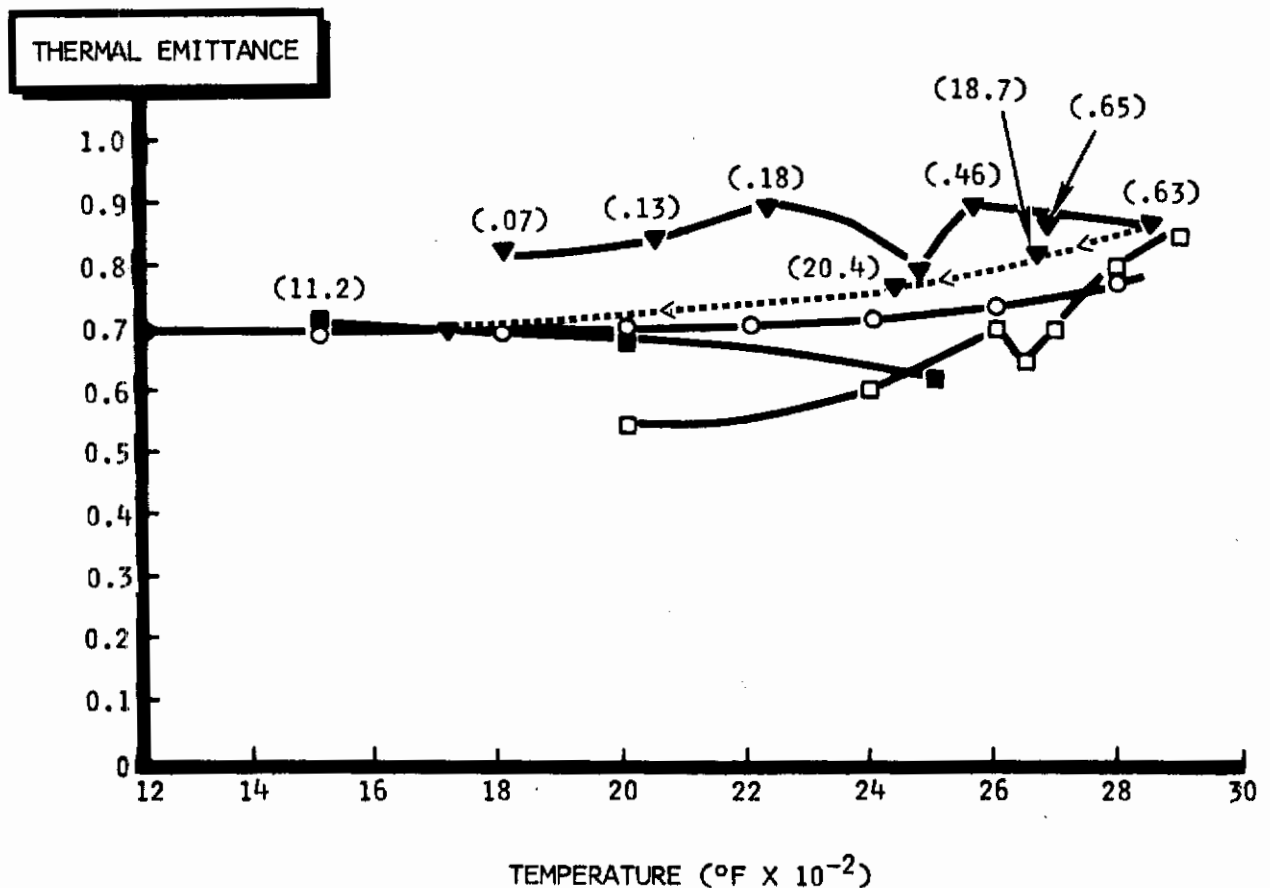
Figure 17.   Thermal Emittance of Oxidation Protective Coatings on Columbium

CURRENT COATINGS

Reference 32, which is a recent review of refractory metal coating technology, previously cited, contains emittance information regarding current coatings. Data in figure 17 for columbium coatings are from this reference. It states that all state-of-the-art coatings (for columbium) have an emittance between 0.6 and 0.8, regardless of temperature and oxidizing pressure. Regarding silicide coatings on TZM at 2500°F, the emittance at atmospheric pressure is between 0.5 and 0.7. The high-emittance improvement top-coating for Disil-coated TZM, developed by Boeing, consisting of titanium carbide suspended in a silicone resin, was stable during an entry environment (Reference 41). Reference 42 indicates that no data are available for the major coated tantalum alloy systems.

Table VII, from Reference 43, consists of emittance data for coated columbium and molybdenum alloys. These measurements were made by the ITT Research Institute, and are for some coatings of current interest. It should be noted that the values are at atmospheric pressure and that time at temperature was a major consideration in these measurements. The total normal data are remarkably consistent. The values at 0.655 microns, however, vary considerably in some cases.

Table VII

TOTAL NORMAL EMITTANCE OF COATED TZM AND B66 AT 2600°F

Coating		Total Normal Emittance After Various Times*				
		1 Hr	2 Hr	5 Hr	8 Hr	10 Hr
Pfaudler PFR-6 (modified silicide) on TZM	Batch 1**	0.66(0.60)	0.68(0.60)			
	Batch 2**	0.62(0.52)	0.65(0.54)			
	Batch 2	0.58(0.55)	0.66(0.55)	0.64(0.55)	0.66(0.57)	0.66(0.53)
GT&E (Mo modified Sn-Al) on TZM	Batch 1	0.58(0.58)	9.64(0.55)			
	Batch 1**	0.68(0.66)	0.66(0.66)	0.66(0.57)	0.65(0.57)	0.65(0.58)
	Batch 2**	0.62(0.66)	0.64(0.63)			
Chromalloy W-2 (modified silicide) on TZM	Batch 1	0.68(0.61)	0.64(0.63)	0.65(0.61)	0.70(0.67)	0.71(0.70)
	Batch 2	0.68(0.60)	0.67(0.70)	0.70(0.61)	0.64(0.74)	0.66(0.69)
LTV (two-cycle modified silicide) on TZM	Batch 1	0.58(0.45)	0.64(0.48)	0.66(0.43)	0.65(0.52)	0.65(0.48)
	Batch 2	0.58(0.61)	0.56(0.63)	0.58(0.61)	0.63(0.67)	0.64(0.70)
Chromizing Durak KA modified silicide on B66***	Batch 1	0.46(0.64)	0.43(0.68)	0.49(0.67)	0.44(0.66)	0.45(0.68)
	Batch 2	0.46(0.46)	0.43(0.48)	0.46(0.55)	0.47(0.52)	0.47(0.54)
TRW (Cr-Ti-Si) on B66	Batch 1	0.69(0.44)	0.62(0.50)	0.62(0.55)	0.66(0.51)	0.65(0.47)
	Batch 2	0.66(0.37)	0.59(0.42)	9.69(0.46)	0.66(0.44)	0.64(0.43)

*Excluding approximately 3 hours heat-up time, except as noted. Values in parentheses are the 0.655 μ normal emittance measurements.

**Heat-up time approximately 6 hours.

***Specimen completely destroyed during measurement.

(Taken from Reference 43)

Section VIII

COATING COMPOSITION AND ITS VARIATION

BACKGROUND

Most of the information on oxidation-resistant coatings for refractory metals has evolved from programs which were designed to either improve this oxidation resistance or make it more consistent. For the most part, the treatment has been largely qualitative. Historically, it was not until observation of the failure of silicide coatings under reduced pressure environments that the extent of the problems inherent in such coatings began to be appreciated.

Although the emittance properties of some of the coated refractory metal systems have been reported, examination of much of the data shows an exceedingly broad spread. Thus, the emittance of silicide coatings has been reported to range from 0.2 to 0.8. The problems involved in such measurements have been discussed in Section IV.

In brief, the problems of effecting a correlation between emittance and composition are as follows:

1. The chemical systems used as protective coatings are not emittance-stable in the test and use environment.

2. The optical properties of most of the unoxidized and oxidized components of the coatings are unknown.

3. The reflective properties of the interfacial phases are unknown. In addition, a good theoretical treatment for evaluating the effect of the existence of these multiple interfaces is not available.

4. The effect of surface roughness is ambiguous and difficult to evaluate experimentally.

5. The problems in experimental techniques for measurement of emittance, until recently, were not generally appreciated.

It is apparent from the literature that there is an increasing realization that qualitative examination of coated systems is inadequate if coatings are to have greater utility. Simultaneously, there appears to be an increasing realization in the field of thermal radiation that more precise treatment of practical problems is required. Most of the work in

coatings is still concerned with oxidation resistance and its improvement. It is obvious that a need also exists for correlating emittance with other coating properties including composition.

The recent advent of the electron microprobe has been of considerable benefit. By this technique, much information can be developed about the composition and structure of a coating not possible by older techniques. The results of electron microprobe analyses combined with metallographic and X-ray diffraction analyses will aid materially in the evaluation of properties related to emittance. It should be observed, however, that these techniques employ room-temperature measurements, while the emittance measurement takes place at elevated temperatures. Emittance is known to change with temperature in most materials. Thus, either accurate means for extrapolating room-temperature definition of coating systems to high temperatures must be found, or techniques must be devised for definition of coating systems at the temperatures where the emittance is measured. In addition, satisfactory techniques must be found for measurement of the optical properties of interfaces, especially submerged interfaces. The importance of these interfaces increases as oxidation of the coatings proceeds and as the temperature is increased, due to the optical transparency of the oxides and its increase with temperature.

Methods for obtaining meaningful data on surface roughness, especially in connection with the shape of the surface irregularities, are required. Similarly, some quantitative method is required for measurement of the roughness of submerged interfaces.

VARIATIONS IN PROPERTIES RELATED TO EMITTANCE

Coatings of interest to this program are given in table VIII. Although these are coatings of specific compositions applied to well-established alloys, the exact composition and microstructure will vary due to variables in the coating process. Each coating is discussed in more detail in the subsequent sections. Since all three coatings are of the diffusion type, they have certain similarities.

Table VIII

COATINGS OF INTEREST TO CURRENT PROGRAM

Vendor	Coating	Substrate
TRW	Cr-Ti-Si	Cb-752(Cb-10W-2 to 3Zr)
Chromalloy	W-3 (silicide)	TZM (Mo-0.5 Ti-0.1Zr)
Sylcor	Sn-Al	Ta-10W

In the unoxidized state, the coatings are generally made up of layers
of intermetallic compounds with varying stoichiometry. Superficially, even
in the unexposed condition, the coatings are likely to have a thin layer of
amorphous oxide resulting from room-temperature oxidation. Beneath this
thin layer of oxidized material, there may be several layers of the coating
and substrate constituents in distinctively different ratios of combination.
The first subsurface layer may be entirely the principal coating constituent
containing other components in solid solution. The concentration of this
constituent is progressively diminished as the substrate is approached. On
the other hand, the constituents of the substrate become progressively
greater in concentration as the substrate is approached. Since all the
coatings are of the diffusion type, the composition of individual layers
will be influenced by the temperature and time of the coating process. The
surface of the substrate itself may be a solid solution of coating constit-
uents, alloying agents, and modifiers.

Generally, demarcations between the different diffusion zones or bands
is fairly well defined and sometimes quite sharp. This separation again
will be determined largely by the temperature and time, but also by the
amount and location of the reservoir which is supplying the diffusing spe-
cies, whether it be the substrate alloy, a precoating solid solution in the
substrate, or the coating pack or "bisque." It may, in the case of the con-
stituents of the coating derived from the pack, be determined by the amount
of halide activator added to the pack or the rate of loss of the activator
from the pack.

While the demarcation of the diffusion bands may be fairly sharp, it
cannot be specified that the interface between the different bands will be
smooth. The thickness of the different diffusion zones and their exact com-
position will vary considerably as the result of the coating process envir-
onment. Coatings from the same pack show substantial variation merely as
the result of temperature variations inherent in the coating process.
Batch-to-batch variations may be even greater.

The composition of the diffusion bands of such coatings can be expected
to change if the coating is subjected to temperatures near or above that at
which the coating is applied. Such an effect is certainly encountered upon
oxidation with the added complication of progressive oxidation. Such oxida-
tion proceeds inwardly, but not necessarily uniformly, since cracks, fis-
sures, and pipes may be present. Such irregularities may be derived from
mismatch between the thermal expansion coefficients of the substrate and
coating. In general, the principal oxide component on the surface of an
exposed coating will be that of the main coating constituent, since a reser-
voir of that constituent is present. Other constituents present in the
coating system, however, can preferentially diffuse into, and enrich, the

surface oxide, the fastest diffusing elements providing the greatest enrichment. Simultaneously, high temperatures and, in some cases, low pressures may cause a depletion of certain constituent oxides in the coating surface as a result of volatilization. The extent of such depletion will be effected by vaporization, and the replacement by diffusion, and, also, the availability of the most volatile constituents.

Thus the composition, microstructure, thickness, etc, of a coating are dynamic variables, determined by many factors, and cannot be stated in any practical way with any degree of certainty.

EMITTANCE RELATIONSHIPS IN COATING

Virtually, the only attempt to treat the emittance of coated systems is that of Richmond (Reference 44). He derived the following equation for relating the normal spectral emittance ϵ_{SN} of an optically inhomogeneous, partially transmitting coating over an opaque substrate to the thickness and optical properties of the coating and the reflectance of the substrate at the coating-substrate interface:

$$\epsilon_{SN} = 1 - \left[\rho_N + (1-\rho_N)(1-\rho_i) \frac{(1-\beta)Me^{\sigma D} - (1+\beta)Oe^{-\sigma D}}{MNe^{\sigma D} - OPe^{-\sigma D}} \right] \quad (15)$$

where

ρ_N is the normal reflectance

ρ_i is the reflectance of the coating-air interface for internally incident diffuse radiant flux

$\beta = \sqrt{K/(K + 2S)}$

$\sigma = \sqrt{(K)(K + 2S)}$

D = coating thickness (millimeters)

K = absorption coefficient (millimeters^{-1})

S = backscattering coefficient (millimeters^{-1})

ρ_s = reflectance of the substrate for diffuse radiant flux incident on the coating-substrate interface from within the coating

$$M = (1 + \beta) - \rho_s (1 - \beta)$$

$$N = (1 + \beta) - \rho_i (1 - \beta)$$

$$O = (1 - \beta) - \rho_s (1 + \beta)$$

$$P = (1 - \beta) - \rho_i (1 - \beta)$$

This equation assumes no spectral selectivity. It is probably valid in its application over a narrow portion of the spectrum. Over the much broader wavelength range of thermal radiation, considerable difference in spectral selectivity occurs, and the optical properties as functions of wavelength must be known.

It must be pointed out, that even for the homogeneous portions of the oxidation-resistant coatings, we do not generally know the true thickness of the partially transmitting coating. Neither do we know the absorption coefficients or the backscattering coefficients. Furthermore, even the index of refraction of many of the components of coatings are not known.

SELECTED COATINGS

Certain similarities exist in the chemistry of the three commercial coatings being investigated during the course of this program. Oxidation protection is attained through the selective oxidation of the coating constituents to form an adherent, stable, protective oxide on the surface. This oxide is continually grown by the further oxidation of fresh constituents supplied by the coating reservoir. When a coating system is exposed to a high-temperature environment, chemical reactions will occur at the coating surface, within the coating, and between the coating and the substrate. As these reactions progress, the chemical constitution and physical characteristics of the coating will continue to change. The reactions that occur are not only dependent on the exposure environment, but also on the residual coating constituents and their location in the coating. Even under exposure to constant environmental conditions, the reaction mechanism can change as the availability of certain species decreases.

The nature of coating reaction mechanisms is quite complex. Only recently have investigations been conducted to delineate the mechanisms of coating protection and/or failure. The more comprehensive studies have concentrated on understanding the basic reactions that occur with pure coating materials and simple coating systems — the only logical approach to a complex problem. Commercial coatings contain modifiers that may be dispersed throughout the coating or concentrated in distinct layers in the coating. The behavior of some of these modifiers has been investigated under certain conditions. However, many effects are unknown, especially under

high-temperature, low-pressure conditions. Part of the difficulty in analyzing the behavior of these modifiers lies in understanding the diffusion phenomena occurring in multicomponent systems. Thermodynamic calculations must also be treated with some reservations due to the reduced activity of species in solution with the major coating constituents.

COATING-SUBSTRATE REACTIONS

The coatings under investigation, table VIII, are all applied by a diffusion process at a temperature below the designed exposure temperatures. The silicide coatings are formed in situ by the reaction of metal halide vapors with the substrate, and the aluminide coatings are formed by partially reacting an aluminum-containing slurry with the substrate. When the coating system is exposed to a high-temperature environment, the coating constituents will continue to diffuse down the chemical potential gradients. During the coating application process, the reactive elements are continually supplied to the surface of the coating. Diffusion through the primary coating phase is the rate-controlling step. The diffusion processes occurring during environmental exposure are somewhat different. The excess of reactive species is no longer present or is quickly consumed. The diffusion zone between the substrate and coating can only grow at the expense of the coating. The diffusion rates are also different, since diffusion through a phase other than the primary coating phase is generally rate controlling. The net result of coating-substrate diffusion is the formation of phases with higher substrate metal content, a reduction in the amount of primary coating phase, and a reduction in the substrate thickness. In order to properly evaluate diffusion data, the factors that may affect the diffusion process should be considered. Diffusion can occur through the bulk of the crystal lattice or through highly conducting channels such as grain boundaries, dislocation lines, and chemical inhomogeneities. At lower temperatures, the bulk of the diffusion occurs through these channels. At higher temperatures, lattice diffusion becomes more rapid and, in many cases, contributes the bulk of the diffusion process. Interstitials either added as modifiers or present as impurities may be expected to influence lattice diffusion rates. In general, published data on coating-substrate diffusion is rather poor for complex commercial coating systems and should be used only as a guide. The amount of interdiffusion must be determined after environmental exposure.

The most important aspect of coating-substrate diffusion is the reduction in the protective lifetime of a coating. The lower silicides are not as protective as the disilicides, and the lower aluminides may be expected to behave in a similar manner. The effects of this diffusion on coating emittance is completely unknown. However, the principal effects are expected to be related to the change in the composition of the surface phases and to the thickness of the primary radiating species.

During the initial portion of high-temperature exposure, relative to the total lifetime of a coating, the only important environmental parameter that will affect coating-substrate diffusion is the temperature. After continued exposure, depletion of certain coating constituents will change the concentration of the diffusing species and, therefore, the diffusion rates. However, since diffusion-controlled processes normally follow the parabolic rate law, coating diffusion may be expected to be extremely slow during later stages of oxidation and, therefore, relatively insensitive to environmental parameters such as air pressure or flow rates.

COATING-ENVIRONMENT REACTIONS

The behavior of a coating surface is distinctly dependent on the environment to which it is exposed. All commercial coatings undergo high-temperature, low-pressure degradation due to a change in oxidation mechanism. All coating materials have appreciable high-temperature volatility, especially under vacuum conditions. The environmental effects may be divided into three regimes depending upon the major reaction mechanism that is operative: (1) a stable oxide forms on the surface and the coating is considered to be protective; (2) the continuous oxide is disrupted, cannot form, or is not stable; (3) coating constituents only vaporize. The conditions that correspond to each of these regimes produce surface phases of different chemical composition and physical geometry. The emittance behavior of a coating may be expected to correspond to the environmental regime to which it is exposed. The coatings being investigated have been evaluated under high-temperature and low-pressure conditions. These data can be used to establish an experimental plan for emittance evaluation.

The environmental parameters that must be considered when evaluating coating behavior are gas composition, pressure, temperature, time, and gas velocity. The bulk composition of the reacting gaseous species is essentially that of air in most applications that warrant knowledge of the emittance properties of refractory metal coatings. The effects of pressure, temperature, and time on the life of refractory metal coatings have recently been investigated by Perkins (Reference 45), Bartlett (Reference 46), and Priceman (Reference 47).

The low-pressure, high-temperature failure of the silicides has been related to the high-temperature chemical behavior of the silicides in the presence of oxygen. The failure of tin-aluminide coatings is related to the boiling point of tin.

High gas velocities may both affect the rate of chemical attack on a coating and produce physical damage due to high shear forces. Solid/gas reactions normally involve a series of five steps: (1) diffusion of reactants to the solid surface; (2) adsorption of reactants on the surface; (3) reaction on the surface, including diffusion through condensed product

phases; (4) desorption of the gaseous products of reaction; and (5) diffusion of the products away from the surface (References 48 and 49). A coherent protective oxide is formed on the surface when the reaction rate is controlled by step 3, which involves diffusion through the protective oxide. Step 5 may contribute to reaction due to the increased loss of the oxide due to vaporization, and therefore, loss of diffusion barriers. However, this effect may be expected to be slight. In general, high gas velocities are not expected to greatly accelerate chemical reaction in the regime where a protective oxide is formed. Coating evaluation in dynamic oxidizing tests substantiate this conclusion, as long as coating defects are not present (Reference 50).

Low-pressure failure of coatings can be related to the formation of gaseous phases and porous oxides. A moving gas layer will essentially reduce the thickness of the boundary layer adjacent to the coating and, therefore, increase the concentration gradient and diffusion rates for reactants and products to and from the surface. Under such conditions, gas velocity effects may be expected to accelerate coating deterioration and changing emittance properties. Unfortunately, no significant experimental data have been gathered on the reaction of coatings to high-velocity, low-pressure (below 1.0 Torr) gas streams.

High-velocity gas shear effects on coating behavior have been evaluated in only a cursory manner. Flow of a glassy mixture, consisting principally of silicon dioxide, on the surface of silicide coatings has been observed in Mach 3 flow tests (Reference 34) and in rocket thrust chambers (Reference 39). Reduction in the thickness of the protective oxide by this mechanism may be expected to affect the emittance behavior of a coating system.

CHROMALLOY W-3 ON TZM MOLYBDENUM

Molybdenum-disilicide coatings on molybdenum alloys have been studied more extensively than any other coating system. The addition of modifiers to the coating has been investigated. However, they produce only slight improvement in high-temperature life. The most beneficial effect of the modifiers is the prevention of low-temperature failure. Most commercial coatings contain over 90 percent $MoSi_2$. The W-3 coating has a proprietary composition. However, preliminary analysis of supplied coatings indicates that about 5 percent MoB is formed through the addition of boron to this coating as a modifier. The molybdenum-silicon metallurgical system contains three intermetallic phases: $MoSi_2$, Mo_5Si_3, and Mo_3Si. Commercial disilicide coatings applied by pack cementation are almost totally the $MoSi_2$ phase. The W-3 coating contains a small percentage of MoB dispersed throughout the coating. The Mo_5Si_3 phase is relatively minor in the as-applied condition and the Mo_3Si phase does not appear. At normal service temperatures the Mo_5Si_3 phase will grow at the expense of the $MoSi_2$ phase and the substrate. The recent report by Bartlett is the only available data on the growth rate

of Mo_5Si_3 (Reference 51). When proper consideration is given to the factors that may influence diffusion and growth rates, this data can be used for guiding experiment design. The actual thickness of the Mo_5Si_3 and $MoSi_2$ phases should be measured after completion of the experiment.[3] As can be seen from figure 18, negligible growth of Mo_5Si_3 will occur at a temperature of 2000°F or below. Therefore, any series of experiments run at this temperature would not be affected by the growth of Mo_5Si_3 at the coating-substrate interface.

The structure of the oxide film grown on $MoSi_2$ coatings can vary considerably depending on the oxidation conditions. Bartlett (Reference 46) has discussed the morphology of films grown on bulk $MoSi_2$ samples, and his results may be considered to be applicable to W-3 coating oxidation at high temperatures. (The boron addition to the coating may be expected to alter the low-temperature behavior of the oxide film.)

The oxide films grown at 1650°F and 1830°F had two different morphologies. One structure contained rectangular platelets of molybdenum oxides in a glassy SiO_2 phase. The other structure had negligible amounts of molybdenum oxide platelets, but contained circular islands of cristobalite. Both structures contained a large number of dark spots that were not identified. The oxide films grown at temperatures above 2100°F contained no dark spots or molybdenum oxide. Only crystobalite islands in a glassy matrix were observed. The growth of these islands was observed to be slow at 2100°F as may be expected, since the devitrification rate of silica at this temperature is low. The boron modifier in W-3 may be expected to increase the devitrification rate of the glassy layer, due to the reduction in viscosity of the glass.

The structure of the oxide film will definitely affect the optical properties of the oxide, which in turn will affect the emittance of the coating system. The emittance of the system may, therefore, be expected to be dependent on the oxidation conditions. In addition to temperature, nucleating agents either in the coating or in the atmosphere may contribute to the change in oxide structure and emittance.

When $MoSi_2$ oxidizes, depletion of silicon occurs, converting the coating adjacent to the oxide to Mo_5Si_3. The lifetime of these coatings has been related to the time necessary for conversion of all the $MoSi_2$ to Mo_5Si_3 by both this reaction and reaction with the substrate. As oxidation proceeds, the emittance of the coating system may be expected to be affected by the growth of Mo_5Si_3. The influence of this phase on emittance is dependent upon the optical properties of the oxide layer on the surface as well as the difference in properties between $MoSi_2$ and Mo_5Si_3. However, on the basis of the work presented in Reference 2, it is probable that there is little difference between the emittance of these two compounds. The oxide grown on silicide coatings in the nonprotective, high-temperature, low-pressure region

PHASE THICKNESS (MICRONS)

(REFERENCE 51)

MINUTES
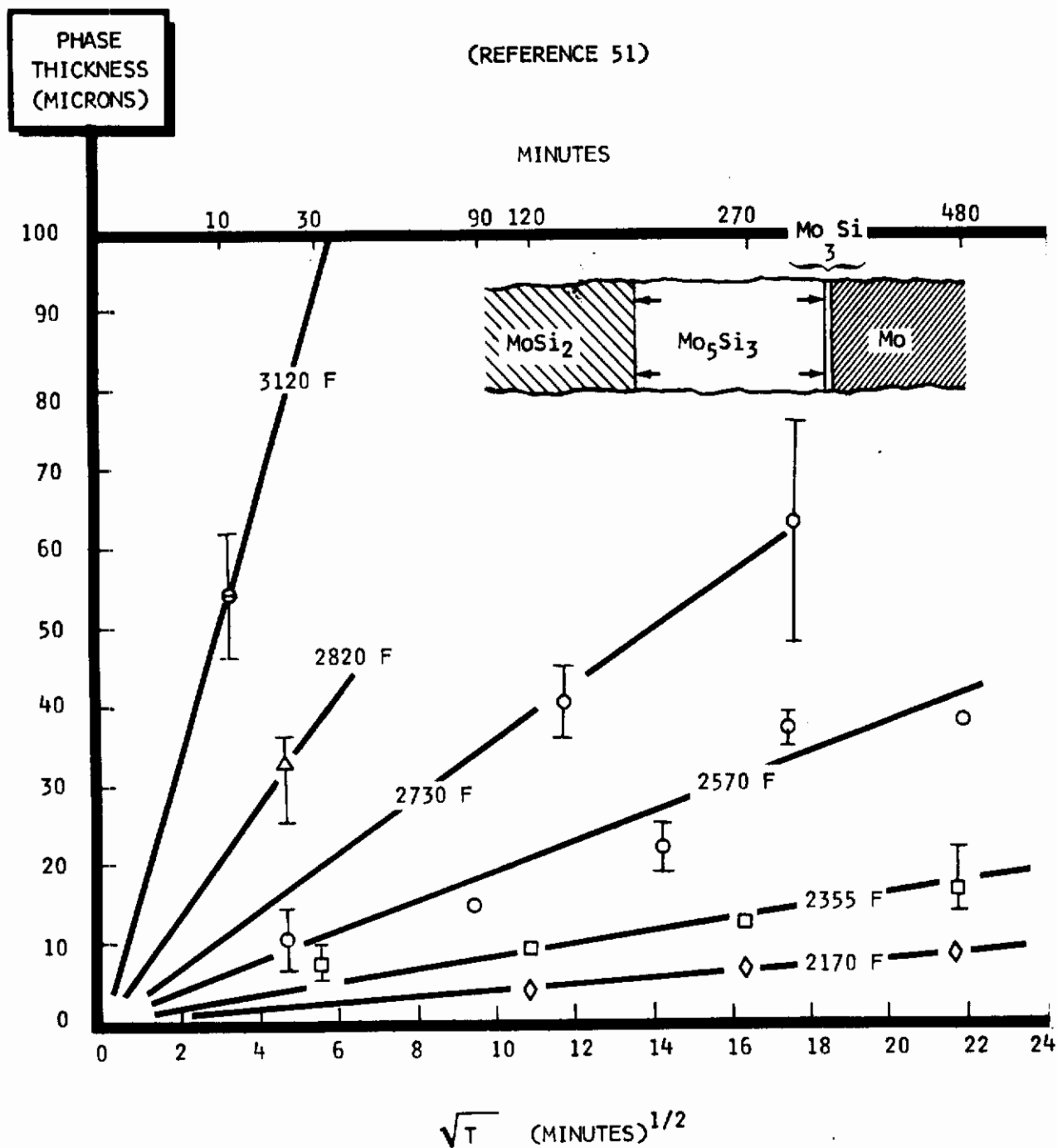
Figure 18.   Parabolic Growth of the Mo_5Si_3 Layer in the $MoSi_2$/Mo Coating System

is quite complex in structure and composition. Under these conditions, the SiO_2 film may become unstable. The chemical reactions and mechanisms that occur under these conditions are discussed by Bartlett (Reference 51). The effect of this pressure-temperature regime on coating composition and structure is quite complex, and the effect of this structure on emittance may be significant. The regions of characteristic oxide film grown on $MoSi_2$ are shown in figure 19, and data for low-pressure failures is shown in figure 20.

The emittance measurements performed on molybdenum-disilicide coatings have shown considerable scatter. Variation occurs not only between vendors, but between samples processed under identical conditions. Figure 21 is intended to demonstrate the variation obtained. Runs one and two were duplicate specimens, supposedly processed under identical conditions.

<u>SYLCOR R505F Sn-Al ON Ta-10W</u>

The structure of aluminide coatings has not been investigated to the extent of silicide coatings. The most recent and complete description of the coating composition and structure was supplied by the coating supplier and confirmed by microprobe and X-ray diffraction analyses at Philco. The slurry is composed of 27.5 percent by weight Al, 6.9 percent by weight Mo, the remainder being tin. The structure of the coating after processing has three distinct zones. The surface layer, approximately 2.7 mils thick, consists of a matrix of beta-tin with dispersed particles of $MoAl_3$ and aluminum. The $MoAl_3$ particles tend to concentrate on the surface. Surface X-ray analysis indicates 60 to 70 percent by weight $MoAl_3$. The second layer is predominantly $TaAl_3$, approximately one mil thick. A very thin layer of $TaAl_2$ exists at the metal-coating interface. The tungsten from the Ta-10W alloy is concentrated in the $TaAl_3$ and $TaAl_2$ phases. Little solid solubility of Al in Sn occurs (Reference 53).

When the coating is exposed to an oxidizing atmosphere at high temperatures, the aluminum will oxidize to form a protective Al_2O_3 layer. According to L. Sama (Reference 54), tin oxides are formed at temperatures below 2000°F. The stability of the tin oxides and molybdenum oxides, however, is somewhat questionable. Several tin oxides have been reported in the literature (Reference 53). However, the interaction of these oxides with the molybdenum oxide and aluminum oxide has not been investigated.

The low-pressure, high-temperature failure of the Sn-Al coatings has been related to the boiling point of tin. Preoxidation or addition of refractory materials such as molybdenum has not significantly improved low-pressure behavior.

The correlation of compositional changes with emittance behavior is a difficult task, due to the complicated nature of this coating. References

LOG ATM OXYGEN PRESSURE

(FROM REFERENCE 51)

*LOW-TEMPERATURE NONPROTECTIVE FILM (SOMETIMES REFERRED TO AS "SILICIDE PEST")
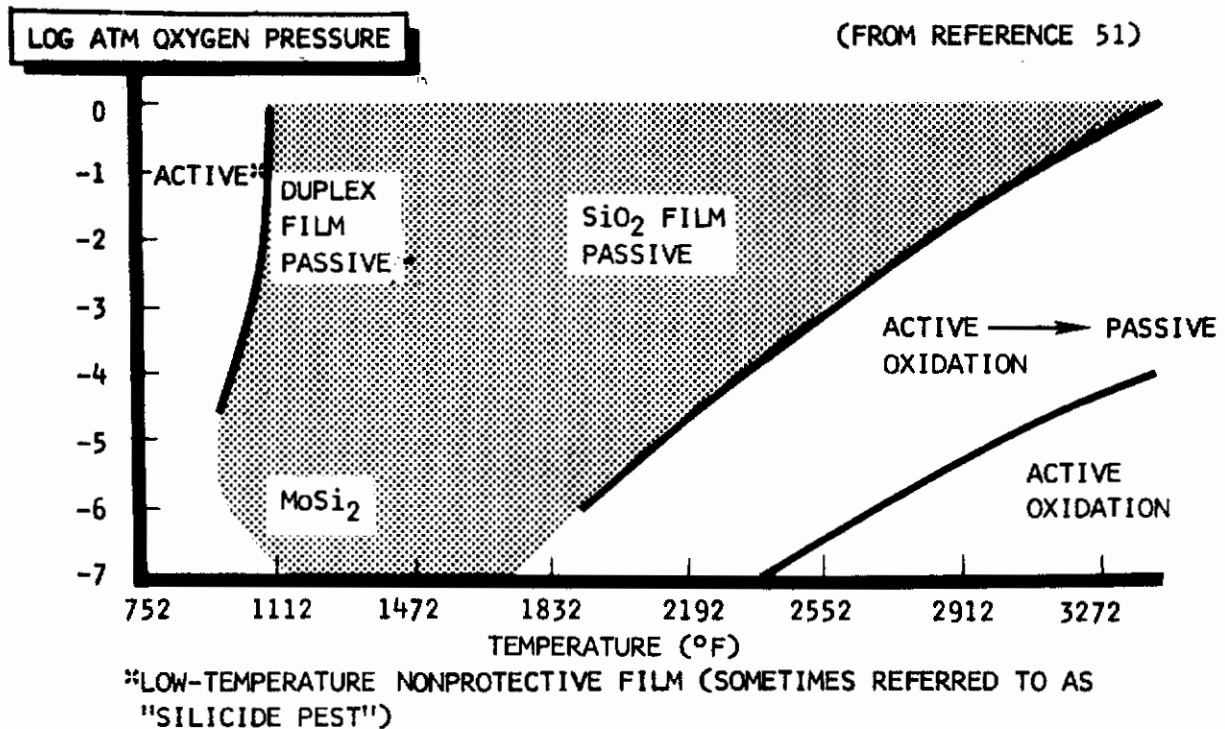
Figure 19.   Oxide Films Grown on $MoSi_2$

TEST PRESSURE, MM Hg

(FROM REFERENCE 52)

NOTE: TEMPERATURES ARE UNCORRECTED OPTICAL VALUES
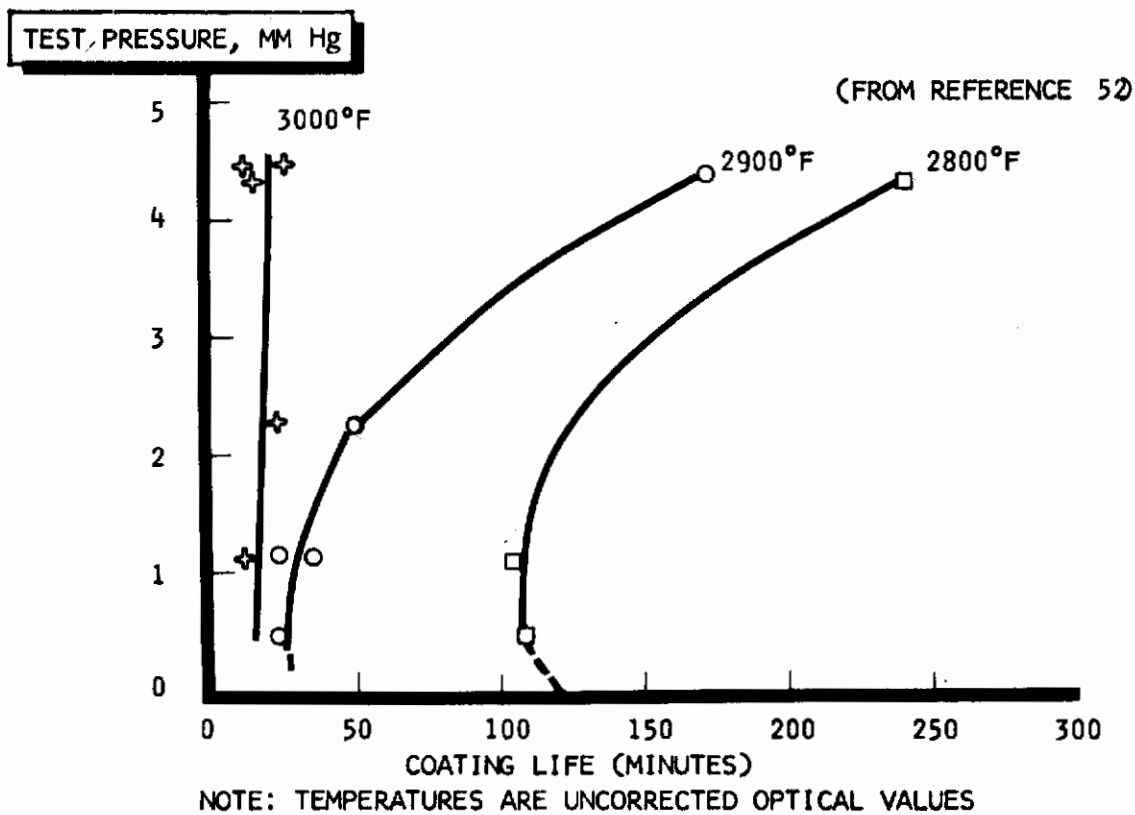
Figure 20.   Protective Life of W-3 Coating on Molybdenum in Low-pressure Oxidation Tests

VENDOR C = REF 51   ●   RUN NO. 1

— — — VENDOR B = REF 51   O   RUN NO. 2

□———□ VENDOR A = REF 54   ✖   RUN NO. 1

                                              △   RUN NO. 2

BASE METAL = Mo – 0.5 Ti
COATING = COMMERCIAL SILICIDE
DUPLICATE SPECIMENS
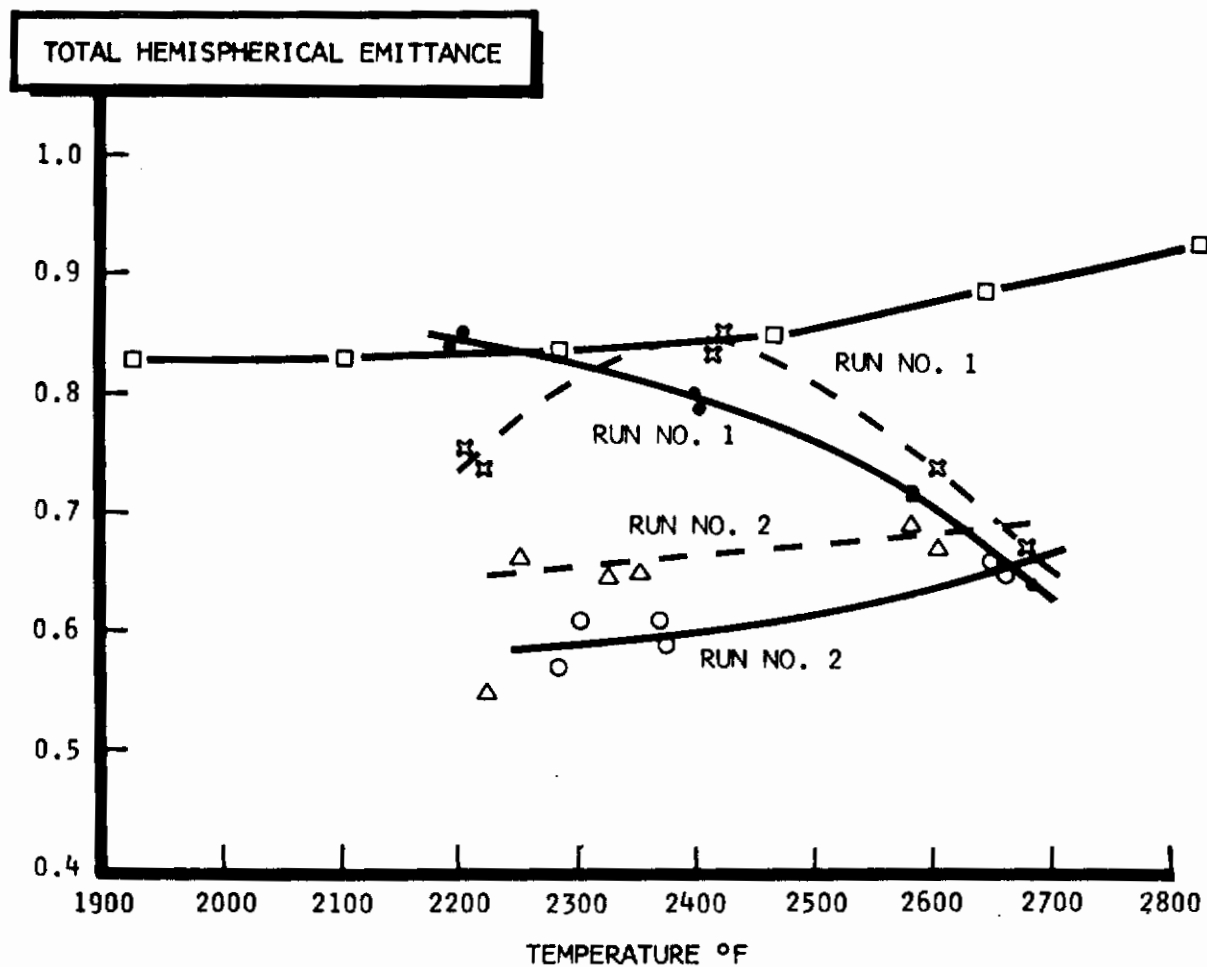
Figure 21. The Emittance of Molybdenum-Disilicide Coatings in Vacuum

to quantitative work agree that the emittance of the coating increases upon oxidation. Leggett el al. (Reference 55) report an increase of total normal emittance from 0.18 to 0.76 upon oxidation at 3200°F.

TRW COATING (Ti-Cr-Si) ON COLUMBIUM 752

The Ti-Cr-Si coatings are applied by a two-stage process. In the first stage, titanium and chromium are diffused into the substrate by a reduced pressure pack cementation process. The second stage is a reduced pressure cementation process for forming a silicide coating. The resulting structure is described in Reference 56. This structure consists of several diffusion zones. The surface layer is a disilicide of the type $(Cb,Cr,Ti...)Si_2$ which evidences several distinct phase boundaries representative of various concentrations of Cb,Cr, and Ti. Beneath the disilicide band are lower silicides of the type $(Cb,Cr,Ti...)_3Si_2$ and $(Cb,Cr,Ti...)_5Si_3$, and beneath this, a solid solution region comprised of Cr,Ti, and Si dissolved in the columbium matrix. Based on the examination of coatings applied to the similar D-43 alloy, when Cb-752 is used as the substrate, tungsten from the alloy substrate can be expected to be distributed throughout the coating phases, whereas the zirconium from the alloy is not expected to appreciably diffuse into the coating.

Test data included in Reference 56 shows that oxidation exposure at 1800°F of the Ti-Cr-Si coating did not significantly alter either the coating microstructure or the compositional profile across the Cr-Ti-Si alloy. On the surface, the composition is representative of an oxide-metal mixture, suggesting that only a thin superficial layer on the coating was converted completely to an oxide phase. The majority of the coating is still a disilicide, evidencing an increase in columbium and a decrease in chromium and titanium concentrations upon approaching the coating-substrate interface. It is also evident that the chromium and titanium are diffusing toward the surface of the coating to react with oxygen.

Reference 56 reveals, further, that on oxidation at 2500°F, the chromium in the Cr-Ti-Si coating migrates very rapidly to the coating surface, while titanium and columbium diffuse toward the surface at somewhat slower rates. After 4 hours at 2500°F, the surface oxides are basically Cr_2O_3 and TiO_2, with a subsurface silicate having formed adjacent to the disilicide phase. After 50 hours (one atmosphere), the majority of the chromium had evaporated from the coating, possibly as a result of both pure chromium and chromium oxide evaporation. The absence of Cr_2O_3 on the scale surface suggests the vaporization of the oxide. The oxides remaining on the coating surface after 50 hours are essentially SiO_2 and TiO_2 with a subsurface mixture of silica and possibly the complex oxide $TiO_2 \cdot Cb_2O_5$. Beneath the oxide scale is the remaining disilicide coating, which has been enriched with upwards of 15 percent by weight columbium. Lower silicide bands adjacent to the

substrates show evidence of having grown considerably in width. The substrate region beneath the silicide coating contains only silicon in solid solution, with all the chromium and titanium having diffused from the original substrate diffusion zone into the outer regions of the coating. The latter three observations characterize the failure mechanism of the coating. The $CbSi_2$ and lower silicide phases are considerably less oxidation-resistant than the originally formed chromium and titanium-rich disilicide, and the depletion of chromium and titanium from the substrate renders the system more susceptible to localized failure at coating cracks or fissures.

Tests reported in Reference 56 showed that the surface oxides remaining after 4 hours at 2700°F were basically TiO_2 and SiO_2. The oxides adjacent to the disilicide, on the other hand, were Cr_2O_3 and silica. At 2700°F, the vaporization rate of chromium (oxide) from the coating apparently exceeded the rate at which Cr could diffuse to the surface, leaving basically the oxides of silicon and titanium. The disilicide immediately adjacent to the oxide scale is a chromium-rich disilicide phase. At reduced pressures, silicon also vaporized from the coating as the volatile SiO phase, resulting in progressive recession of the coating surface. There was an absence of titanium and a low concentration of chromium in the substrate beneath the silicide, and also, the peak in the tungsten content was near the substrate-coating interface. The two coating constituents diffuse outward very rapidly at 2700°F, thereby, depleting the substrate. However, the reason for the peak in the tungsten concentration is not clear.

Section IX

PRELIMINARY EXPERIMENTS TO SHOW THE RELATIONSHIP BETWEEN COATING EMITTANCE,

COMPOSITION, AND ENVIRONMENT

BACKGROUND AND PURPOSE

Initial experiments were run in order to determine the variation in emittance values, chemistry, coating thickness, and surface roughness that would be encountered in typical batches of coated refractory metals. This series of tests was conducted as a prelude to other tests to be run in the ensuing phases of the program and served to orient the planning of the recommended comprehensive emittance program. (Refer to Section II.)

SPECIMEN PREPARATION

Disc specimens 0.975 (±0.015) inch in diameter by 0.020 (±0.001) inch thick, suitable for the emittance measurement specimen holders, were obtained from sheet stock. Cb-752 and Ta-10W discs were punched and the edges radiused with emery cloth on a lathe. TZM molybdenum discs were machined from the sheet stock in order to avoid laminations. The discs were electrolytically alkaline cleaned and pickled as shown in table IX.

The discs were inspected, weighed, measured for thickness and diameter, and sent out for coating as follows:

1. TZM molybdenum: W-3 coating, Chromalloy Division of Chromalloy Corp, West Nyack, New York

2. Cb-752 columbium: Cr-Ti-Si coating, TRW Equipment Laboratories, Thompson-Ramo Wooldridge, Inc, Cleveland, Ohio

3. Ta-10W tantalum alloy: Sn-Al coating, Sylcor Division, Sylvania Electric Products, Hicksville, New York

Table IX

PICKLING METHODS FOR SUBSTRATE METALS PRIOR TO COATING

1. TZM molybdenum

   Cleaner solution: 10 parts (by weight) NaOH
        5 parts (by weight) KMnO4
       85 parts (by weight) water

   180°F for ten minutes

   Pickle solution: 15 parts (by weight) HCl
       15 parts (by weight) H_2SO_4
       10 parts (by weight) CrO_3
       60 parts (by weight) water

   Room temperature for 10 minutes

2. Cb-752

   Pickle solution: 45 parts (by volume) HNO_3 (at 42° Bé)
        5 parts (by volume) HF (60 percent by weight, solution)
       50 parts (by volume) water

   Room temperature for one minute

3. Ta-10W

   Pickle solution: 50 parts (by volume) H_2SO_4 (66° Bé)
       25 parts (by volume) HNO_3 (42° Bé)
       25 parts (by volume) HF (60 percent, by weight, solution)

   Room temperature for one minute

The coated discs were inspected, weighed, and measured for thickness and surface roughness. These measurements are shown in tables X, XI, and XII, and visual inspection results of the parts are given in table XIII.

Table X

COATED MOLYBDENUM SPECIMENS

(TZM MOLY/CHROMALLOY SILICIDE)

Sample No.	Coating Thickness Per Face (Mils)	Total Coating Weight (mg)	Surface Roughness (Microinches)[1]		
			Low	High	Weighed Avg
M-1	1.2	78	22	33	26
M-3	1.3	64	20	36	26
M-4	1.2	76	24	36	30
M-5	1.3	82	24	33	27
M-6	1.3	77	22	33	27
M-7	1.15	72	21	30	24
M-8	1.3	61	21	28	24
M-10	1.25	79	23	34	28
M-11	1.3	75	22	36	28
M-12	1.3	81	20	33	24
M-14	1.35	80	24	37	29

NOTE:

(1) Measured on the face used for emittance measurements. Brush Surf-indicator, 0.030-inch cutoff. Four full passes 45 degrees apart.

Table XI

COATED COLUMBIUM SPECIMENS

(Cb-752/TRW Cr-Ti-Si)

Sample No.	Coating Thickness Per Face (Mils)	Total Coating Weight (mg)[2]	Surface Roughness (Microinches)[1]		
			Low	High	Weighed Avg
C- 1	3.1	345	40	63	53
C- 2	3.3	357	36	62	44
C- 3	3.2	350	37	60	45
C- 4	3.1	338	40	65	50
C- 5	3.2	361	35	53	40
C- 6	3.0	329	30	50	39
C- 7	3.1	345	39	74	53
C- 8	3.2	347	40	58	50
C- 9	3.2	339	43	70	58
C-10	2.9	325	38	60	47
C-11	3.0	324	34	55	40
C-12	3.3	350	30	50	38
C-13	3.4	351	32	55	37
C-14	3.3	341	35	60	45
C-15	3.3	326	33	65	45
C-16	2.9	336	40	75	52
C-17	3.3	357	28	50	36
C-18	3.1	342	35	55	46
C-19	3.2	346	35	60	46
C-20	2.8	307	38	60	44
C-21	3.2	359	32	55	42
C-22	3.1	346	30	65	43
C-0[3]	(Uncoated)	(Uncoated)	23	33	27

NOTES:

(1) Roughness measured on the face used for emittance measurements. Brush Surfindicator, 0.030-inch cutoff. Four full passes 45 degrees apart.

(2) Weight corrected for loss caused by grit blasting (40 mg) as determined with specimen No. 0. Since grit blasting may vary, coating weight is only approximate.

(3) Grit blasted, not coated.

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Table XII

COATED TANTALUM SPECIMENS

(Ta-10W/SYLCOR TIN ALUMINIDE)

Sample No.	Coating Thickness Per Face (Mils)	Total Coating Weight (mg)[3]	Surface Roughness (Microinches)[1]		
			Low	High	Weighed Avg
T-2	4.6	403	160	200	174
T-3	4.4	414	170	230	191
T-5	5.4	474	150	220	175
T-6	4.9	425	170	250	200
T-8	5.5	468	160	220	181
T-9	6.0	415	250	340	300
T-10	5.1	439	200	260	231
T-12	5.3	440	200	270	229
T-13	5.0	410	180	260	227
T-14	5.5	480	200	280	242
T-15	5.9	466	280	410	345
T-16	6.1	491	280	370	328
T-5[2]			200	300	249
T-9[2]			250	350	292

NOTES

(1) Measured on the face used for emittance measurements. Brush Surfindicator, 0.030-inch cutoff. Four full passes 45 degrees apart.

(2) Roughness remeasured after heating specimens to 2000°F.

(3) Weight corrected for loss from grit blasting (11 mg) as determined with one specimen. This may not be uniform, so coating weight should be considered approximate.

Table XIII

VISUAL INSPECTION OF AS-RECEIVED COATED SPECIMENS

1. Chromalloy W-3 Coated TZM

   Discs showed mottled surfaces with varying shades of color. All discs had circumferential cracks on the edges.

2. Cr-Ti-Si on Cb-752

   All specimens had split edges. Surface crazing was apparent at approximately 100 magnification.

3. Sn-Al on Ta-10W

   Considerable color variation from part to part. Grain size of surface structure varied from part to part (about 10 to 1 grain diameter ratio). No edge cracks.

TEST METHODS

The coated discs were examined in accordance with table XIV. Selected specimens were exposed to 1500°F and 2000°F temperatures in air and argon during measurement of the total normal emittance, and room-temperature spectral emittance and chemical composition determinations were made before and after exposure. Compositional analyses were performed by X-ray diffraction and electron microprobe X-ray techniques at Aeronutronic Division of Philco Corporation (Reference 57). These were, in general, only single sample tests intended to indicate trends in behavior of the coatings for future guidance.

SURFACE ROUGHNESS

Surface roughness of the as-coated specimens was determined with a Brush Surfindicator, using a 0.003-inch radius diamond stylus and the 0.030-inch cutoff setting. Passes were made at 45-degree spacings on the same surface used for emittance, electron microprobe, and X-ray diffraction determinations.

X-RAY DIFFRACTION

A General Electric, Model XRD-5, X-ray diffractometer, employing a copper k-alpha radiation source, was used in the X-ray diffraction analysis. The angular location and relative intensities of the peaks of the X-rays defracted from the specimen were recorded on a Leeds-Northrup strip-chart recorder. The recorder was calibrated as a function of the scanning angle in degrees. The estimated percent of each constituent of the specimen was obtained from the relative intensities of the peaks. The instrument settings and slit systems were identical for all samples.

Table XIV

TEST PROCEDURE FOR PHASE I EXPERIMENTS

Substrate	Cb-752					TZM Molybdenum					Ta-10W								
Coating	TRW Cr-Ti-Si					Chromalloy W-3					Sylcor Sn-Al								
Specimen No. (1)	C-1	C-5	C-9	C-2	C-3	M-1	M-7	M-10	M-4	M-5	T-10	T-8	T-13	T-2	T-3	T-14	T-15	T-12	T-16
As-received Room temperature spectral reflectance	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Profilometer measurements	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Microprobe analysis	X					X					X								
X-ray diffraction		X	X				X	X				X	X						
Total Normal Emittance																			
1500°F air		X							X					X					
2000°F air				X			X								X				
1500°F argon					X					X						X			
2000°F argon			X					X											X

Table XIV

TEST PROCEDURE FOR PHASE I EXPERIMENTS (CONT)

Substrate	Cb-752					TZM Molybdenum					Ta-10W								
Coating	TRW Cr-Ti-Si					Chromalloy W-3					Sylcor Sn-Al								
Specimen No. (1)	C-1	C-5	C-9	C-2	C-3	M-1	M-7	M-10	M-4	M-5	T-10	T-8	T-13	T-2	T-3	T-14	T-15	T-12	T-16
After Exposure																			
X-ray diffraction		X	X	X	X		X	X	X	X				X	X	X			X
Microprobe analysis		X					X								X				
Room temperature spectral reflectance		X	X	X	X		X	X	X	X				X	X	X	X	X	X

NOTE:

(1) Room temperature spectral reflectance and Profilometer measurements were made on 10 specimens of each coating material.

ELECTRON MICROPROBE X-RAY ANALYSIS

The samples were prepared for microprobe analysis by sectioning, mounting in an electrically conductive resin, and polishing using standard coated refractory metals metallography procedures. An ARL (Applied Research Laboratories, Inc, a subsidiary of Bausch and Lomb) electron microprobe X-ray analyzer was used for this analysis. The sample was placed in the microprobe and aligned so that the traverse was in a direction normal to the sample interface. The ARL microprobe was adjusted to scan three element channels simultaneously. Two lithium fluorides and an ADP (ammonium dihydrogen phosphate) monochromator were used to isolate the characteristic radiation. The intensity scales were adjusted using element standards so that 100 percent chart deflection represented pure components. Each reported element was step-scanned with a one-micron beam spot size. In most cases, one-micron or 2-micron steps were taken and traverses were made at several locations. At each step, the instrument acceleration voltage was held constant and integration of the fluorescent radiation was made against the sample current so that the results would be semiquantitative. The results are presented in relative intensity as recorded from the microprobe. This corresponds to the approximate weight percentage. The only correction attempted was for background.

Projections of both the electron backscatter images, sample current images, and characteristic X-ray images on an oscilloscope were used to locate and identify inclusions and dispersed phases.

ROOM-TEMPERATURE EMITTANCE MEASUREMENT

Hohlraum Apparatus

The room-temperature spectral emittance data was inferred from reflectance values obtained from a Hohlraum-type reflectance apparatus, figure 22. This type of measurement, developed by Gier, Dunkle, and Bevans (Reference 58) yields a reflectance value which can be used to obtain the spectral emittance of opaque specimens by difference:

$$\epsilon_\lambda = 1 - \rho_\lambda \tag{16}$$

The equipment used consists of a Model 13-U Perkin-Elmer double-beam spectrophotometer which measures and records the radiant energy in the 2- to 25-micron wavelength region (Reference 59).
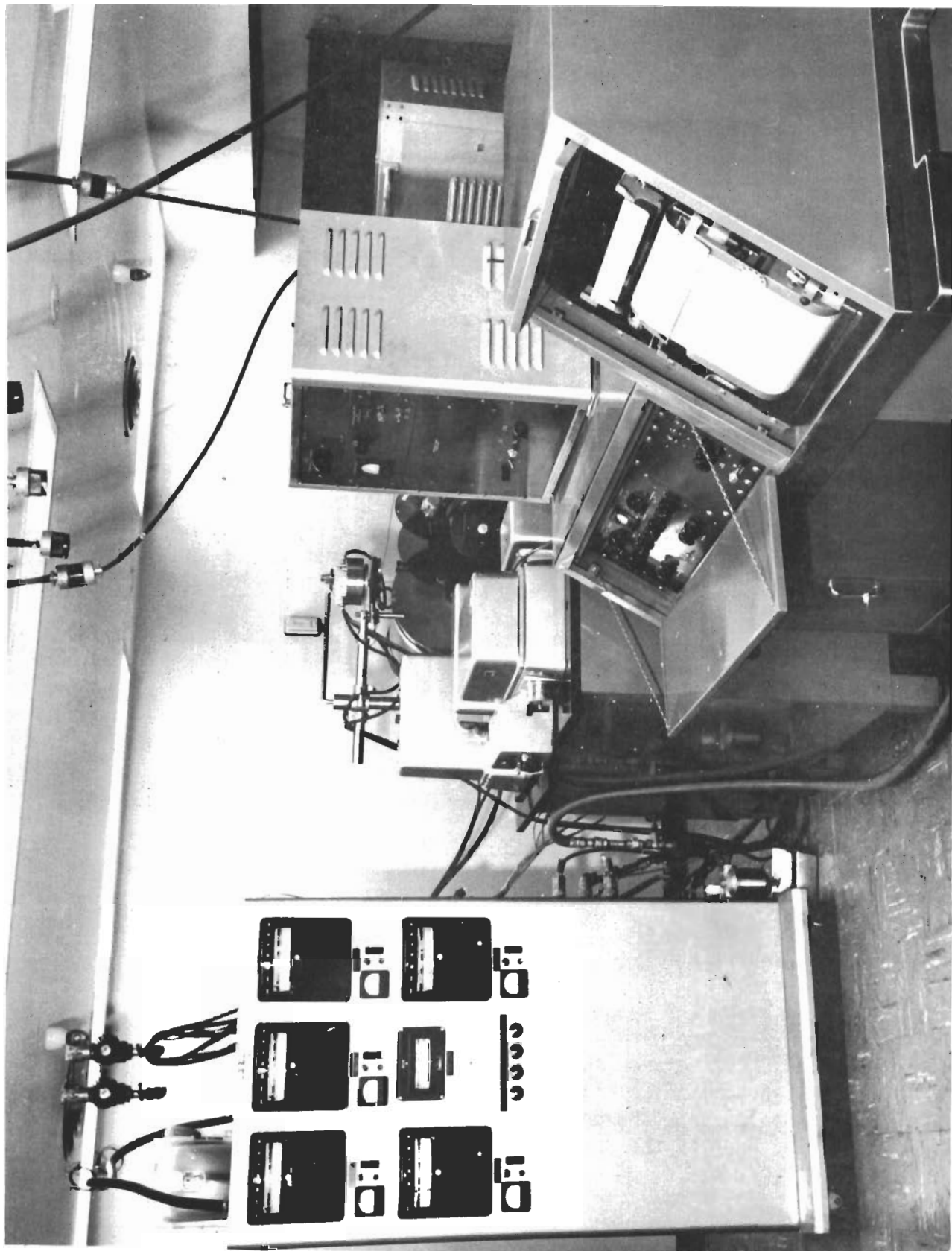
Figure 22. Perkin-Elmer Spectrophotometer With Hohlraum Reflectance Attachment

The original Nernst-Glower source compartment is circumvented and the Hohlraum cavity is mounted behind the instrument. Auxiliary mirrors bring the two new beams to focus at the original sample positions. The beam geometry of the basic spectrophotometer has been retained, insofar as possible, in order to minimize errors. A secondary chopper with a larger diameter blade was used, and two aperture stops were added to prevent stray radiation. The new chopper was modified from a stock assembly of the same type as the original, in order to assure minimum error in phasing and beam balance and to permit the use of standard Perkin-Elmer checkout and adjustment of the chopper components.

The specimen, cooled from the rear by circulating water, is inserted into an oven so that the specimen surface is flush with the rear wall of the oven. The other walls of the oven irradiate the specimen in a hemispherical fashion, and the energy is reflected from the surface of the specimen. One beam of the double-beam spectrophotometer is focused on the specimen and the other beam is focused on the hot rear wall of the oven. The oven cavity is mounted concentrically to its axis so that it can be rotated 90 degrees to permit obtaining a 100 percent reference line by viewing two portions of the hot rear wall of the cavity. The cavity is then rotated back into the sample position, and since the specimen is very cold compared with the cavity temperature, its self-emission is insignificant, and the instrument measures only the sample reflectance. The ratio of the energies in the two beams, as recorded by the spectrophotometer, is then proportional to the Hohlraum reflectance.

The actual reflectance value is calculated at each wavelength by the following divisions:

$$\rho_\lambda = \frac{\text{Distance from zero line to specimen line}}{\text{Distance from zero line to 100 percent line}} \tag{17}$$

Beckman DK-2

A Beckman DK-2 spectroreflectometer which has been modified to obtain absolute reflectance values (Reference 60) was used to measure the room-temperature reflectance in the 0.5- to 2.5-micron region. This instrument uses a magnesium-oxide-coated integrating sphere which has a diffusing screen to eliminate the dependence of the specimen reflectance values on the reflectance of the sphere coating.

TOTAL NORMAL EMITTANCE MEASUREMENT AND SPECIMEN EXPOSURE

The total normal emittance values presented in this report were obtained by the sliding specimen technique, References 61 and 62. The basic principle of this technique is illustrated in figure 23 where a cylindrical blackbody with a specimen mounted internally on a sliding push rod is viewed by a radiometer. The radiometer alternately measures the radiant flux emanating first from the blackbody cavity and then from the surface of the specimen which is moved rapidly to the forward position, thus blocking the energy radiated from the cavity.

The cylindrical susceptor cavity, which has a sufficient length-to-diameter ratio for its wall emittance and configuration to provide an effective blackbody (Reference 13) is heated by a high-frequency induction coil to the desired test temperature. Temperature gradients in the susceptor are minimized by adjusting the coil spacing to provide a uniform isothermal wall along the length of the cavity. A water-cooled aperture is provided at the front of the cavity to prevent spurious radiation from entering the detector optical path. If the aperture were not used when the specimen is positioned at the front of the cavity during test runs, energy from some portion of the furnace might be diffusely reflected from the front of the specimen into the detector system, thereby producing an erroneously high signal. The energy emanating from the aperture at a near normal angle is collected by the optical system and focused onto the detector. A filter may be placed in front of the detector to provide broad band-pass measurements.

The specimen is mounted on a suitable push rod and positioned in the cavity through the rear of the susceptor. In the cavity, the specimen is uniformly heated by radiation from the hot walls of the cylinder to an equilibrium temperature which is the same as that of the inner cavity surfaces. When the specimen has reached the equilibrium temperature, a blackbody emittance value is obtained by reading the total energy radiated from the cavity and setting the detector output to a convenient location on the recorder. The actual distance between the detector zero line and the blackbody energy reading then will correspond to 100 percent emittance. Figure 24 shows a typical energy trace. With the specimen at the rear of the cavity (position A), the energy is at the blackbody energy level. As the specimen is moved rapidly forward (position B), the energy emanating from the aperture decreases until the instant the specimen reaches the front of the cavity (position C). The specimen is held in the forward or test position for several seconds, during which time, the energy level decreases at a slower rate as a result of specimen cooling. The specimen is then moved to the back of the cavity to prepare for subsequent runs. The knee in the
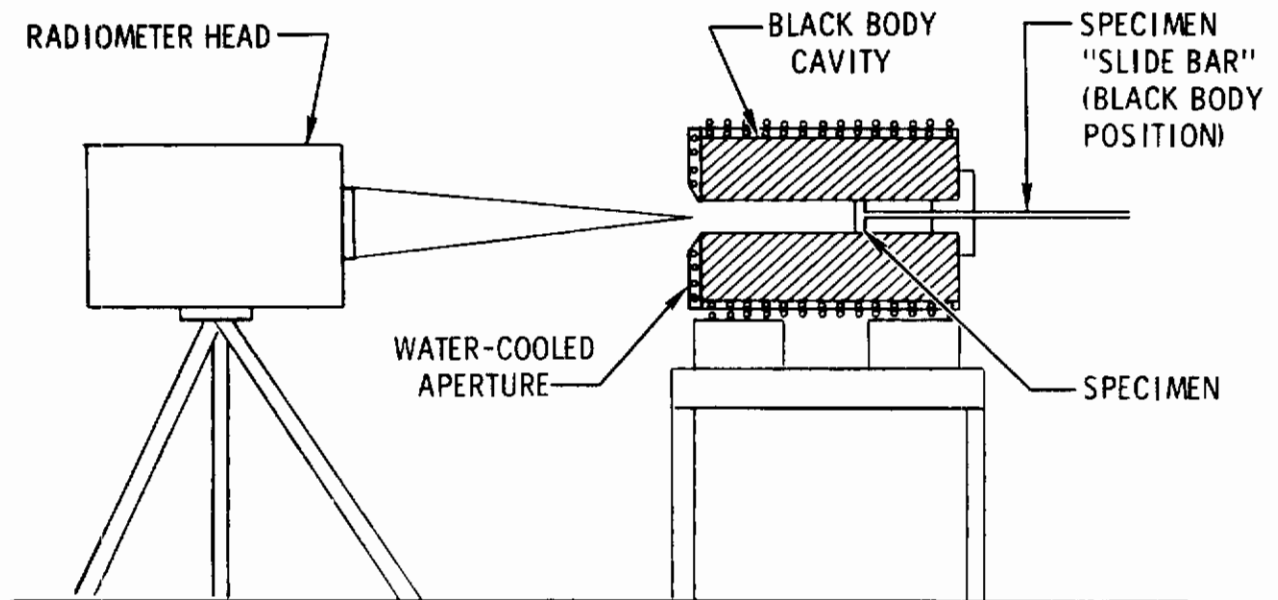
Figure 23. Principle of Sliding Specimen Emittance Measurement Apparatus
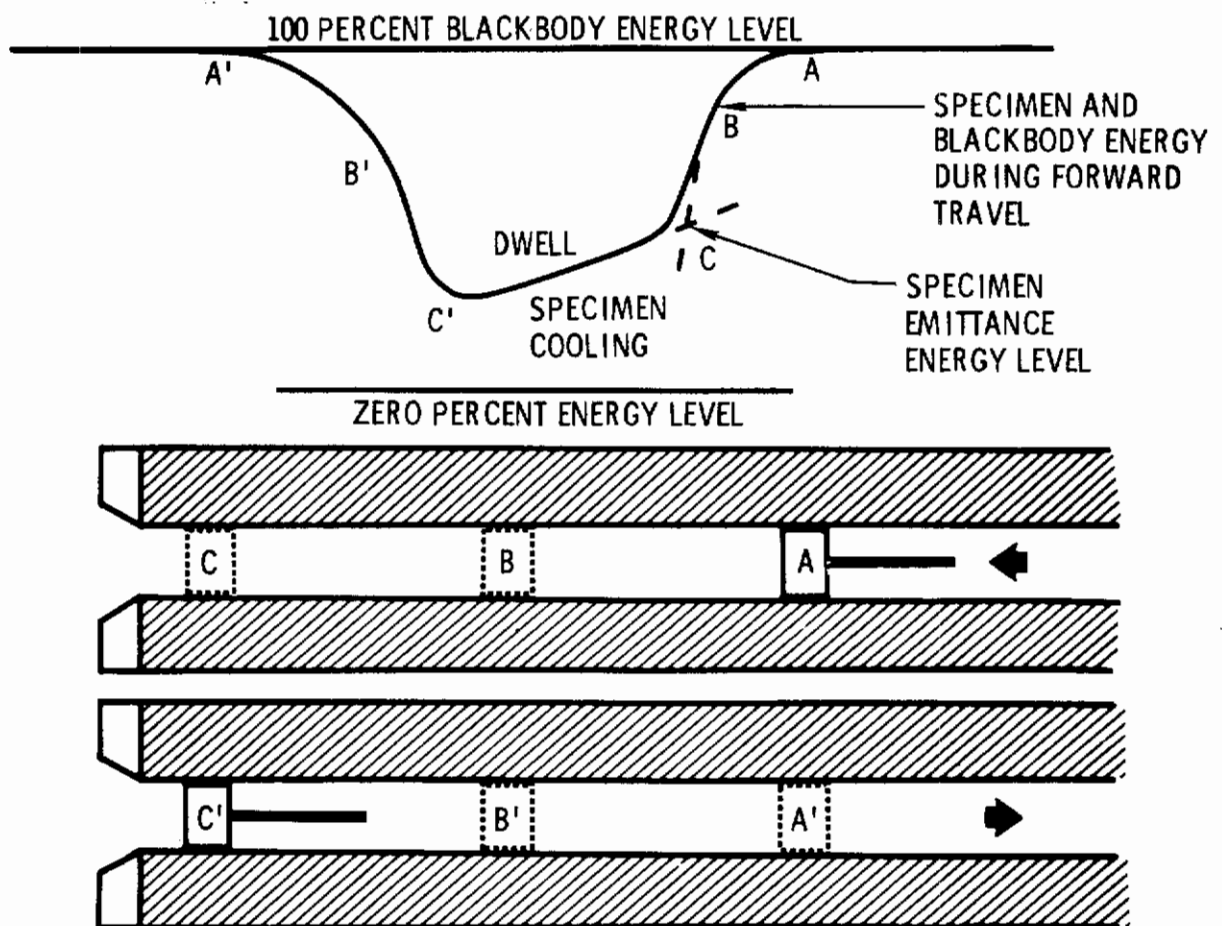
Figure 24. Typical Energy Trace for Push-Pull Emittance Apparatus

curve at position C is the point at which the energy emitted corresponds
to that of the specimen at the test temperature. The emittance is the ratio
of the specimen energy level at position C to the blackbody energy level
at position A expressed as a decimal value.

The main advantage of the sliding specimen apparatus is that the temp-
erature of the sample need not be measured directly by a thermocouple with
the usual attendant thermocouple problems. With the specimen located deep
inside the isothermal cylindrical blackbody cavity, the temperature of the
specimen reaches and is maintained at the cavity temperature. The determi-
nation of the blackbody cavity temperature (which is also the sample temp-
erature) can be made by using a conventional optical pyrometer. The temp-
erature of the cavity can be measured to within 10°F with the pyrometer by
a practical observer. This error is negligible, since the specimen is at
the same temperature as the cavity and emittance values are normally a very
weak function of temperature for small changes in absolute temperature.

For the measurement of total normal emittance in an air atmosphere,
the cavity is open to ambient room air. In the performance of the total
normal emittance test in argon, the cavity was enclosed in a thin-wall,
stainless-steel tube which was water cooled at both ends. The cavity was
viewed through a KBr window which was attached to the front end of the
water-cooled tube by an O-ring seal. The handle of the push rod passed
through a water-cooled Teflon sliding seal at the rear of the chamber. To
assure that the argon was clean and had no oxygen present, it was passed
through an argon train which consisted of a dehumidifier, a titanium chip
furnace, and a tube with molecular sieve material. The argon was fed into
the front of the chamber, passed through the cylindrical blackbody cavity,
and exhausted out of a restricted tube in the rear of the chamber. To faci-
litate in the initial purge of the chamber, a low-capacity, vacuum-roughing
pump was used and the chamber pressure alternated. During test runs, the
chamber was kept at a slight positive pressure of about one inch of mercury.

TEST RESULTS

CORRELATION OF ROOM-TEMPERATURE AND ELEVATED-TEMPERATURE EMITTANCE VALUES

The room-temperature spectral emittance curves of the 2000°F air-
exposed specimens of the three coatings were integrated over the energy
distribution of a 2000°F blackbody. The values obtained agree closely with
the total normal emittance values of these specimens determined at 2000°F.
Correlation was within 0.005 for each coating, as shown in the following:

	W-3 Coating	Cr-Ti-Si Coating	Sn-Al Coating
ϵ_N - Measured at 2000°F	0.75	0.80	0.82
ϵ_N - Integrated room-temperature spectral emittance	0.745	0.796	0.825

This correlation indicates that emittance values inferred from room-tempera-
ture reflectance measurements are useful for trend studies of these coat-
ings up to 2000°F.

SURFACE-FINISH/EMITTANCE CORRELATION

Surface roughness measurements of the as-received specimens are given
in tables X, XI, and XII.

The chromalloy W-3 coated TZM discs show a relative smooth surface
with little variation from part-to-part within the batch of 11 specimens
(6-microinch variation between the average reading for the maximum and mini-
mum roughness). Figure 25 shows the envelope of spectral emittance values
for the as-received W-2 coated TZM specimens. The envelope represents the
extreme values of emittance over the 0.5- to 20.0-micron range, within
which the emittance values of the individual specimens lie. Thus, the as-
received (nonexposed) specimens show an average emittance variation of about
0.05 and a maximum variation of 0.15 for the group of 11 parts. Because of
the small variation in surface roughness, this emittance variation is attri-
buted primarily to factors other than surface roughness.

The TRW Cr-Ti-Si coated Cb-752 specimens also show only minor varia-
tions in surface roughness of the as-coated parts. For the group of 22
specimens, the maximum average roughness is 58 microinches and the minimum
roughness 36 microinches. Figure 26 shows the envelope of spectral emit-
tance values of 10 specimens which were measured in the as-coated condition.
The average maximum variation of emittance is about 0.07, slightly more
than the W-3 coated molybdenum parts. Contrary to what might be expected,
the lower emittance curve of figure 26 is defined principally by specimen
No. C-9, which has the highest surface roughness of the group, and the
upper boundary is principally defined by specimen No. C-5, which has com-
paratively low surface roughness. However, it is expected that the small
variation in roughness within this group of specimens is of minor signifi-
cance with respect to emittance variation.

The Sylcor Sn-Al coated Ta-10W parts had comparatively high surface
roughness and high variation from part-to-part and around the same part.
Average roughness varied from 174 to 345 microinches within the group of 12

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BASE METAL:		TZM molybdenum
COATING SYSTEM	TYPE:	W-3 silicide
	APPLIED BY:	Chromalloy
	THICKNESS:	1.15 to 1.35 mils per face
	WEIGHT:	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

As-coated condition. Emittance determined from room temperature reflectance data.
11 specimens

Figure 25. Envelope of Emittance Variation of Chromalloy W-3 Coated TZM

BASE METAL:		Cb-752 Columbium
COATING SYSTEM	TYPE:	Cr-Ti-Si
	APPLIED BY:	TRW
	THICKNESS:	2.8 to 3.4 mils per face
	WEIGHT:	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

As-coated condition. Emittance determined from room temperature reflectance data. 10 specimens.

Figure 26. Envelope of Emittance Variation of TRW Cr-Ti-Si Coating on Cb-752

as-coated specimens. Figure 27 shows the envelope of spectral emittance values for these specimens. The emittance spread varies from 0.08 at the short wavelengths up to 0.27 at longer wavelengths. No clear-cut correlation of total emittance and surface roughness was evident from this group of specimens. Although there was a significant roughness spread, there were insufficient data points in the high roughness range. Some tendency toward correlation was obtained by comparing roughness and spectral emittance. Figure 28 shows the effect of roughness on emittance at 2 and 15 microns. There appears to be a tendency of emittance to increase with roughness in the low wavelength range, and the opposite effect to occur at the higher wavelengths. A greater number of specimens as well as improved surface characterization are required to more clearly correlate emittance and sur-face factors.

EFFECT OF ENVIRONMENTAL EXPOSURE

Chromalloy W-3 Coated TZM Molybdenum

Figures 29 and 30 show the effect upon spectral emittance of exposure in argon at 1500°F for 65 minutes, and 2000°F for 50 minutes, respectively. These single sample tests show an increase in emittance of about 0.10 be-tween 3 and 5 microns for the 1500°F exposure (specimen M-5), and a slight decrease of emittance above 5 microns wavelength for the 2000°F exposure (specimen M-10). Table XV presents the X-ray diffraction surface analyses of the coated molybdenum specimens before and after exposure. The 2000°F argon-exposed sample (M-10) shows only a transition of the minor constit-uent MoB from the delta to the beta phase. This is consistent with the low diffusion reaction rates expected at this temperature, as indicated by figure 18 (Bartlett, Reference 51).

Figures 31 and 32 show the effect upon spectral emittance of exposure in air at 1500°F for 48 minutes, and 2000°F for 42 minutes. It is seen that the emittance increases upon exposure, and this increase appears to be more pronounced at selected wavelengths and higher temperatures. Figure 33 shows the composition of an as-coated specimen, and figure 34 shows the structure of 2000°F-air specimen after exposure as determined by electron microprobe X-ray analysis. No significant compositional changes are shown to have occurred other than a small growth of the lower silicide layer at the substrate-coating interface. X-ray diffraction results (table XV) indicate the formation of 2 to 5 percent MoO_2 on the surface of the 2000°F-air specimen.

BASE METAL:		Ta-10W
COATING SYSTEM	TYPE:	Sn-Al
	APPLIED BY:	Sylcor
	THICKNESS:	4.4 to 6.1 mils per face
	WEIGHT:	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

As-coated condition. Emittance determined from room-temperature reflectance data. 12 specimens.
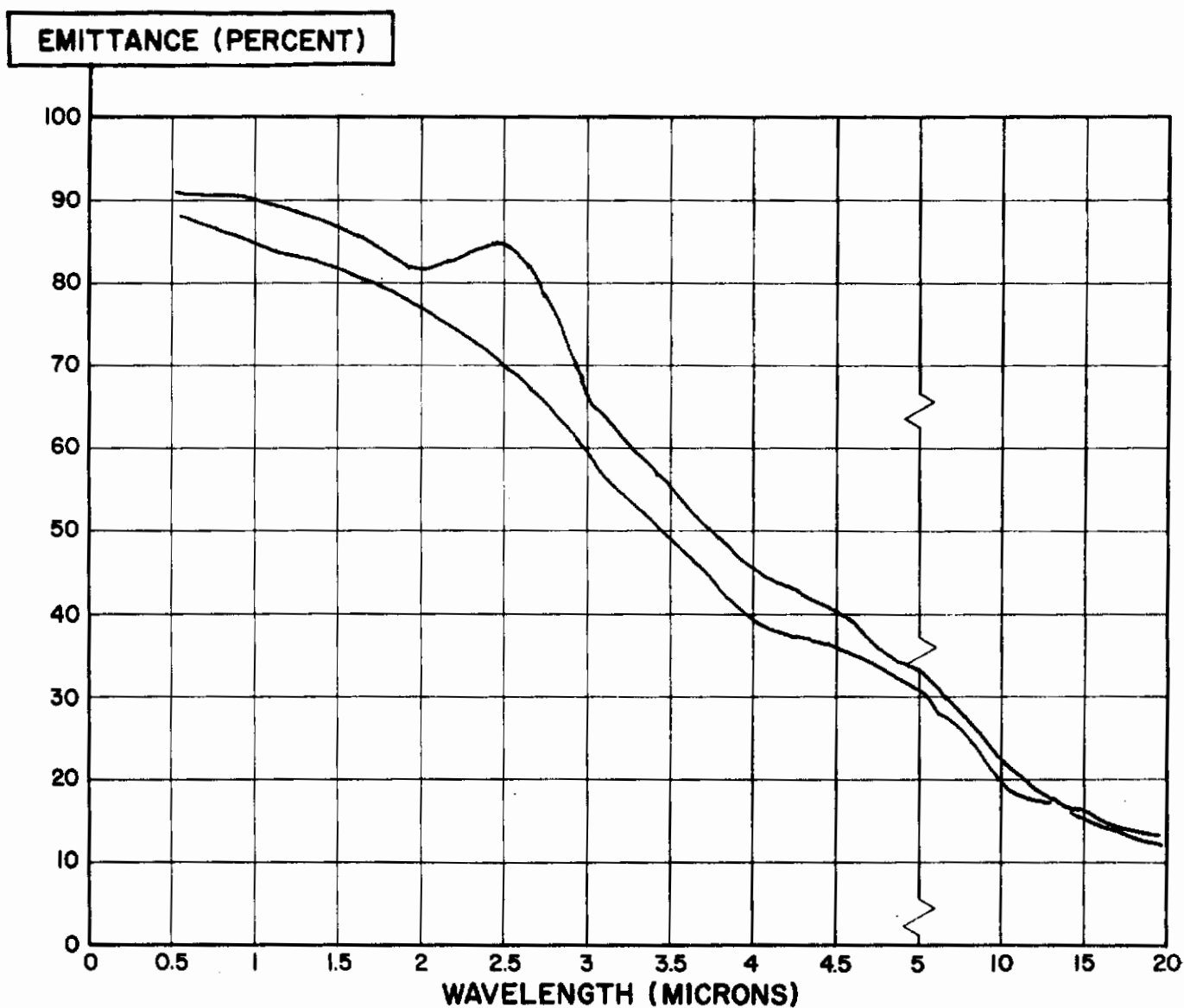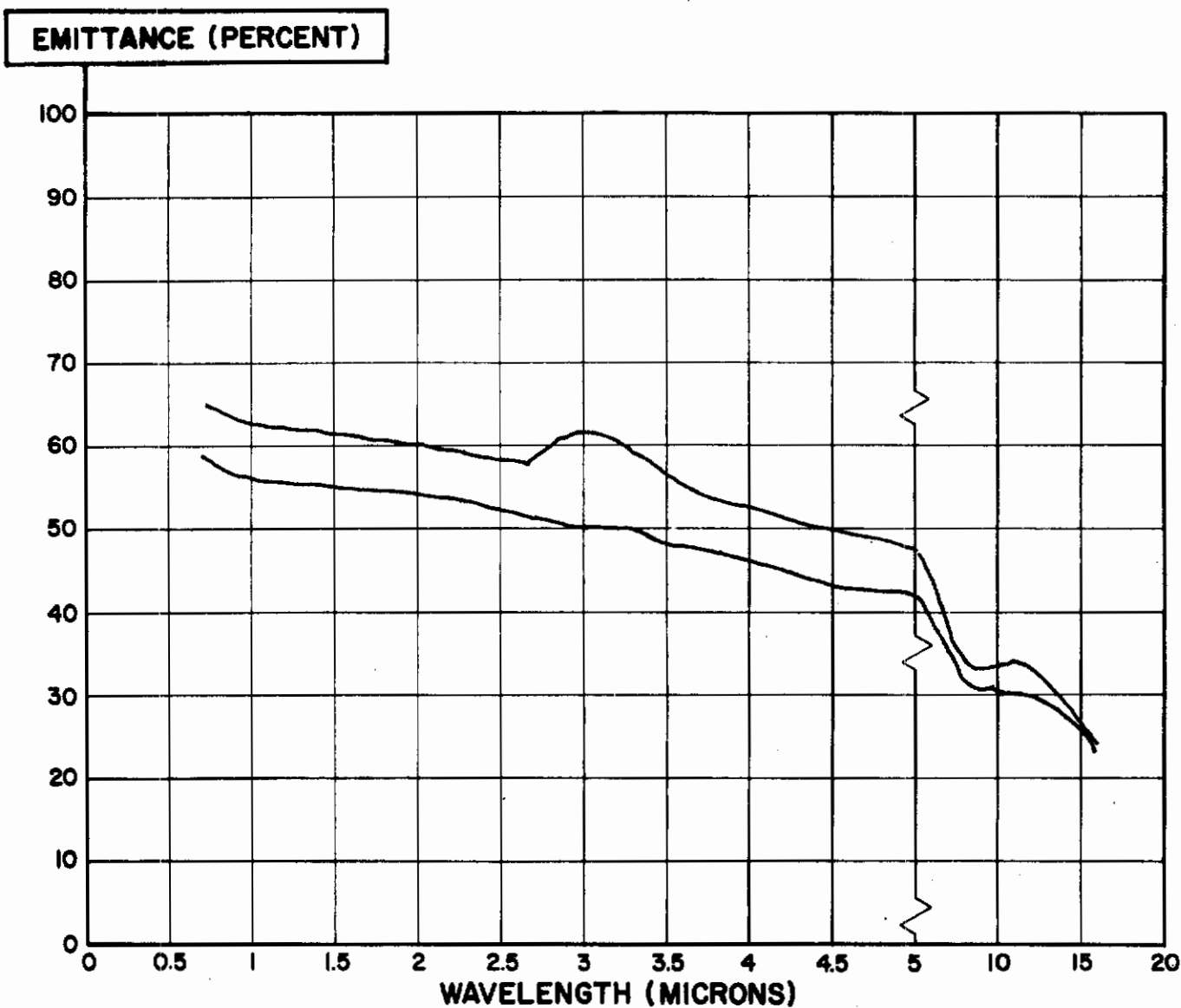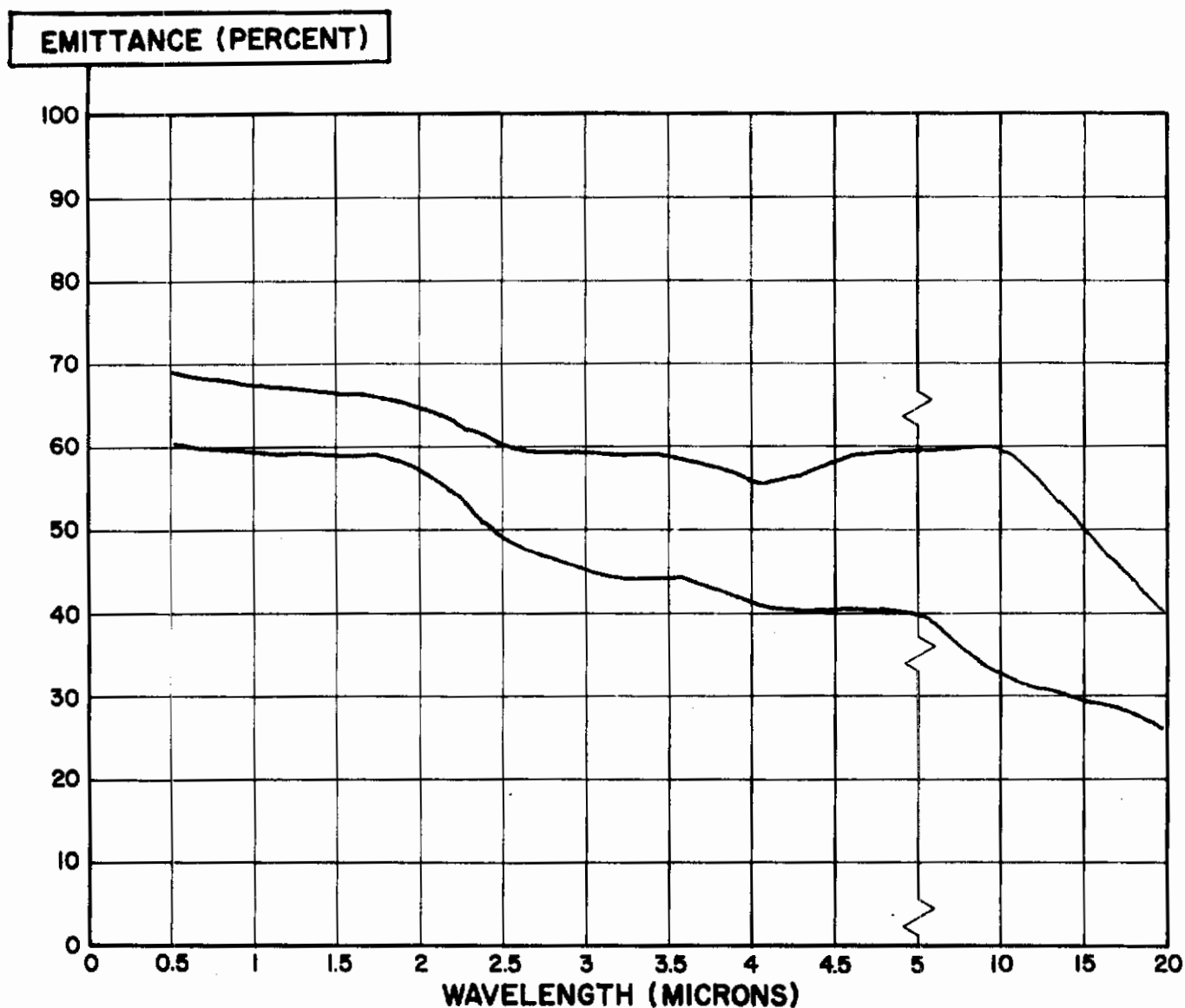

Figure 27. Envelope of Emittance Variation of Tin-Aluminum Coated Ta-10W Specimens

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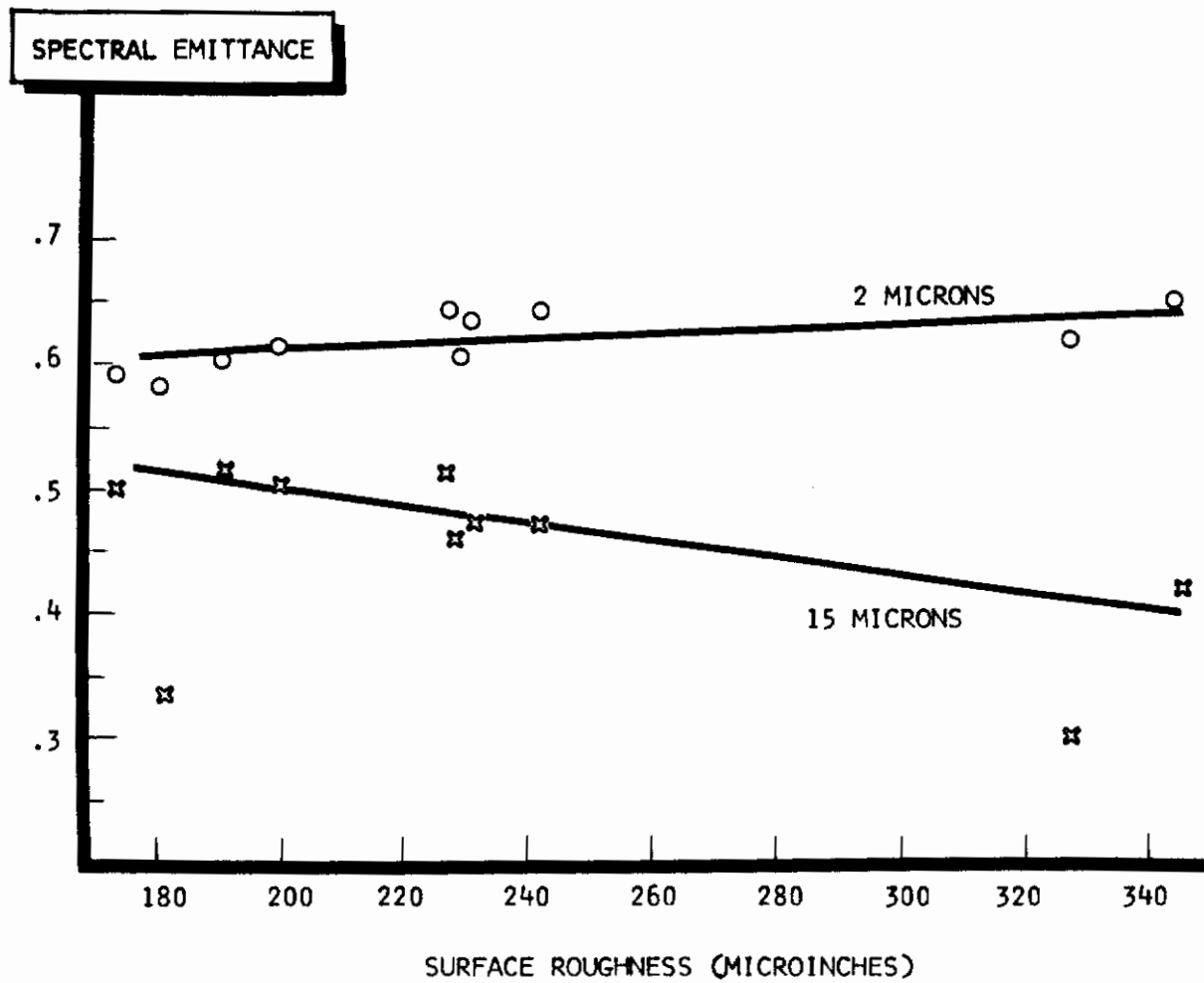
Figure 28. Effect of Surface Roughness on Spectral Emittance of Sn-Al Coated Ta-10W

BASE METAL:		TZM Molybdenum (Specimen M-5)
COATING SYSTEM	TYPE:	Chromalloy W-3 Silicide
	APPLIED BY:	Pack
	THICKNESS:	1-3 mils per face
	WEIGHT:	82 mg

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

        a. As received

        b. After 65 minutes exposure at 1500°F in argon

Emittance determined from room temperature reflectance data
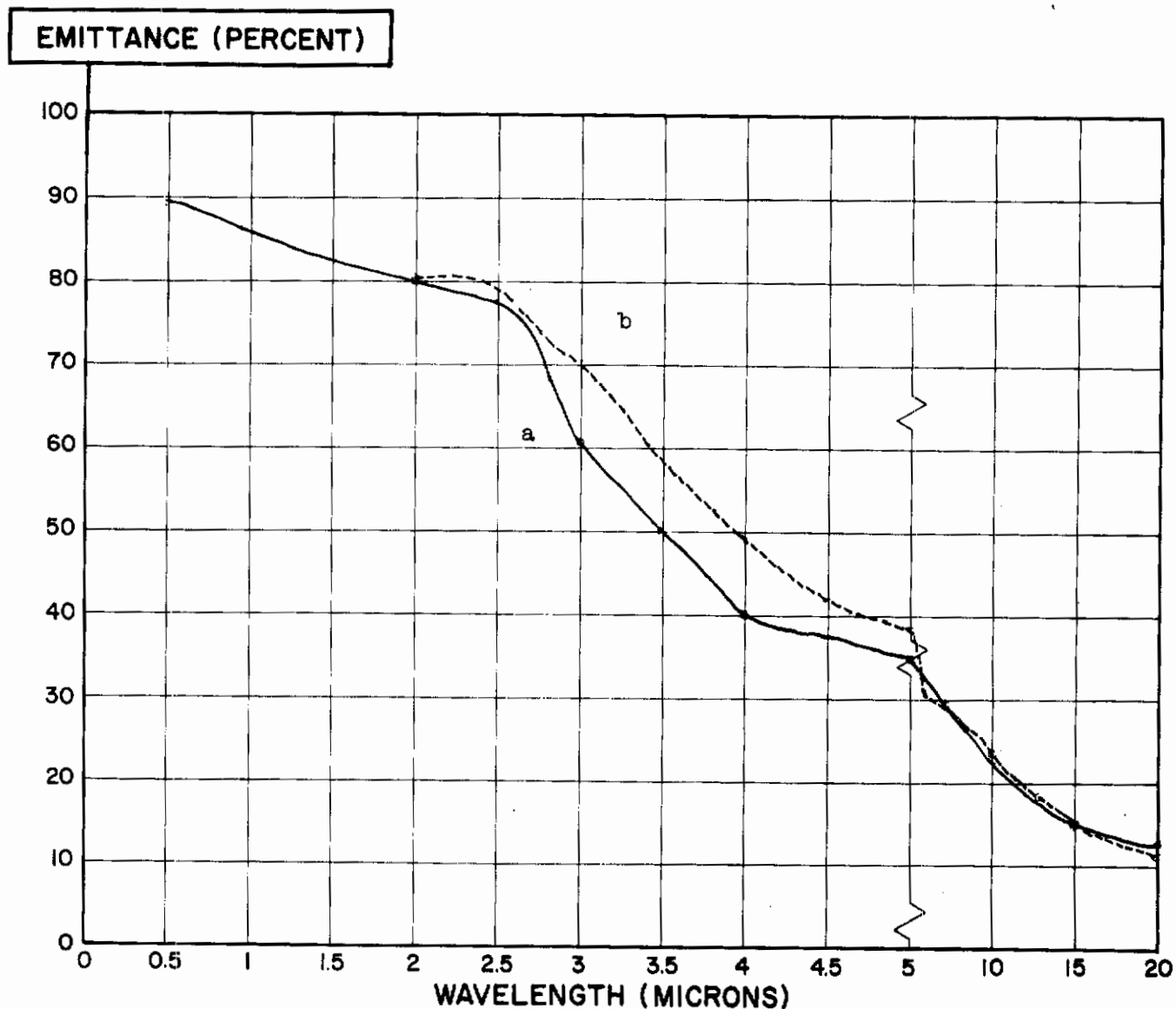
Figure   29.   Effect of 1500°F Exposure in Argon on the Spectral
Emittance of Chromalloy W-3 Coated Molybdenum

BASE METAL:		TZM Molybdenum (Specimen M-10)
COATING SYSTEM	TYPE:	Chromalloy W-3 Silicide
	APPLIED BY:	Pack
	THICKNESS:	1.25 mils per face
	WEIGHT:	79 mg

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

a. As-received

b. After 50 minutes exposure at 2000°F in argon

Emittance determined from room temperature reflectance data

EMITTANCE (PERCENT)

WAVELENGTH (MICRONS)
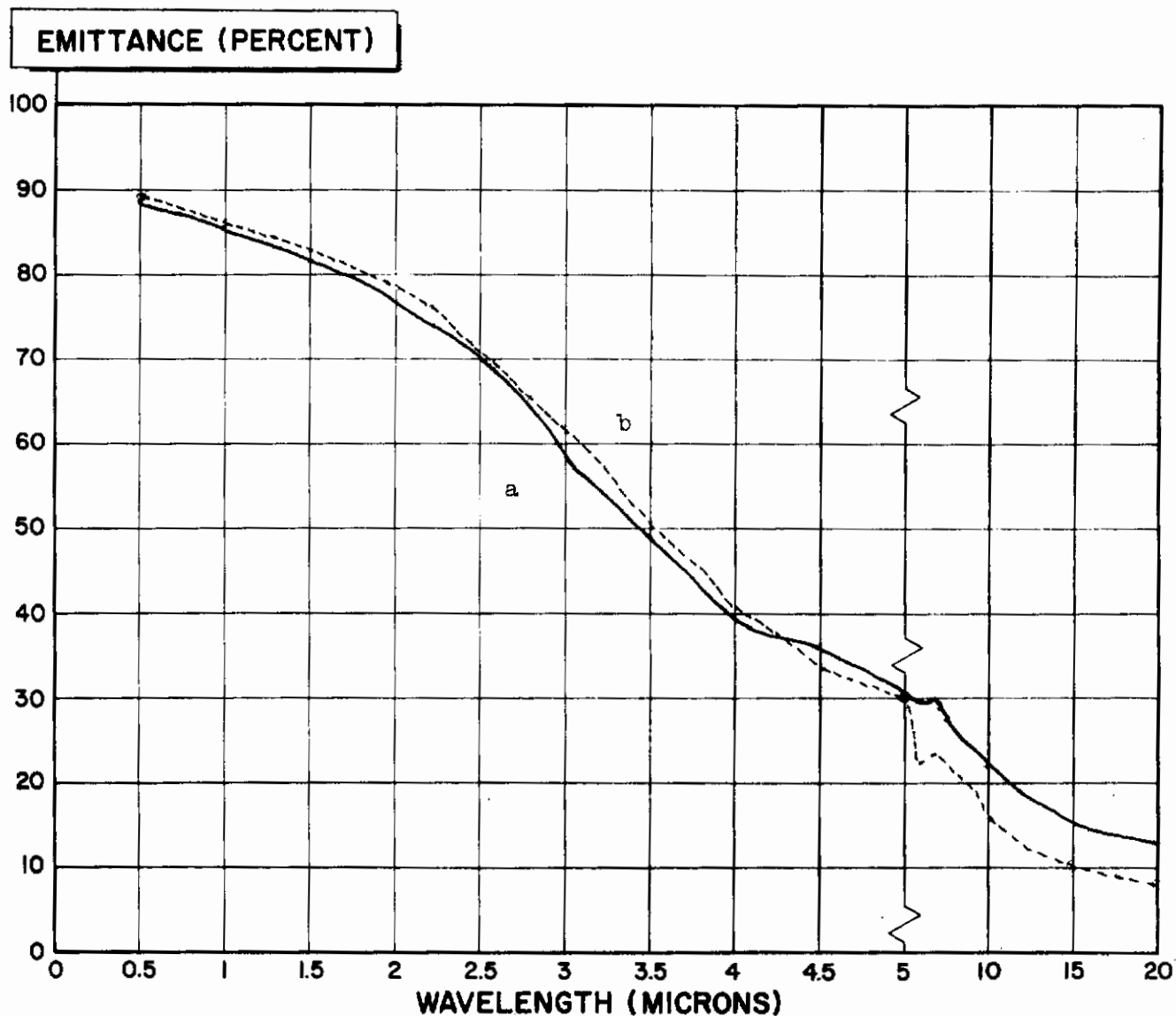
Figure 30. Effect of 2000°F Exposure in Argon on the Spectral Emittance of Chromalloy W-3 Coated Molybdenum

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Table XV

X-RAY DIFFRACTION RESULTS OF CHROMALLOY W-3

Coated TZM

Sample No.	Condition	Chemical Compounds and Estimated Relative Quantity (Weight Percent)			
		$MoSi_2$	β MoB	MoO_2	Other
M-10	As-received	90-95	2-5		2-5 percent δ MoB
M-7	As-received	95	5		
M-5	After exposure: 1500°F argon	95	5		
M-10	After exposure: 2000°F argon	95	5		
M-4	After exposure: 1500°F air	95	5		
M-7	After exposure: 2000°F air	95		2-5	Possibly low percent Mo_2B

BASE METAL:		TZM Molybdenum (Specimen M-4)	
COATING SYSTEM	TYPE:	Chromalloy W-3 Silicide	
	APPLIED BY:	Pack	
	THICKNESS:	1.2 mils per face	
	WEIGHT:	76 mg	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

    a. As received

    b. After 48 minutes exposure at 1500°F in air

Emittance determined from room temperature reflectance data
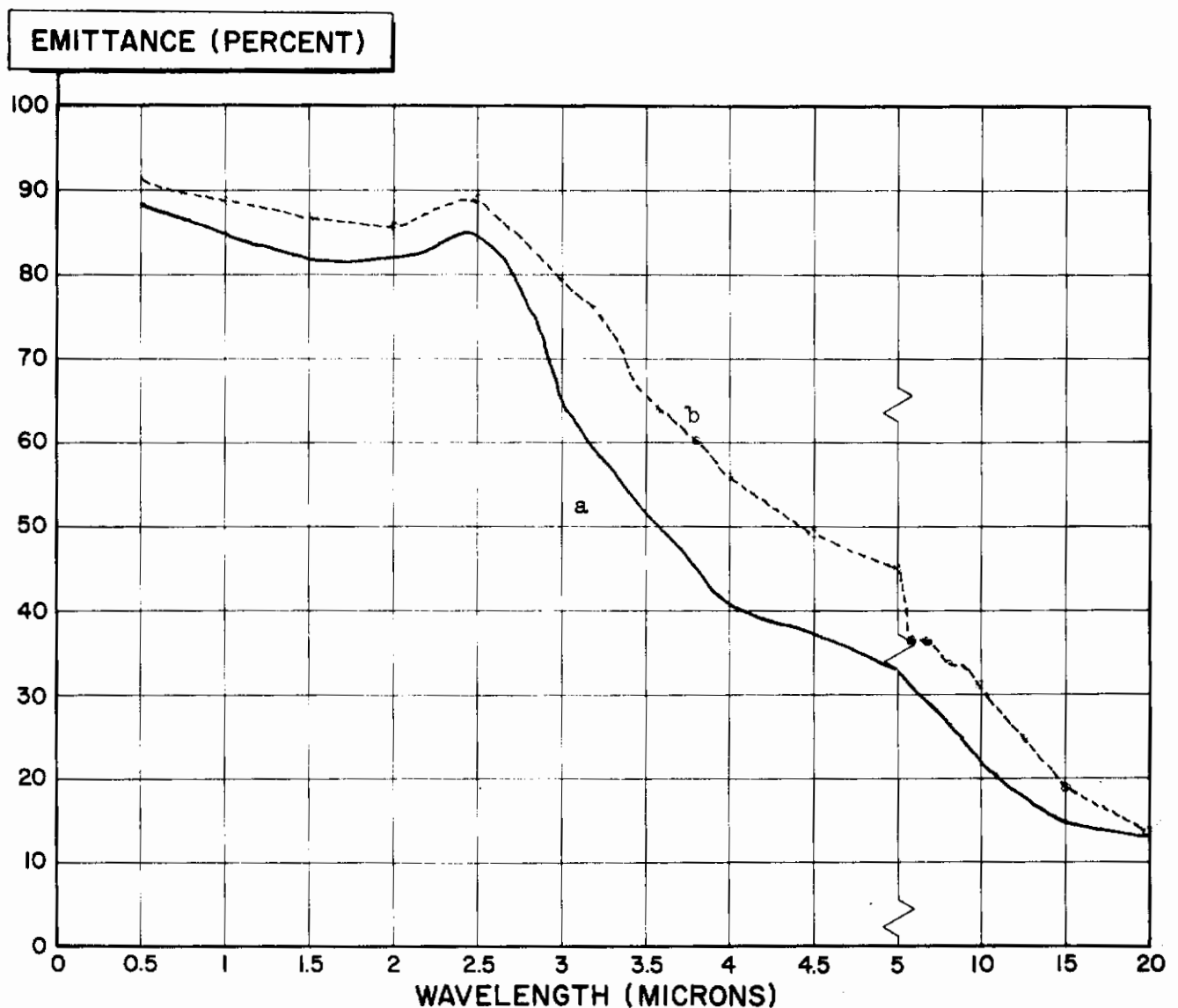
Figure 31. Effect of 1500°F Exposure in Air on the Spectral Emittance of Chromalloy W-3 Coated Molybdenum

BASE METAL:		TZM Molybdenum (Specimen M-7)
COATING SYSTEM	TYPE:	Chromalloy W-3 Silicide
	APPLIED BY:	Pack
	THICKNESS:	1.15 mils per face
	WEIGHT:	72 mg for 1 inch diameter disc

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

a) As-received

b) After 42 minutes at 2000°F in air.

ε_N = .75 measured at 2000°F

= .745 integrated R.T. spectral emittance
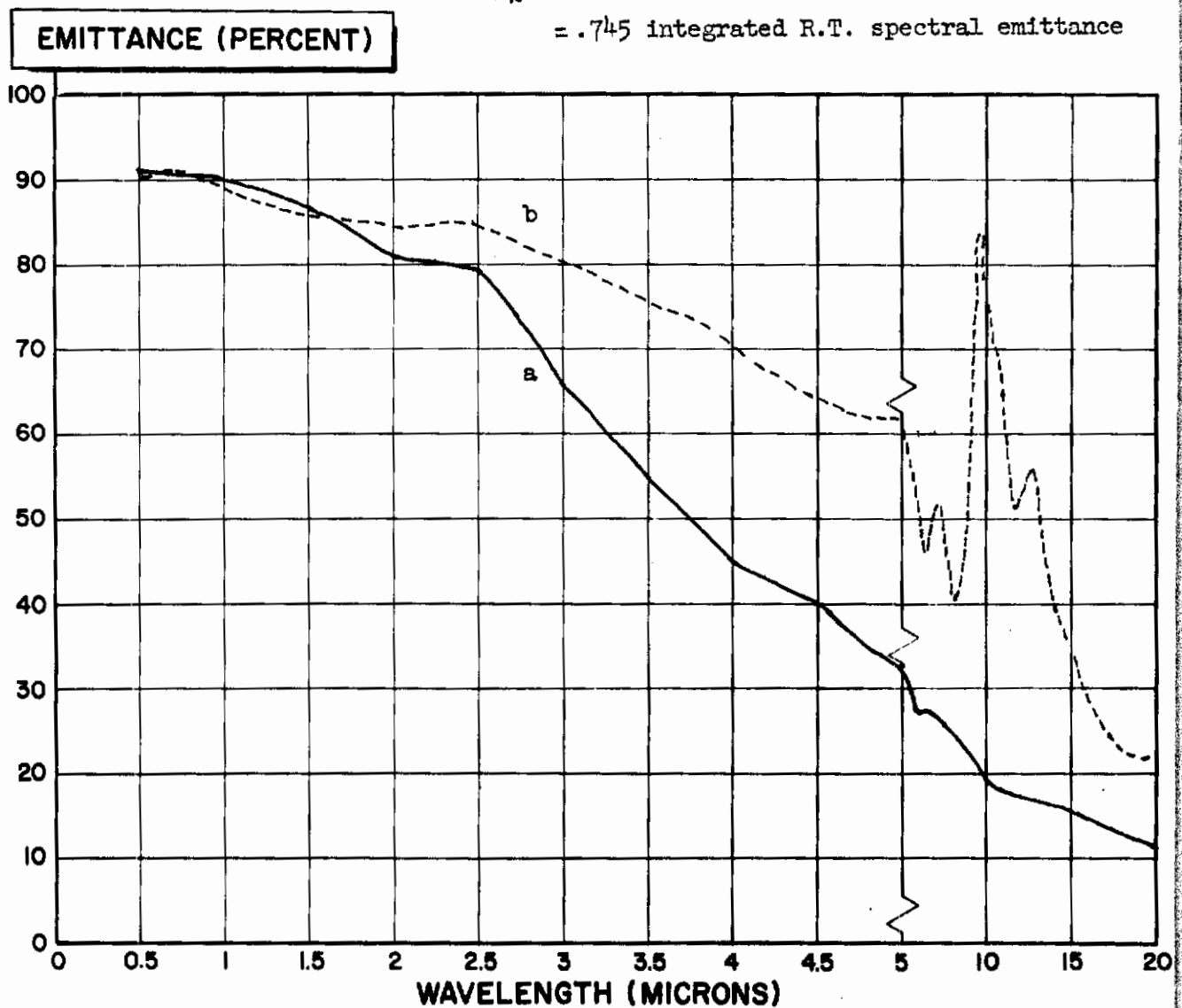
Figure 32. Effect of 2000°F Exposure in Air on the Spectral
Emittance of Chromalloy W-3 Coated Molybdenum

ZONE	POINT	RELATIVE INTENSITY				HYPOTHESIZED COMPOUNDS OR ALLOYS
		Mo	Si	Ti	Zr	
1	1A	55	34		Tr	MoSi$_2$
	1B	68	18		Tr	SMALL INCLUSIONS OF Mo$_5$Si$_3$ OR MoSi$_2$ MoB
2	2A	78	16		Tr	Mo$_5$Si$_3$
3	3A	91			0.5	BORON DIFFUSION ZONE
4	4A	99			0.5	TZM ALLOY SUBSTRATE

Tr – INDICATES TRACE

NO TITANIUM DETECTED

52 μ   2-4 μ
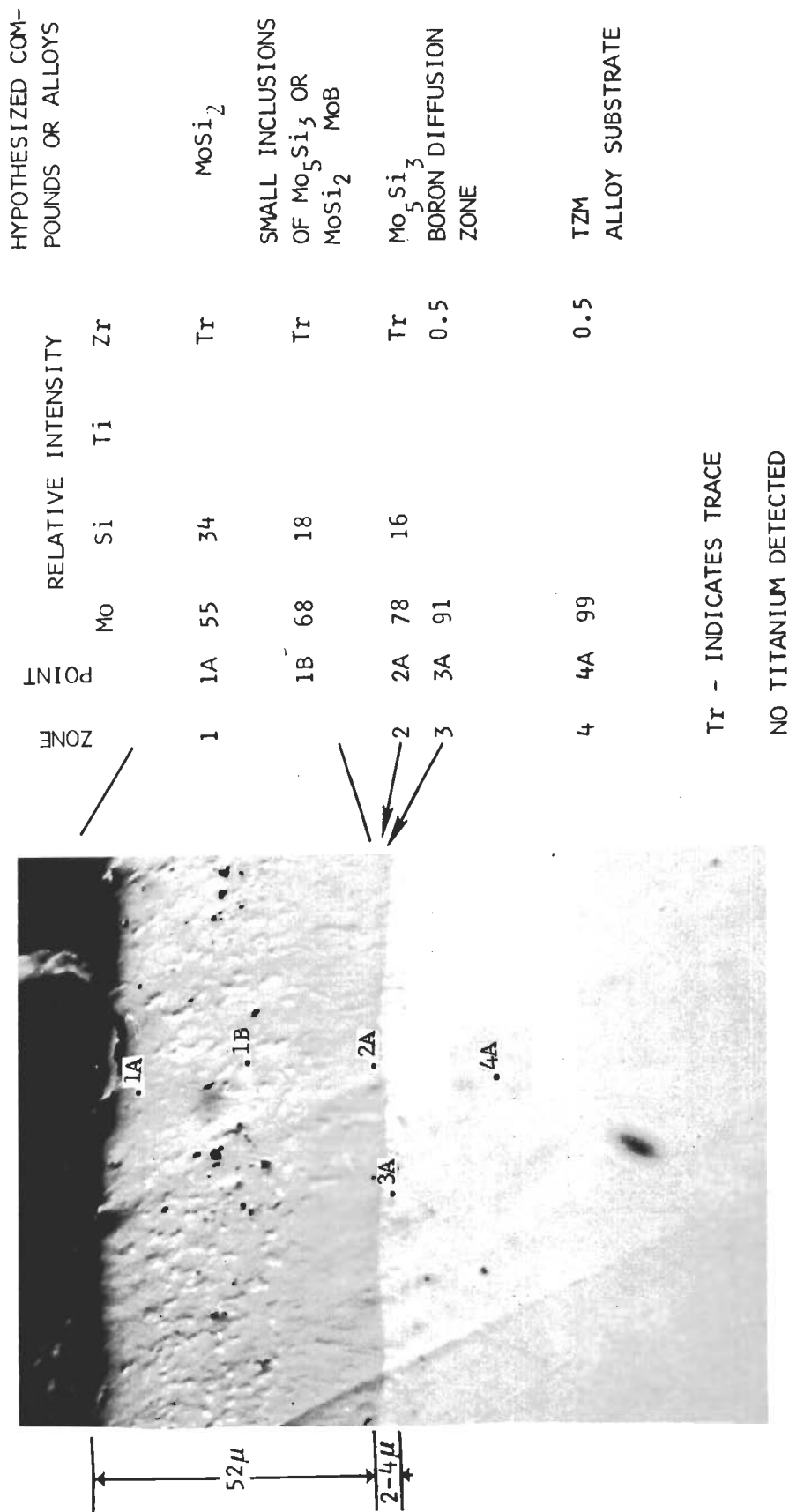
Figure 33. Photomicrograph and Microprobe Data for Chromalloy W-3 Coating in As-coated Condition (Specimen M-1)

ZONE	POINT	Mo	Si	Ti	Zr	HYPOTHESIZED COMPOUNDS OR ALLOYS
1	1A	55	39		Tr	$MoSi_2$
	1B	61	27		Tr	SMALL INCLUSIONS OF Mo_5Si_3 OR $MoSi_2$, MoB
2	2B	80	19		Tr	$Mo_5Si_3 > 2$
3	3A	85			Tr	BORON DIFFUSION ZONE
4	4A	99			0.5	TZM ALLOY SUBSTRATE

Tr - INDICATES TRACE
NO TITANIUM DETECTED
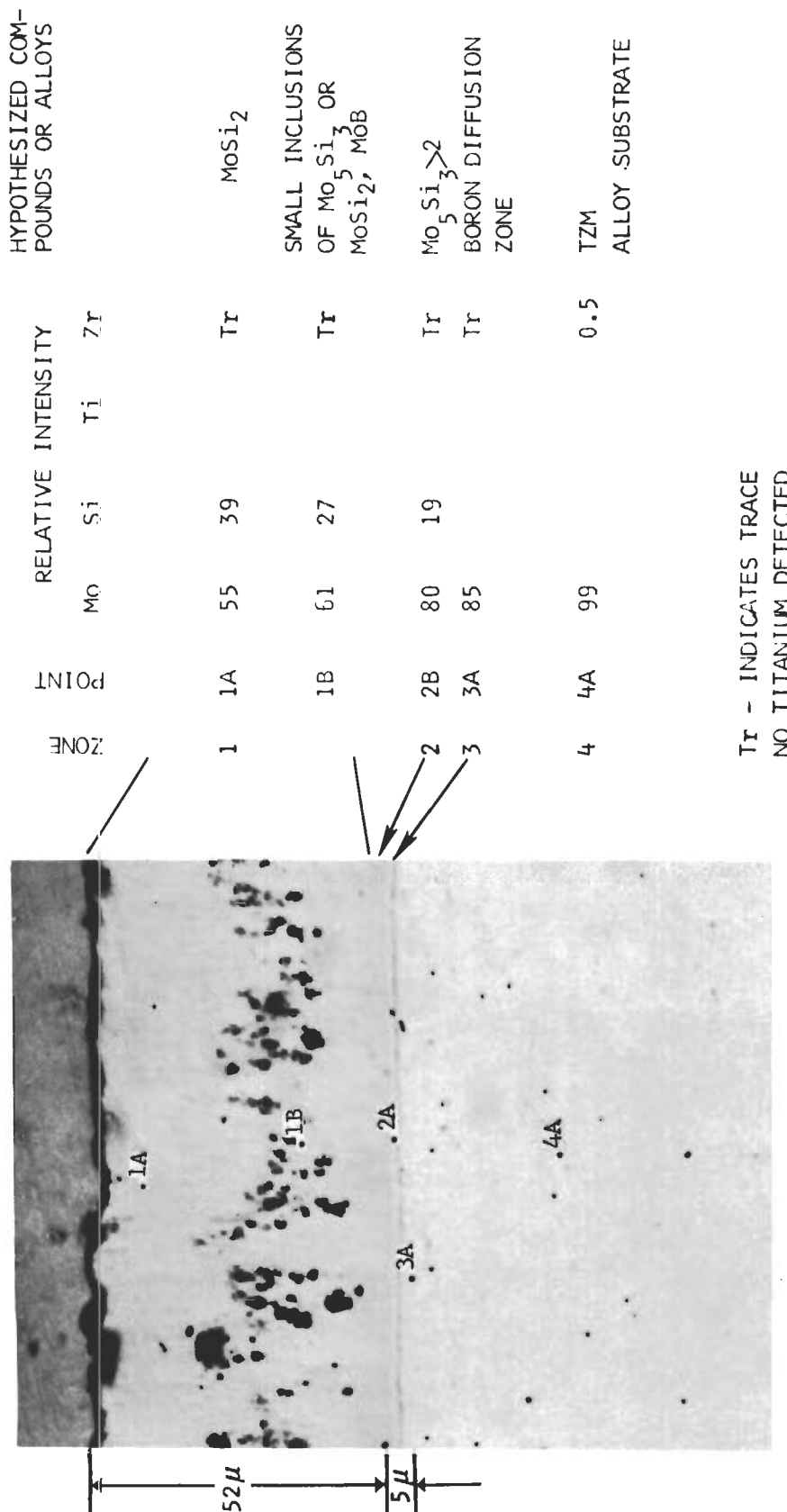
Figure 34. Photomicrograph and Microprobe Data for Chromalloy W-3 Coating After 2000°F Air Exposure for 42 Minutes (Specimen M-7)

Figure 35 shows the variation of total normal emittance with time of exposure at 1500°F and 2000°F. After an initial increase, the emittance is seen to level-off with little change for the times and temperatures studied.

Cr-Ti-Si Coated Cb-752

Figure 36 and 37 show the effects of exposure in argon at 1500°F and 2000°F on the spectral emittance. A fairly small emittance increase occurred below about 2.5 microns, with possibly a slight emittance decrease above this wavelength. X-ray diffraction surface analyses of the columbium specimens are given in table XVI. While no compositional changes were detected from 1500°F-argon exposure, the formation of 10 percent of the lower silicides from 2000°F-argon exposure is indicated.

The effects upon spectral emittance of exposure in air at 1500°F and 2000°F are shown in figures 38 and 39. Comparison of the 1500°F-air exposure with the argon exposures indicates little effect from air at this temperature and time (46 minutes) of exposure. However, the 2000°F-air exposure shows a considerable emittance increase over the entire wavelength range measured. X-ray diffraction data indicate no surface alternation in the case of the 1500°F exposure, and the formation of 5 percent lower silicide and 5 percent silica for the 2000°F exposure. Figures 40 and 41 show the coating microprobe analyses for an as-received and the 2000°F-air specimens. Little change throughout the coating structure is indicated.

Figure 42 shows the total normal emittance variation with exposure time. A significant change is observed only for the 2000°F-air-exposed specimen.

Sn-Al Coated Ta-10W

Figure 43, 44, 45, and 46, show the effect upon emittance of exposure of the Sn-Al coatings at 1500°F and 2000°F in argon and air. In all cases, the emittance significantly increased throughout the wavelength range of interest. The emittance of the 2000°F-air-exposed specimen increased 0.25 to 0.30 fairly uniformly with wavelength, and the other specimens increased about half this amount. Table XVII contains the X-ray diffraction results of the Sn-Al coatings, and figures 47 and 48 show photomicrographs and microprobe analyses of an as-received specimen, and the specimen subjected to 2000°F exposure in air. X-ray diffraction results of the air-exposed specimens show the formation of Al_2O_3 on the surface, the amount increasing with exposure temperature. In addition, the surfaces of the air-exposed specimens show from 50 to 80 percent concentrations of tin, in contrast to

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CHROMALLOY W-3 COATING ON TZM

	SPECIMEN	EXPOSURE
O	M-4	1500°F – AIR
□	M-7	2000°F – AIR
△	M-5	1500°F – ARGON
⊙	M-10	2000°F – ARGON
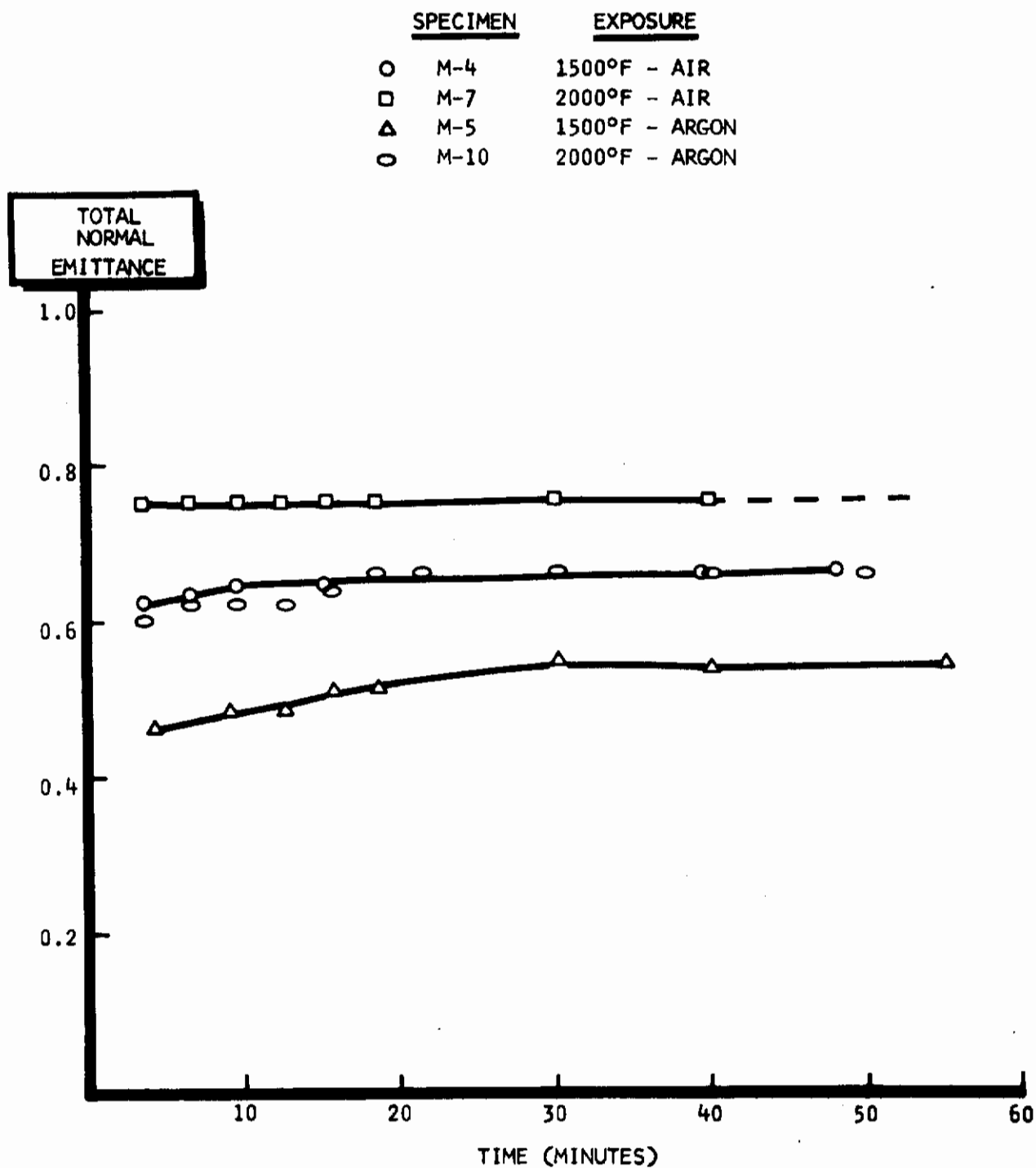
Figure 35.   Total Normal Emittance Variation With Elevated Temperature
Exposure Time for Chromalloy W-3 Coating

BASE METAL:	Cb-752 Columbium (Specimen C-3)		
COATING SYSTEM	TYPE:	TRW Cr-Ti-Si	
	APPLIED BY:	Pack	
	THICKNESS:	3.2 mils per face	
	WEIGHT:	350 mg	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

      a. As-received

      b. After 45 minutes exposure at 1500°F in argon

      Emittance determined from room temperature reflectance data
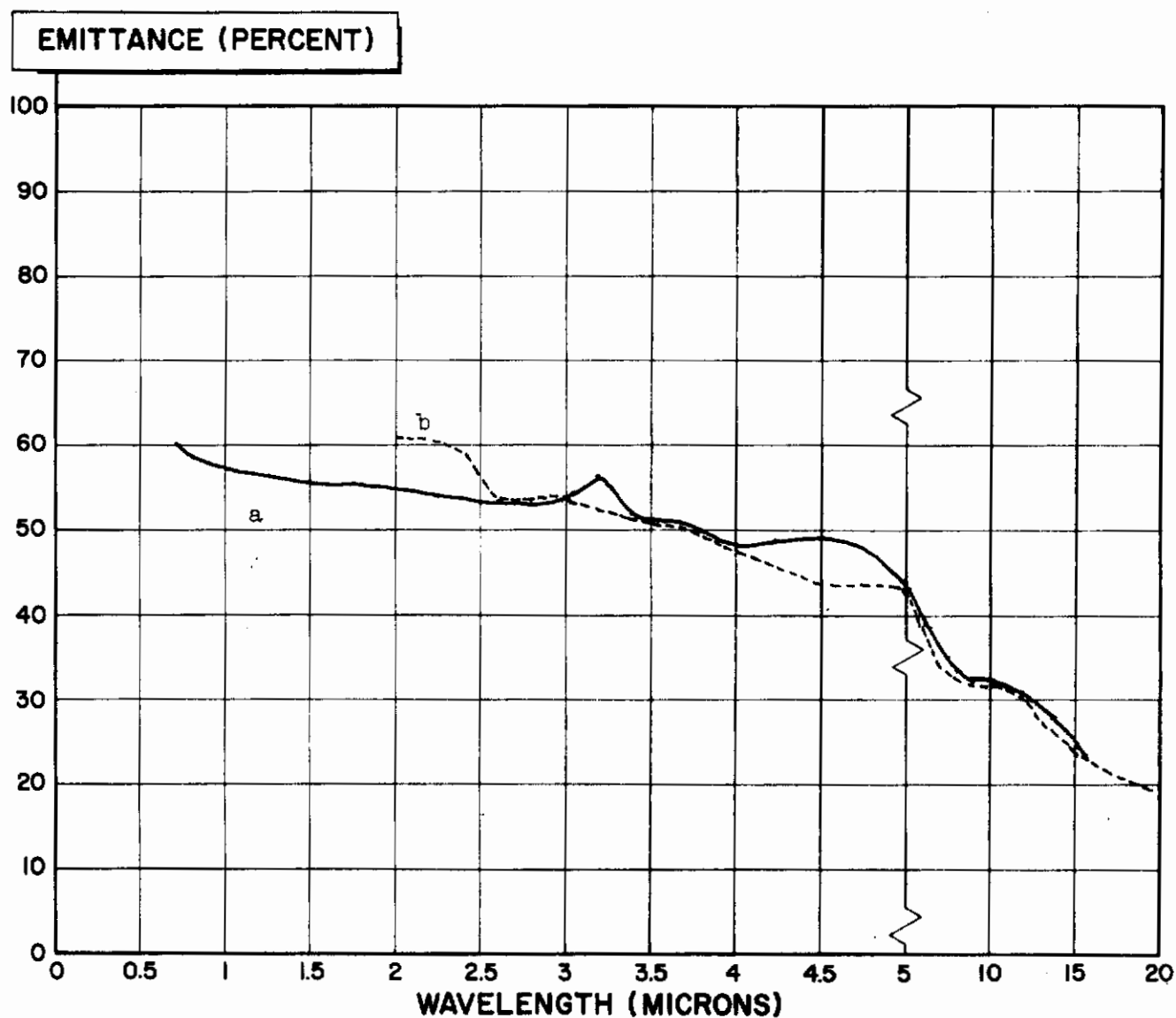
Figure 36. Effect of 1500°F Exposure in Argon on the Spectral Emittance of Cr-Ti-Si Coated Columbium

BASE METAL:	Cb-752 Columbium (Specimen C-9)		
COATING SYSTEM	TYPE:	TRW Cr-Ti-Si	
	APPLIED BY:	Pack	
	THICKNESS:	3.2 mils per face	
	WEIGHT:	339 mg	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

a. As-received

b. After 60 minutes exposure at 2000°F in argon

Emittance determined from room temperature reflectance data
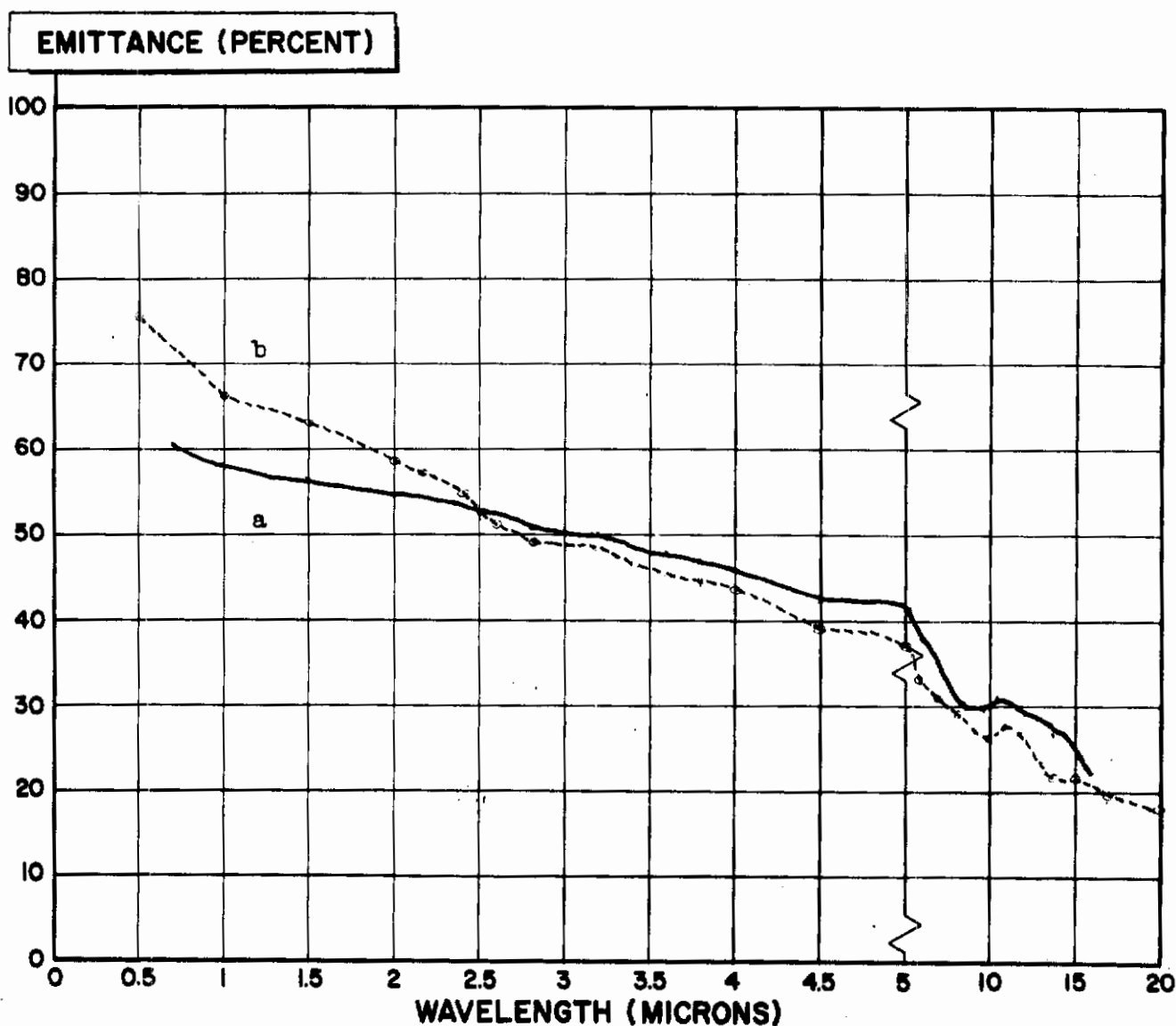
Figure 37. Effect of 2000°F Exposure in Argon on the Spectral Emittance of Cr-Ti-Si Coated Columbium

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Table XVI

X-RAY DIFFRACTION RESULTS OF Cr-Ti-Si COATED Cb-752

Sample No.	Condition	Structure	Compounds
C-5	As-received	Hexagonal C40 structure(1) a_0 = 4.565 angstroms c_0 = 6.385 angstroms	Limits of $(Cr_{0.5} Ti_{0.5}) Si_2$ to a maximum limit of: $(Cr_{0.67} Ti_{0.12} Cb_{0.2}) Si_2$. 100% (Cr-Ti-Cb complex) Si_2 intermetallic
C-9	As-received	Identical with C-5	Identical with C-5
C-3	After exposure: 1500°F argon	Hexagonal C40 structure very similar to C-5 and C-2 (1)	100% (Cr-Ti-Cb complex) Si_2 intermetallic
C-9	After exposure: 2000°F argon	Hexagonal C40 structure very similar to C-9 (as-received) (1)	90% (Cr-Ti-Cb complex) Si_2 intermetallic 5% Cb_5Si_3 5% Cr_3Si
C-2	After exposure: 1500°F air	Hexagonal C40 structure a_0 = 4.57 angstroms c_0 = 7.46 anstroms	Limits of $(Ti_{0.53} Cr_{0.47}) Si_2$ to $(Cb_{0.22} Cr_{0.63} Ti_{0.15}) Si_2$ 100% (Cr-Ti-Cb complex) Si_2 intermetallic

Table XVI

X-RAY DIFFRACTION RESULTS OF Cr-Ti-Si COATED Cb-752 (CONT)

Sample No.	Condition	Structure	Compounds
C-5	After exposure: 2000°F air	Hexagonal C40 structure very similar to C-5 (as-received)(2)	90% (Cr-Ti-Cb complex) Si_2 intermetallic 5% Cb_5Si_3 5% cristobalite (SiO_2)

NOTES:

(1) a_0 and c_0 are crystallographic axis lengths.

(2) Sample warpage made a_0 and c_0 determinations inaccurate due to nonplanar surfaces.

BASE METAL:		Cb-752 Columbium (Specimen C-2)	
COATING SYSTEM	TYPE:	TRW Cr-Ti-Si	
	APPLIED BY:	Pack	
	THICKNESS:	3.3 mils per face	
	WEIGHT:	357 mg	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

a. As-received

b. After 46 minutes exposure at 1500°F in air

Emittance determined from room temperature reflectance data
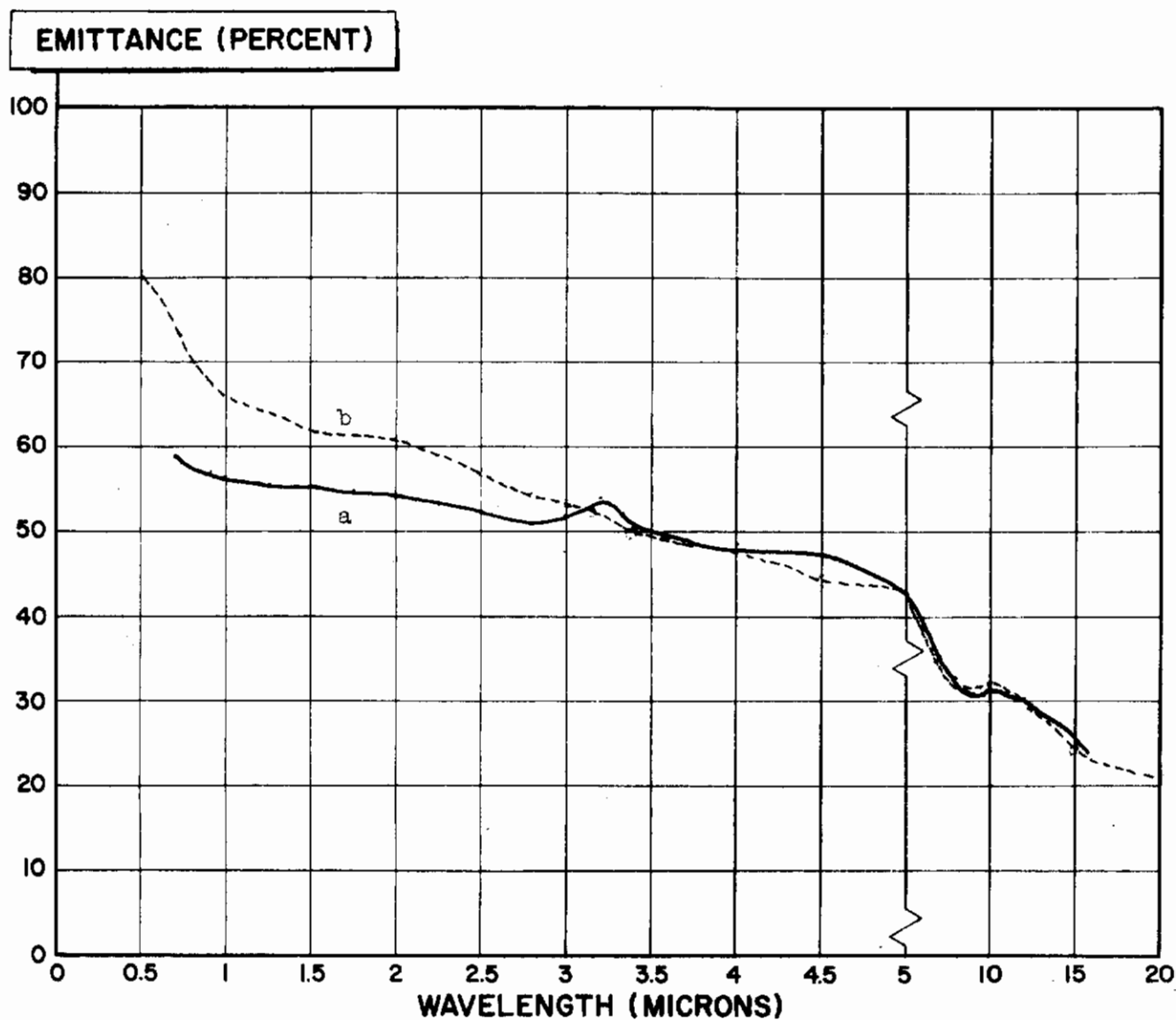
Figure 38. Effect of 1500°F Exposure in Air on the Spectral Emittance of Cr-Ti-Si Coated Columbium

BASE METAL:	Cb-752 Columbium	(Specimen C-5)
COATING SYSTEM	TYPE:	TRW Cr-Ti-Si
	APPLIED BY: Pack	
	THICKNESS: 3.2 mils per face	
	WEIGHT: 361 mg	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

    a. As-received

    b. After 81 minutes exposure at 2010°F in air

Emittance determined from room temperature reflectance data

$$\epsilon_N = .80 \text{ measured at } 2000°F$$

$$\epsilon_N = .796 \text{ integrated R.T. spectral emittance}$$
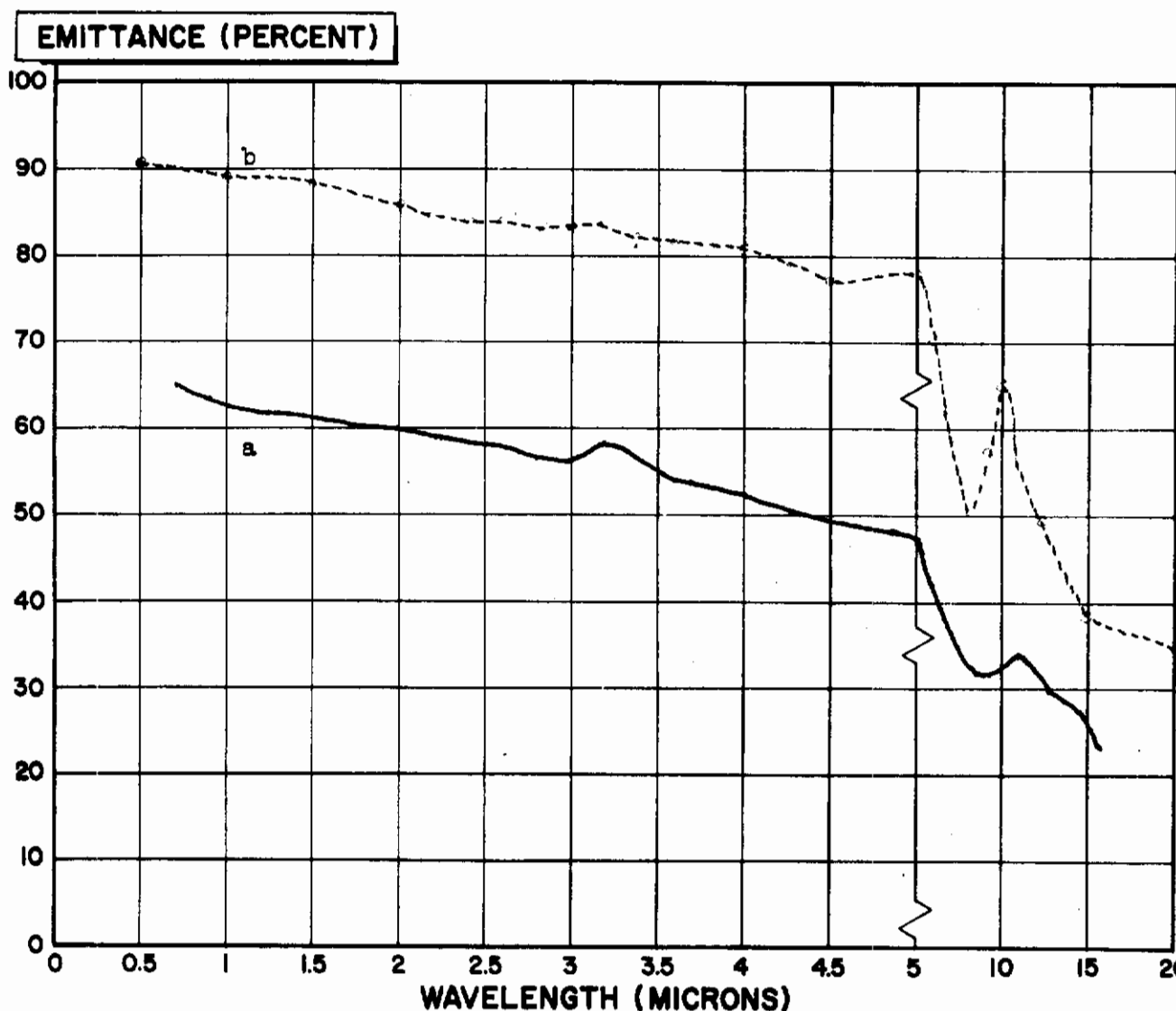
Figure 39. Effect of 2000°F Exposure in Air on the Spectral Emittance of Cr-Ti-Si Coated Columbium

ZONE	POINT	Cb	Zr	W	Si	Cr	Ti	HYPOTHESIZED COMPOUNDS OR ALLOYS
				RELATIVE INTENSITY				
1	1A	8	>1		45	22	10	(Cr,Ti,Cb)Si$_2$
	1B	17	>1	>1	42	22	7	
2	2A	20	>1	1	28	27	7	TRANSITION ZONE
3	3A	31	1	4	40	6	7	(Cb,Ti,Cr)Si$_2$
	3B	41	1	4	37	3	5	(Cb,To,Cr)$_5$Si$_3$
	4A	77	1	7	37	3	5	INTO CrTi – DIFFUSION ZONE
4	4B	90	3.5	9		0	0	
5	5A	90	3.5	9				ALLOY SUBSTRATE Cb 752

INDICATES LINEAR VARIATION OF RELATIVE INTENSITY FROM POINT A TO B

70μ   2-8μ   30μ   6μ

.1A   .1B   3A   3B   4A   4B   .5A

Figure 40.   Photomicrograph and Microprobe Data for Cr-Ti-Si Coating in As-coated Condition (Specimen C-1)

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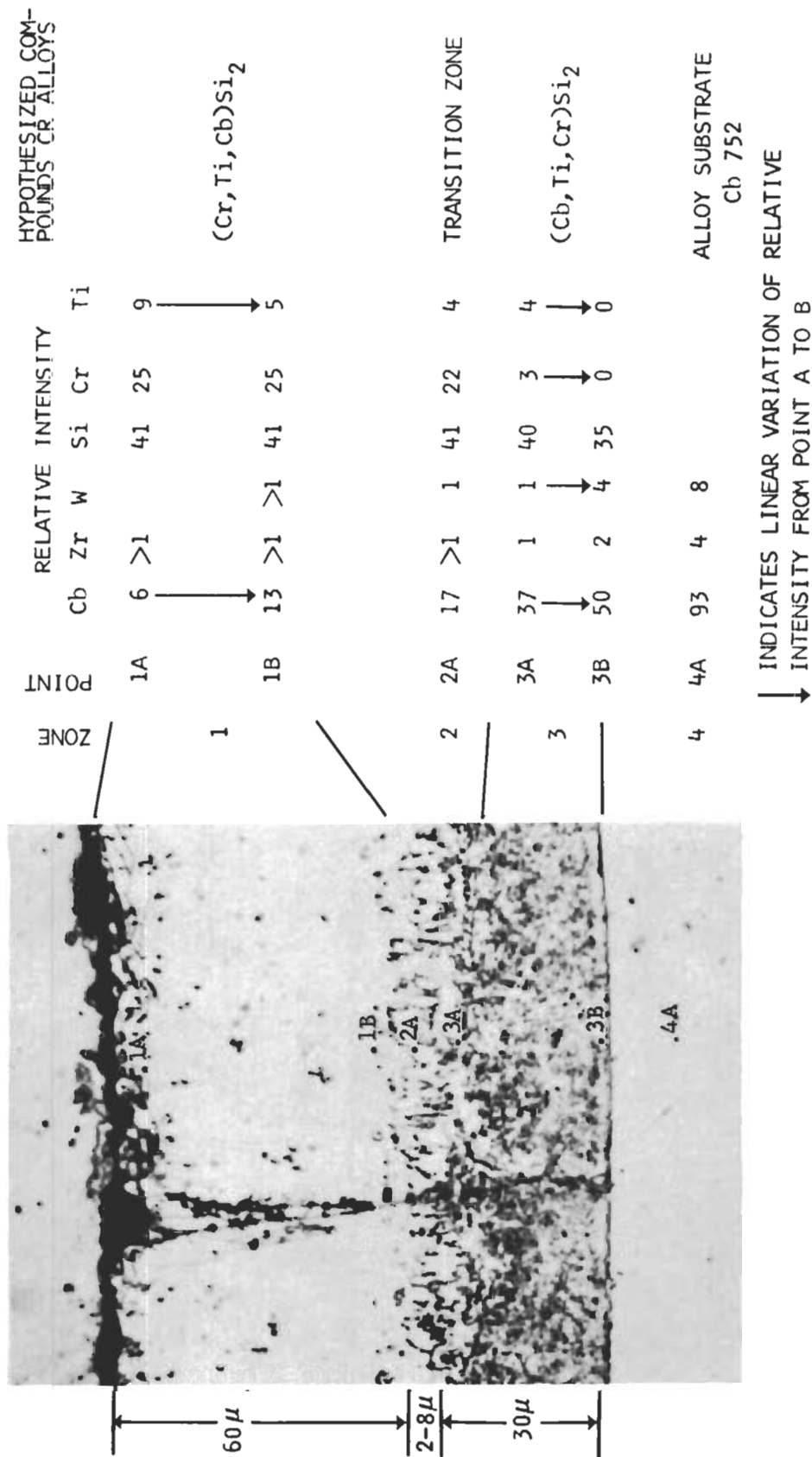
Figure 41. Photomicrograph and Microprobe Data for Cr-Ti-Si Coating After 2000°F Air Exposure for 81 Minutes (Specimen C-5)

TRW CR-TI-SI COATING ON CB-752

SPECIMEN	EXPOSURES
O C-2	1500°F – AIR
□ C-5	2000°F – AIR
△ C-3	1500°F – ARGON
O C-9	2000°F – ARGON
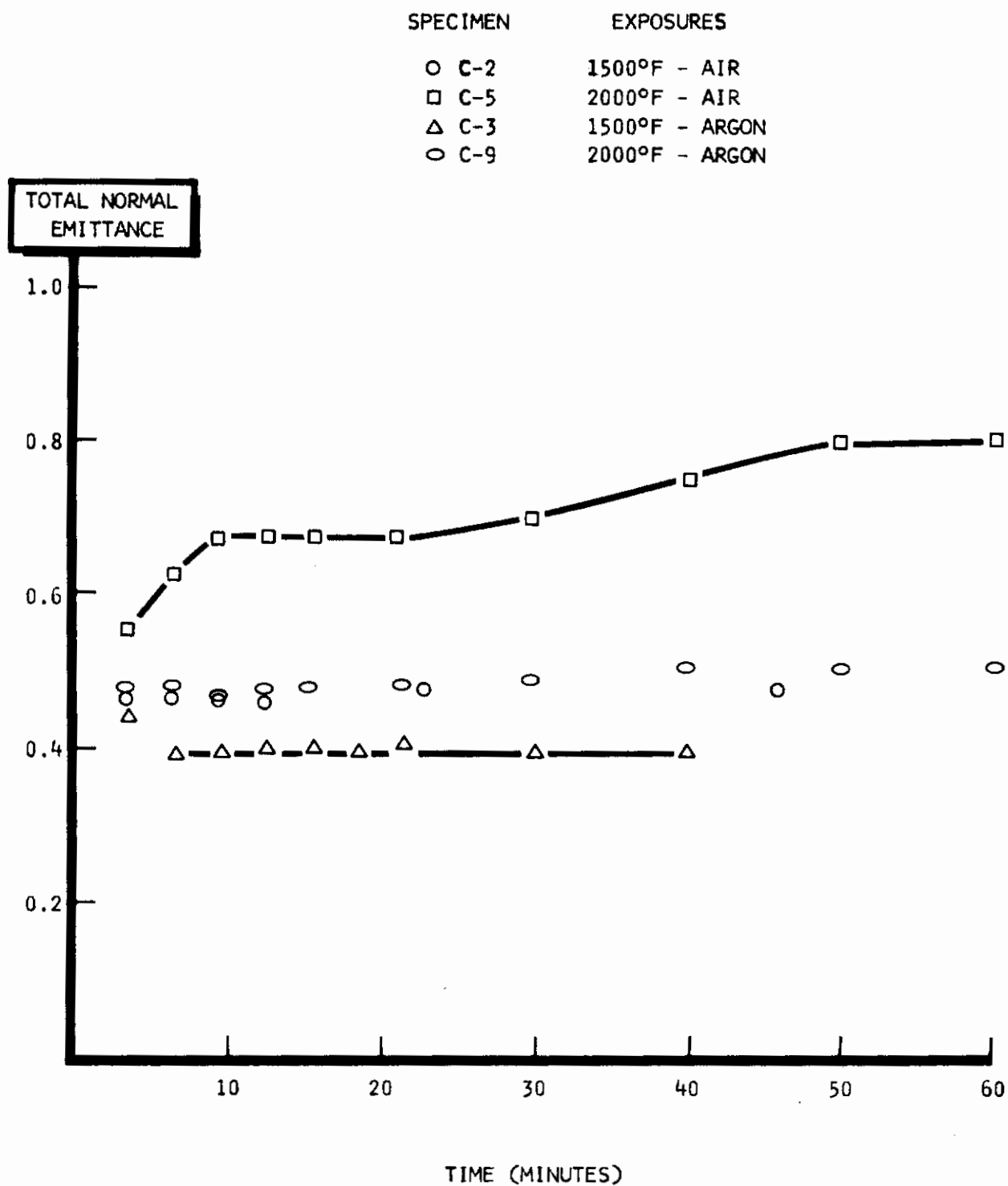
Figure 42. Total Normal Emittance Variation With Elevated
Temperature Exposure Time for Cr-Ti-Si Coating

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BASE METAL:		(Specimen T-16)	
		Ta-10W	
COATING SYSTEM	TYPE:	Sylcor Sn-Al	
	APPLIED BY:	Slurry	
	THICKNESS:	4.9 mils per face	
	WEIGHT:	425 mg	

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

    a. As received

    b. After 45 minutes exposure at 1500°F in argon

Emittance determined from room temperature reflectance data
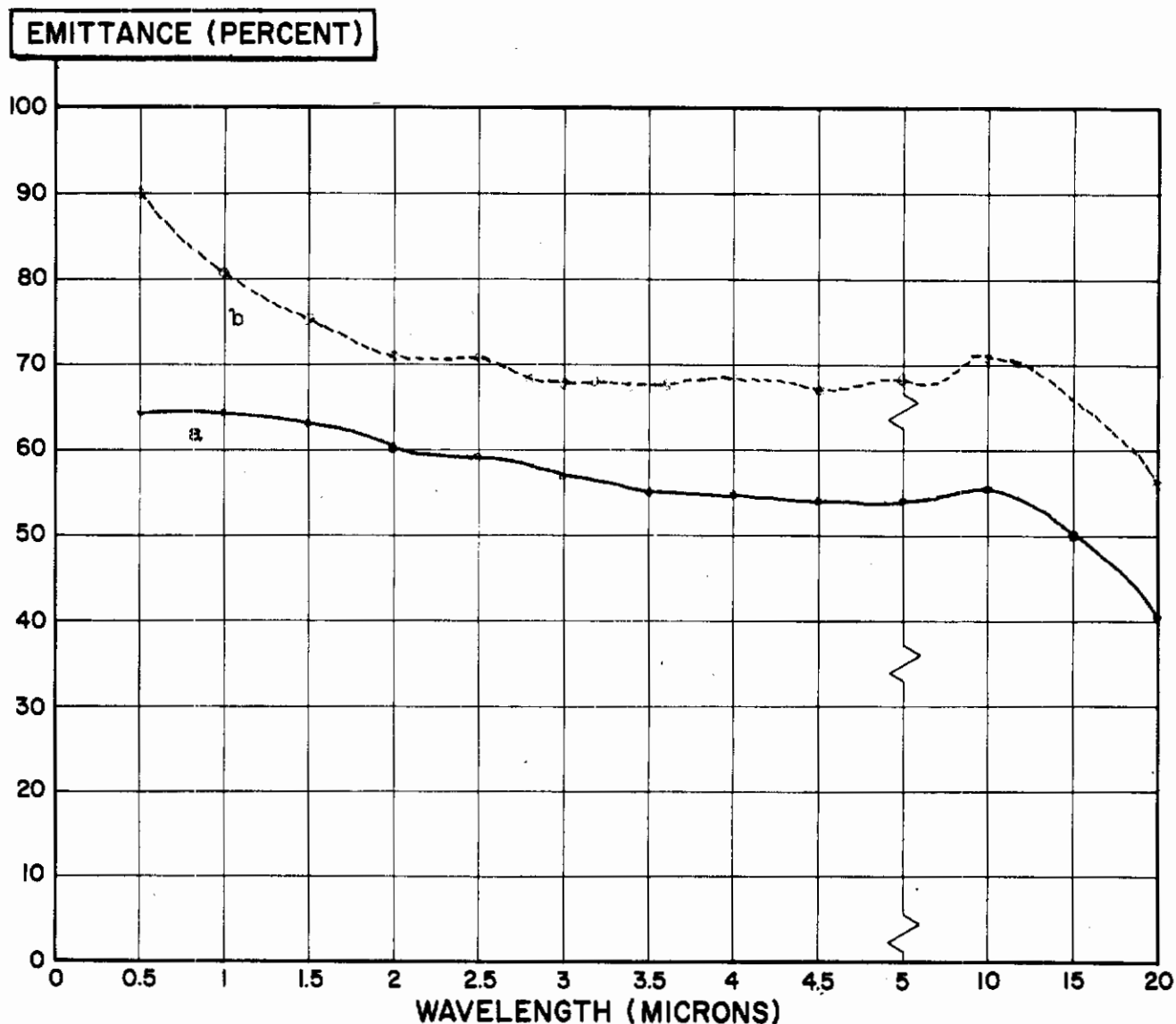
Figure 43. Effect of 1500°F Exposure in Argon on the Spectral Emittance of Sn-Al Coated Tantalum

BASE METAL:		Ta-10W (Specimen T-14)
COATING SYSTEM	TYPE:	Sylcor Sn-Al
	APPLIED BY:	Slurry
	THICKNESS:	5.5 mils per face
	WEIGHT:	480 mg

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

      a. As-received

      b. After 50 minutes exposure at 2000°F in argon

      Emittance determined from room temperature reflectance data
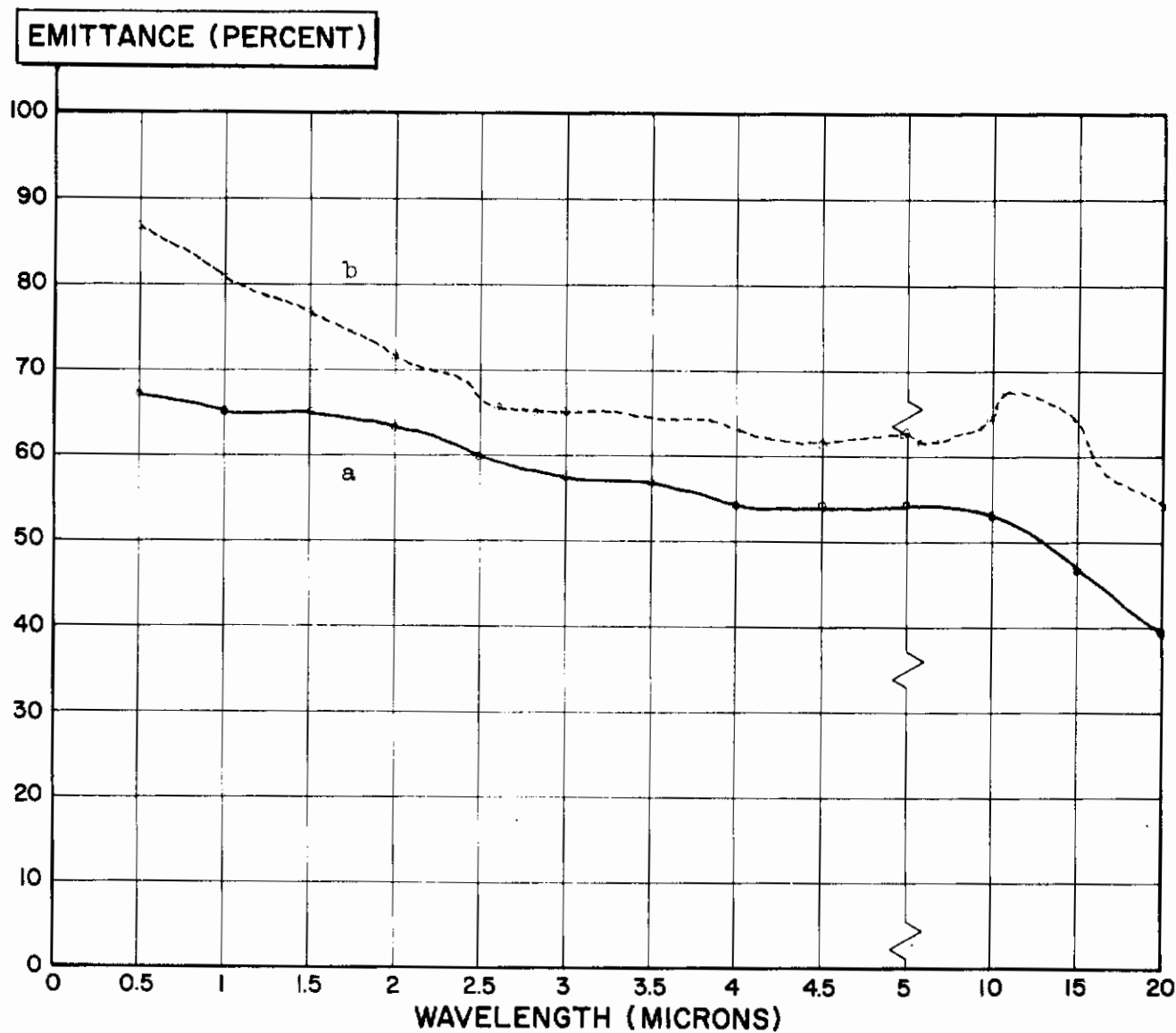
Figure 44.   Effect of 2000°F Exposure in Argon on the
Spectral Emittance of Sn-Al Coated Tantalum

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BASE METAL:		Ta-10W (Specimen T-2)
COATING SYSTEM	TYPE:	Sylcor Sn-Al
	APPLIED BY:	Slurry
	THICKNESS:	4.6 mils per face
	WEIGHT:	403 mg

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

a. As received

b. After 67 minutes exposure at 1500°F in air

Emittance determined from room temperature reflectance data
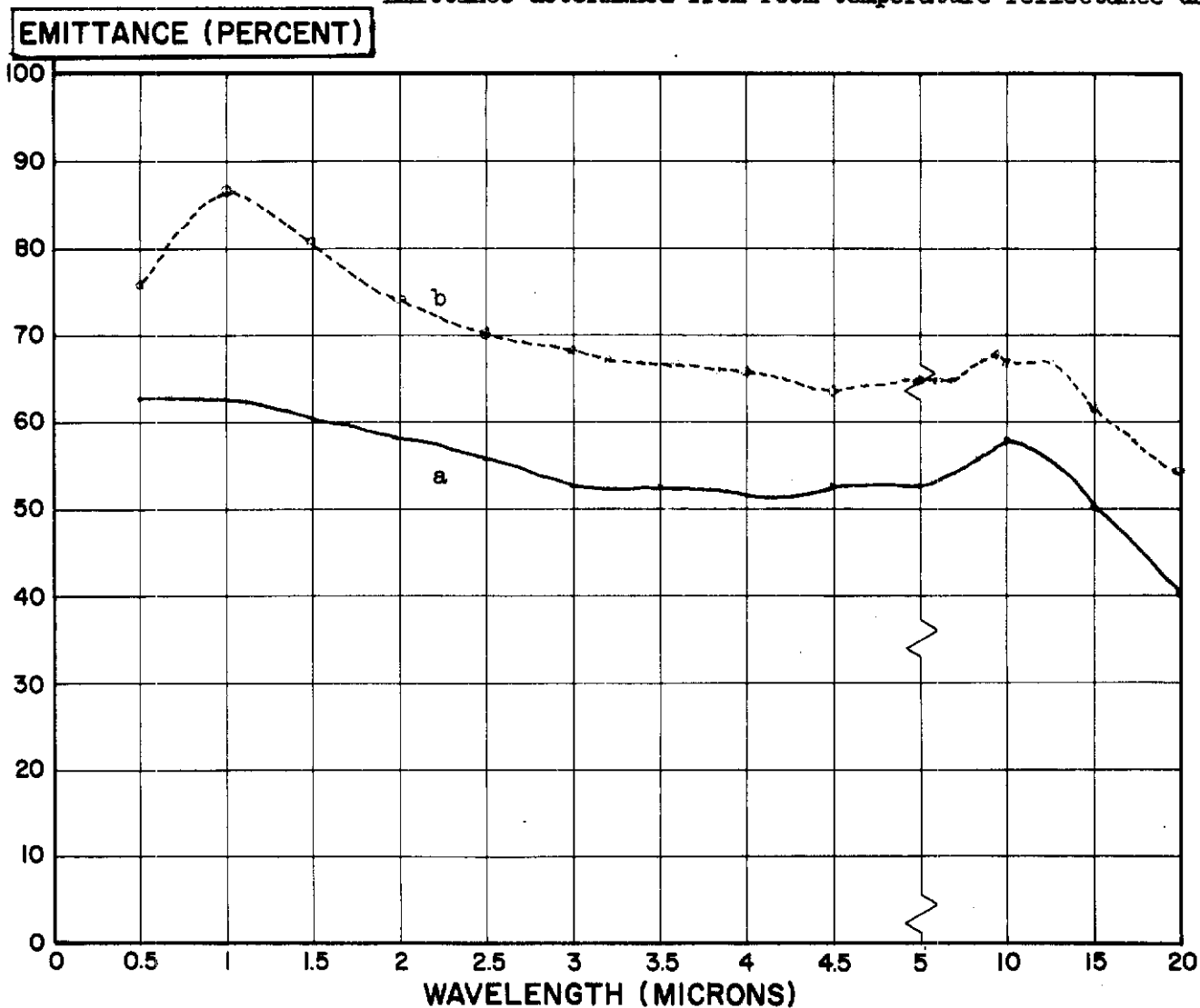
Figure 45. Effect of 1500°F Exposure in Air on the Spectral Emittance of Sn-Al Coated Tantalum

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BASE METAL:		Ta-10W (Specimen T-3)
COATING SYSTEM	TYPE:	Sylcor Sn-Al
	APPLIED BY:	Slurry
	THICKNESS:	4.4 mils per face
	WEIGHT:	414 mg

TEST CONDITIONS AND SPECIMEN PRECONDITIONING:

    a. As received

    b. After 52 minutes exposure at 2000°F in air

Emittance determined from room temperature reflectance data

ϵ_N = .82 measured at 2000°F

ϵ_N = .825 integrated R.T. spectral emittance
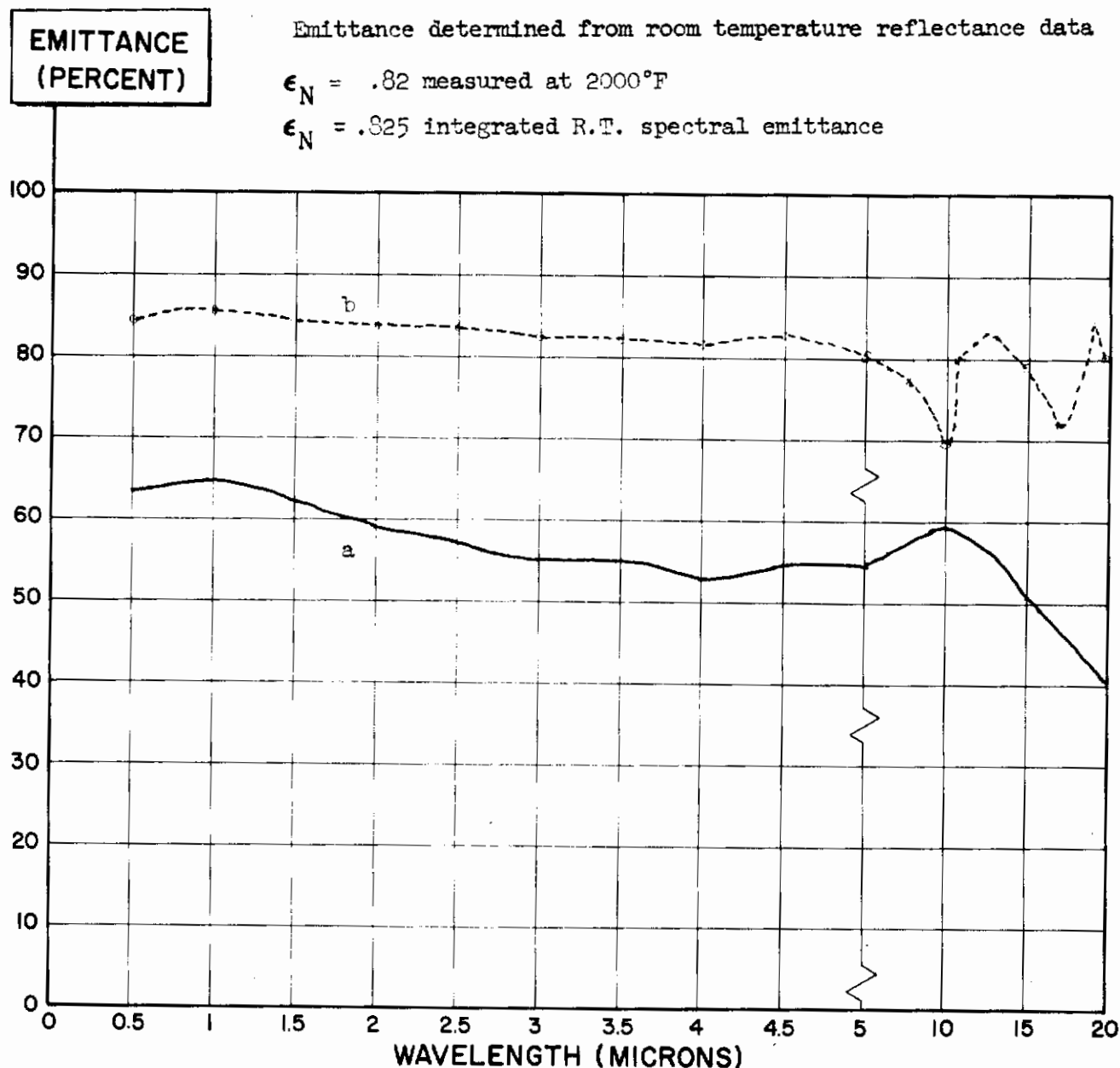
Figure 46. Effect of 2000°F Exposure in Air on the Spectral Emittance of Sn-Al Coated Tantalum

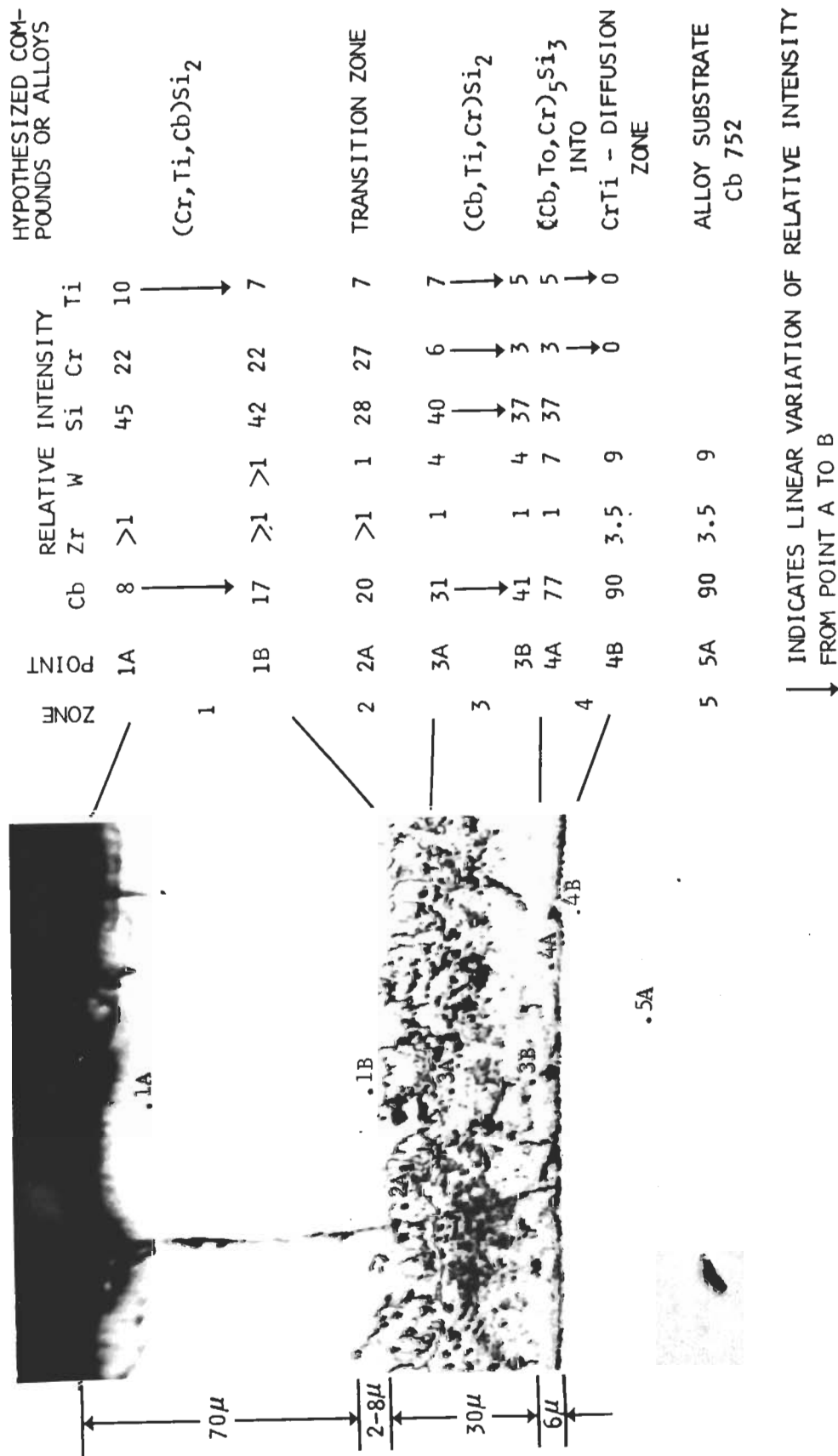121

Table XVII

X-RAY DIFFRACTION RESULTS OF Sn-Al COATED Ta-10W

Sample No.	Condition	Chemical Compounds and Estimated Relative Quantity (Weight Percent)			
		β Sn	$MoAl_3$	Al_2O_3	Other
T-8	As-received	20-30	60-70		5-10% unknown, 7 lines unidentified
T-13	As-received	15-25	60-70		5-10% unknown, 3 lines unidentified
T-16	After exposure: 1500°F argon	45-55	30-45		5-10% unknown, 7 lines unidentified
T-14	After exposure: 2000°F argon	20-25	60-70		10-15% unknown, 7 lines unidentified
T-2	After exposure: 1500°F air	50-60	30-40	Trace	2-5% unknown, 2 lines unidentified
T-3	After exposure: 2000°F air	70-80	10-15	5-10	2-5% unknown, 2 lines unidentified

ZONE	POINT	RELATIVE INTENSITY					HYPOTHESIZED COMPOUNDS OR ALLOYS
		Al	Sn	Mo	Ta	W	
1	1A		95	Tr			βSn
	1B	27	6	36			MoAl₃
	1C	85					Al
	1D	34	34		33		Ta
2	2A	26	7	26	18		TRANSITION ZONE
3	3A	30			43	2	TaAl₃
4	4A	15			52	5	TaAl₂
5	5A				78	9	Ta-10W ALLOY SUBSTRATE
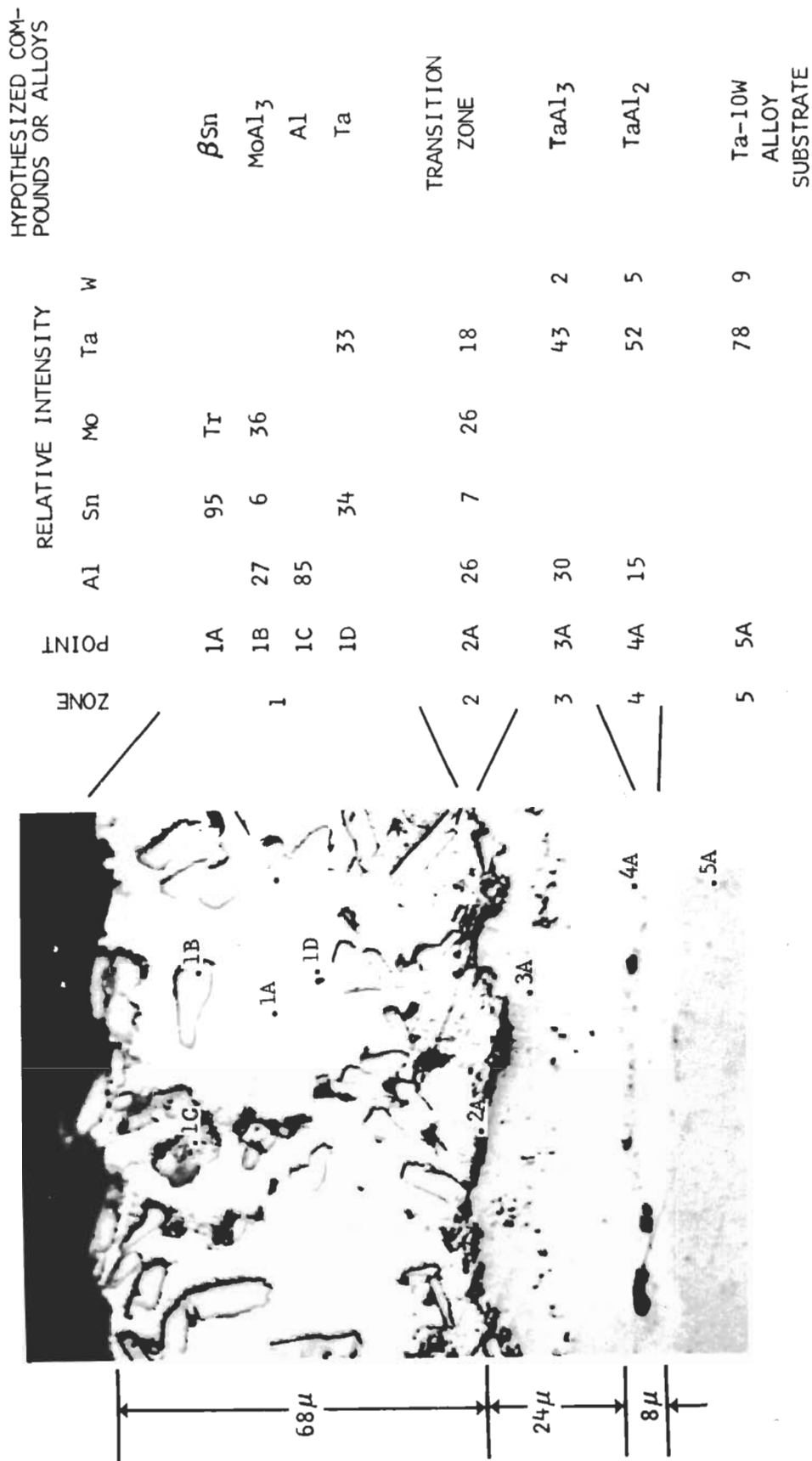
Figure 47. Photomicrograph and Microprobe Data for Sn-Al Coating in As-received Condition (Specimen T-10)

ZONE	POINT	RELATIVE INTENSITY					HYPOTHESIZED COMPOUNDS OR ALLOYS
		Al	Sn	Mo	Ta	W	
	1A		98				βSn
1	1B	28	16	36			MoAl$_3$
	1C	12	12		70	5	Ta
2	2A	31	2	27	27	1	TRANSITION ZONE
	3A	30	3		54	2	TaAl$_3$
3	3B	19			67	5	TaAl$_2$
	3C	11			76	7	Ta$_2$Al
4	4A				94	8	Ta-10W ALLOY SUBSTRATE
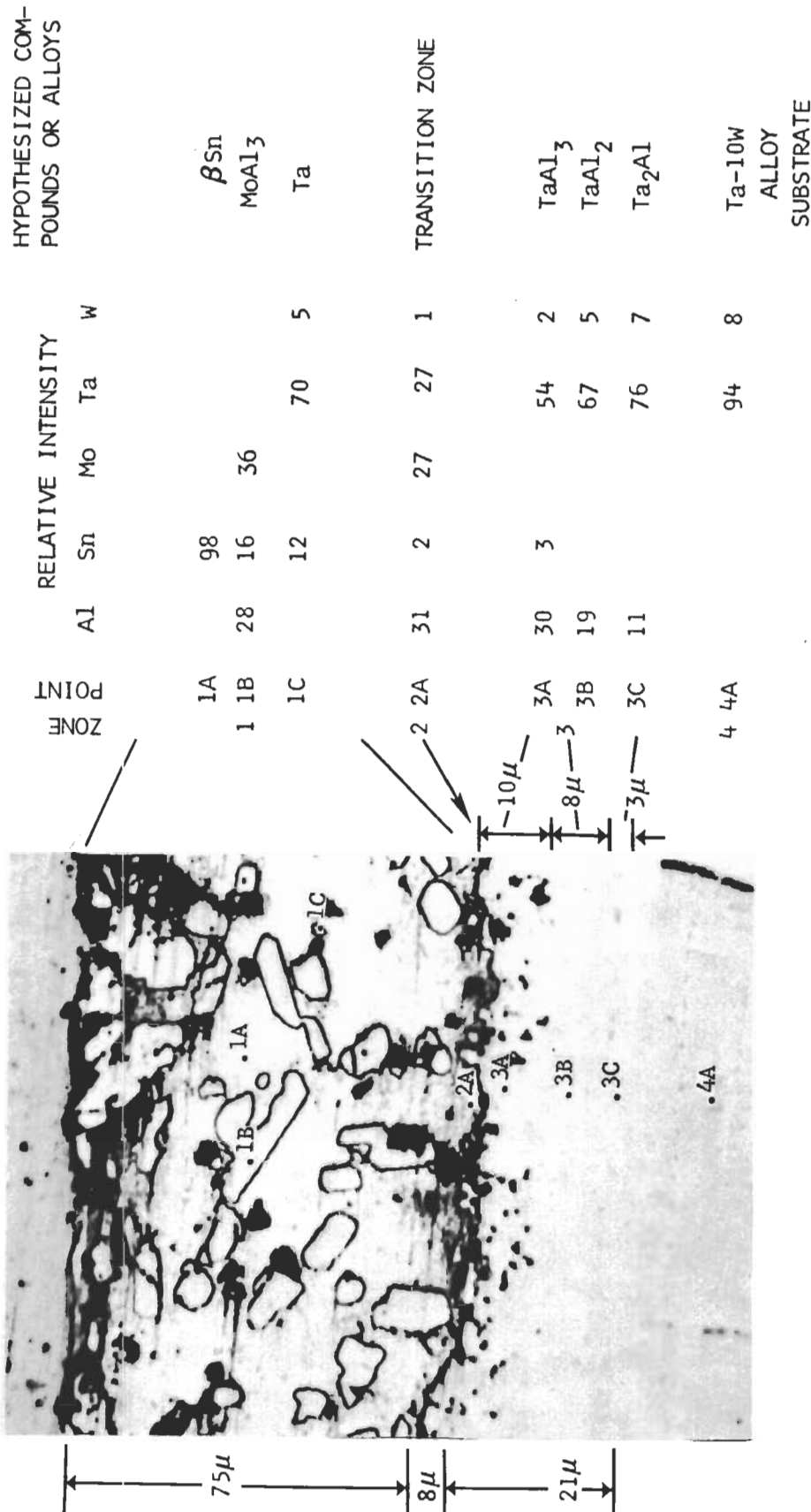
Figure 48. Photomicrograph and Microprobe Data for Sn-Al Coating After 2000°F Air Exposure for 52 Minutes (Specimen T-3)

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concentrations of 15 to 30 percent in the as-received coating surfaces. Corresponding decreases of the $MoAl_3$ phase occurred. The 1500°F-argon specimen also showed, to a lesser extent, the surface tin increase and the $MoAl_3$ decrease, whereas, the 2000°F-argon specimen was not appreciably affected in this manner.

The total normal emittance variation with exposure time is shown in figure 49. Since the spectral emittance values measured before and after exposure show a substantial emittance increase for all specimens, increase apparently occurred during the first few minutes of exposure.

DISCUSSION OF RESULTS

W-3 COATED MOLYBDENUM

Although not detected by microprobe or X-ray diffraction analysis, silica is expected to exist on the air-exposed specimen surfaces, as discussed in Section VIII. This silica may form as a thin, continuous-surface film at 2000°F, and as a discontinuous film or as segregated islands in the 1500°F temperature range exposure. Another mechanism expected to occur on the surface is a roughening effect caused by selective oxidation or vaporization. These reactions, combined with the detected formation of molybdenum oxide, are believed to account for the emittance increase of the 2000°F-air exposure, the lesser increase at 1500°F in air, and the relative emittance stability during exposure in argon.

These results point out the need for the following:

1. Improved characterization of the coating surface to detect the very thin oxide films and clusters which are known to form upon oxidation of these coatings

2. Improved techniques to allow measurement of surface roughness of oxidized coatings

3. Determination of the emittances of compounds such as the various oxides of molybdenum, which have not been found in the literature

Cr-Ti-Si COATED Cb-752

Of the four specimens exposed at 1500°F and 2000°F in air and argon, only the 2000°F-air specimen showed significant emittance variation, except for emittance increases in the wavelength region of about 0.5 micron, where

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SYLCOR SN-AL COATING ON TA-10W

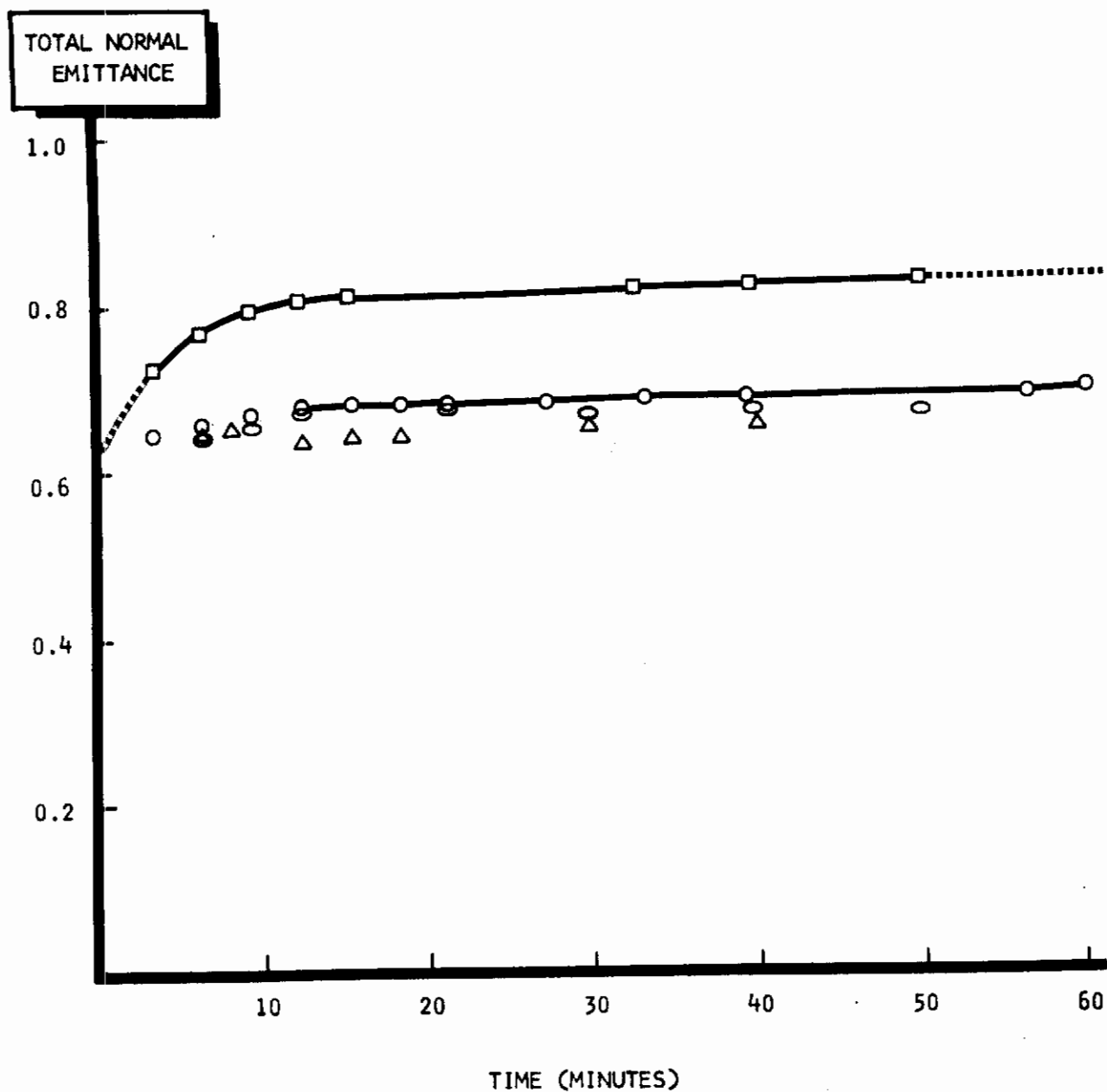| SPECIMEN		EXPOSURE
O	T-2	1500°F - AIR
□	T-3	2000°F - AIR
△	T-6	1500°F - ARGON
O	T-14	2000°F - ARGON

Figure 49. Total Normal Emittance Variation With Elevated
Temperature Exposure Time for Sn-Al Coating

the emittances of all specimens increased sharply after exposure. The emittance of the 2000°F-air sample increased on the order of 0.25 over the entire wavelength range. The emittance increase above about 5 microns for this sample can be, at least, partially accounted for by the formation of silica, the existence of which was verified by X-ray diffraction. Gadd (Reference 56) reports that exposure of the Cr-Ti-Si coating in air at one atmosphere, at temperatures up to 2300°F, showed essentially a parabolic weight gain. At 1800°F, the protective oxide was found to be silica, containing considerable chromium and titanium, either as independent oxides or in solid solution. Exposure at 2500°F resulted in an initially formed surface scale of essentially Cr_2O_3, with lesser quantities of the oxides of titanium and silicon. Continual exposure at 2500°F resulted in a rapid loss of chromium, leaving a scale consisting of SiO_2, TiO_2, and possibly the complex oxide $TiO_2-Cb_2O_5$. Based on this data, a small amount of Cr_2O_3 would be expected to form during exposure in one atmosphere of air at 2000°F. Since Cr_2O_3 has a high emittance in the one- to 15-micron range, this compound may be a possible explanation for the marked emittance increase which occurred from air exposure, but not from the argon exposure at 2000°F.

Sn-Al COATING ON Ta-10W

In contrast to the silicide coatings, the emittance of the Sn-Al coating increased significantly from both air and argon exposure at both 1500°F and 2000°F. Al_2O_3, detected on the surfaces of the air-exposed specimens, does not account for the emittance increase caused by argon exposure, nor does it explain the emittance increase below about 5 microns for the air-exposed samples. Although exposure, particularly in air, shows increased tin concentration on the surface as detected by X-ray diffraction, the photomicrograph (figure 48) of the exposed sample suggests a surface tin depletion and the increased exposure of the $MoAl_3$ phase.

Again, improved surface characterization is required to account for the observed emittance increase of this coating upon exposure. Priceman and Sama (Reference 47) have found that tin oxide starts to form at about 1400°F upon exposure of the Sn-Al coating in air at one atmosphere, and that this oxide remains to above 2000°F. Tin oxide was not detected in this preliminary investigation.

Section X

COMPREHENSIVE EMITTANCE PROGRAM

PURPOSE

The basic purpose of this Phase I report is to plan an emittance measurement program that will provide the thermodynamicist with reliable emittance information for refractory metal-coating systems so that adequate thermal calculations can be made. The ultimate goal is to provide the design data that would be required during the next 5 years. An additional purpose is to provide information which will enable coatings to be designed with known and reproducible emittance properties.

PROBLEM

Four problems must be recognized. They involve coating environment, coating processing, the measurement of emittance properties, and the associated use of such properties in thermal calculations. The emittance properties of a **refractory-metal/coating** system are functions not only of the chemistry and other physical properties of the coating, but also, of its environment. The environment includes temperature, partial pressures of the atmospheric constituents, various types of radiation, the velocity of gases passing over the surface, and variations of all these with time. The emittance properties of coatings can be expected to vary depending upon the control exercised by the processor and the inherent reproducibility of the coating. It is not known whether the current practices used to yield reproducible oxidative preventive coatings will also yield reproducible emittance properties. Accurate heat-transfer calculations for surfaces radiating to space require the use of total hemispherical emittance values. Such values are difficult to measure above 2500°F except in a vacuum. The more readily obtainable total normal emittance values are not necessarily adequate in place of total hemispherical values. Heat-transfer calculations between surfaces may be subject to serious error if spectral emittance data are not used. This depends, however, on the amount emittance varies with wavelength. Spectral normal values are being obtained on this current program at temperatures up to 3000°F, and their use would represent a large improvement in thermal calculations. Ideally, spectral hemispherical values are needed. Methods to determine these values up to 3000°F are not available. Directional emittance data may also be needed to permit careful heat-transfer calculations between surfaces. This need is dependent upon the extent to which coatings depart from diffuse radiation.

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Further examination is also required of typical vehicle and engine designs involving thermal calculations to determine the magnitude of the errors inherent in the use of simplified calculations rather than more complex ones employing spectral and directional emittance properties. A preliminary examination was made of the need for spectral and directional property information in Section V of this report. Additional study is required.

PROGRAM PLAN

The idealized program plan is divided into four phases:

Phase A - Effect of Environment on Emittance

Phase B - Relationship of Processing Control Parameters to Emittance

Phase C - Thermal Calculations

Phase D - Special Emittance Properties

PHASE A - EFFECT OF ENVIRONMENT ON EMITTANCE

1. Select coatings that are important for each alloy of interest (e.g., columbium, molybdenum, tantalum, and possibly tungsten).

2. Request one batch of specimens from each selected source.

3. Screen samples by measurement of the following physical properties to ensure that samples to be used are uniform. Set aside samples that differ significantly from batch average.

   a. Coating thickness

   b. Coating weight

   c. Surface roughness

   d. Spectral emittance inferred from room-temperature reflectance

   e. Composition (selected samples only), using means that will especially measure composition of the outer surface layer

4. Subject selected samples to various conditions of atmospheric pressure, temperature, and time-exposure in accordance with table XVIII.

Note: Do not expose samples to conditions which previously have been found to cause premature coating failure in programs designed to measure oxidative prevention qualities of coatings.

5. Measure spectral normal and total hemispherical emittance at elevated temperature and reduced pressure conditions during cycling period. Select measuring times so as to show variation with a minimum of determinations. Since total normal emittance is easier to measure than total hemispherical, it may be used as a guide. In addition, these two properties will be equal for diffuse materials.

6. Measure the following properties of exposed samples at suitable selected intervals to show trend with a minimum number of measurements:

   a. Spectral emittance inferred from room-temperature reflectance

   b. Composition of selected samples as in item 3e.

   c. Surface roughness

7. Measure spectral emittance properties of single compounds which are constituents of coatings so as to identify coating components responsible for emittance performance.

8. Expose coatings in a hypersonic tunnel under the following conditions:

   a. Mach 6 gas flow velocity, 3400°R stagnation temperature, and 140,000-foot pressure altitude. Typical suitable test facilities include (1) a hypersonic wind tunnel of the type located at FluiDyne Engineering Corp, Minneapolis, Minnesota, or (2) an arc-heated (plasma) tunnel of the type located at Purdue University, Lafayette, Indiana.

   b. Mach 20 gas flow velocity, 12,000°F stagnation temperature, and 140,000-foot pressure altitude. Suitable test facilities, now under development, include the magnetohydrodynamic facilities now being developed by the General Electric Co., and by Wright-Patterson Air Force Base.

Table XVIII

TEMPERATURE, PRESSURE, AND TIME-EXPOSURE CONDITIONS FOR

ESTABLISHING EFFECT OF ENVIRONMENT ON EMITTANCE

Temperature of conditioning atmosphere	1400°F, 2000°F, 2500°F, and 3000°F
Partial pressure of oxygen in the conditioning environment of dry air	Laboratory space vacuum simulation, e.g., 10^{-7} mm Hg, 10^{-2} mm Hg, 1 mm Hg, and 152 mm Hg
Time of exposure to conditioning environment	a. Cycle at space vacuum for 5-minute intervals* 50 times b. Cycle for 15-minute periods at 10^{-2} to 152 mm Hg up to 200 times** c. Cycle for 1.5-hour periods at 10^{-2} to 152 mm Hg up to 200 times**

* Store at 10^{-7} mm Hg between measurements.

** Current coatings cannot withstand 200 exposure cycles above 2500°F and at low pressures.

9. Measure emittance of coatings, if possible, during tunnel operation. Measure properties listed in item 3, before and after exposure.

10. Subject coatings to simultaneous exposure of space vacuum, elevated temperature, and ultraviolet light within hot measuring chamber while monitoring spectral emittance by means of sliding specimen technique. The coating should be cycled from the cold to hot zone in the chamber without breaking vacuum.

PHASE B - RELATIONSHIP OF PROCESSING CONTROL PARAMETERS TO EMITTANCE

1. Sampling

   a. Examine process specifications or other control documents used in coating application to determine process limits (i.e., temperature limits, pack composition limits, vacuum-furnace limits, and other controls).

   b. Coat test specimens in laboratory at each limit, high and low of each parameter being controlled. Also, combine process parameters. Use different batches of pack materials even though composition is said to be identical.

   c. Distribute test specimens throughout retorts along with production or other parts being coated. If parts are being slurry coated, coat parts at different times throughout the day and at upper and lower thickness limits.

   d. Have suppliers coat five test specimens distributed throughout a production batch, if possible, and repeat this procedure **every 3 months for one year**.

2. Testing

   a. Upon receipt, subject samples to the following tests:

      (1) Spectral emittance inferred from room-temperature reflectance

      (2) Surface roughness

      (3) Coating weight and thickness

      (4) Surface composition and composition through cross section (selected specimens)

b. Select samples representing average and extreme conditions found in item 2a.

    (1) Subject selected samples to several temperature, pressure, and time-exposure conditions found critical in Phase A, and determine spectral and total normal emittance under these temperature and pressure conditions.

    (2) After exposure to conditions in item 2b.(1), determine spectral emittance, inferred from room-temperature reflectance measurements.

PHASE C - THERMAL CALCULATIONS

1. Examine vehicle and engine designs, both current and proposed, which could include use of refractory metals.

2. Select typical situations wherein spectral emittance and directional emittance properties may be involved.

3. Make conventional heat-transfer calculations employing graybody and diffuse assumption and compare results with calculations based upon spectral and directional properties.

4. Survey thermodynamic calculation groups in Aerospace Industry and ask whether spectral and directional property data is needed and, specifically, how it would be used.

PHASE D - SPECIAL EMITTANCE PROPERTIES

1. Improve total hemispherical emittance measuring techniques for use in air atmospheres and especially for temperatures above 2500°F. Find means of eliminating thermocouples.

2. Make angular spectral reflectance measurements at room temperature of coated refractory metals which previously have been exposed to elevated temperatures and reduced pressures. From these measurements, infer angular emittance and, thereby, extent to which surfaces probably exhibit diffuse radiation properties.

3. If item 2 indicates appreciable departure from diffuse radiation properties, make angular spectral emittance measurements at elevated temperatures and reduced pressures.

4. Develop a means of making spectral hemispherical emittance measurements.

RELATION OF CURRENT PROGRAM TO COMPREHENSIVE PROGRAM

As explained in Section II, the current program includes only a part of the work outlined in this section (Section X, "Comprehensive Emittance Program"). Part of each of the four Phases, A through D, is either included or is very similar. Until additional data are available from the current program, it would seem premature to implement any larger part of this idealized expanded program. Most of the problem areas presented under Phases A through D can be defined better when additional data are available.

In particular, it should be noted that the program under Phases A and B involves many samples. The use here of statistical methods is indicated, but until real data are available showing the variations and the factors that cause the variations, the setting up of detailed experimental plans would not appear warranted.

Section XI

SUMMARY

1. The emittance characteristics of coated refractory metals used on aerospace vehicles and engines are extremely important in applications involving radiant cooling and the exchange of heat. Heat loss and exchange are basically controlled by the Stefan-Boltzman expression wherein emittance times a constant, times the absolute surface temperature raised to the fourth power equals the heat loss (or absorption) in Btu/ft^2 sec.

2. The coated refractory metal exterior surfaces of vehicles which operate in the hypersonic regime, including cruise and reentry vehicles, are convectively heated by passage through the atmosphere. These surfaces are cooled almost solely by radiation of heat to space. This same method may be used to great advantage for cooling thrust chambers and nozzle extensions of space engines.

3. In order to calculate the temperature of the exterior skins of such vehicles, it is necessary to know the total hemispherical emittance of the coated metal. Much existing emittance data, especially above 2500°F, are total normal emittance data and do not equal hemispherical values unless the coatings are radiatively diffuse. The extent to which current coatings are diffuse is unknown.

4. In order to calculate the heat exchange rate within enclosures and between hot structural parts of the vehicles, it is generally necessary to know the spectral emittance of the surfaces involved. Large errors may be made if spectral data are ignored and total emittance is used. This is especially true where radiative transfer dominates, such as at higher altitude, in space, and at hypersonic temperatures.

5. Both strength of a refractory metal and protective life of the coating on a refractory metal are strongly temperature-dependent. Emittance affects the coating-metal system performance solely by the effect it exerts upon the system temperature.

6. The emittance of a coated refractory metal is a function of its environment. The emittance is generally a function of the partial pressures of the environment constituents, high temperature, and time. The emittance varies as the coating chemistry responds to its environment.

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7. Heating the as-received silicide coatings, TRW Cr-Ti-Si on colum-
bium 752 and chromalloy W-3 on TZM molybdenum, in air at 2000°F,
markedly increased emittance. Similar heating of these silicide
coatings in argon did not increase emittance. Heating Sylcor tin-
aluminide-coated tantalum in argon, as well as in air, increased
emittance. These changes are probably associated with oxide
formation for the silicide coatings and possibly with metallic tin
depletion in the outer surface of the tin-aluminide coating. It
appears that procedures for detecting very thin oxide layers must
be used.

8. The chemistry and distribution of chemical species in the afore-
mentioned coatings is actually known or may be inferred with a good
degree of reliability at atmospheric pressure to about 2500°F.
Such knowledge is limited above 2500°F and also at combinations of
temperatures above 2000°F and reduced pressures. Most is known
about the silicide coatings.

9. The coatings are extremely complex optically, and while some theory
exists which purports to relate the optical properties of non-
homogeneous materials to spectral emittance, the application of
such theory is difficult, partly because simple optical constants
of the coating constituents are unknown. In any case, it would
appear that the best, even to be hoped, would be the experimental
identification of the dominant optical mechanism for a particular
coating-system/environment range, and thereby, the establishment
of quasi-theoretical relationships.

10. The effect of high Mach number airstreams upon the emittance
properties of refractory metal coatings is unknown. It is surmised
that emittance will only be affected if the coating constituents
are soft enough to flow at service temperature when subjected to
aerodynamic shear forces or if oxide layers are not adherent.
Aerodynamic shear loads are actually quite low as shown by calcula-
tions.

11. Little relationship was found between spectral emittance properties
and surface roughness within the single batches of coatings tested.
It is probable that the roughness variations encountered were in-
sufficient to be significant.

12. Spectral normal emittances were inferred from room-temperature re-
flectance measurements made on single batches of refractory coat-
ings in the as-received condition. For the three coatings, in the
order given in item 7, the greatest spectral emittance variation
between individual specimens (10 to a batch) taken at 2 microns was

0.54 to 0.60, 0.78 to 0.82, and 0.54 to 0.60, respectively. The effect of elevated temperature on this variation was not determined.

13. For these three coatings, it was found that the total normal emittance measured at 2000°F equaled the total normal emittance calculated by integrating the areas under spectral curves inferred from room-temperature reflectance data. This means that easily obtained reflectance data are probably valid for trend studies up to 2000°F for the coatings measured.

14. Extreme exposure conditions for real situations during which external surface emittance is a significant performance parameter typically involve cyclic exposure times above 2000°F. For lifting reentry vehicles, these exposure times are not greater than 15 minutes; for hypersonic cruise vehicles, not greater than 2 hours; and for radiation-cooled engines and associated parts, not more than 5 minutes. Pressures for the vehicles would lie between 1 and 10 mm Hg, and for the engines from 0.01 mm Hg to space vacuum. Pressures on the interior surfaces of vehicles could be static pressure corresponding to altitude. These should be considered as typical situations, and not as limits.

15. A comprehensive emittance program which recognizes the significance of items 1 through 14 has been prepared and is presented in Section X.

Section XII

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COATING SUPPLIER QUESTIONNAIRE

The suppliers of the three coating systems studied were requested to furnish information concerning the general processing techniques employed and the coating properties. In reply to several questions, TRW referred to the report of an investigation of the Cr-Ti-Si coating (Reference 56). Where indicated, sections of this report are extracted as required. The questions asked and the replies which were received are as follows:

COATING PROPERTIES

    1. What is the composition of the coating?

        a. How was the composition determined (e.g., microprobe)?

        b. How does the composition vary through the thickness of the coating?

Replies to these questions were as follows:

Sylcor: The composition of the slurry applied is 65.6 percent Sn, 27.5 percent Al, and 6.9 percent Mo. The coating after heat treatment consists of an inner layer of $TaAl_3$ and an outer layer of 80 to 90 percent Sn and the remainder Al in which elongated crystals of $MoAl_3$ are embedded. The coating has been analyzed by electron probe and X-ray diffraction.

TRW: Elements present in coating are Cr, Ti, Si, and substrate constituents. The as-applied coating consists of three distinct layers in the silicide overlay plus a substrate diffusion zone (Reference 56). These layers are shown schematically in figure 50. The element concentration profile shown in the figure was determined by microprobe analysis on D-43 columbium alloy coated under the conditions indicated in replies to questions 1 and 2 under "Coating Processing."

    2. How does the composition vary from lot to lot and among parts within the same lot?

Replies to this question were as follows:

Sylcor: No statistical composition analyses have been made.

COATING
SURFACE

| | SUB-STRATE | DIF-FUSION ZONE | | SILICIDE | ZONE | |

PHASE THICKNESS (MICRONS)

| | SUB-STRATE | 18μ | 5μ | 8μ | 37μ |

ELEMENT CON-
CENTRATION
(ATOMIC
PERCENT)*

Element							
Cb	93	93	49	39	15	11	4
W	7	7	7	7	4	4	0.5
Zr	1	1	0.1	–	–	–	–
Cr	–	–	17	12	6	14	20
Ti	–	–	23	15	10	6	9
Si	–	–	4	26	65	65	66

(Cb,Ti)$_3$ (Si, W,Cr)$_2$ ——— |←——— (Cr,Ti, Cb, W) Si$_2$ ———→|

OR

(Cb,Ti,Cr)$_5$ (Si, W)$_3$
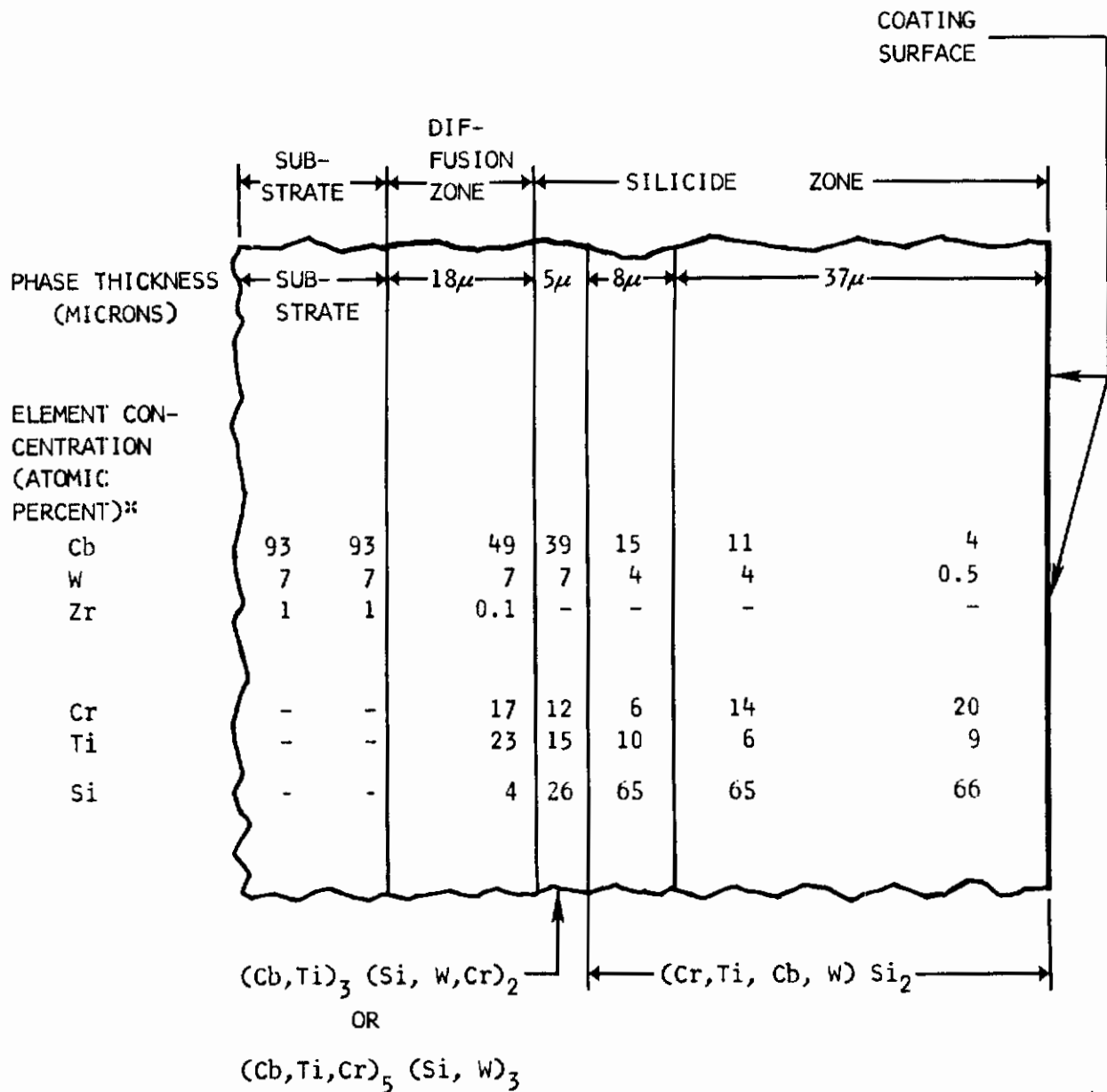
* ATOMIC PERCENT CONCENTRATION EQUALS WEIGHT/MOLECULAR WEIGHT X 100. THE
PHYSICAL LOCATION OF THE NUMERICAL VALUES INDICATES THE APPROXIMATE LOCATION
WITHIN THE SPECIMEN TO WHICH THEY APPLY.

Figure 50. Schematic Drawing of TRW Cr-Ti-Si Coating on D-43 Columbium Alloy

TRW: Reproducible — based on metallographic analysis and oxidation control data. No batch-to-batch microprobe data are available. Composition of coating may vary from location to location in the coating retort due to thermal gradients in the furnace.

3. How does the composition change with environmental experience?

Replies to this question were as follows:

Sylcor: When the coating is exposed to an oxidizing environment at elevated temperatures, two major reactions occur. One, the $TaAl_3$ interdiffuses with the substrate to form $TaAl_2$. A one- to 2-mil layer is converted in one hour at 2300°F or higher. Two, the Al in the Sn-Al phase forms a layer of Al_2O_3 which actually does the protecting. At very high temperatures, the Sn is lost gradually, but slowly, by vaporization. At temperatures below 2300°F, Sn oxides are formed in addition to Al_2O_3. In a vacuum or in an inert gas, Sn starts to boil away at 2300°F or higher, since no coherent Al_2O_3 film is formed.

TRW: Referred to Reference 56 from which the following is extracted.

"Exposure of the Cr-Ti-Si coating in air at one atmosphere, at temperatures up to 2300°F, is accompanied by a weight gain which is essentially parabolic in nature (for at least 200 hours). At 1800°F, the protective oxide is essentially silica, containing considerable chromium and titanium either as independent oxides or in solid solution. Exposure of the Cr-Ti-Si coating in air at 2500°F and above results in an initial weight gain, followed by a significant weight loss for a considerable period of the exposure. At 2500°F, the initially formed surface scale is essentially Cr_2O_3, with lesser quantities of the oxides of titanium and silicon. Continual exposure at 2500°F results in the rapid loss of chromium, either by chromium or chromium oxide vaporization, eventually leaving a scale consisting of the oxides SiO_2, TiO_2, and possibly the complex oxide $TiO_2 \cdot Cb_2O_5$. The remaining disilicide coating is continually depleted of chromium and titanium, and enriched in columbium, until the disilicide can no longer sustain the formation of the protective oxide system. The less oxidation-resistant lower silicides (also columbium-rich) continually grow in width during the elevated temperature exposure. As the exposure temperature increases above 2500°F, the increased diffusion rates and accelerated loss of chromium correspondingly reduce the coating protective life.

"Reduced pressure oxidation of the Cr-Ti-Si coating at 2500°F again results in the rapid loss of chromium from the coating. However, this evaporation is accompanied by the additional loss of silicon via SiO volatilization. The enhanced loss of coating elements by vaporization at the reduced pressures greatly accelerates the failure mechanism characteristic of the Cr-Ti-Si coating. Failure of the Cr-Ti-Si coating by a wear-out type

mechanism is basically the result of three phenomena: (1) depletion of chromium from the disilicide and from the protective oxide system, (2) enrichment of the disilicide and the oxide scale with columbium, and (3) depletion of coating elements from the substrate. The latter factor is associated with the increased susceptibility of the substrate to crack or fissure formation in the coating during thermal cycling."

4. What emittance measurements have been made on the coating?

    a. Unexposed?

    b. Exposed? (Conditions and test method.)

Replies to these questions were as follows:

Sylcor: Emittance measurements have been made on this class of coating at Douglas (Reference 55), Convair (Reference 63), and Martin.

Douglas Data (T-111)

Condition	Total Normal Emittance
As-coated	0.18 (at 80°F)
Oxidized at 3200°F	0.76 (at 80°F)

Convair Data (T-111)

Condition	Temp °F	Total Normal Emittance
As-coated	RT	0.18
As-coated	2200	0.25
As-coated	2700	0.28
After 5 oxidation cycles to 2700°F	RT	0.65
	2700	0.68

Please see references for techniques used.

TRW: None at TRW.

5. Can you refer us to any customers who have conducted emittance measurements on your coatings?

Replies to this question were as follows:

Sylcor: Refer to reply to preceding question 4.

TRW: Boeing, McDonnel, Lockheed.

6. Has the surface finish of the coating been characterized? To what degree can it be controlled?

Replies to these questions were as follows:

Sylcor: The surface finish of the coating has not been characterized.

TRW: No.

7. Has the thermal expansion coefficient of the coating been determined?

Replies to this question were as follows:

Sylcor: The thermal expansion coefficient of the coating has not been determined.

TRW: No - would vary with composition across the coating.

COATING PROCESSING

1. What is the composition of pack or slurry? What are the major and minor impurities?

Replies to these questions were as follows:

Sylcor: The composition of the slurry is 65.6 percent Sn, 27.5 percent Al, and 6.9 percent Mo. There are only trace impurities (i.e., less than 100 ppm) in these powders.

TRW: Pack process.

Cr-Ti Cycle	Silicon Cycle
60 part, by weight, Cr, 40 part, by weight, Ti, with one part, by weight, halide salt added (KF,NaF,CrCl$_3$...)	100 part, by weight, Si, with 0.5 part, by weight, halide salt added (NaF,KF)
Major impurities - Fe,Zr,Al	Commercially available silicon — not ultrapure

Chromizing Corporation: Active ingredients are primarily silicon and some boron. Dougle-pack method, that is, two runs in separate packs of similar composition.

2. What are the processing conditions (e.g., time, temperature, atmosphere)?

Replies to this question were as follows:

Sylcor: Processing is one hour at 1900°F in vacuum of less than one-micron pressure.

TRW:

Cr-Ti Cycle	Silicon Cycle
8 hours 2300°F 10^{-2} mm Hg pressure (air)	4 to 6 hours 2300°F to 2100°F 10^{-2} mm Hg pressure (air)

3. Are any posttreatments of the coating employed?

Replies to this question were as follows:

Sylcor: There are no posttreatments.

TRW: No.

4. What requirements exist for surface condition and finish of the substrate prior to application of the coating?

Replies to this question were as follows:

Sylcor: No rigid requirements for surface finish before coating. Can be etched or grit blasted.

TRW: Deburred by abrasive tumbling, hand sanding, etc. Cleaned, degreased, etched to remove any oxide or surface scale.

5. How does the surface finish of the substrate affect the surface finish of the coating?

Replies to this question were as follows:

Sylcor: Very little relationship between surface finish of substrate and surface finish of coating.

TRW: Coating surface reflects prior surface roughness. However, highly polished substrate surface cannot be retained after coating.

6. How accurately can the thickness of the coating be controlled?

Replies to this question were as follows:

Sylcor: Thickness can be controlled plus or minus 20 percent on most surfaces. In recesses or hard to get at places, the coating thickness variation may be much higher.

TRW: t ±0.004 inch.

7. What quality control measures are used?

Replies to this question were as follows:

Sylcor: Thickness, weight changes, visual and microscopic surface examination, and control samples for destructive evaluation are used as quality control measures.

TRW: Micrometer measurements and metallographic examination

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13. ABSTRACT The role of emittance in refractory metal coating performance was reviewed and analyzed for the purpose of orienting the planning of a comprehensive program to provide accurate and proper emittance data for thermal calculations needed in the design of advanced aerospace vehicles and engines. The following was found: Coated refractory metals are used and are planned for future use on reentry and hypersonic cruise vehicles which are cooled almost solely by the radiation of heat to space. Space engine nozzles and extensions fabricated of coated refractory metals may be cooled to advantage by radiation. Emittance values have a profound effect on the rate of heat rejection, and thereby, on the metal-coating system temperature which, in turn, controls coating life and metal strength. The emittance of a coated refractory metal is a function of its environment which includes temperature, time, partial pressures of the atmospheric constituents, and the free-stream velocity of the atmosphere under extreme temperature conditions. Total hemispherical emittance values are needed for thermal calculations involving exterior vehicle and engine surfaces that radiate to space, but for calculations between surfaces, the use of spectral emittance values is indicated if emittance varies appreciably with wavelength. Most emittance data in the literature are total normal data which do not necessarily equal total hemispherical data unless the coatings

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ABSTRACT (Continued)

radiate diffusely. The extent to which refractory metal coatings display diffuse radiation is not known.

As an aid in planning the comprehensive program, a number of preliminary emittance experiments were performed. Heating as-received silicide-coated columbium and molybdenum alloys and one tin-aluminide-coated tantalum alloy to 2000°F in air caused a marked increase in emittance which, for the silicide coatings, was associated with oxide formation. The total normal emittance of these coatings measured at 2000°F was found to equal the total normal emittance calculated by integrating the spectral curve (as a function of a 2000°F graybody) inferred from room temperature reflectance data. This indicates that the shape of the spectral curve at 2000°F is not a strong function of temperature.

A comprehensive emittance program is presented for possible future action. It covers the effect of cyclic environmental exposure on emittance, including exposure in a hypersonic tunnel; the relationship of coating process control parameters to emittance; the significance of various types of emittance properties in thermal calculations; and recommendations concerning the determination of special emittance properties such as angular emittance.