UNCLASSIFIED

AD 419028

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

UNCLASSIFIED

64-5

WADD-TR-60-370
Part III

THERMAL RADIATION PROPERTIES OF MATERIALS
PART III

TECHNICAL REPORT NO. WADD-TR-60-370, PART III
AUGUST 1963

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D.C., for sale to the general public.

Copies of this report should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

FOREWORD

This report was prepared by the Institute of Engineering Research, University of California at Berkeley, California, under USAF Contract AF33(657)-7793. This contract continued the research on radiation properties of materials which was begun under Contract AF 33(616)-6630, initiated under Project 7360 "Materials Analysis and Evaluation Techniques", Task No. 736001 "Thermodynamics and Heat Transfer". It was administered under the direction of the Air Force Materials Laboratory, Aeronautical Systems Division, with Mr. R. A. Winn acting as Project Engineer.

Part I of this report covered the work done from the initiation of the project in July 1959 to September 1960, and Part II from September 1960 to December 1961. This report, Part III, is the final report on this project. The research was conducted under the direction of R. A. Seban, Professor of Mechanical Engineering, with assistance, during the phase covered by this final report, from E. Andersen, M. Dillenius, L. Jones, J. Tsuji and B. Pearce.

ABSTRACT

The effect of temperature on the normal spectral emittance in the range from 1 to 15 microns is demonstrated for certain polished metals and some oxidized and coated metals by a comparison of absorptances measured at room temperature and emittances measured at temperatures of the order of 2000°R to 2500°R. The emittances were obtained in a system designed and constructed in the previous phase of this research and these results are affected by the less than optimum operation of this system, by which contamination of the sample occurred, irregularly but consistently. A major diversion of effort thus occurred in attempts to ameliorate this difficulty, but without complete success. A large part of the results do appear to be satisfactory, though in this conclusion reliance must be placed on the results of other investigators to an extent greater than was first anticipated.

The results for platinum, nickel, and iron reveal at high temperature the correspondence with the Hagen-Rubens law which is implied by available results on the total normal emittance, though the correspondence in this spectral range must be attributed to anomalous effects. With oxides and with coated materials the effect of temperature on the spectral values appears to be small and localized, though with some materials these are indications of permanent changes in the emittance as the period of exposure to high temperature is increased.

This technical documentary report has been reviewed and is approved.

ROBERT E. BROCKLEHURST
Assistant Director
Materials Physics Division
AF Materials Laboratory

LIST OF FIGURES

SECTION I

APPARATUS AND TECHNIQUE

INTRODUCTION

The objective of this research was the determination of
the effect of temperature on the normal spectral emittance of
certain metals and coated metals. This was accomplished
experimentally by the measurement of the spectral normal
absorptance at room temperature in a cavity reflectometer and
the spectral normal emittance at high temperature in a system
devised for this purpose. The effective spectral range of
both devices was from 1 to 25 microns but practically all of
the measurements were limited to the more convenient 1 to 15
micron range of the NaCl optics and monochrometer prism.

A major impediment to the unambiguous achievement of the
experimental objectives was encountered in operating diffi-
culties with the system for the measurement of the normal
spectral emittance and the major and most harmful problem was
associated with contamination of the sample. The origin of
this difficulty was apparently in inadequate oxygen removal
from the system and the continued effort to ameliorate this
and other minor problems diverted much of the effort from the
real objectives of the research. A serious consequence too,
was the ambiguity introduced into all of the results for the
spectral emittance, in consequence of which considerable
interpretation of the results is required and more reliance
than should be necessary needs to be placed on other exper-
imental results. These operating difficulties are considered
in detail in the Appendix, where the system is described
completely.

SPECTRAL EMITTANCE SYSTEM

The essential components of this system are comprised of
a reference cavity and a sample heater contained in an en-
closure which can initially be evacuated and subsequently
charged with argon. This sytem has been described before
(2, 3) and is described in detail in the Appendix, and only its
essential aspects are considered here. Of these, the sample
heater is the most important; basically this is a small cavity

---

furnace in front of which the 7/8 inch diameter disc sample is mounted on a sample holder made of molybdenum sheet; a water cooled radiation shield contained in the furnace door provides the aperture through which the sample is viewed. The reference cavity is a graphite tube, mounted centrally in a heater core, with a center line coinciding with the center line of the sample heater, and this center line is in the horizontal plane. A moveable mirror, with its axis vertical, is situated midway between the front of the cavity and the sample itself; by rotation of this mirror radiation emerging either from the sample or from the cavity can be directed through a window in the side of the enclosure into the optical system which directs it onto the inlet slits of a Perkin Elmer Model 98 Monochrometer. Fig. 1 shows schematically the arrangement of these components.

Particularly because of the difficulties that were encountered, note must be taken of the reasons for the design of this system, with two furnace-type heating units contained within the enclosure. In both, heating is provided by tungsten wires, wound on ceramic cores, and insulated externally by additional ceramic and low temperature insulation. In the case of the sample, this type of heating, involving irradiation of the back of the sample, was chosen so that the sample could be of the disc type, of a size usable directly in the Gier Dunkle cavity, and other reflectometers used for room temperature measurements. Such immediate interchange would not have been possible, for instance, with systems in which the sample is heated by the passage of an electric current through it, though admittedly such systems involve a minimum of material for the heater system and thus reduce the possibility of the retention of foreign gas in the enclosure in which the sample is contained. The situation of the cavity within the enclosure was made so that a single line of sight would exist for both the cavity and the sample, though in addition, the level of operating temperature that was anticipated, in excess of $2800^{O}R$, made necessary the use of heater wires that required a vacuum or an inert gas environment.

Operation of this system commenced with the introduction of a sample mounted on a molybdenum sample holder. The sample thermocouple wires of 30 ga. platinum-platinum 10% thodium or of 30 ga. chromel-alumel, were spot welded individually to the back of the sample in the center region and the wires were carried through ceramic insulators away from the sample to the thermocouple therminal block. The system was then closed and evacuated to a pressure of 1×10^{-3} mm Hg, this pressure then being maintained for an hour or more before argon was introduced to give a final total pressure slightly above atmospheric
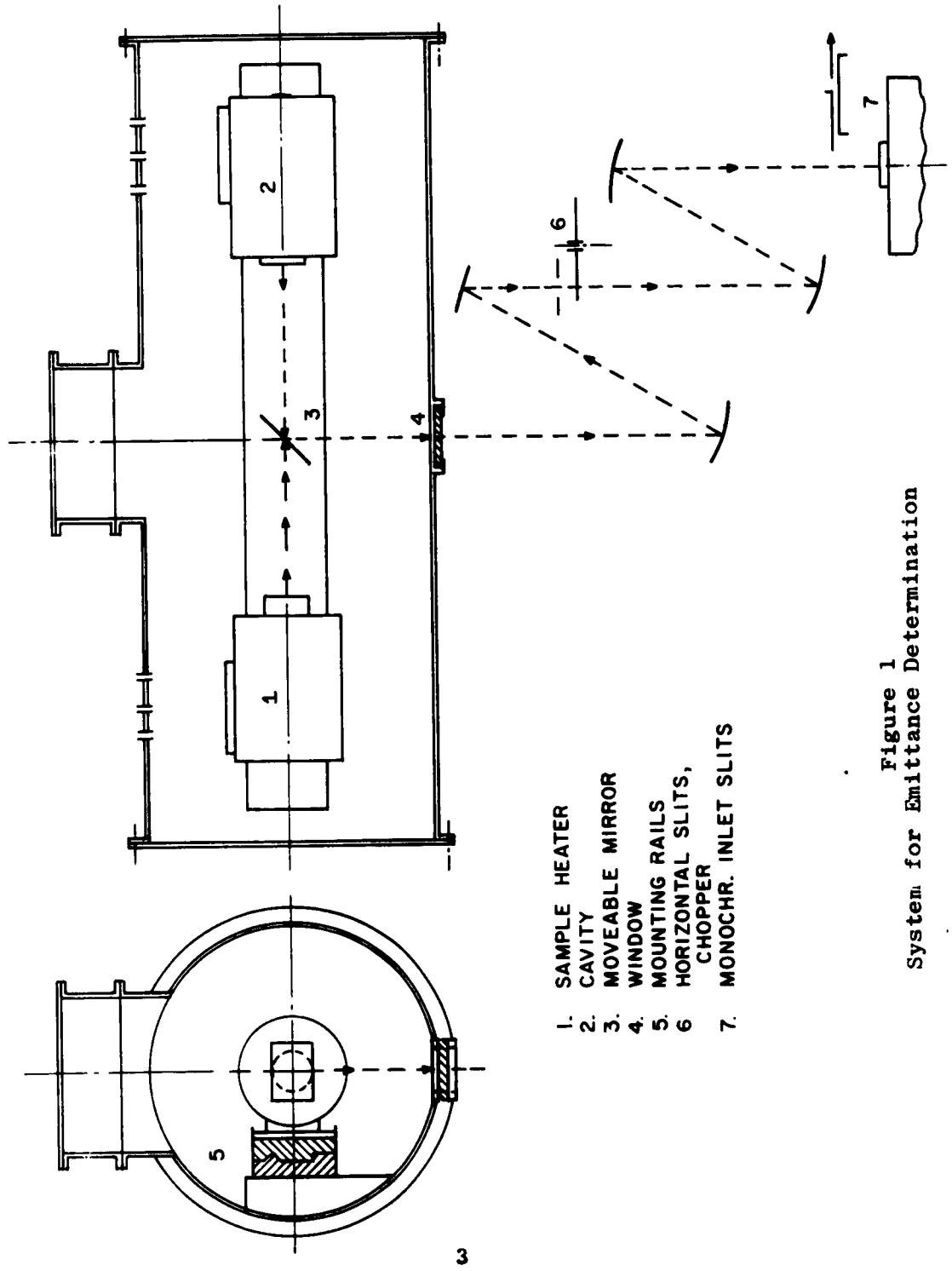
2

1. SAMPLE HEATER
2. CAVITY
3. MOVEABLE MIRROR
4. WINDOW
5. MOUNTING RAILS
6. HORIZONTAL SLITS, CHOPPER
7. MONOCHR. INLET SLITS

Figure 1
System for Emittance Determination

3

pressure. Heating of sample furnace and cavity could then commence, with electrical supply under manual control with a current limit. Voltage increases then resulted in operating temperature levels in a period of two to three hours, when steady temperature conditions would exist and observation could begin.

At any wave length setting on the monochrometer, the essential observations were the output (zero level) with a black shutter at room temperature in the inlet optics and the output when either the sample or the cavity was observed by rotation of the mirror. Besides the sample or the cavity, contributions to the output could be made by all of the optical components up to the chopper location, if any of these existed at a temperature above the room temperature of the reference sight. Analysis[2] indicated that such additions were not expected because the argon assisted in the cooling of the moveable mirror and this could be confirmed by a sight on the mirror when placed normal to the exit window immediately after exposure to the cavity or to the sample. When, in some situations, the system was operated with vacuum, small contributions to the output at long wave lengths could arise from the mirror and the results were corrected for this, primarily from the output detected from a direct sight on the mirror.

In the simplest sense, the ratio of the output signals, S_c from the cavity and S_s from the sample, could then be interpreted as

$$\frac{S_s}{S_c} = \epsilon s \frac{E_s - E_o}{E_c - E_o}$$

1.1

The emissivity of the sample, ϵ_s, was then obtained from this relation, the monochromatic emissive powers E for a black body being specified as E_o, corresponding to room temperature; E_s, corresponding to the sample temperature as indicated by its therocouple; E_c, corresponding to the cavity temperature as indicated by the thermocouple located at the back of the cavity.

The area viewed at the sample, or at the front of the cavity, was in the vertical direction determined by horizontal slits located at an image position near the chopper, the height normally used was about 2.4 mm. The horizontal width of the viewed area was determined by the slit opening of the monochrometer, and was essentially the same. The maximum slit opening normally used was 1 mm.

Operating procedures varied to some extent but usually observations were made at increments of 0.2 microns for wave

4

lengths from 1 to 3 microns and at half micron increments there-
after. Reproducibility was checked by repeating readings after
the initial spectral traverse. The single beam operation re-
quires considerable time, and a single spectral determination
required a period of about forty-five minutes.

Other sample temperatures, differing not too greatly from
the initial temperature, could be obtained in about an addition-
al hour.

Power was shut off after the final determination and the
system cooled to room temperature in about five hours. Then the
system could be opened and the sample removed.

ROOM TEMPERATURE ABSORPTANCE

Absorptances at room temperature were determined by a
cavity reflectometer of the Gier-Dunkle type; this and its mode
of operation has been described (1, 4) and the errors usually
associated with it have been considered. One additional source
of error could arise in its use with metals the surfaces of
which have become rough due to thermal ageing. If this rough-
ness is sufficient to destroy the specularity of the sample and
yet is not great enough to make it a diffuse reflector then the
radiation emerging from the cavity may originate from an
appreciable part of the cavity near the exit hole. Because the
exact geometrical nature of the reflection is unknown in these
cases the error is not assessable; if it is assumed that the
reflectance is constant over a definite angle with respect to
the angle of incidence, it can be shown that the error in the
reflectance due to the cavity opening might be as much as 7%.
This is a disastrous error in the evaluation of absorptance for
a metallic surface.

Reflectance readings were also made in most cases with the
Beckmann DK-2 spectro-reflectometer, as an adjunct to the
determinations of room temperature reflectance with the cavity
reflectometer. With specular samples, appraised against an
MgO reference, there is an error corresponding in magnitude to
one reflection from the sphere wall. If the degree of non-
specularity is such that most of the reflection occurs to a
region near the inlet port, the correction may still be the
same. Because of the ambiguties the Beckmann readings are
not in general reported for metallic surfaces, but the ratio
of non-specular to "total" reflection is reported as an index
of the degree of roughness of metallic surfaces. Associated
with these values are deductions from roughness measurements
obtained with a Talysurf profilometer.

5

TEST SEQUENCE

The normal sequence of operations on a given sample involved: a) roughness determination on Talysurf indicator, b) absorptance determination at room temperature with cavity reflectometer and DK-2, c) emittance determination at high temperature in emittance system, d) absorptance determination at room temperature with cavity reflectometer and DK-2, e) roughness determination. These steps were not always followed in detail, and for many samples the roughness records were not taken; steps b, c, d, were quite well followed and steps b and d indicated the degree of "reversibility" that had been obtained. Particularly in view of the contamination problem that existed in the emittance system, this was an important appraisal.

6

SECTION II

SPECTRAL EMITTANCE OF METALS

INTRODUCTION

Smooth samples of platinum, nickel, copper, molybdenum and iron were subjected to the test sequence indicated in the prior chapter, with emittance values determined at temperatures between $1800^{\circ}R$ and $2200^{\circ}R$, so that the prime index of temperature effect is in the comparison of the absorptance measured at room temperature and the emittance measured at high temperature, the temperature ratio then being of the order of three and one half. Comparisons between measured emittances at different temperature levels are not possible with accuracy because the temperature ratio is too small and this restriction on the temperature ratio arose in turn from the operating problems with the emittance system. Also, in all cases, continued exposure of the sample in the emittance system ultimately resulted in values of the emittance that were significantly higher than the initial values thereof, with subsequent absorptance values also much higher than the original values. While in the cases for which results are quoted there was no visual evidence that contamination had occurred, it can also be shown that a film with a transmittance only a little less than unity could also account for the disparity in the results.

A primary comparison for results of this type is to the normal emittance that is predicted from the optical properties that are specified by the classical free electron theory and in particular, to examine the dependence of the spectral emittance on temperature in comparison to the dependence of the electrical conductivity on the temperature. The Drude theory, specified for a single charge carrier, is the simplest specification for the spectral dependence of the optical properties of metals. It is accorded almost universal textual presentation, with some variability of its algebraic form, that chosen here corresponds to the presentations in Pepperhoff[5] and Rutgers[6]. The real and imaginary parts of the "index of refraction" are then given by the relations

$$n^2 - k^2 = 1 - \left(\frac{\lambda}{\lambda_1}\right)^2 \left[1 + \left(\frac{\lambda}{\lambda_2}\right)^2 \right]^{-1} \qquad 2.1$$

$$2nk = \left(\frac{\lambda}{\lambda_2}\right)\left(\frac{\lambda}{\lambda_1}\right)^2 \left[1 + \left(\frac{\lambda}{\lambda_2}\right)^2 \right]^{-1} \qquad 2.2$$

The normal absorptance is given by the Fresnel relation as:

$$\alpha = \frac{4n}{(n+1)^2 + k^2}$$
2.3

In Eqns. 2.1 and 2.2 the wave length $\lambda_1 = \sqrt{\frac{\pi m c^2}{N e^2}}$ is on the long wave length side of the region for which is predicted a rapid rise of the absorptance to unity. This wave length cannot be predicted, because neither the effective electron mass m nor the number of free electrons per unit volume N are known precisely. Measurements of the optical properties in the short wave length region have indicated a value of $\lambda_1 = 0.17$ microns for copper. It should be of the same order, but somewhat greater, for the other metals considered here. The wave length $\lambda_2 = \frac{2\sigma_0}{c}\lambda_1^2$ is approximately a bound on the short wave length side of the region in which n and k become of the same order of magnitude. Here σ_0 is the DC conductivity.

There is in the literature a very considerable examination of the degree to which Equations 2.1 and 2.3 can be used to correlate measured values of the optical constants, and in particular whether the values of λ_1 and λ_2 deduced in this way indicate a conductivity σ_0 that corresponds to the D. C. value. Generally this is not so, and Givens[7] indicates that lower values are usually indicated, the reduction from the D. C. value envolving factors like two to five. Schultz,[8] however, by careful measurements on copper, gold, and silver, concluded that the D. C. values could be obtained.

There is no general algebraic combination of Equations 2.1, 2.2 and 2.3 which gives an explicit specification of the absorptance in terms of λ_1 and λ_2 but there are numerous approximations which do so for limited spectral ranges. The most useful here are the expression of Mott and Zener, for $5\lambda_1 < \lambda < \lambda_2/10$

$$\alpha = \frac{2\lambda_1}{\lambda_2}$$
2.4

and the "Hagen Rubens" expression for $\lambda > \lambda_2$

$$\alpha = \sqrt{\frac{2\lambda_1^2}{\lambda\lambda_2}} = \sqrt{\frac{c}{\lambda\sigma_0}}$$
2.5

8

The latter forms a common specification for the absorptance of metals; it has been integrated over the spectral range to obtain expressions for the total normal emittance and it has been used in conjunction with the Fresnel equations, integrated for angular dependence, to relate the total normal to the total hemispherical emittance.

The absorptance specified by Equation 2.5 is indicated as curve H, for $530^{\circ}R$ and $2000^{\circ}R$, on all the figures giving the results, the value of the conductivity being taken from Reference 9. The Mott-Zener expression, Equation 2.4, is indicated also as curve M, based on the same conductivity and a value of λ_1 which is, except for copper, merely an estimate; for copper $\lambda_1 = 0.17$; and the estimates are platinum 0.20, molybdenum, 0.20, nickel 0.20, iron 0.20. These values are not illogical and the curves given by Equations 2.4 and 2.5 can be regarded as asymptotic for the absorptance that is given by the Drude theory in the region.

Additional absorption of radiation occurs, particularly in the short wave length regions, for all except the alkali metals and this is usually interpreted as an additional contribution to the optical constants as specified by Equations 2.1 and 2.3. If bound oscillators are assumed, this addition can be made analytically and such formulations commonly appear. Alternatively, Beattie and Conn[10] appraised the difference between the measured optical constants and those estimated from the Drude theory as the consequence of internal photoelectric absorption. For the transition metals the spectral region in which such additional effects are important extends far into the infra-red, to the region of ten microns, and is the dominant effect in the value of the absorptance, so that the values there are very much greater than those that are indicated by Equation 2.4.

The presentation of the results first emphasizes the experimental values; the absorptances determined at room temperature and the emittances determined at elevated temperature are shown as curves and these are identified on the caption sheet for the figure on which they appear by the temperature associated with them, the atmosphere in which the result was obtained, and the history of high temperature exposure subsequent to the prior indication thereof. Lines are shown for the absorptance given by Equation 2.4, designated as M and for Equation 2.5, designated as H, calculated on the basis that has been indicated. The caption sheets also contain values for the fraction of the reflection that was indicated to be non-specular by the results obtained from the Beckmann DK-2 reflectometer, and the sheets contain also values of peak to peak roughness and the lateral spacing between peaks as deduced from the

9

records obtained from the Talysurf indicator.

In the presentation of the results for the emittance there are shown curves for those "initial" values of this quantity which agree with expectation. Only one curve is shown for the "anomalous" higher values of the emittance that were obtained after longer periods of exposure in the emittance system and this curve represents the relatively constant value obtained after a relatively long exposure. For platinum, nickel and copper the intermediate behavior is discussed in greater detail by Andersen [11].

PLATINUM

Platinum samples were polished with aluminum oxide, cleaned with water and then subjected to absorptance and emittance determinations. Three different samples were used, and the results were all similar to those for the No. 3 sample that are presented on Figure 2, on which Curve A represents the initial absorptance determination at room temperature. Thereafter the sample was aged for 3 hours and the absorptance was measured again to give essentially the same values as Curve A. Three additional hours of aging at $1960^{\circ}R$ produced a slight reduction in absorptance at wave lengths greater than 3 microns. This is indicated by Curve B. The difference with respect to Curve A is so small as to be almost within the error of the absorptance determination but the difference is consistent and in accord with the expected consequence of some stress relief in the surface.

Next, the sample was put into the emittance system and three determinations were made, with the results given by Curves 1, 2, and 3. Beyond 10 microns the indicated absorptances tended to constant values. This was appraised as an error in measurement so that the results for that range are now shown. After these three emittance determinations the sample was removed from the emittance system and the absorptance at room temperature was determined again, to yield the results given by Curve C. The absorptances are above the prior values and there is a marked increase near 9 microns. In general, however, the differences are relatively small and in contrast to subsequent experience, at least the order of the original absorptance was maintained to this point.

The sample was next introduced into the emittance system for determinations at higher temperatures. Curve 3 was essentially reproduced but then successively higher values of emittance were obtained, terminating, after 58 additional hours, at the values of emittance given by Curve 4. This situation was typical of the other platinum samples also, and of the

10

other metallic samples, except copper, as well. After a certain period of residence in the emittance system, higher values of emittance were obtained.

The final room temperature absorptance is given by Curve D, and these absorptances are far in excess of the initial values. The fraction of the non-specular reflectance indicated by the Beckmann determination, and tabulated with the caption of Fig. 2, reveals the result of the roughness developed on the surface of the specimen. The roughness was, by error, not determined for this sample but Sample No. 4, giving similar final results for emittance and reflectance, indicated a peak to peak roughness of 2.5 microns, with a lateral spacing of about 25 microns.

NBS PLATINUM

A single sample of platinum, prepared by the National Bureau of Standards as a "standard" sample, was similar to the platinum samples except that it had been aged by heating in air at a temperature of 2742°R for one hour, followed by a cooling period of the order of twelve hours, as described in Reference 12. The resulting surface was slightly rough, as indicated by the fraction of non-specular reflection in the initial condition, in comparison to that given for the platinum sample on Figure 2.

Curve A of Figure 3 gives the initial room temperature absorptance: at short wave lengths the values are practically identical to Curve A of Figure 2, while at long wave lengths they are similar to Curve B of Figure 2. The irregularity in the absorptance near 6 microns that is indicated by Curve A of Fig. 3 appears however to be unique to the NBS sample.

The first emittance determinations were made early in the experimental program with a flat bottom cavity for which the emittance apparently departed significantly from unity at long wave lengths. The emittances then obtained are given by Curves 1 and 2 of Figure 3 and these are terminated at 6 microns, the apparent limit of reliability of the results. Actually the values indicated at longer wave lengths were almost constant at the terminating values and Curve 2 extended to 25 microns at this constant value.

Curve B of Figure 3 is the absorptance at room temperature after these initial emittance determinations. It is lower than Curve A at long wave lengths, but in small amount and in essence reversibility was preserved up to this stage of the examination.

Six months later two additional emittance determinations were made, at 1960°R and at 2390oR and these emittances, shown

11

Figure 2

SPECTRAL EMITTANCE OF PLATINUM

Sample No. 3

Curve	Temp., ^{O}R	Atmos.	Interval Heating Time	Date
A	530	Air	3 hrs at T = 1210°R	7-11-62
		Vac	3 hrs at T = 1960°R	7-13-62
B	530	Air		7-18-62
1	2190	Vac.	1 hr. at T > 2190°R	8-13-62
2	2125	Argon	48 hrs at T > 2000°R	8-15-62
3	2490	Argon	4 hrs at T > 2200°R	8-15-62
C	530	Air	30 hrs at T = 2560°R	8-16-62
4	2600	Vac.	17 hrs at T = 2660°R	8-22-62
D	530	Air		8-23-62
M_1, H_1	530			
M_2, H_2	2000			

DK-2 fraction non-specular

Date	Wave length 0.5	1.0	1.5	2.0	2.5	Remarks
7-10-62	0.06	0.01	0	0	0	Mechanically polished
7-16-62	0.06	0.01	0	0	0	After ageing period on 7-13-62
7-18-62	0.09	0.03	0.01	0.01	0.01	After Curve B
8-23-62	0.86	0.82	0.79	0.75	0.72	After Curve D

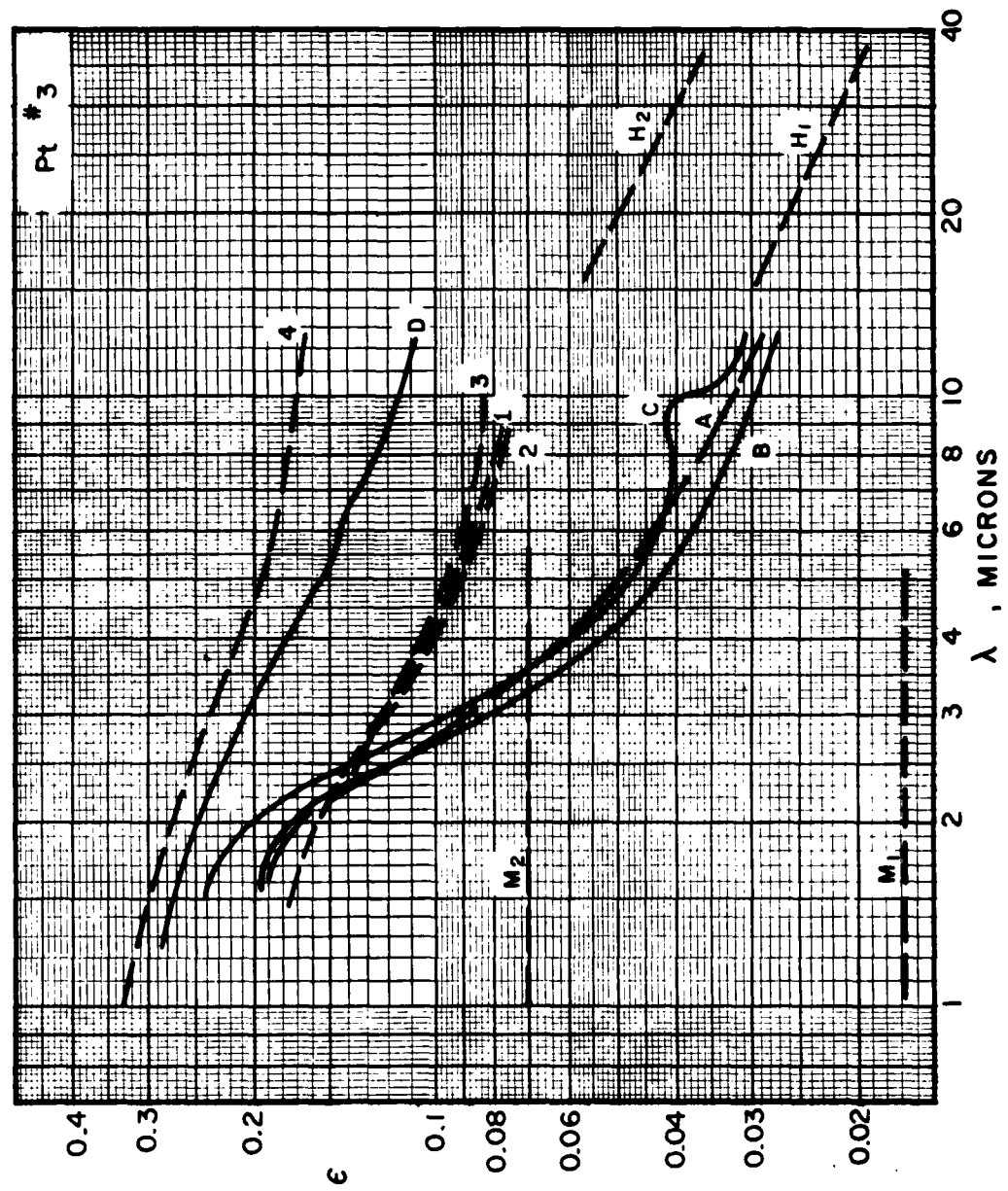| Date	Roughness, microns Peak to Peak	Lateral	Remarks
7-10-62	0.025	10	Mechanically polished
7-16-62	0.025	10	After Curve A
7-18-62	0.025	10	After Curve B

Figure 2

13

Figure 3

SPECTRAL EMITTANCE OF NBS PLATINUM

Curve	Temp. ^{o}R	Atmos.	Interval Heating Time	Date
A	530	Air		5-1-62
1	1960	Argon	1 hr at $T > 1960^{o}R$	5-3-62
2	1995	Argon	23 hrs at $T > 1960^{o}R$	5-4-62
B	530	Air		5-22-62
3	1960	Argon	11 hrs at $T > 1950^{o}R$	11-7-62
4	2390	Argon	1 hr at $T > 2300^{o}R$	11-8-62
C	530	Air		1-9-62
M_1, H_1	530			
M_2, H_2				

DK-2, fraction non-specular

| | Wave Length | | | | | |
Date	0.5	1.0	1.5	2.0	2.5	Remarks
5-1-62	0.3	0.11	0.073	0.057	0.049	As received
3-17-63	0.45	0.392	0.35	0.32	0.29	After Curve C

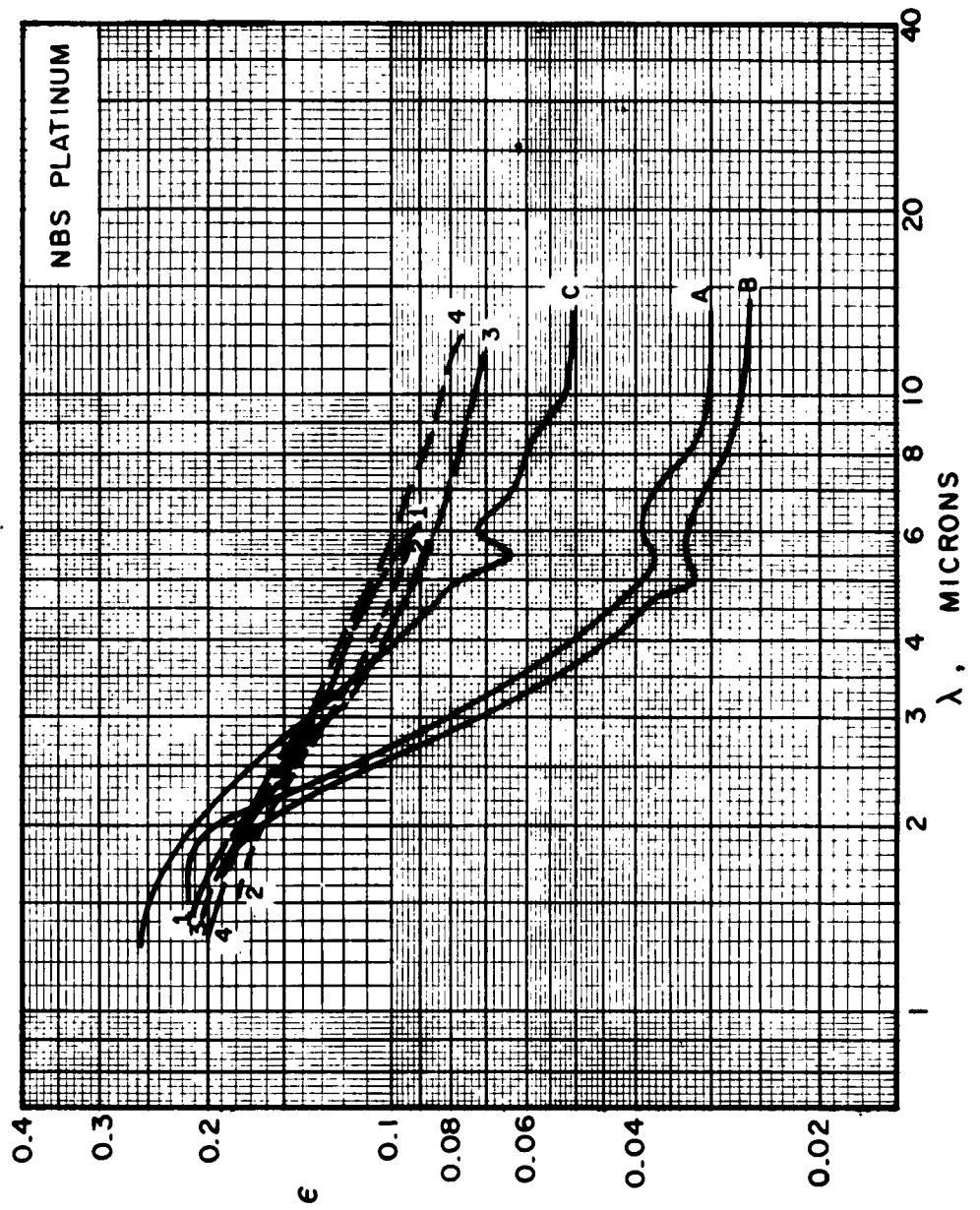| | Roughness, microns | | Remarks |
Date	Peak to Peak	Lateral	
5-1-62	0.12	10	As received
4-2-63	0.15	20	After Curve C

Figure 3

15

as curves 3 and 4, are of the same order as the initial values, and are more consistent in the temperature effect indicated at long wave lengths. These emittances are also essentially the same as those indicated for platinum by Curves 1, 2, and 3 of Fig. 2.

The final determination of room temperature absorptance was made at a much later time and, strangely, the original value of absorptance was not realized but rather the higher values given by Curve C were obtained. It was still later when the DK-2 determinations were made and these indicated only a slight increase in roughness.

NICKEL

A number of nickel samples were examined, all were first polished with aluminum oxide, and cleaned with water. The results exhibited here are those for Sample No. 7, and these are typical of the experience with this material. Curve A of Fig. 4 represents the values of the absorptance at room temperature of the polished nickel. This curve also represents within 5% the absorptance of 9 different samples, though some others indicated an absorptance 40% higher. The reason for the latter difference is not clear, differences in polishing technique could have been a factor. Curve A however does represent the values of greatest confidence and also agrees with other data on nickel.

Curve A also indicates the reflectance of nickel samples aged in vacuum for three hours at 1060°R and three additional hours at 1960°R. Another sample, No. 10, maintained the reflectance at the values given by Curve A after four hours of ageing at a temperature of 2470°R. There is apparently little stress relief which would tend to alter the reflectance of the polished material.

Curve 1 of Fig. 4 represents the emittance obtained at 2280°R after four hours in the emittance system at that temperature. Similar results were obtained with Sample No. 10 after one hour at 2395°R.

Emittance determinations were continued with Sample No. 7 after the initial determination, with slightly higher sample temperatures. The indicated emittance increased and Curve 2 of Fig. 4 indicates the final values after a total of fifty-two hours in the system. A large increase in emittance was produced, and the succeeding determination of absorptance at room temperature as shown by Curve B indicates that much of this increase was permanent. The DK-2 results, (taken much later in time)

indicate that the specularity of the sample had almost vanished and the surface indicator revealed a peak to peak roughness of the order of 6 microns.

MOLYBDENUM

Samples of molybdenum were cut from the 0.005 inch thick sheet that was used for the sample holders; the samples were cleaned with acetone but were not polished. The initial roughness of the material indicated peak to peak values of less than 0.25 microns, and a relatively larger component of non specular reflection. Curve A of Fig. 5 gives the initial absorptance of this sample.

Curves 1 and 2 of Fig. 5 represent the emittance found from successive determinations at two temperatures; similar values were found for initial determinations with other similar samples. The subsequent absorptance at room temperature, given by Curve B, indicates that changes occurred during the residence of the sample in the emittance system though the situation of the values found for the emittances makes it appear that such changes occurred after the emittance determinations had been completed.

Another molybdenum sample, of the same type, having the same initial absorptance, was aged in a vacuum furnace for one hour at $2292^{O}R$ at a pressure of 1×10^{-5} mm Hg and the absorptance was determined at room temperature after this ageing. This final absorptance was practically the same as that given by Curve B of Figure 5, except that in this latter case the absorptances were slightly lower in the region of ten microns. It is for this sample that the fraction of non-specular reflection is given in the caption of Fig. 5 and, after ageing, there was no major change in the surface profile of the sample. Clearly, however, the nature of the surface was altered even during the one hour heating period. Abbott[13] has noted similar experience with molybdenum even with better vacuum conditions.

IRON

A limited investigation was conducted on two iron samples for spectral absorptance and emittance determinations. The two samples were cut from a pure iron sheet and polished with aluminum oxide and cleaned with water. Due to the susceptibility of iron to oxidation, all absorptance and emittance measurements were taken as soon as possible after the sample had been polished. In the case of unavoidable intervals between absorptance and emittance measurements, the samples were kept in a low humidity environment in order to retard any oxidation that

17

Figure 4

SPECTRAL EMITTANCE OF NICKEL

Sample No. 7

Curve	Temp. ^{O}R	Atmos.	Interval Heating Time	Date
A	530	Air		8-13-62
1	2160	Vacuum	1 hr at T = 2260°R	8-29-62
2	2570	Vacuum	48 hrs at T > 2260°R	8-31-62
B	530	Air		9-4-62
M_1, H_1	530			
M_2, H_2	530			

DK-2, fraction non-specular

	Wave length					
	0.5	1.0	1.5	2.0	2.5	Remarks
Date						
8-13-62	0.04	0	0	0	0	Mechanically polished
1-24-63	1	1	1	1	1	After Curve B

	Roughness, microns		Remarks
Date	Peak to Peak	Lateral	
8-13-62	0.025	25	Mechanically polished
1-24-63	7.5	25	After Curve B

Figure 4
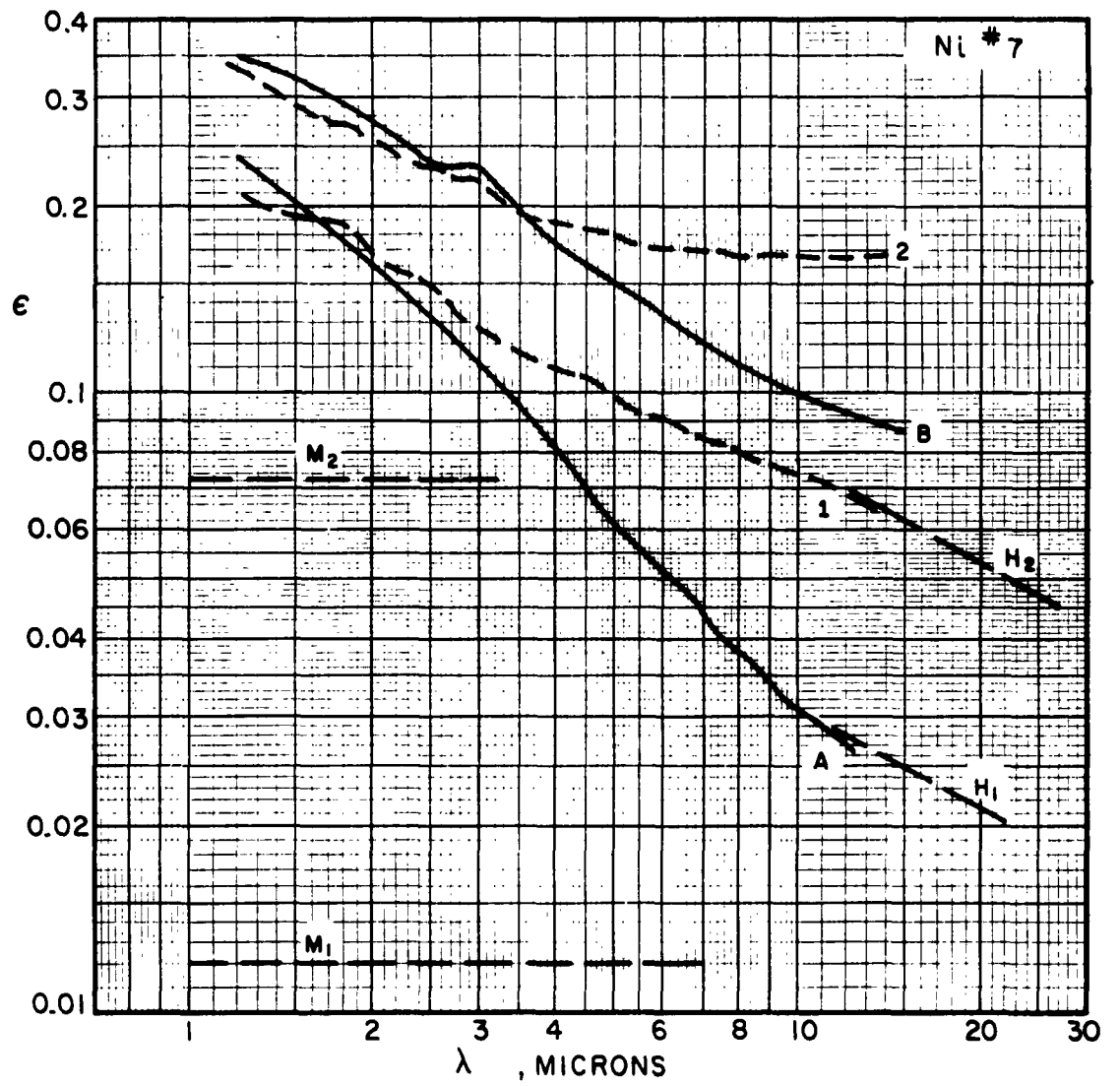
19

Figure 5

SPECTRAL EMITTANCE OF MOLYBDENUM

Sample No. 1

Curve	Temp. ^{O}R	Atmos	Interval Heating Time	Date
A	530	Air		12-3-62
1	2000	Argon	1 hr at T > 2060°R	1-10-63
2	2240	Argon	8 hrs at T > 2060°R	1-10-63
B	530	Air		1-23-63
M_1, H_1	530			
M_2, H_2	2000			

DK-2 fraction non-specular

		Wave length				
Date	0.5	1.0	1.5	2.0	2.5	Remarks
1-29-63	0.706	0.445	0.282	0.199	0.150	DK-2 and roughness measurements are for a different sample, but identical to the sample used for Curve A

Roughness, microns

Date	Peak to Peak	Lateral
1-29-63	5	13

Figure 5

21
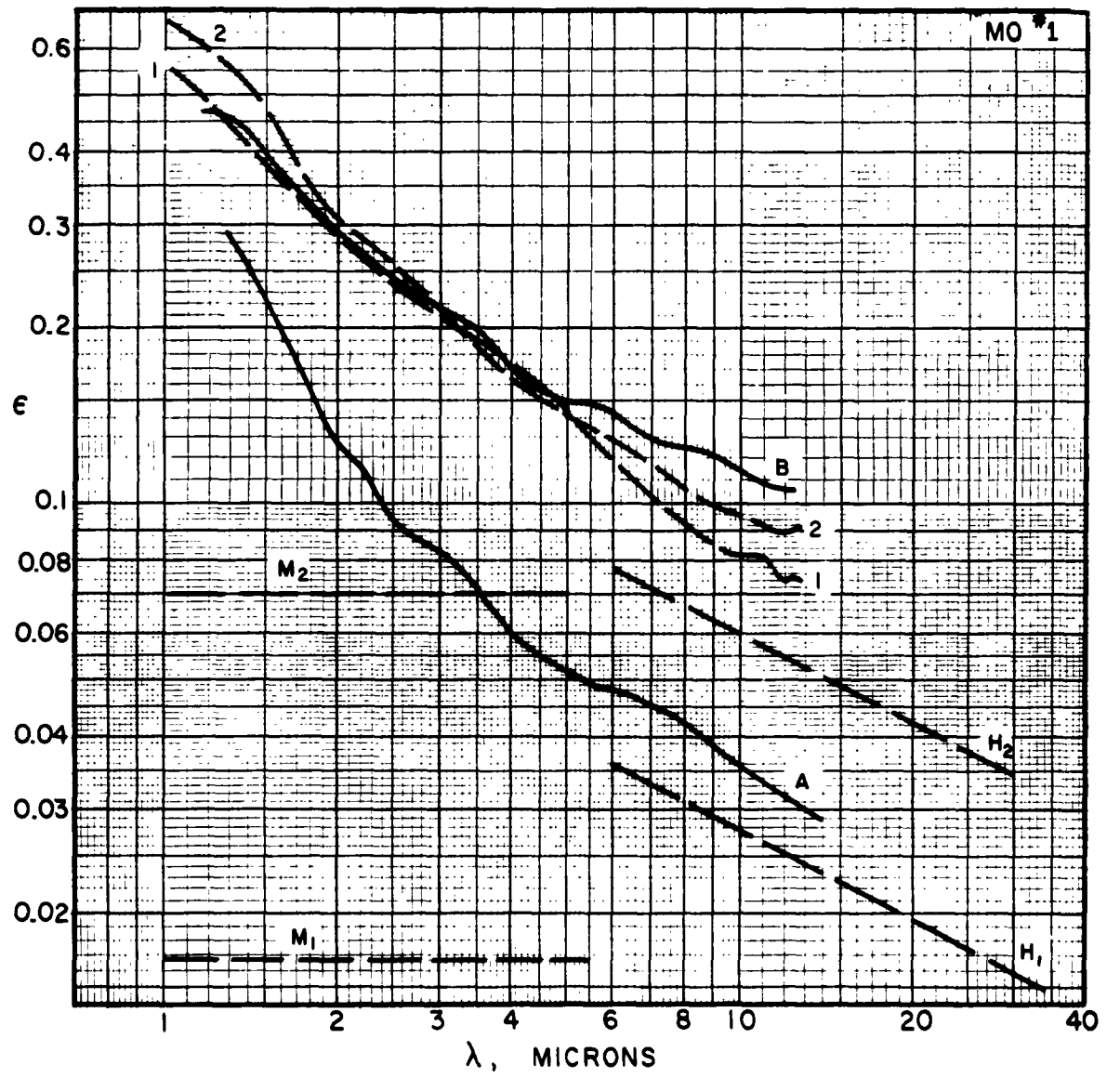
Figure 6

SPECTRAL EMITTANCE OF IRON

Sample No. 2

Curve	Temp. $^\mathrm{o}$R	Atmos.	Heating Time	Date
A	530	Air		4-18-63
1	1940	Argon	$2\frac{1}{2}$ hrs at T = 1904$^\mathrm{o}$R	4-24-63
2	2370	Argon	24 hrs at T > 1200$^\mathrm{o}$R 5 hrs at T > 1200$^\mathrm{o}$R	4-25-63
B	530	Air		4-26-63
M_1, H_1	530			
M_2, H_2	2000			

DK-2, fraction non-specular

	Wave length					
	0.5	1.0	1.5	2.0	2.5	Remarks
Date						
4-23-63	0.03	0.01	0	0	0	After Curve A
4-26-63	0.40	0.26	0.2	0.18	0.16	After Curve 2

Roughness, microns

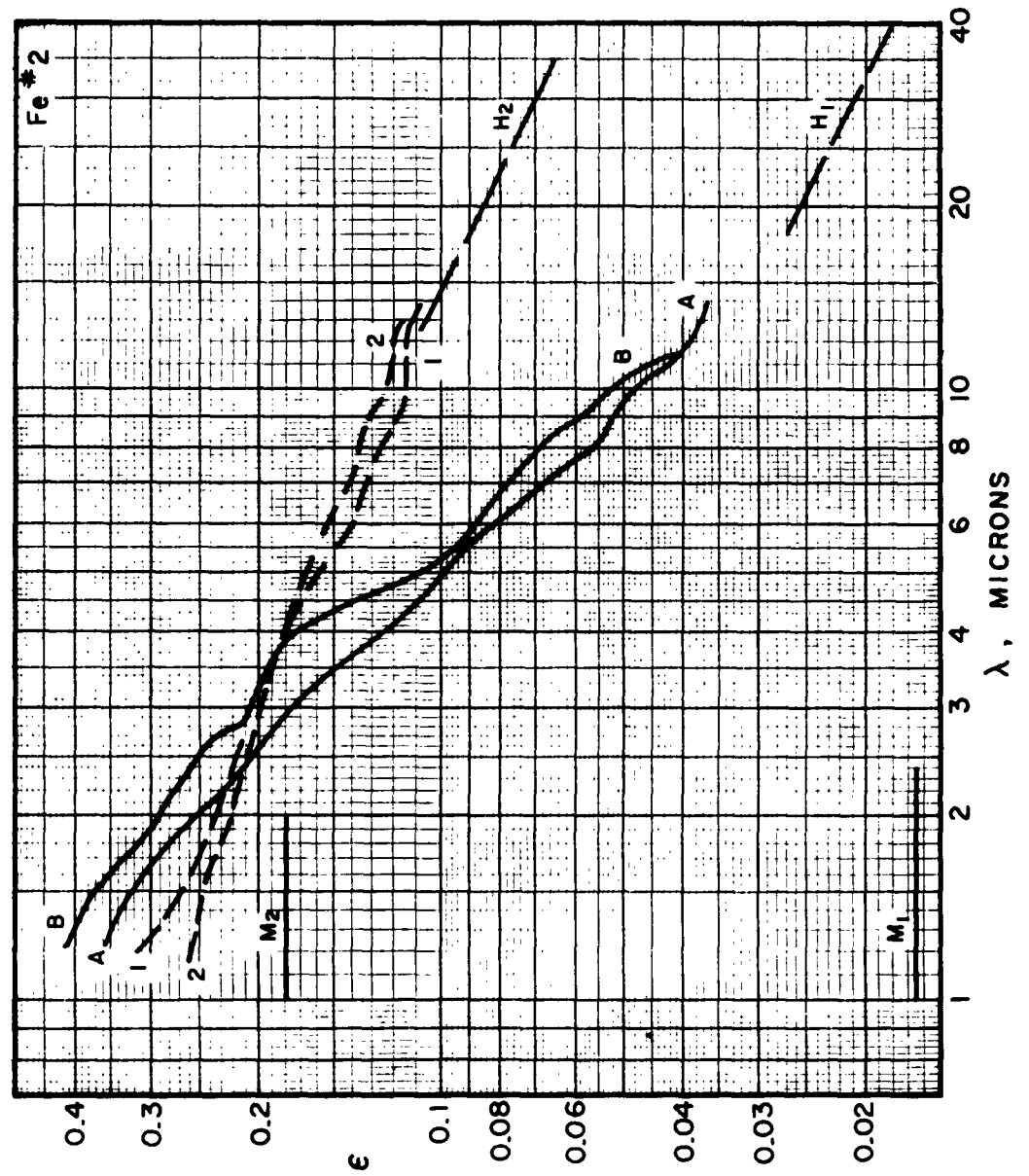| Date	Peak to Peak	Lateral	Remarks
4-23-63	0.05	10	After Curve A
4-26-63	0.5	50	After Curve B

22

Figure 6

23

might otherwise occur.

Curve A of Fig. 6 represents the values of the absorptance at room temperature obtained from both freshly polished samples. In the spectral emittance determinations at elevated temperature ambiguities arose in the data obtained from sample No. 1. This data differed sufficiently enough from the expected results so that omission was warranted and only data for sample #2 is presented herein.

The properties of iron differ from the metals investigated in that iron undergoes a phase change from the $\propto$ to the λ^1 phase at 2000°R. The two emittance runs shown by Curves 1 and 2 of Figure 6 were made in order to show the change in emittance of the material between the two phases.

Curve 1 of Figure 6 represents the emittance values obtained for the $\propto$ phase at 1940°R after $2\frac{1}{2}$ hours in the emittance system at that temperature. Following this run, the temperature of the sample was increased to 2370°R and held for five hours to assure completion of the phase change throughout the material. Curve 2 represents the emittance values obtained for the sample temperature of 2370°R and the emittance values are seen to be lower than Curve 1 for wavelengths less than 4 microns.

Due to the slow sample cooling time that occurs in the emittance apparatus, the sample was assumed to have transformed back to the $\propto$ phase for the subsequent determination of the absorptance at room temperature as shown by Curve B in Fig. 6. The high values of the room temperature absorptance after the high temperature emittance runs as compared to the room temperature absorptance of the freshly polished sample indicate permanent changes in the surface of the sample. The surface changes are evident by comparison of the DK-2 and roughness results obtained before and after the high temperature emittance runs for sample #2. The DK-2 results indicate that the specularity of the sample had decreased and the surface indicator showed an increase to 0.5 microns of the peak to peak roughness. Due to the decrease in specularity and subsequent increase in the diffuse component, the increase of Curve B over Curve A may be partially accounted for on the basis of the error that occurs for diffuse reflection due to the opening in the bottom of the absorptance apparatus.

COPPER

Three samples of copper were tested under generally similar conditions and the results for sample #3 as shown on Fig. 7 are characteristic of all the samples. These results are clearly

affected by oxidation and possibly by deposits and none of
them can be regarded as fundamental but they show the interest-
ing sequence obtained by thermal ageing of a sample which was
first mechanically polished. Curve A shows the absorptance
obtained in that condition; it is typical of other quotations
for mechanically polished copper and, remarkably, is represented
fairly by an extrapolation of the Hagen-Rubens equation. The
Mott-Zener approximation, really applicable in this spectral
region, gives an absorptance of 0.003.

After three hours of ageing at $810^{O}R$ the room temperature
absorptance changed to Curve B. The variation is strange and
some oxidation may have occurred. Three more hours of heating
at $1660^{O}R$ produced the room temperature absorptance revealed by
Curve C. There is definite evidence of stress relief in the
decreased absorptance at long wave lengths but the increases
near 1 micron must be regarded as anomalous. The absorptance
there is far above the value of 0.02 which would be regarded
as typical for electropolished copper.

Curve 1 shows the emittance obtained at $2235^{O}R$ after forty-
five hours at this temperature in vacuum. This is essentially
the minimum emittance obtained. Prior and subsequent emittances
where higher than the minimum values by as much as 0.01, with
the values obtained after 75 hours tending to be high by that
amount. The values of the emittance are probably too high but
the striking feature is the relative independence with respect
to wave length except in the region near 10 microns. This is
the kind of spectral dependence indicated by the Mott-Zener
approximation.

The ratio of the reflectances associated with the measured
emittance to that associated with the Mott-Zener absorptance is
0.976; thus a film with a transmittance of about $\sqrt{0.976}$
would rationalize the two values. Alternatively, the selection
of an electrical conductivity at half its D.C. value would make
the Mott-Zener approximation correspond with the experimental
results. Both views are plausible.

After removal of the sample from the emittance system the
room temperature absorptance was determined and the ageing was
continued in a vacuum furnace at $2235^{O}R$ so that the total time
at this temperature was increased to 102 hours. Curve D re-
presents the absorptance that was typical of three determinations
that were made during this final heating period; two others
were slightly higher. There is no specific rationalization for
the excess of the absorptance at room temperature, given by
Curve D, over the emittance at high temperature, given by Curve
1. Actually the positions should at least be reversed and the

25

Figure 7

SPECTRAL EMITTANCE OF COPPER

Sample No. 3

Curve	Temp. ^{O}R	Atmos.	Interval Heating Time	Date
A	530	Air		7-13-62
B	530	Air	3 hrs at T = 810°R	7-19-62
C	530	Air	3 hrs at T = 1660°R	7-23-62
1	2235	Vacuum	17 hrs at T = 2200°R 75 hrs at T = 2200°R	7-31-62 8-1-62
D	530	Air		8-15-62
H_1	530			
M_2, H_2	2000			

DK-2, fraction non-specular

Date	0.5	1.0	1.5	2.0	2.5	Remarks
7-11-62	0.11	0.03	0.01	0	0	Mechanically polished
7-17-62	0.40	0.21	0.07	0.03	0.02	After aging 3 hrs at 810°R
7-23-62	0.33	0.22	0.11	0.06	0.04	After Curve C
8-2-62	0.95	0.98	0.98	0.97	0.96	After Curve 1

Roughness, microns

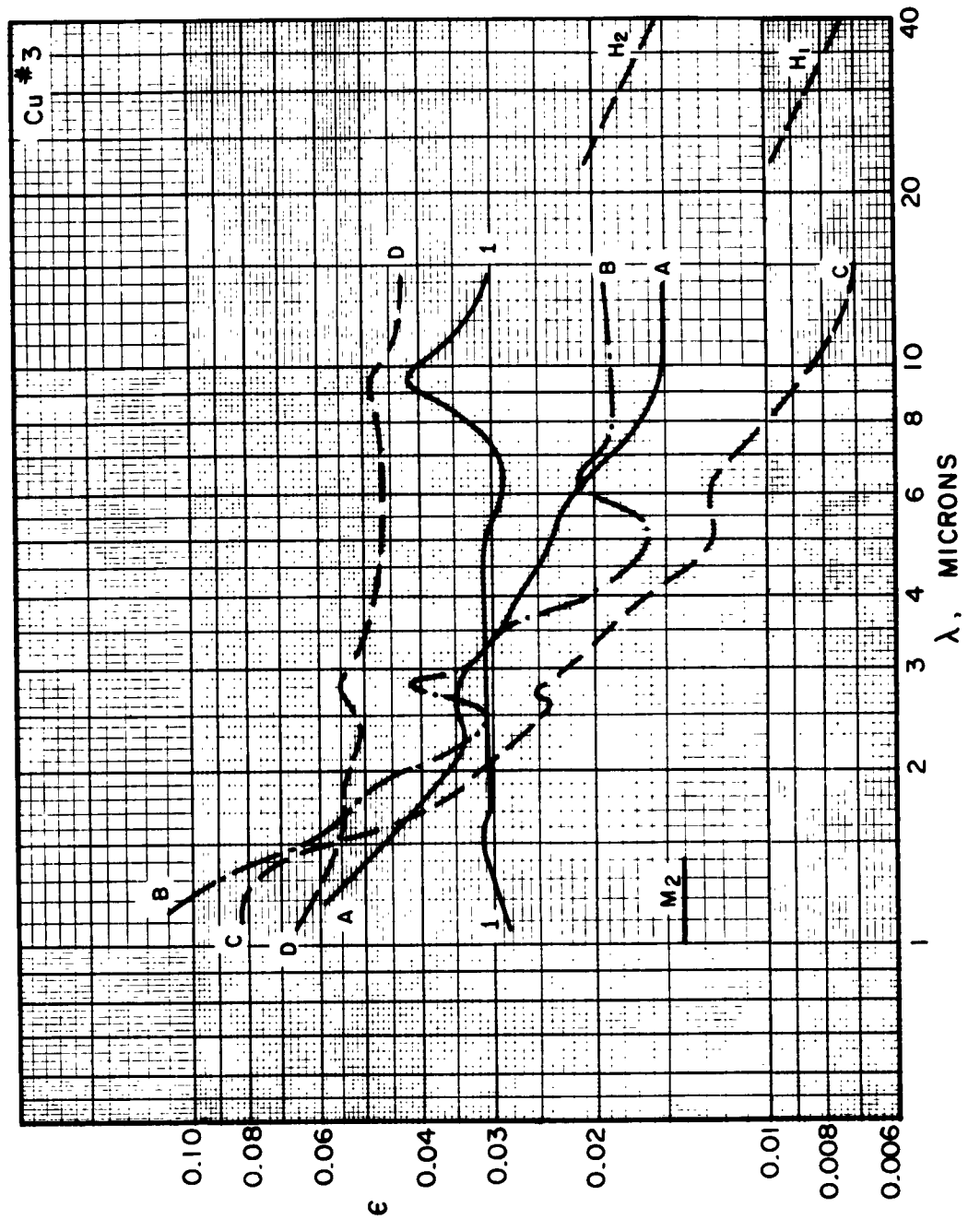| Date	Peak to Peak	Lateral	Remarks
7-11-62	0.02	5	Mechanically polished
7-17-62	0.02	5	After aging 3 hrs at 810°R
7-23-62	0.05	10	After Curve C
8-2-62	4	50	After aging period on 8-1-62

Figure 7

27

excess of the final absorptance may be due to the formation of
a film having a transmittance of the order of 0.97, or of error
in the final absorptance measurement because of the non
specularity of the surface. The absorptance is so low in the
case that the maximum error in the reflectometer due to surface
non-specularity could account completely for the magnitude of
the absorptance that is given by Curve D.

THE ANOMALY IN THE EMITTANCE MEASUREMENTS

The ultimate increase in the emittance at high temperature,
illustrated particularly by the results that have been indicated
for platinum and for nickel, but found to some extent for
molybdenum and iron as well, cannot be regarded as conclusive
because of the variable difficulties with contamination that were
experienced with the emittance system. Clearly, the deposition
of a thin layer of absorbing material on the surface of the
sample would produce such an increase. If it can be assumed for
such a film that interference effects will be averaged out
either by variations in thickness or scattering processes within
it, then the normal reflectance of the surface can be calculated
on an energy basis as

$$ r = r_1 + \frac{r_2(1 - r_1^2) t^2}{1 - r_1 r_2 t^2} \qquad\qquad 2.6 $$

where r_1 is the reflectance of the air-film interfact, r_2 is
the reflectance of the film-metal interface, and t is the
transmittance of the film. If r_1 is near zero and r_2 is near
unity, then the ratio of the reflectance with the film to the
reflectance of the metal surface will be approximately the
square of the transmittance of the layer. Should the difference
between the "initial" and "final" emittance be due to the
formation of such a film, then the ratio of the reflectances
associated with these emittances will be approximately the
square of the transmittance of the film. A like interpretation
can be associated with the "initial" and "final" absorptances
at room temperature. Table 1 gives these ratios, with the
subscript on the reflectance denoting the curve for the
absorptance or emittance with which it is associated.

28

Table 1

Platinum	λ	2	4	6	8	10
Figure 2	$\dfrac{r_4}{r_3}$	0.86	0.89	0.89	0.90	0.89
	$\dfrac{r_D}{r_A}$	0.92	0.87	0.90	0.90	0.91
Nickel Figure 5	$\dfrac{r_2}{r_1}$	0.89	0.92	0.91	0.90	0.89
	$\dfrac{r_B}{r_A}$	0.87	0.89	0.92	0.92	0.93

The tabulation indicates that the assumption of a film having a transmittance of the order of 0.95 would rationalize the results for these two metals. In view of the contamination problems that did occur, this interpretation cannot be ignored and the higher "final" emittances and absorptances must therefore be regarded as a possible consequence of malfunction of the emittance system. Other interpretations are possible, however, and it is appropriate to at least cite them here. It has already been noted that the effect of the increased non-specularity that was found in the "final" condition of the samples could produce errors in the determination of the room temperature absorptance, though the magnitude thereof would probably not attain the level of the ratios in Table 1. Also, while an alteration in the degree of specularity of the surface would not to the first order affect the accuracy of the determination of the emittance in the emittance system, a basic effect would begin to occur. This can be considered in the limit, for which the surface can be visualized to become so rough as to be completely diffuse. Then the normal emittance would become identical with the hemispherical value and this hemispherical value, as a lower limit, would be the same as the value for a smooth surface. This would result in an increase of 20 to 30% in the measured normal emittance. This is not as much as observed and indicated by the reflectance ratios of Table 1, (i.e. an increase in emittance from 0.10 to 0.13 gives a reflectance ratio of 0.96) but this effect could also contribute to the observed effect.

29

Finally, there is the unknown effect of the crystal growth, that produces the surface irregularity, on the optical properties of the surface itself.

Recent evidence, obtained by means of room temperature absorptance measurements on samples of polished nickel and polished platinum after various periods of ageing at temperatures above $2300^{O}R$, at pressures of $3x10^{-5}$ mm Hg and below, has never resulted in final absorptances as high as those indicated on Figs. 2 and 4. Rather, values typical of the initial values, Curves A, have been maintained. And there has also been no substantial increase in the sample roughness. Thus it appears that the high final values of emittance and absorptance that are indicated in Figs. 2, 3 and 4 are most probably the consequence of either contamination or chemical reaction.

RELATION OF THE EMITTANCE TO THE DRUDE THEORY

In considering the relation of the values of emittance to the prediction of the Drude theory, it is assumed tacitly that the "initial" values of the emittance are correct, that is unaffected by what ever phenomena result in the subsequent increase in the emittance. Support for this view is only inferential in terms of comparison with other results for the emittance at similar temperatures; such comparisons, made in the following sections, do provide a basis for this interpretation.

For platinum, nickel, and iron, the values of the absorptance at room temperature at long wave lengths are remarkably close to the prediction of the Hagen Rubens equation, Eqn. 2.5, based on the D. C. conductivity as given in reference 9. This is the kind of correspondence that has led to the historic recommendation for the use of Eqn. 2.5 for the specification of the absorptance, and the position of Eqn. 2.4 shows the kind of extrapolation of Eqn. 2.5 that is involved, for this equation should be valid only when the absorptance is less than that given by Eqn. 2.4. In this respect it must be recalled that in this latter relation the absorptance is inversely proportional to wave length λ_{l} , and the value of λ_{l} was chosen arbitarily. The value λ_{l} = 0.20 was used; smaller values hardly seen realistic, and substantially smaller values would be needed to move the intersection of Eqn. 2.4 and 2.5 to the spectral region in which the results still correspond with Eqn. 2.5

For the transition metals, anomalous absorption effects produce the absorptances that are increasingly greater than the indication of the Drude theory. Insofar as is conceived the total emittance for radiation at room temperature, the Hagen Rubens law is quite adequate, for with the maximum in the

30

spectral emissive power near 10 microns, and only 10% of the energy at wave lengths shorter than $7\frac{1}{2}$ microns, the departure of the spectral absorptance from Equation 2.5 at shorter wave lengths is of no consequence.

The emittance at high temperature can be compared on Fig. 2, 4, 5 and 6 to the indications of Eqn. 2.4 and 2.5 for a temperature of 2000°R, with the effect of differences between this and the sample temperature approximated satisfactorily in the small range that is involved by considering the absorptance given by Eqn. 2.5 to depend on the square root of the absolute temperature, and from Eqn. 2.4 directly on the absolute temperature. The gross interpretation is of improved coincidence with the Hagen Rubens relation at these higher temperatures. This is in part expected, for the decrease in the conductivity decreases the wave length λ_2, as can be seen also from the movement to shorter wave lengths of the intersection of Eqn. 2.4 and 2.5. The spectral emittance is a little lower than the prediction of Eqn. 2.5 but still close enough to make it valid and to sustain it as a basis for the calculation of the total emittance. The reason for the coincidence must be in a just appropriate alteration of the "anomalous" effects on the optical constants to balance the alteration in the free electron effect at the shorter wave lengths as that is indicated by Eqn. 2.4.

Compared to the transition metals, for copper those absorption mechanisms contributing to the optical properties as additions to the free electron effects are significant only at wave lengths shorter than 1 micron and in the spectral region considered here any experimental departure from that theory must be associated with surface effects. The susceptibility of copper to work hardening and the effect of surface strain on the optical properties of the surface layer are well known and for copper in particular the initial reflectance depends strongly on the polishing technique that is employed. Also, the large conductivity of copper lowers the absorptance, so that the value given by Eqn. 2.4 is 0.003, and the lower limit at which Eqn. 2.5 ought to apply is about 100 microns. Thus the fact that the absorptance at room temperature of mechanically polished copper is given in magnitude by Eqn. 2.5 ranks as one of the purest kinds of coincidence. In reference 2 it was indicated how higher values could be obtained by stressing the surface additionally via roughening with sandpaper and lower values by electropolishing the surface. The attainment of absorptances as low as those indicated by the Drude theory requires special care; Shultz[8] has done this. In the present instance annealing accomplished some reduction in absorptance via stress relief, the reduction is relatively small and may have been affected by oxidation in the imperfect vacuum system that was used.

31

In the emittance system a radical alteration of the
spectral dependence of the emittance was achieved, with a
substantial degree of spectral invariability. This is the
trend of Eqn. 2.4, though the measured absorptances are still
more than twice the theoretical indication. At the temperature
of 2235^OR substantial evaporation occurred and the surface,
though rough, was clean.

COMPARISON TO OTHER RESULTS

A comparison to the present results for the "initial"
values of the emittance to similar values that are available in
the literature is particularly important because of the
assumption that has been made of the correctness of these
initial values despite the subsequent anomalous behavior of the
determinations made in the emittance system. Figures 8 through
10 each contain one of the curves for the measured spectral
emittance. For all metals except the NBS platinum, curves are
shown for the results of Price[14] who obtained results for
emittance for wave lengths up to 4 microns. For nickel and
copper there are available the results of Hurst[15] and for
the NBS platinum "standard" the results of Harrison[12].

For completeness the values of the room temperature absor-
ptance are also shown, with the curves terminated at about 2
microns to simplify the presentation. Comparison for these
values is made to the absorptances as given by Pepperhoff[5]
(page 54; the presentation there is on so small a scale that
the replot of this information on Figures 8 to 10 is scarcely
accurate to 0.01).

For platinum the emittance determined here is lower than
that found by Price; if Eqn. 2.5 is presumed to approximate the
temperature dependence of the emittance, then the absorptance
at 2520^OR should be only 8% above that at 2150^OR. In fact, with
the exception of molybdenum, all of the Price results appear to
be high.

The values of the emittance at 2390^OR for the platinum
standard are on Fig. 8 compared to the results reported by
Harrison[12] for the same material. Here points are shown,
selected from the tabulation of those results, for temperatures
of 2520^OR and 1980^OR.

For nickel Figure 9 shows that the present results for the
emittance at 2160^OR agree well with those of Hurst, and are
about 40% lower than those of Price. For molybdenum, shown on
Figure 9, the present results are high, due probably to the
formation of a film on the sample even at the beginning of the
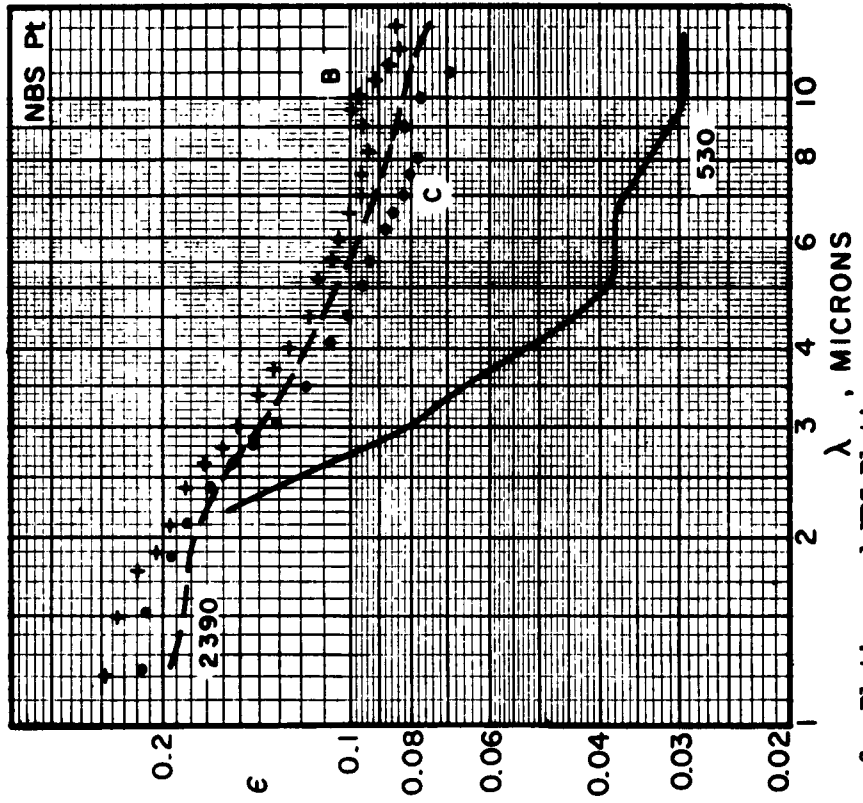emittance determination. This effect has already been noted

32
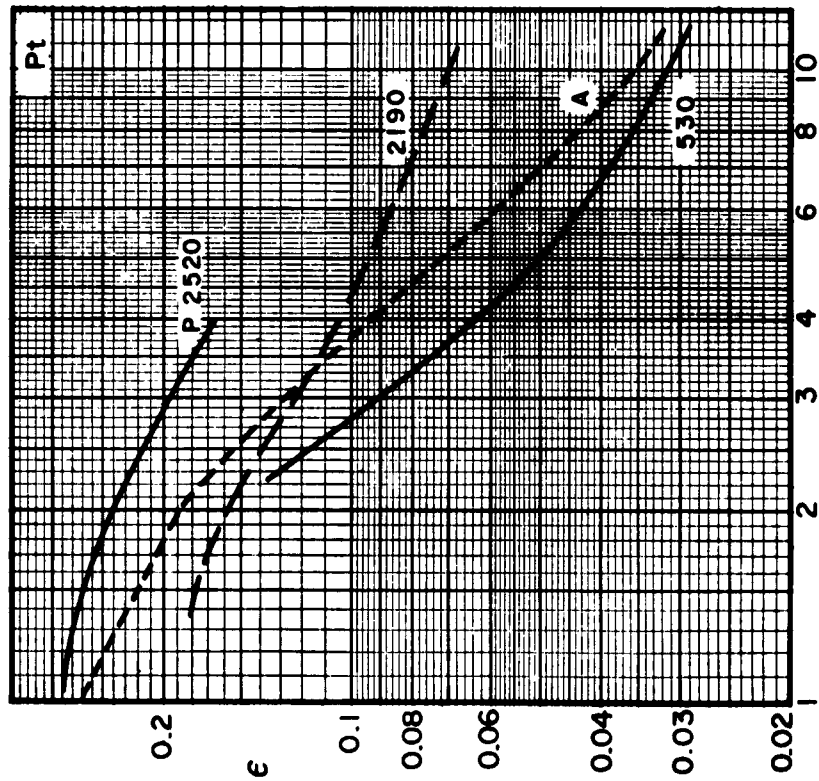
Figure 8 Comparison of Spectral Emittances for Platinum and NBS Platinum

Curves: P_t, 530°R, 2190°R from Fig. 2; NBS P_t, 530°R, 2390°R from Fig. 3; P, Price 2520°R;
A, Pepperhoff 530°R; B, Harrison 2520°R; C, Harrison 1980°R

33
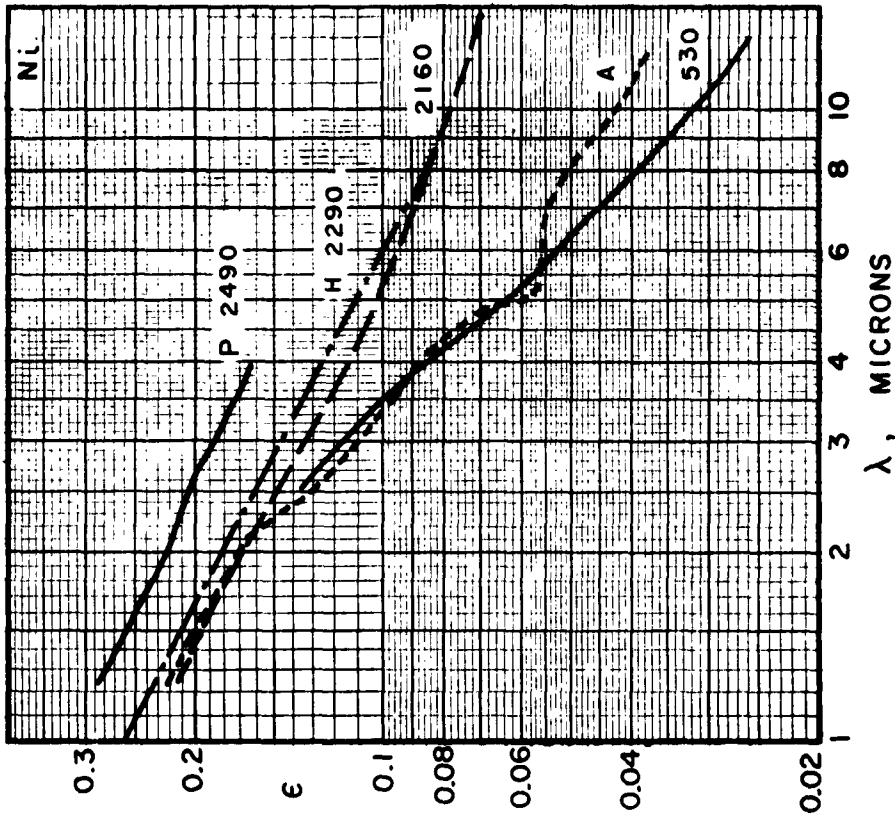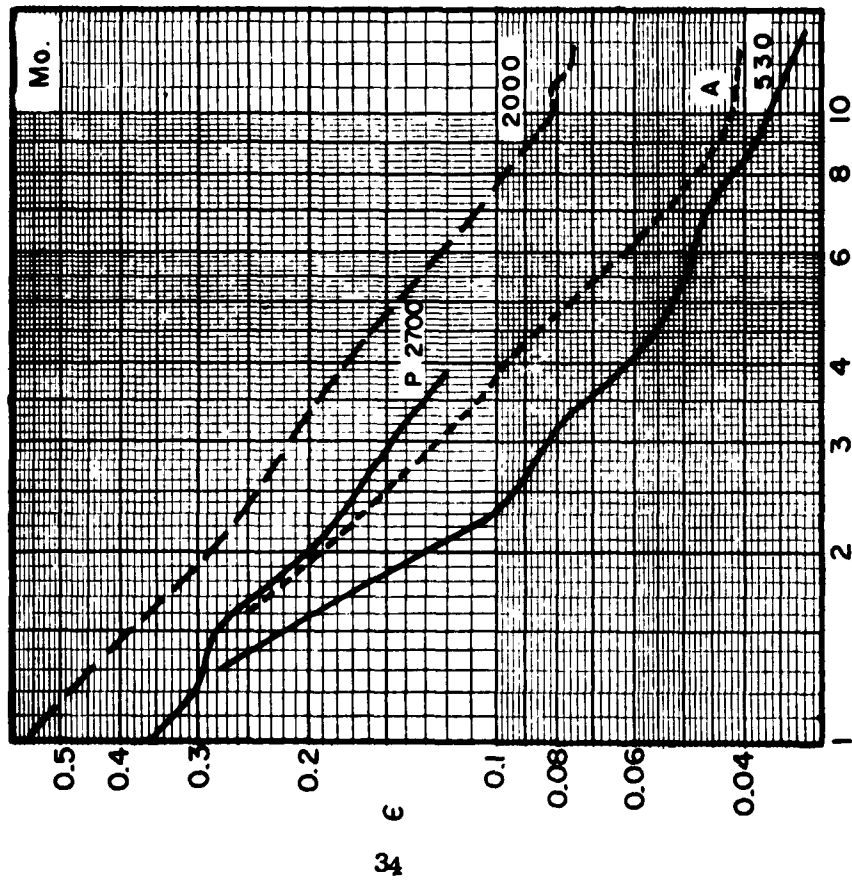
Figure 9 Comparison of Spectral Emittances for Molybdenum and Nickel

Curves: Mo, 530°R, 2000°R from Fig. 5; Ni, 530°R, 2160°R from Fig. 4; P, Price 2700°R and
2490°R; A, Pepperhoff 530°R; H, Hurst 2290°R

34
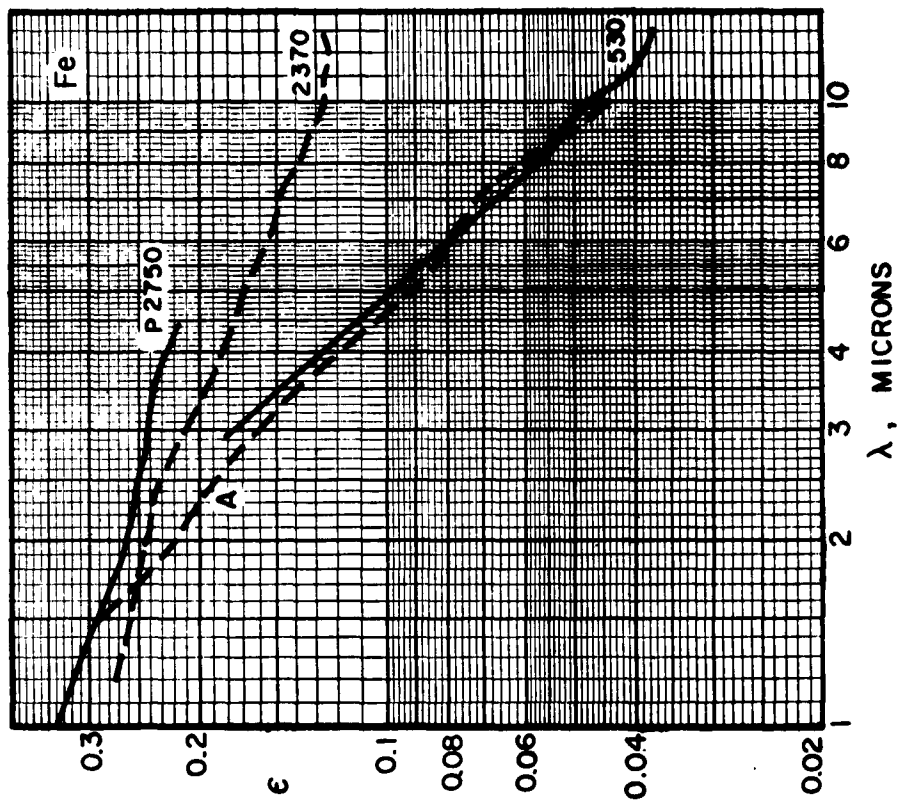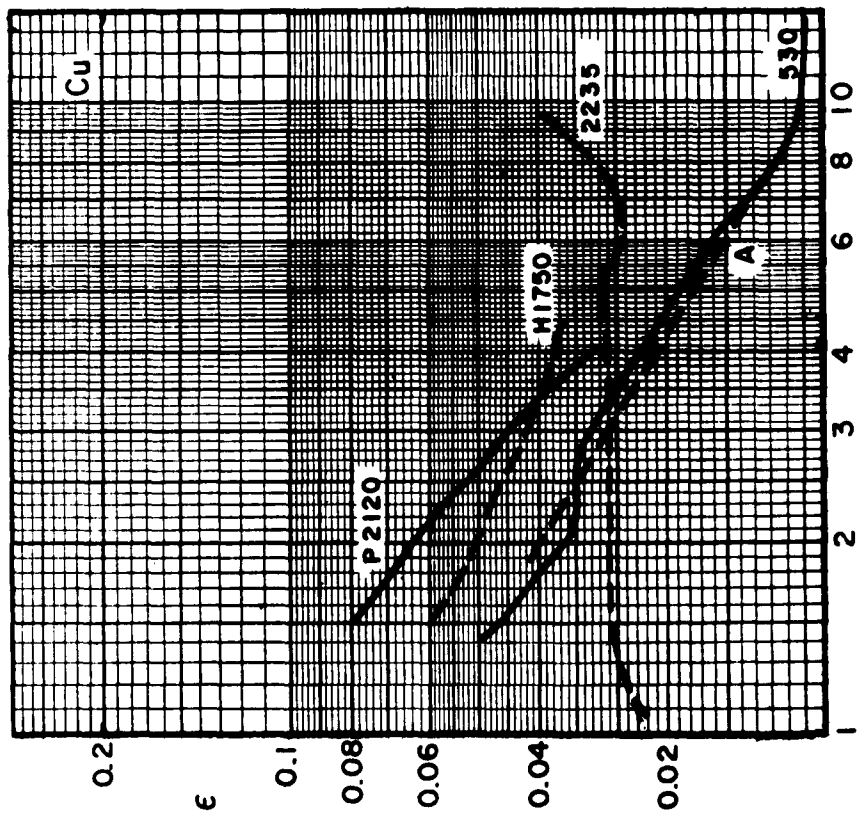
Figure 10 Comparison of Spectral Emittances for Copper and Iron

Curves: Cu, 530°R, 2235°R from Fig. 7; Fe, 530°R, 2370°R from Fig. 6; P, Price 2120°R
and 2730°R; A, Pepperhoff 530°R; H, Hurst 1750°R

35

in respect to the lack of coincidence, in this case, with the prediction from Eqn. 2.5.

For iron, shown on Fig. 10, the absorptance obtained at room temperature is seen to agree quite well with similar data presented in Pepperhoff. In order to compare the emittance values obtained for a sample temperature of 2370^OR to the data presented by Price, Eqn. 2.5 was used and the emittance at 2730^OR consequently found to be 6.0% above that at 2370^OR. With this correction the data would still be slightly lower than that presented by Price for the same temperature.

For copper, shown on Fig. 10, the present results differ both in magnitude and in spectral dependence from those of Hurst and of Price, with the present results, as noted before, being in closer accord with the relatively constant value of the emittance which would be predicted by the Drude theory.

Another appraisal of the present results consists in the comparison of the total normal emittances calculated from them with the results of direct measurement. Table 2 contains a comparison for 2000^OR; for this the present results, near 2000^OR were corrected to 2000^OR by assuming a dependence on the square root of the temperature. Comparison values are obtained from the results of Abbott[13], the curves given by Rutgers[16], and from empirical equations tabulated by him for the total emittance.

TABLE 2

Total Normal Emittance at $2000^{\circ}R$

	Rutgers	Abbott	Present	Empirical Rutgers p. 157
Platinum	0.105	0.113	0.112	0.133
Nickel	0.165		0.121	0.133
Molybdenum	0.086[1]	0.17	0.20	
Iron			0.19	0.16[3]
Copper	0.024[2]		0.032	

(1)   estimated from total hemispherical emittance of 0.105

(2)   estimated from total hemispherical emittance of 0.03

(3)   estimated from a total hemispherical emittance calculated as 0.18

The results given by Abbott appear to be preferable and for platinum the correspondence of total values calculated from the present results is excellent. The present results for molybdenum appear to be high, and Abbott's values, as discussed by him, may be also. For the other metals, the correspondence with available information is adequate.

37

SPECTRAL EMITTANCE OF OXIDIZED AND COATED METALS

INTRODUCTION

As a metal is oxidized, the oxide film is at first thin, uniform in thickness, and homogeneous, and the absorptance of the surface is still largely controlled by the reflectance of the metallic substrate, modified by the effect of the film as can be predicted from the available theory for thin film optics. As oxidation progresses the oxide layer tends to become of variable thickness and internally inhomogeneous and the inhomogeneity provides for scattering which drastically reduces the transmittance of the surface layer and consequently diminishes radically the influence of the substrate on the reflectance of the surface. The reduction of transmission by scattering is of course spectrally dependent and will be greater for wave lengths less than the order of the scale of the inhomogeneity.

While the surface layers considered here are basically dielectric and thus have low surface reflectances when in homogeneous form, the reflectance of the inhomogeneous layer depends critically on the samll but finite absorption index of the material. As long as the scattering is substantial, a small internal absorption will lead to a high reflectance because of multiple reflections in the layer. If the absorption increases, as by a spectral approach to the frequency of an internal oscillator, the scattering will enhance the absorption and the effect of multiple internal reflections will diminish so that the reflectance of the surface will approach that of the homogeneous material.

In a homogeneous layer of material in which it can be considered that interference effects are averaged out, as by slight variations in the layer thickness, the reflectance of the surface can be approximated by Eqn. 2.6. If such a layer is visualized and attention is limited to a small spectral region within which there is an absorption region that can be specified by a classical oscillator, and if the layer is thick enough so that its transmittance is zero at the oscillator frequency, then if such a layer is situated upon a surface of high reflectance the reflectance of the system will also be high, except for a lower value in the region of the oscillator, where the transmittance will be near zero. If instead this layer is inhomogeneous with enough scattering to make the transmission zero throughout the spectral range considered then the form of the reflectance will still be the same, high away from the resonance point because of multiple reflections within the layer and lower at the resonance

38

point. Alternatively, considering a homogenous layer on a
black surface, the reflectance of the system will be essentially
zero away from the resonance point and higher at the resonance
point at the same value as with the substrate of high reflect-
ance. With scattering, the reflectance of the system will be
the same as with the highly reflecting substrate and in fact is
independent of the substrate material.

Thus, with a layer of dielectric material on a metallic
substrate the attainment of low reflectances within appreciable
spectral regions requires the scattering produced by inhomo-
geneity and sufficient internal absorption to eliminate the
effect of multiple reflections. With the oxides of polyvalent
metals this is attained through a number of absorption bands.
While these are known to some extent (see Lecompte[16], p. 789),
the level of information is scarecely adequate for any prediction
of reflectance.

In turning to the effect of temperature on the emittance of
such systems, estimates thereon can be made only on the assump-
tion that increases in temperature will tend to broaden slightly
the absorption bands, and for poor absorbers this should reduce
slightly the variation of emittance in such regions, and in-
creasing the emittance at the minima that should be located
there. In general, these effects are expected to be small and
to be reversible. In addition, because of the dependence of
the properties on the extent of inhomogeneity, structural
changes produced by increases in temperature could influence the
properties; such changes would be discovered also in a sub-
sequent change in the properties at room temperature.

In measurements made previously[2] on oxides and on coated
materials, some temperature dependence on the emittance was
found; it was small and localized at high wave lengths and,
because the samples on which the initial and final absorptances
were measured at room temperature were not the same, question
still remained about distinctions between reversible and irre-
versible effects. While this difficulty was removed with the
present emittance system, the overall situation was not much
improved because of the problem with contamination in the
emittance system. The conclusion that can be made is the same
as before, that the reversible effects of temperature are rel-
atively small and restricted in spectral extent.

Results are presented for oxidized Inconel and oxidized
Kanthal, these two are "standard" samples prepared by NBS, and
for a few of the coated materials for which results had been
presented before[2].

39

OXIDIZED INCONEL

The oxidized Inconel sample was prepared by the National Bureau of Standards, presumeably according to the technique specified by Harrison[12]. The results obtained with it begin with the first measurement of absorptance at room temperature, given by Curve A of Fig. 11a. Operation in the emittance system then produced results for the emittance at temperatures of 2256, 2519, and 2646°R, these results for the lowest and highest temperatures are shown on Fig. 11 as points; the values for the temperature of 2519°R were located between these points. Subsequently the absorptance was measured at room temperature as Curve D. The reduction in absorptance from its initial value was surprising for in this case there was no other evidence to indicate contamination and evidence from other samples would imply that the consequence of contamination would have been to increase the absorptance.

On Fig. 11b the emittances at the two temperatures are now shown as curves and the points are the emittances reported by Harrison[12] on the same kind of sample at a lower temperature of 1440°R and at a temperature of 2340°R, typical of the present measurements. While Harrison's values at 2340°R are somewhat lower than the present values, the disparity between them is within the deviation between samples quoted by him. Thus the present values agree with those of Richmond to the extent of the deviation that he quotes. The deviation with oxidized inconel may be considerable, Harrison[17] earlier quoted values giving emittances at 2520°R about 0.03 above the present values; earlier work, reported in Reference 2, gives substantially lower values of emittance, obtained from oxidized surfaces which were originally smooth. The sensitivity of the emittance of oxidized Inconel to the original condition of the surface prior to oxidation has been noted by Harrison and also demonstrated by the measurements of total normal emittance made by Sully[18] on Nimonic 75 and on nickel and stainless steel.

The present results for emittance indicate a very small increase as the temperature is increased, but the relative temperature effect is inconsistent with respect to the initial absorptance, in reference to which the increase is relatively small considering the temperature difference that is involved. Harrison's results show a relatively greater temperature effect between 1440°R and 2340°R.

OXIDIZED KANTHAL

The oxidized Kanthal was a "standard" sample prepared by the National Bureau of Standards according to the procedures indicated in ref. 12, and this sample was subjected to a series

of determinations of the same type as used with the oxidized
Inconel sample. Unfortunately, contamination did occur during
operation of the emittance system, to a degree detectable by
visual observation of the sample and thus the basic appraisal
of the system was not possible in the way intended by this
sample.

Fig. 12a shows the results, beginning with the initial
determination of absorptance at room temperature, and followed
by an absorptance determination at a temperature of $1390^{\circ}R$.
Only these two results correspond in general to the values given
in Ref. 12. The correspondence is, in fact, very close for wave
lengths between 2 and 9 microns, with deviations at higher wave
lengths which, between the measured absorptance at room temp-
erature and the NBS values at $1440^{\circ}R$, are rational in terms of
the trend of the emittance at higher temperature.

The two curves which represent the emittance are associated
with the second and fourth determinations of a series of four
which all give similar results. Examination of the sample after
the first determination already showed evidence of contamination
so that the high values given by curves 1 and 2 are ascribed to
this effect. Curve C, for the absorptance at room temperature
obtained after the emittance determination, shows the permanent
increase that resulted from the contamination. A comparison
between curves C and 2 still shows a temperature effect that is
similar to that implied by the comparison of Curve A and the NBS
results for the emittance.

At a later time a similar series of determinations was made
on this sample, with the results indicated on Fig. 12b by curves
D and E, for the initial and final absorptance at room temperature,
and curves 3 and 4 for the intervening emittance determinations.
Curve D is the same as curve C; the absorptance at room temp-
erature did not change in the interval. The emittances are
almost the same at wave lengths up to 8 microns and this invar-
iability with temperature is similar to what is indicated by
Curve A and the NBS results for the emittance. An increase of
emittance with increase in temperature is indicated at wave
lengths above 8 microns, with a maximum gain near 11 microns.
Thus, despite the apparent contamination, the relative effect of
temperature on the emittance is preserved. Notably, the final
room temperature absorptance, given by Curve E, is practially
the same as the initial absorptance of this series of determi-
nations. Clearly during these latter emittance determinations
no further contamination of the sample occurred.

41

Figure 11

SPECTRAL EMITTANCE OF NBS OXIDIZED INCONEL

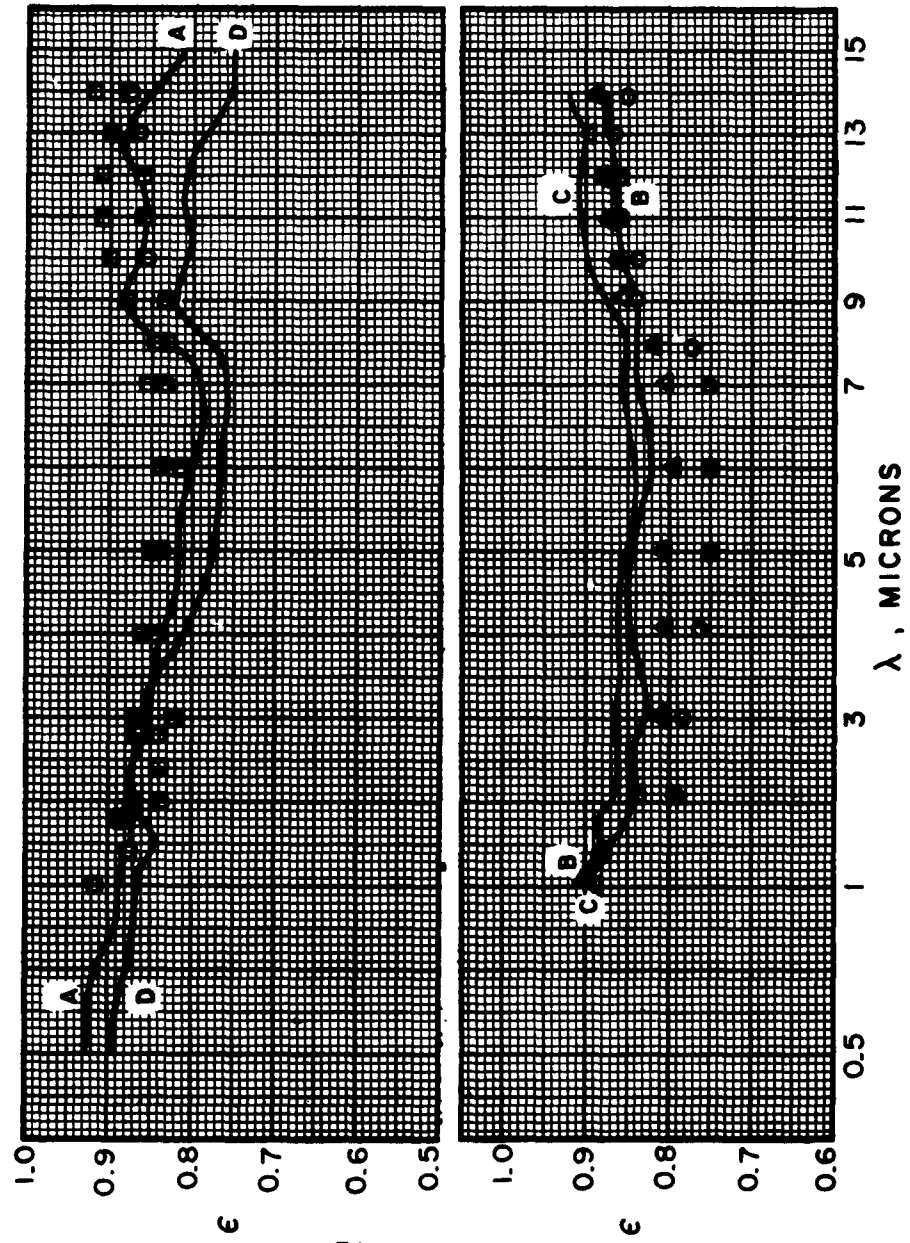| Curve	Temp. ^{o}R	Atmos.	Interval Heating Time	Date
A	530	Air		1-16-63
B, ▽	2256	Argon	2 hrs at T = 2250°R	1-24-63
C, ▢	2646	Argon	2 hrs at T = 2640°R	1-24-63
△	2340*	Air		
○	1440*	Air		
D	530	Air		1-25-63

*Ref. 12, pg. 85 and pg. 92

Figure 11

43

Figure 12

SPECTRAL EMITTANCE OF NBS OXIDIZED KANTHAL

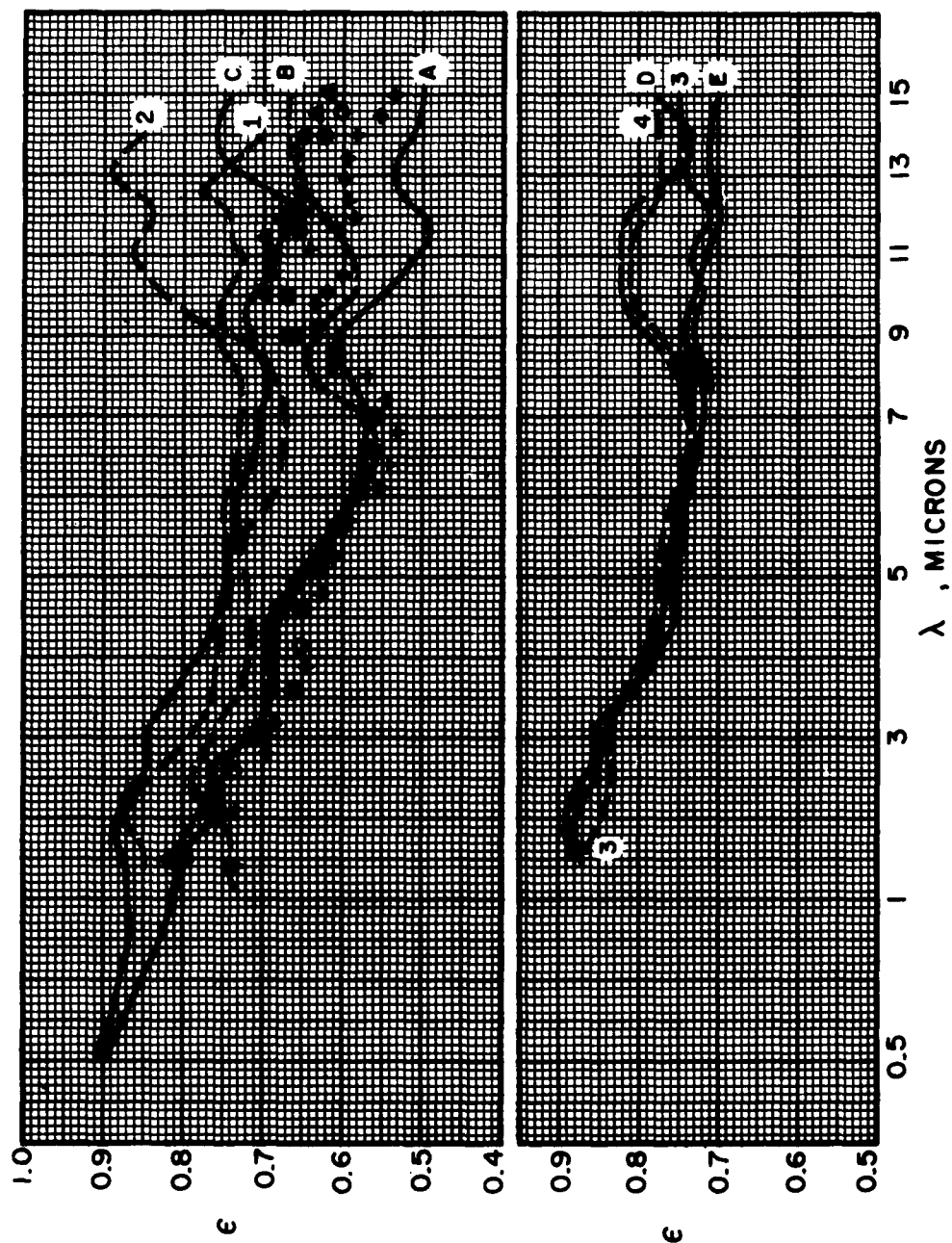| Curve	Temp.°R	Atmos.	Interval Heating Time	Date
A	530	Air		1-16-63
B	1395	Air	2 hrs at T - 1395°R	1-21-63
1	2410	Argon	26 hrs at T - 2400°R	2-28-63
2	2454	Argon	5 hrs at T - 2450°R	2-28-63
C	530	Air		3-6-63
D	530	Air		4-30-63
3	2064	Argon	2 hrs at T - 2000°R	5-2-63
4	2440	Argon	2 hrs at T - 2440°R	5-8-63
E	530	Air		5-13-63
0	1960*	Air		
+	1440*	Air		
△	2340*	Air		

*Ref. 12, Pg. 75, 78, 82.

44

Figure 12

45

CHROMALLOY W2

A sample of Chromalloy W2 was cut from a sample which had
been used previously in a total emittance determination in air
at 2260°R. The sequence of determinations with this sample
began with an emittance determination, with the results given
by Curve 1 of Fig. 13. In the sequence of emittance deter-
minations which followed, difficulty was encountered with the
thermocouple attachment and all subsequent runs involved the
assumption of a sample temperature giving an emittance of about
0.73 at 2 microns. The subsequent room temperature absorptances
confirm this value, but of course temperature invariability is
then assumed in the 2 micron region. Modest errors here would
not, however, affect substantially the emittance results at
wave lengths greater than 4 microns.

The emittance determinations, resulting in curves 1
through 3, indicated a continued increase in emittance. Curve
4 shows an alteration at shorter wave lengths, and this
emittance, at 2495°R, is fairly well confirmed by the following
determination of absorptance at room temperature, which gave
the values shown by circles on Fig. 13. Thus these points,
and Curve 4, would indicate only a small dependence of
emittance on temperature, localized in the region from 3 to 7
microns and a slightly larger one beyond 10 microns.

Two further emittance determinations produced further in-
crease in the emittance, but the final absorptance, given by
the points shown as triangles, remains almost the same as the
previous one up to 7 microns, with marked differences at higher
wave lengths. Thus the final three runs indicate a larger
dependence on temperature than does the initial set.

The apparent development of an absorptance maximum at 10
microns is an interesting but uninterpreted point. It exists
also in the determinations made with the second sample.

After measurements had been made with a second sample,
then an additional sample was cut from the piece from which all
of the samples were obtained and measurements were made on them
of room temperature absorptance. Comparison was then made be-
tween the results reported in reference 2, the No. 2 sample of
this series, and a third sample, and the absorptances were
consistent only at wave lengths below three microns. At higher
wave lengths the absorptance reported in Ref. 2 was much less
than the latter two, and these diverged after 7 microns. It
appears that the coating is seriously non-uniform spatially, and
transparent enough initially to produce an appreciable con-
tribution from the substrate at long wave lengths. This might

46

explain part of the effect found in Fig. 13 in the observation of different parts of the sample in successive emittance and absorptance determinations.

Results obtained with the second sample of Chromalloy W2 are shown on Fig. 14b. In this case the initial absorptance, given by Curve A, is higher at long wave lengths than the initial emittances of the first sample for which results are shown on Fig. 13 because of the differences in the samples. The emittance determination given by Curve 1 of Figure 14b, shows an immediate reduction in the emittance at short wave lengths, to values slightly lower than found with the first sample and a variation at long wave lengths rather typical of the final absorptance of the first sample. The final absorptance at room temperature, Curve B, is again different from the emittance in the long wave length region, but rather in the opposite way found with the first sample.

This kind of anomalous behavior was also found with the similar coated material, XP6789, for which one sample was investigated, with the results shown on Fig. 14a. Here the trends are similar to those shown for the second Chromalloy sample on Fig. 14b. The coating appears to have changed during heating, and a substantial temperature effect is apparent in the long wave length region when the final emittance and room temperature absorptance determinations are compared.

CHROMATE ON 420 SS

Results have been reported[1] for a "chromate" coating on various types of substrates, the substrates having no influence on the radiation properties and the reported results demonstrated essential equivalence between the absorptance at room temperature and that measured at a sample temperature of 1500°F. One of these samples, with a substrate of 420 stainless steel, was examined in the emittance system to determine if this temperature independence would be preserved at higher temperatures.

Fig. 15 shows the results obtained from two emittance determinations and the initial and final room temperature absorptance measurements. These differ because in the interval between the emittance determinations the major part of the coating evaporated from the sample. The initial absorptance, Curve A, and the emittance, Curve 1, at 2348°R reveal an almost negligible effect of temperature. At long wave lengths there is a small increase in the emittance at the elevated temperature.

Figure 13

SPECTRAL EMITTANCE OF CHROMALLOY W2

Sample No. 1

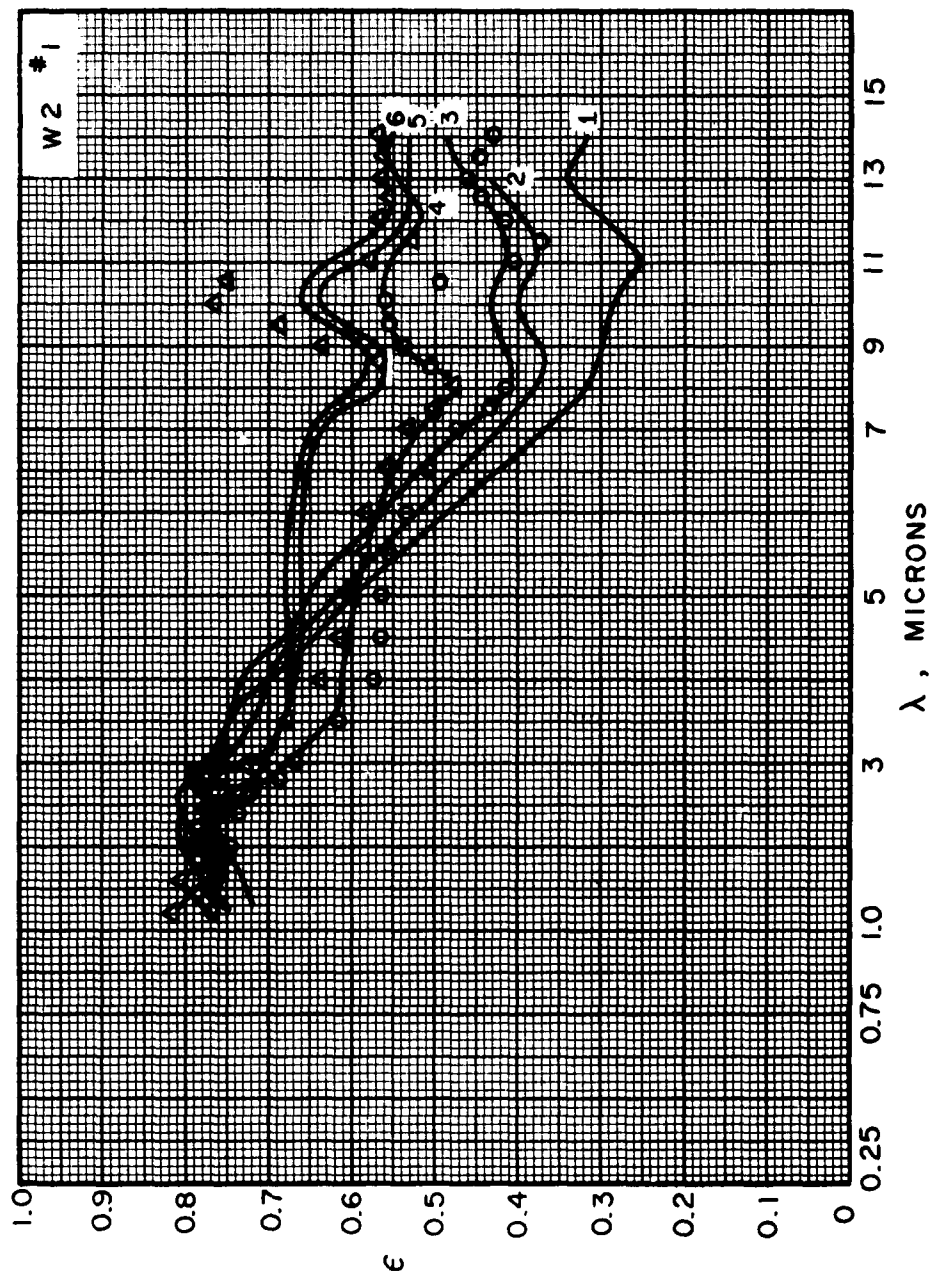| Curve	Temp. ^{O}R	Atmos.	Interval Heating Time	Date
1	1880	Argon	2 hrs at T = 1800°R	11-14-62
2	2110	Argon	27 hrs at T = 2100°R	11-15-62
3	2405	Argon	20 hrs at T = 2400°R	11-16-62
4	2495	Argon	3 hrs at T = 2495°R	11-16-62
◉	530	Air		1-8-63
5	2010	Argon	5 hrs at T = 2000°R	1-22-63
6	2310	Argon	3 hrs at T = 2300°R	1-22-63
△	530	Air		1-23-63

Figure 13

49

Figure 14

SPECTRAL EMITTANCE OF XP 6789 AND OF CHROMALLOY W2

a) XP 6789

Curve	Temp.°R	Atmos.	Interval Heating Time	date
1	2040	Argon	2 hrs at T = 2000°R	2-22-62
A	530	Air		2-27-62
2	2560	Argon	8 hrs at T = 2560°R	3-27-62
3	2760	Argon	2 hrs at T = 2760°R	3-29-62
B	530	Air		5-10-62

b) W-2, No. 2

Curve	Temp.°R	Atmos.	Interval Heating Time	Date
A	530	Air		2-29-63
1	2550	Argon	2 hrs at T = 2500°R	3-4-63
B	530	Air		3-6-63

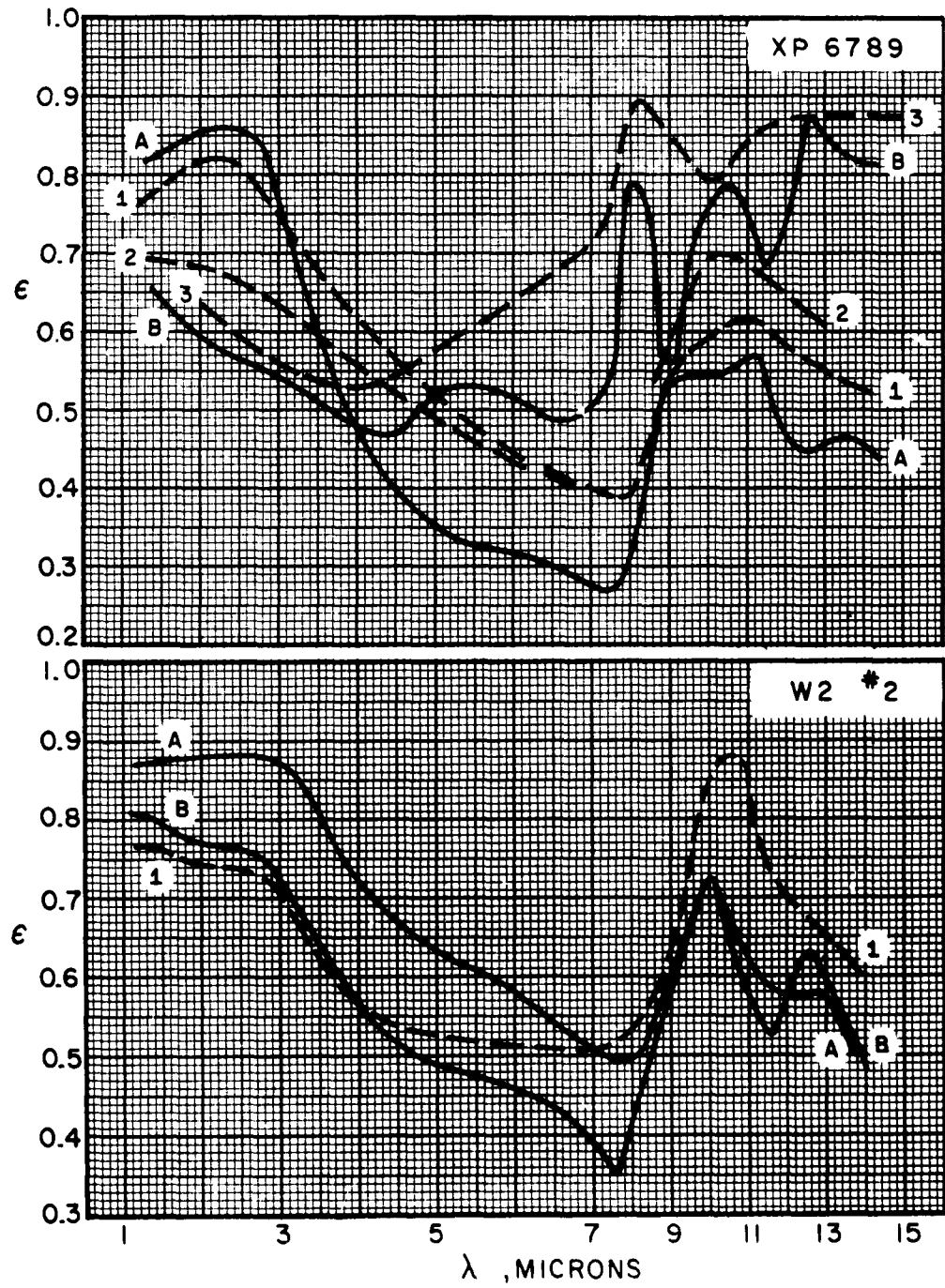Figure 14

51

After the first emittance determination the temperature was raised to 2545°R and in the 2 hour interval before the next test was begun the coating apparently evaporated completely from the sample. Curve 2 indicates the great reduction of emittance, to values almost typical oi the substrate material. The final absorptance, Curve B, is about the same; this implies that the temperature dependence of the substrate (and what coating remained) is also quite small.

CHANGE VOUGHT II + IX + TiO$_2$

This material had been investigated before[2], at room and at elevated temperatures, but a verdict on the effect of temperature on the emittance could not be rendered decisively because of apparent differences in the samples used for room temperature absorptance and high temperature (1660°R) emittance. One of the original reflectance samples was again subjected to the measurement of room temperature absorptance and essentially the original[2] results were obtained. This is Curve A of Fig. 16. Emittance determinations were then made and Curves 1 and 2 show the initial general correspondence with the room temperature absorptance, followed by higher values at later times for wave lengths less than 9 microns. Visual inspection after this determination revealed that the reddish color of the original specimen had been lost, and there was evidence, through deposit on the radiation shield, of the loss of the outer part of the coating. The final room temperature absorptance is also higher and tends to be of the order of the last emittance determination, though there are significant local differences.

Curve 2 is terminated at 2 microns because of apparent errors in the sample temperature determination which resulted in the indication of lower emittances at wave lengths shorter than 2 microns.

The emittance indicated by Curve 2 is like that given earlier[2] for the spectral emittance at 1600°R, but the variability between the samples that was demonstrated at that time prevents much generalization of this correspondence. The final absorptance, Curve B, is similar to that found before[2] from a sample cut from another sample which had been heated in air at a temperature of 3060°R. In that vase, and in this one also, exposure to higher temperature resulted in a loss of material or a change in material which produced a permanent increase in the absorptance in the short wave length region.
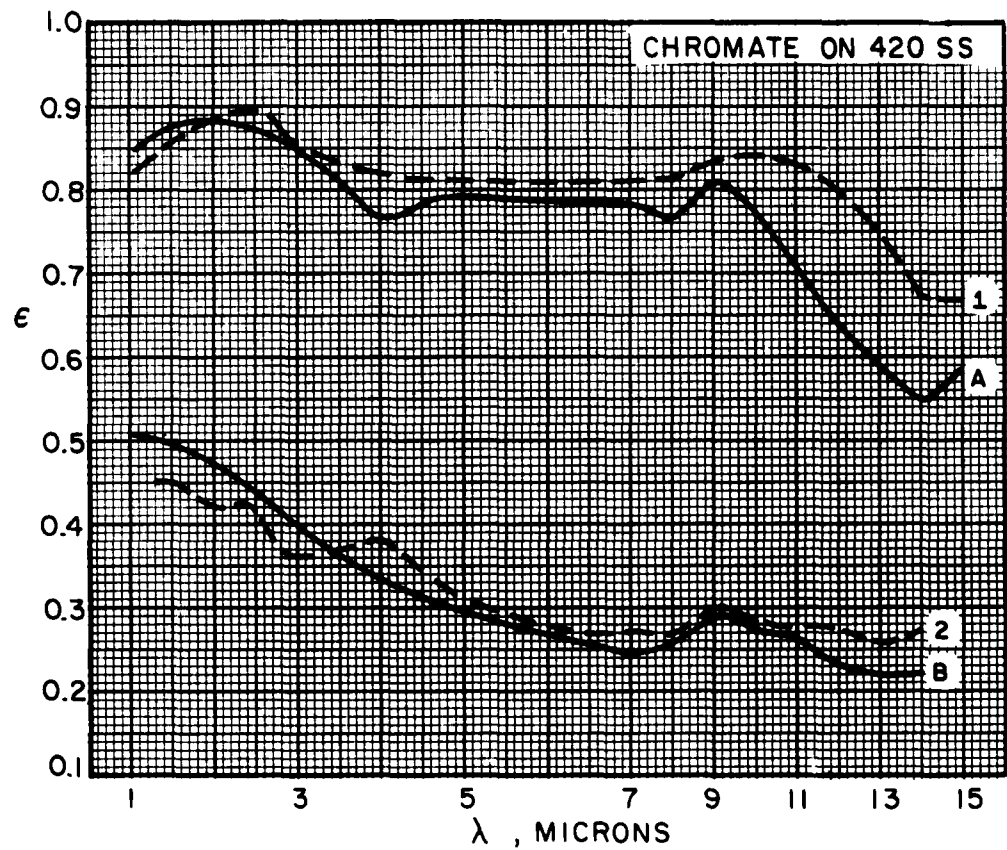
52

Figure 15

Spectral Emittance of

Chromate on 420 Stainless Steel

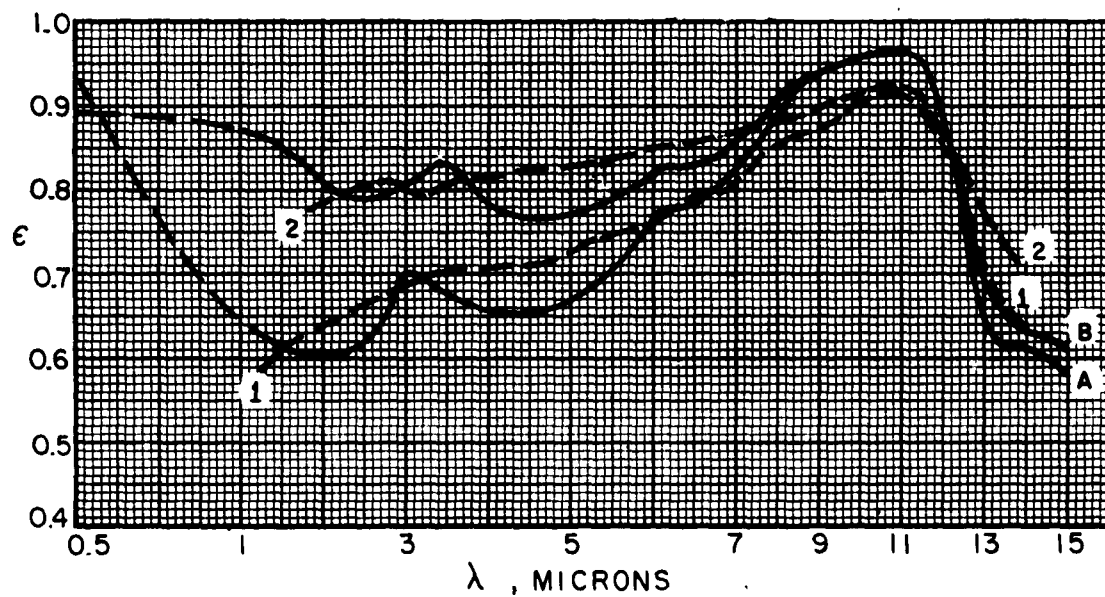| Curve	Temp.^{O}R	Atmos	Interval Heating Time	Date
A	530	Air	-	3-5-63
1	2348	Argon	2 hrs	3-7-63
2	2545	Argon	2	3-7-63
B	530	Air	-	3-8-63

Figure 16

Spectral Emittance of

Chance Vought II + IX + T_iO_2

Curve	Temp. ^{O}R	Atmos.	Interval Heating Time	Date
A	530	Air		9-9-62
1	1854	Argon	4 hrs	9-5-62
2	2330	Vacuum	30 hrs at 1400°F	9-6-62
B	530	Air		9-10-62

APPENDIX

The Spectral Emittance System

INTRODUCTION

The system used for the determination of the spectral
emittance has been described[2,3] in essentially its original
form. Relatively few permanent changes have been made but the
description of the system is here given rather completely both
as a convenience and also as a basis for the indication of the
operating problems that were encountered. It has already been
noted on a number of locations in the report that the system
to this time has been unsatisfactory on the score of contam-
ination of the sample holder, and at times of the sample, that
occurred in an irregular temporal pattern associated with the
temperature of the sample heater and the time for which heating
was maintained. Mention of this problem is continued in the
description of the parts of the system and the final section
contains a review of the problem itself.

SYSTEM AND ENCLOSURE

The basic components of the system are a reference cavity
and a sample heating furnace, mounted on rails with their dxes
coincident and in the horizontal plane. Fig. 1, a plan view of
the system, shows them schematically, contained within the
enclosure. Located centrally between them is a mirror turning
about a vertical axis which intersects the common axis of the
cavity and the sample. This mirror is turned, against stops,
by a selsyn motor located within the enclosure, to enable the
passage of radiation either from the cavity or from the sample
through the window in the side of the enclsosure. An off-axis
parabolic mirror, located outside the enclosure, receives this
radiation and produces an image at a location near the chopper,
where there are located horizontal slits to limit the height of
the observed area. Beyond this point, an off axis spherical
mirror and a plane mirror provide a second image at the inlet
slits of the monochrometer. The width of the area observed at
the sample or the cavity is determined by the opening of these
slits and is almost the same as the slit width. The monochrometer
is a Perkin Elmer Model 98, with the thermocouple detector out-
put entering a Perkin Elmer Model 107 amplifier. The amplifier
output is read on a Brown-Rubicon precision indicator.

The enclsoure is a steel tank which is 16 inches in diameter
and 36 inches long, with flanged ends and flanged nozzles on the
center top and center side. A heavy steel rail within the tank
provides support for the sample heater, cavity, and moveable

55

mirror. Cooling water lines pass through the tank walls, and also wires for the electric heating, current supply and thermocouple wires; all wires pass through the wall via Conex fittings.

There are three water cooling circuits within the tank, for the jacket of the cavity, for the jacket of the sample heater, and for the door and the water cooled shield on the sample heater. Initially, Swage-lock fittings connected these circuits to the tubes that passed through the tank wall, later these fittings were removed and all connections were made by soft soldered couplings in an effort to eliminate any possible leakage. This actually gave no apparent improvement and difficulty arose on one occasion due to a leak at one of the soldered connections.

The original evacuation system, used in obtaining all of the results that are described here, made use of a mechanical vacuum pump capable of reducing the pressure in the tank to less than one micron, as indicated by a NRC thermocouple gage. The combined leak and out gassing rate varied, improvements in the system resulted in a final indicated rate of 1.0 liters per second at 2 microns. In operation, a pressure of one micron was maintained for two or more hours; argon was then introduced through a system which included a dessecator, to a final pressure of about one pound per square inch gage. In certain instances, indicated on the results, argon was not introduced but rather the system was heated and operated under vacuum, with the pump in continuous operation. In such operation the system pressure was of the order of 5 microns, due in part to the inferior operation of the pump during that period.

CAVITY

The cavity itself was a graphite tube, 0.5 inch in internal diameter with a length of 2.7 inches, with a conical base as indicated in Fig. 17. This cavity was used subsequent to June 1962 as a substitute for the earlier similar unit indicated in Ref. 2, which had a flat instead of conical base. The original unit was found to have an emittance substantially less than unity at wave lengths above 7 microns due apparently to specular reflection from the flat base. The front of the tube is constricted to an opening 0.3 inches in diameter.

The graphite tube is contained in a thin ceramic tube, on which secondary heater windings are carried and this assembly is enclosed in another ceramic tube on which the primary heater is wound. Another ceramic tube enclosed this and is in turn sheathed with a 0.12 inch thick molybdenum sleeve for

56

longitudinal temperature equalization. All ceramic is refractory alundum and the tungsten heating wires are embedded in refractory cement. Fiberfrax was initially and is finally used for external insulation. From June 1962 to December 1962 bubble zirconia was used as external insulation on the premise that some of the contamination problems arose from the Fiberfrax insulation. Since these problems continued with the use of the zirconia it was ultimately replaced by Fiberfrax to realize the better thermal insulation obtained with that material.

The primary heater is made of 80 mil tungsten wire. A secondary heater at the front of the cavity is of 40 mil wire and another at the rear is of 80 mil wire. These secondary heaters are also a revision of the original design. Heating current is supplied from transformers having primary voltage supplied through Variacs; all control is manual.

Platinum-platinum 10% rhodium thermocouples are located in the base of the cavity and at the front edge of the cavity. Checks were made by inserting a thermocouple into the cavity through the orifice, with good agreement between this thermocouple and the thermocouple at the back of the cavity. At one period, prior to December 1962, difficulty was experienced due to apparent deterioration of the thermocouple in the back of the cavity, so that its response diminished, and for the period cavity temperatures were determined from optical pyrometer observations, corrected for the transmittance of the optical system. In all cases this observation was available as a check.

SAMPLE HEATER

The internal construction of the sample heater is the same as that of the cavity, except that only one 80 mil tungsten heater is used. As in the cavity, the external insulation was for a time of bubble zirconia instead of Fiberfrax, but replacement was made in December 1962. In this unit particularly, the higher thermal resistance of Fiberfrax was needed because of the smaller thickness of the external insulation. Fig. 18 shows the major details of the unit and is the same figure as used before [2].

Fig. 19 gives greater detail of the method of sample support, the sample holder shown being the final form used for this component. This was cut from 0.005 inch thick molybdenum sheet and when the contamination problem was severe a new holder was used for each new sample. Three tabs cut from the sheet were folded back to hold the sample, three others projected forward to enter the space between the ceramic ring in the furnace door and the water cooled shield. Additional tabs

57

FIBERFRAX

GRAPHITE

ALUNDUM

STEEL

ALUNDUM CEMENT
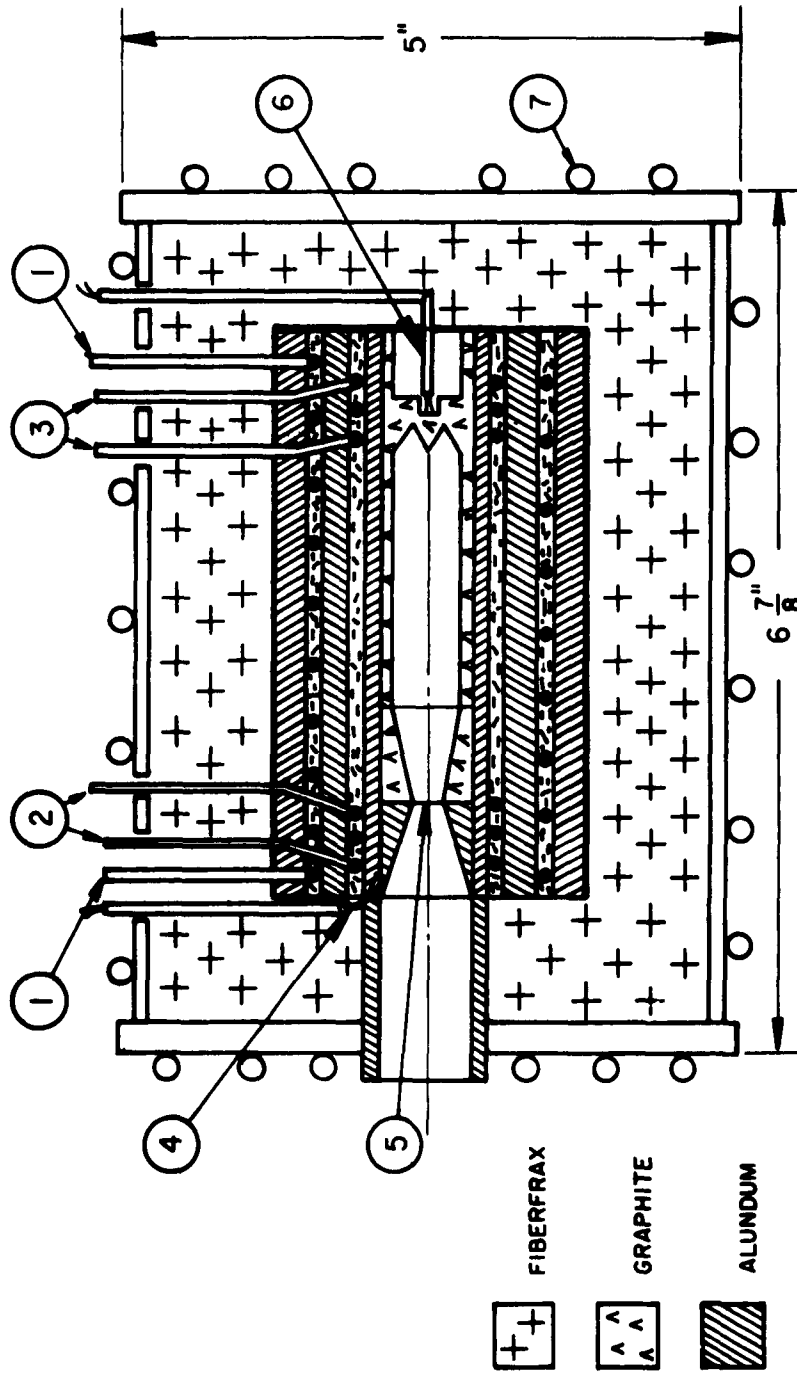
MOLYBDENUM SHEET

1, 2, 3. HEATER WIRES

4. FRONT THERMOCOUPLE

5. ORIFICE

6. BACK THERMOCOUPLE

7. JACKET WATER TUBES

Figure 17
Reference Cavity

cut from the sample holder held the ceramic tube carrying the sample thermocouple wires. A 0.30 inch hole in the front of the sample holder provided the view of the sample.

This sample holder assembly is inserted by opening the door of the furnace and registering the front tabs of the sample holder. The door is then closed; the sample itself enters the opening in the ceramic front ring of the furnace and the ceramic thermocouple tube a recess in that ring. The thermocouple wires, fitted with a connector, are plugged into the mating connector on the terminal board of the sample heater, adjacent to the reference junction for that board. With the door closed and the sample in place, the gap between the face of the sample holder and the water cooled shield is about 0.05 inches.
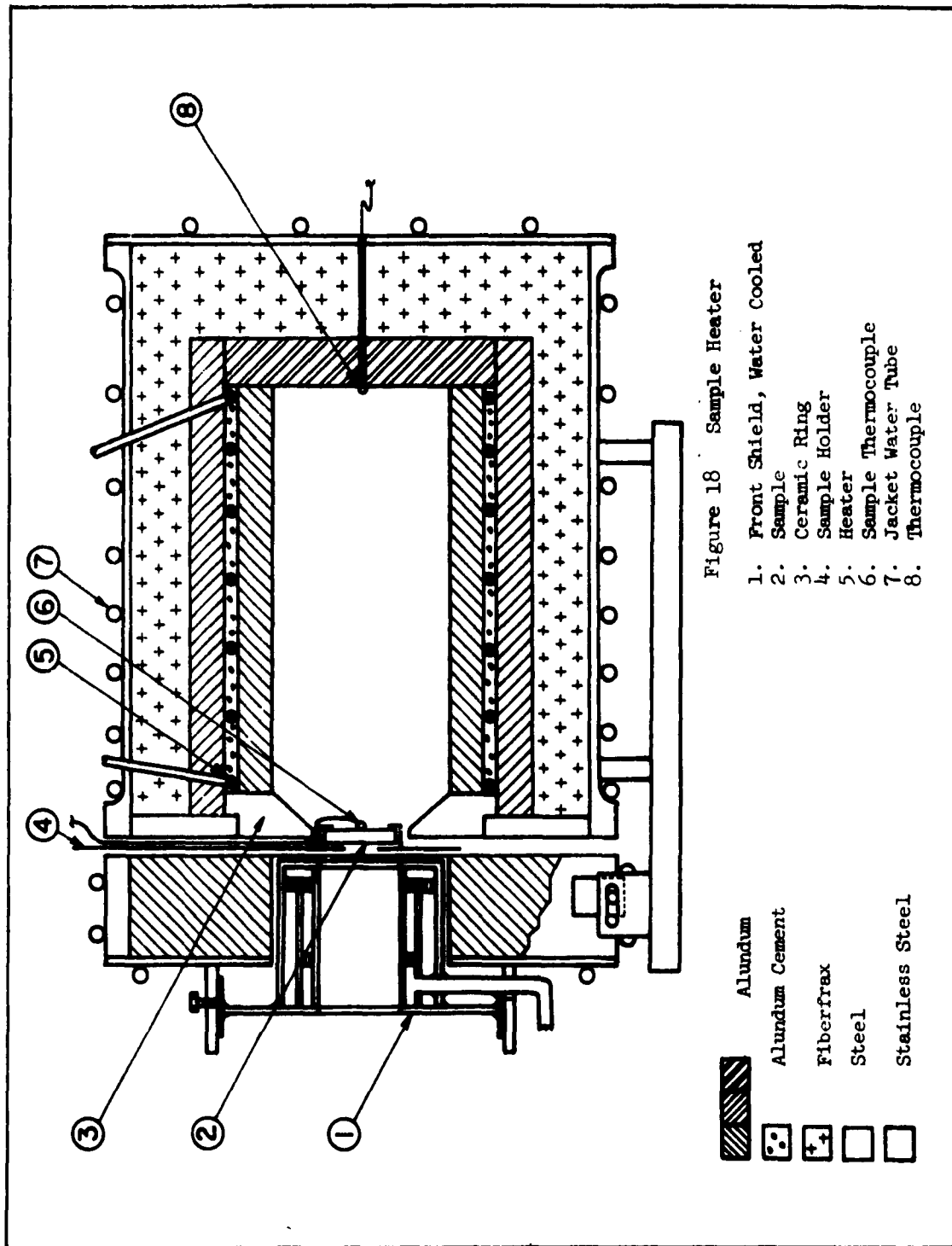
The water cooled shield, shown on Fig. 18, was made of stainless steel, with all seams heli-arc welded. Substantial difficulty was encountered with the joints of the shield at the base of the shield, adjacent to the sample. Very small pin holes developed in this region, and the only solution achieved was to cut back this face and soft solder the seams and entire face. Difficulties of this nature occurred at the beginning of operation and subsequently in a failure of the solder joint. A second shield, fabricated with ostensibly more care, revealed the same difficulties. The final repair of this shield has, however, maintained its integrity for a six month period.

The one inch inside diameter of the shield is honed smooth, to avoid diffuse reflection, and the face of the shield adjacent to the sample holder is painted black to minimize reflection in that area.

EMITTANCE DETERMINATION

The relation of the true emittance to the ratio of the net monochrometer detector responses and the observed temperatures of the cavity and the sample was considered in some detail in Refs. 2 and 3, here the algebra is minimized and the important effects are discussed more qualitatively. This can be divided into a consideration in which it is assumed that the radiosity of the sample is indeed the emission therefrom and another in which additional possible contributions to the radiosity of the samples is considered.

The location of the chopper, outside of the tank and intermediate in the optical path, leads to additional contributions to the detector output from the optics between the

Figure 18 Sample Heater

1. Front Shield, Water Cooled
2. Sample
3. Ceramic Ring
4. Sample Holder
5. Heater
6. Sample Thermocouple
7. Jacket Water Tube
8. Thermocouple

Alundum
Alundum Cement
Fiberfrax
Steel
Stainless Steel

ALUNDUM

ALUNDUM CEMENT

FIBERFRAX

STEEL

Figure 19
Sample Holder

1. SAMPLE THERMOCOUPLE

2. SAMPLE

3. SAMPLE HOLDER, MOLYBDENUM
SHEET.

61
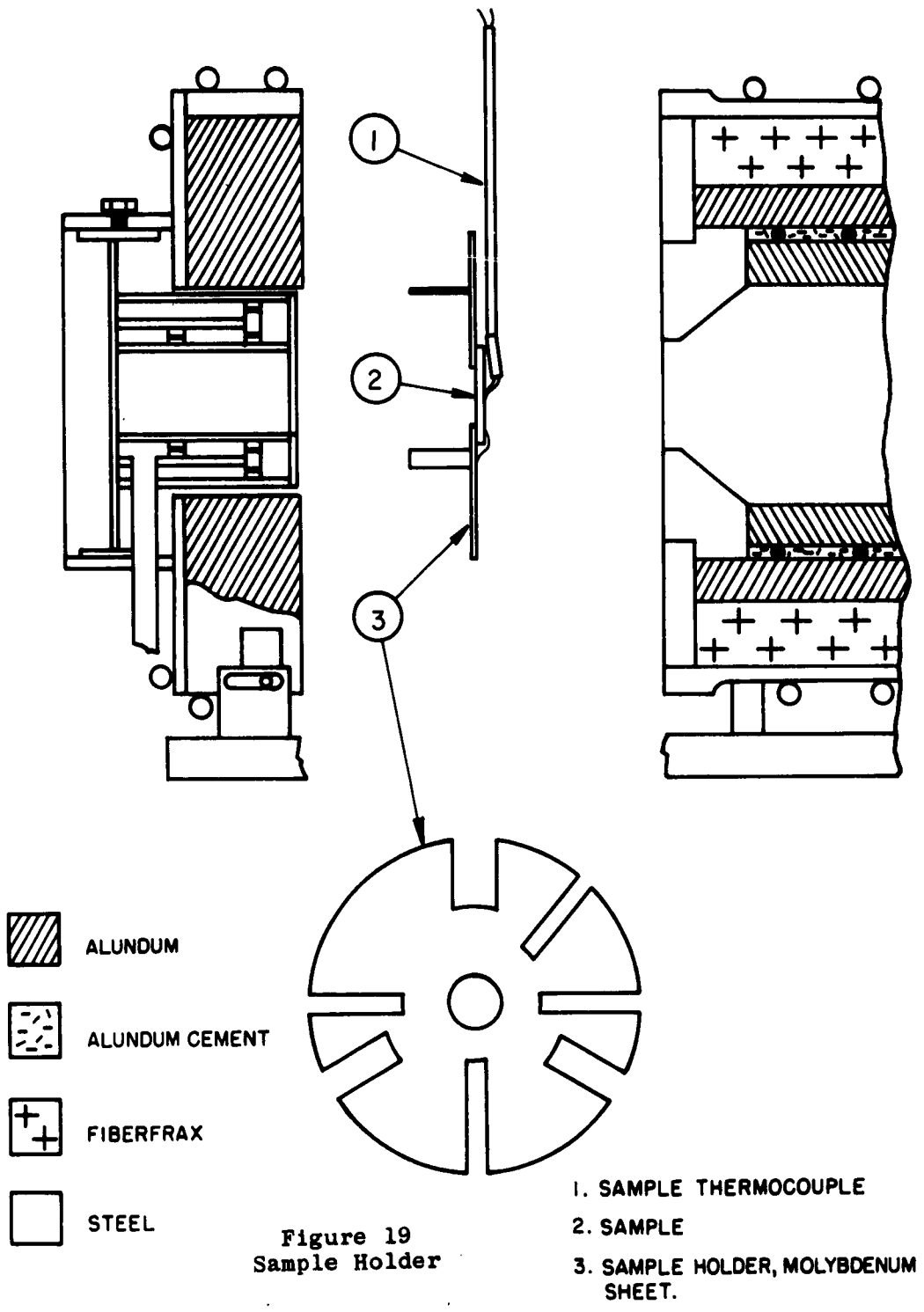
sample and the chopper location. Obviously, the preferred location for the chopper is at the front of the cavity and in front of the sample, but the need for large chopper blades and the internal location of the motor and breaker points in this arrangement led to the compromise represented by the outside location of the chopper. Thus the emission from the internal mirror, the window, and two external mirrors must be accounted for, as well as the transmittance of the window. The ratio of the detector responses for the sights on the sample and on the cavity then is complicated even when the negligible contribution of the two external mirrors is neglected.

$$\frac{S_s}{S_c} = \frac{\epsilon_s(E_s - E_o) + (1 + r_s r_M)\frac{\epsilon_M}{r_M}(E_M - E_o) + [r_M^2 r_S + 1 - r_M^2 r_S r_w]\frac{\epsilon_W}{r_M}(E_W - E_o)}{(E_c - E_o) + \frac{\epsilon_M}{r_M}(E_M - E_o) + \frac{\epsilon_W}{r_M}(E_W - E_o)} \quad A.1$$

here ϵ, r, E denote the emittance, reflectance and monochromatic emissive power of the component indicated by the subscript: c, cavity; m, mirror; w, window; s, sample, o, room temperature.

If the emittance is calculated from Eqn. 1.1

$$\frac{S_s}{S_c} = \epsilon_s \frac{E_s - E_o}{E_c - E_o} \quad 1.1$$

then a comparison with Eqn. A.1 indicates the error associated with the emittance calculated from Eqn. 1.1. These are in general negligibly small, except for the large error that can occur due to heating of the internal mirror as that can occur during operation with a vacuum. If only the mirror is considered to be at a temperature above that of the reference sight, then the ratio of the emittance ϵ_{s1}, indicated by Eqn. 1.1 to the true value, given by Eqn. A.1 is:

$$\frac{\epsilon_{s1}}{\epsilon_s} \cong \frac{1 + (1 + r_s r_M)\frac{\epsilon_M}{r_M \epsilon_s}\frac{(E_M - E_o)}{(E_s - E_o)}}{1 + \frac{\epsilon_M}{r_M}\frac{(E_M - E_o)}{(E_c - E_o)}} \quad A.2$$

As an example, with sample and cavity temperatures of 2500°R, surroundings at 530°R, and an (impossibly) high mirror temperature of 1000°R, with ϵ_M = 0.15 and r_M = 0.85, then

62

if the sample were to be metallic with an emittance of 0.10 at 10 microns, the value of the emittance ϵs, indicated by Eqn. 1.1 would be twice the true value. Even with a vacuum the mirror temperature was doubtless not as large as this but in some instances it was above the temperature of the surroundings. Then a spectrometer response could be observed when the mirror was placed normal to the line of sight immediately after an observation on the sample and the final readings were corrected for this additional contribution to the response. This is an undesireable feature of vacuum operation of this system which was designed for use with an argon atmosphere. With the gas atmosphere the internal mirror is cooled by free convection and the heating problem then does not exist.

In addition to possible errors contributed by the optics of the system, there is an additional contribution from those effects which may cause the radiosity of the surface of the sample to differ from its actual emission. Irradiation of the sample occurs from the ceramic ring in the door of the sample furnace, "seen" by the sample through the gap between the sample holder and the black face of the water cooled shield. The angle factor involved is of the order of 0.02 and if the temperature of the ceramic were to be the same as that of the sample, and if the sample was a diffuse reflector, then the consequent increase in the observed emittance would be the product of 0.02 and the sample reflectance. This could become significant with a sample which was a poor emitter, but these samples tend to be specular and even with the rough metallic samples it is doubtful that irradiation at almost grazing incidence would be reflected in any substantial amount in the normal direction.

OPERATIONAL PROBLEMS WITH THE SPECTRAL EMITTANCE SYSTEM

Because of operational difficulties with the system for spectral emittance measurements a dual objective was imposed on all of the work which led to the results which have been presented in this report. On one hand, the program was pursued in an attempt to determine the effect of temperature on the spectral emittance for a significant number of materials, while on the other hand attempts were made to eliminate the problem of contamination of the sample, which as has been indicated, introduced uncertainty into the results that were obtained and likewise limited the scope of the program both in number of materials and in the maximum temperatures that were obtained.

The contamination was apparent by alteration of the appearance of the molybdenum sample holder and of the sample itself. This varied in severity and extent, and in extreme

63

cases deposition occurred on the water cooled shield. The apparent cause was the presence of oxygen in the system and the most consistent adverse reaction was with the tungsten heating wires in the sample heating furnace. This oxygen was present either because of inadequate out-gassing of the ceramic parts of the heating furnace (and also of the cavity furnace), inadequate purging of the argon supply system, or because of leakage in the water cooling system. At various times all of these effects apparently contributed to the difficulty.

During the first part of the program the deposits involved light coatings of blue and brown material near the central parts of the sample holder, with a frequent occurrence of yellow-white material in larger amounts on the outer part of the sample holder and sometimes on the face of the water cooled shield. The darker material was probably a mixture of WO_2 and W_2O_5 and the light material the hydrate of WO_3. The mechanical problem of welding the joints of the radiation shield has already been mentioned and leakage from the water circuit apparently reacted when the yellow deposit and the hydrate appeared. When the shield was definitely sealed this contamination did not occur and to reduce the possibility of such occurrance all the joints in the water tubing within the enclosure, first made with Swage-Lock fittings, were changed to soldered connections. Continued deposit of the blue and brown material occurred, primarily on the back of the sample and the sample holder, though discoloration of the front of the sample holder also occurred. Since both WO_2 and W_2O_5 have sublimation temperatures of the order of $1900^\circ R$, it is hard to visualize their presence on the surface at the temperatures at which the emittances were determined and they may have condensed during the cooling of the system. Their presence, however, did open the possibility for a reaction with the material of the sample itself.

It has already been indicated that in June 1962 the Fiber-Frax insulation was replaced by bubble zirconia on the premise, then held, that the Fiber-Frax insulation was responsible for some of the contamination. At that time also the original reference cavity and cavity heater were replaced. No substantial improvement was produced by the change in insulation and because of the higher thermal conductivity of the zirconia, operating temperatures were seriously limited. The operation with vacuum used in the following period was required to allow temperatures higher than $2000^\circ R$, but such operation was used also at times in connection with the investigation of the contamination problem. The zirconia insulation was removed and replaced with Fiber-Frax in December 1962.

64

REFERENCES

1. Seban, R. A. and Rolling, R. E. "Therman Radiation Properties of Materials, Part I", WADD TR 60-370, Part I, October 1960.

2. Seban, R. A. "Thermal Radiation Properties of Materials, Part II", WADD TR 60-370, Part II, Aug. 1962.

3. Seban, R. A. "System for the Measurement of Spectral Emittance in an Inert Atmosphere", Symposium on Measurement of Thermal Radiation Properties of Solids, Dayton, Sept. 1962. Preprints, Vol. II, page 91.

4. Gier, J. T., Dunkle, R. Bevans, J. "Measurement of Absolute Spectral Reflectivity from 1 to 15 Microns" Jour. Opt. Soc. Amer. Vol. 44, 1954, p. 558.

5. Pepperhoff, W., "Temperaturstrahlung". Steinkopf, 1956. Darmstadt.

6. Rutgers, G. W. W. "Temperature Radiation of Solids" in Hanbuch der Physik, Vol. 26. Springer, 1958. Berlin.

7. Givens, M. P., Solid State Physics, Vol. 6, p. 313. Academic Press, New York.

8. Shultz, L. G. "An Experimental Confirmation of the Drude Free Electron Theory of the Optical Properties of Metals for Silver, Gold, and Copper in the Near Infra-Red". Jour. Opt. Soc. Amer. Vol. 44, p. 540, 1954.

9. Goldsmith, A., Waterman, T., Hirschborn, H. "Thermophysical Properties of Solid Materials, Elements"., WADC TR 58-476, Vol. I., 1960.

10. Beattie, J. and Conn, G. "Optical Constants of Metals in the Infra-Red", Phil. Mag. Vol. 46, p. 1002, 1955.

11. Andersen, E. A. "The Spectral Emittance of Metals in the Infra-Red", M. S. Thesis, Univ. of Calif. at Berkeley, June 1963.

12. Harrison, W., Richmond, J., Shorten, F., Joseph, H. "Standardization of Therman Emittance Measurements, Part IV, Normal Spectral Emittance, $800^{\circ}-1400^{\circ}K$", WADC TR 59-510 Part IV, Dec. 1962.

REFERENCES (Cont.)

13. Abbott, G., Alvares, N., and Parker, W. "Total Normal and Total Hemispherical Emittance of Polished Metals, Part II" WADD-TR-61-94, Part II. Jan. 1963.

14. Price, D. "The Emissivity of Hot Metal in the Infra-Red", Proc. Phy. Soc. London, Vol. 59, p. 118, 1947.

15. Hurst, C. "The Emission Constants of Metals in the Near Infra-Red" Proc. Royal Soc. Sec. A, Vol. 142, p. 466, 1933.

16. LeCompte, J. "Spectroscopie dans l' infrarouge" in Handbuch der Physik, Vol. 26. Springer, 1958. Berlin.

17. Harrison, W., Richmond, J. Skramstad, H. "Standardization of Thermal Emittance Measurements, Part III, Normal Spectral Emittance, 800°-1400°K", WADC-TR-59-510, Part III.

18. Sully, A., Brandes, E., and Waterhouse, R. "Some Measurements of the Total Emissivity of Metals and Pure Refractory Oxides and the Variation of Emissivity with Temperature", Br. Jour. of Applied Physics, Vol. 3, p. 97, 1952.