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MEASUREMENTS OF TOTAL HEMISPHERICAL EMISSIVITY OF SEVERAL STABLY OXIDIZED METALS AND SOME REFRACTORY OXIDE COATINGS

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SUMMARY

A description of the apparatus and methods used for obtaining total hemispherical emissivity is presented, and data for several stably oxidized metals are included. The metals which were tested included type 347 stainless steel, tungsten, and Haynes alloys B, C, X, and 25. No values of emissivity were obtained for tungsten or Haynes alloy B because of the nature of the oxides produced. The refractory oxide coatings tested were flame-sprayed alumina and zirconia.

The results of the investigation indicate that strongly adherent, oxidized surfaces of a high stable emissivity can be produced on type 347 stainless steel for which the total hemispherical emissivity varied from 0.87 to 0.91 for temperatures from 600° F to 2,000° F. For this same temperature range, the Haynes alloys tested showed values of total hemispherical emissivity from 0.90 to 0.96 for alloy C, from 0.85 to 0.88 for alloy X, and from 0.85 to 0.89 for alloy 25. Haynes alloy B and tungsten formed nonadherent oxides at elevated temperatures and, therefore, stable emissivities were not obtained.

The results obtained for the flame-sprayed ceramics (alumina and zirconia) showed considerably higher values of total emissivity than those measured for coatings applied by other methods. Emissivity values ranging from 0.69 to 0.44 for aluminum oxide and from 0.62 to 0.44 for zirconium oxide were measured for temperatures from 800° F to 2,000° F.

INTRODUCTION

One of the most effective means of limiting the temperature rise due to aerodynamic heating of supersonic and hypersonic aircraft is the method of radiative cooling. The inherent simplicity, reliability, and low increased weight of this method make it especially desirable.

Since loss of heat by radiation is directly proportional to the total hemispherical emissivity of the surface, it is evident that the emissivity of any surface must be high in order to obtain maximum cooling. Most clean metals have low emissivities and are, therefore, poor radiators. Thus, for effective radiative cooling a coating of some material with a high emissivity must be applied to the clean metallic surface.

One method which may be used to obtain this coating is the oxidation of clean metal in air until the oxide coating is of sufficient thickness to limit continued oxidation. This coating may then possess a high stable value of total hemispherical emissivity. Although large quantities of emissivity data are available in existing technical literature, many of these data are incomplete with respect to the physical properties of the oxide coating produced.

The Pilotless Aircraft Research Division of the Langley Research Center is currently engaged in an investigation of the total hemispherical emissivities of various aircraft construction materials for application to cooling of supersonic and hypersonic aircraft.

Results of measurements of several stably oxidized metals have been previously reported in references 1 and 2. The present report contains data for additional high-temperature metals and alloys such as type 347 stainless steel and Haynes alloys C, X, and 25. Values of total normal emissivity obtained for flame-sprayed alumina and zirconia coatings are included and represent the first measurements on refractory coatings made in this investigation.

SYMBOLS

f	radiation flux, Btu/(sq ft)(sec)
R	rate of radiant energy emission, Btu/sec
T	absolute temperature, ^{o}R
ϵ	total hemispherical emissivity
ϕ	angle of incidence, deg

Subscripts:

b	black body
0	at $\phi = 0$
u	surface of unknown emissivity

APPARATUS

The apparatus used for measurement of total hemispherical emissivity in this investigation is described in detail in reference 1; therefore, only a brief summary is presented herein.

Total hemispherical emissivity may be measured by using either the "filament-in-vacuum" apparatus or the "reference-black-body" apparatus. This investigation employed the reference-black-body apparatus which was especially suitable for a large variety of materials over a wide range of surface conditions. A general view of the test equipment is shown in figure 1.

The black-body target used in this investigation (fig. 2) was a highly oxidized hollow Inconel cone 6 inches in length with an opening at the base of approximately 1 inch and a total apex angle of 8.6°. A recent report (ref. 3) of a theoretical evaluation indicates that this type of reference black body is superior to either a cylindrical or a spherical construction and has an emissivity very near to the theoretical value of 1 (0.997). This reference black body was placed inside a commercially available tube-type furnace which was heated by silicon-carbide resistance elements to provide a heat source for the black body (fig. 3).

The radiant-flux sensing element used to measure total radiation from a radiating source was a commercial total-radiation pyrometer. This pyrometer consisted of a thermopile of 10 thermocouples of chromel-constantan wire connected in series and a lens system for focusing the radiant flux onto the hot junctions which were flattened and blackened for maximum absorption of radiant energy. A water-cooled shield and shutter arrangement was mounted between the sensing pyrometer and any radiating source to prevent extraneous radiation from reaching the pyrometer and to limit the temperature rise of the pyrometer housing. The shutter was opened only when a reading was to be made in order to admit radiation to the thermopile. The sensing pyrometer, water-cooled shield, and specimen rig are shown in figure 4. This specimen rig was designed to hold test specimens of flat strips in a vertical position while being viewed by the pyrometer. A pivoted arm connecting the specimen rig and pyrometer apparatus allows the pyrometer to be rotated through a range of angle of incidence from 0° to 60° for determining the total hemispherical emissivity of the test specimen.

The test specimens were sheet-metal strips $1\frac{1}{2}$ inches wide, 9 inches long, and approximately 1/32 inch thick with expansion slots to prevent buckling at elevated temperatures.

Temperatures of the reference black body and the test specimens were measured by thermocouples of No. 30 (American wire gage) chromel-alumel wire spotwelded to the surfaces. These thermocouples were connected to a standard commercial potentiometer calibrated to read the temperature directly in degrees Fahrenheit. The electromotive-force output of the radiation sensing pyrometer was measured by a precision potentiometer when the pyrometer was set in position to view either the reference black body or the test specimen.

PROCEDURES

It was found that the most convenient procedure to use for the radiation measurements was to determine the radiant-flux intensity from the black body over the entire temperature range rather than to view the black body and test specimen alternately at each temperature. The thermopile used as the radiation sensing element was then considered calibrated and only a periodic check was needed to determine any drift or change.

The calibration curve shown in figure 5 is given in terms of thermopile potential as a function of the absolute black-body temperature. In addition, a scale of relative flux intensity (relative to black-body flux at $1{,}000^{\circ}$ R) is given at the top of the figure. The use of relative values of flux intensity greatly decreases the requirements on the instrumentation since only ratios of relative flux intensities of the test specimen and the black body are necessary for the reduction of emissivity data obtained by the methods used in this investigation. This method of obtaining total emissivity ϵ_u from the ratio of flux intensities R_u/R_b is based on the fact that the absolute temperatures and the areas viewed by the thermopile of the unknown surface and of the black body are made equal. The mathematical derivation of R_u/R_b is fully developed in reference 1. Calibrations of the thermopile and its optical system were made three times during the course of this investigation: once before the tests were begun, once at approximately the midpoint, and again at the conclusion of the tests. No appreciable deviation between calibrations was indicated. (See fig. 5.)

In order to insure consistent data, all metal specimens used in this investigation were cleaned to pure bright metal by mechanical polishing and then were washed in alcohol. After a second bath of distilled water, the test specimens were dried by a hot-air blast. Handling of the test specimens after cleaning was kept to a minimum to avoid possible contamination.

After the test specimens were cleaned, a preliminary test was conducted to determine the adherence, emissivity stability, and resistance to rapid changes of temperature of the oxides produced. The test consisted of heating the strips in still air at various temperatures for periods of time necessary to produce an oxide of stable emissivity at a particular temperature. The adherence of the oxide produced and the ability of the oxide to withstand a rapid temperature change were checked by rapidly lowering and raising the temperature of the strip. The results of this preliminary test indicated the maximum temperature at which an adherent smooth oxide with a stable emissivity could be obtained (up to a temperature limited by the capacity of the test-strip heating system).

After completion of the preliminary test to determine the optimum oxidation temperature, clean test strips were oxidized at this temperature until an oxide coating of stable emissivity was obtained. The procedure indicated the time required to obtain an oxide coating with the desired properties at the given oxidation temperature.

Total normal emissivity of the test strips stably oxidized in this manner was measured over the temperature range from 600° F to the maximum oxidation temperature of 2,000° F. Total hemispherical emissivity was then determined by measuring the radiant-flux intensity at angles of incidence from 0° to 60° over this temperature range. These measurements were used to determine any deviation of the radiant flux from the Lambert cosine law for diffuse emission.

If this test indicates that the emission from the surface of the test specimen is diffuse, the total normal emissivity is identical to the total hemispherical emissivity and no correction is necessary. If the emission is nondiffuse, the total hemispherical emissivity must be obtained by the methods of double integration discussed in reference 1.

TESTS AND RESULTS

Type 347 Stainless Steel and Haynes Alloys C, X, and 25

The nominal chemical compositions of type 347 stainless steel and Haynes alloys C, X, and 25 as obtained from references 4 to 6 are given in table 1. Results of the preliminary test showing the variation of total normal emissivity with time and temperature of oxidation for these materials are presented in figures 6 to 9. The test results indicated that all these alloys form oxide coatings with the desired properties at an oxidation temperature of 2,000° F.

Figure 10 illustrates the results of tests made to determine the time at an oxidation temperature of 2,000° F necessary to produce the required oxide surface. Clean metal specimens were used for this test and the results obtained show that there is no appreciable increase of total normal emissivity after approximately 20 minutes from "time zero" which is the time at which the temperature of the test strip reaches 2,000° F. Thus, the test specimens oxidized for this time have oxide coatings of stable emissivity at all temperatures up to the maximum oxidation temperature of 2,000° F.

After the total normal emissivity of these stably oxidized test specimens was obtained, measurements of the radiant flux at angles of incidence from 0° to 60° were made over the temperature range from 600° F to 2,000° F. This check indicates any deviation from the Lambert cosine law for diffuse emission. The results of this test are shown in figures 11 to 14 where the circle represents the Lambert cosine law for diffuse emission and the test points indicate the experimental data. These figures show that the stably oxidized test specimens emit diffusely over the range of temperature and angle of incidence considered. Therefore, the measured values of total normal emissivity can be taken as the values of total hemispherical emissivity.

Total hemispherical emissivity as a function of specimen temperature is presented for type 347 stainless steel and Haynes alloy C in figure 15 and for Haynes alloys 25 and X in figure 16. Data are given for specimens oxidized for specified times at 2,000° F as well as for the specimens progressively oxidized at various temperatures up to 2,000° F as shown in the temperature time histories of figures 6 to 9. The results indicate that values of total hemispherical emissivity can be obtained for these stably oxidized materials which vary from 0.87 to 0.91 for type 347 stainless steel, from 0.90 to 0.96 for Haynes alloy C, from 0.85 to 0.88 for Haynes alloy X, and from 0.85 to 0.89 for Haynes alloy 25 over the temperature range from 600° F to 2,000° F. The close agreement of these two sets of data indicates that the total hemispherical emissivity of specimens which have been stably oxidized at 2,000° F is essentially independent of the oxidation history at lower temperatures.

Haynes Alloy B

The nominal chemical composition of this nickel-base high-temperature alloy as obtained from reference 5 is given in table 1. Attempts made to produce an oxide coating on Haynes alloy B which would be suitable in aerodynamic applications were unsuccessful because of the nature of the oxides formed at high temperatures. These oxides showed little ability to withstand rapid temperature changes; they consistently spalled when the temperature of the strip was lowered from some oxidation temperature to near room temperature. Another undesirable feature of the coating was

the formation of the characteristic yellow trioxide of molybdenum (MoO_3) which occurs at temperatures near 1,200° F, and at slightly higher temperatures the trioxide will volatilize.

Since the preliminary test indicates that a suitable oxide coating cannot be produced by the methods utilized in this investigation, further study of this material was omitted.

Tungsten

The preliminary test conducted on tungsten to determine the effects of time and temperature on the oxides produced indicated that the oxides formed on this material at elevated temperatures are unsuitable for aerodynamic applications. The results obtained from this preliminary test indicated that this metal is incapable of producing a "self-healing" oxide which will limit continued oxidation. A further undesirable characteristic is the formation of a powdery yellow oxide which has little resistance to abrasion and can be easily rubbed off.

Alumina and Zirconia (Flame-Sprayed Ceramics)

The methods used for heating metallic specimens during measurements of total normal emissivity could not be used for alumina and zirconia (flame-sprayed ceramics) because of the nonconductivity of these materials except at elevated temperatures. Inconel strips, sandblasted and oxidized, were, therefore, used as heating elements and the ceramic coatings were applied to these strips by flame-spraying techniques. This method of heating allows the ceramic coating to be heated to a maximum temperature of 2,000° F.

When the ceramic-coated test specimens were heated during measurement of emissivity, the radiant flux emanated from both the ceramic coating and the underlying metal heater up to a certain limiting thickness of the coating. This limiting thickness is governed by the particle size and the refractive index of the ceramic (ref. 7). Furthermore, the temperature drop through the ceramic surface need not be known, but it must be compensated for in order to obtain reasonably accurate measurements of total normal emissivity. The method used herein was chosen in order to minimize the error resulting from this unknown temperature drop and the effects of radiation from the Inconel heater strip.

The ceramic coating was applied in thicknesses varying from 0 to 0.016 inch. The surface temperature of the Inconel heater strip was measured by thermocouples of No. 30 (American wire gage) chromel-alumel wire spotwelded to the back side of the strip, and this temperature was assumed constant through the heater.

Measurements were then made on each strip over the temperature range from 800° F to 2,000° F and the values of total normal emissivity as a function of coating thickness were plotted for each temperature. A representative plot of zirconia at a temperature of 1,200° F is shown in figure 17. The values of emissivity recorded in this figure were obtained after the test strips reached thermal equilibrium. Thermal equilibrium was determined by taking readings at intervals until no change of electromotive force due to radiant energy was detected. Extrapolation of the linear portion of this curve to zero thickness eliminates the error due to radiation from the Inconel heater strip and to the unknown temperature drop through the coating. The total normal emissivity obtained at zero thickness is considered to be the emissivity of the ceramic at the temperature of the heater strip which was 1,200° F for the data of figure 17.

The temperature drop through the oxide coating was determined by comparing the temperature of the Inconel strip with that measured by a thermocouple of chromel-alumel wire mechanically bonded directly to the ceramic surface. The temperature drops were found to be essentially linear with coating thickness over the range of temperature considered, as shown in figure 18 for alumina.

Total normal emissivity as a function of heater-strip temperature is shown for alumina and zirconia in figure 19. The results indicate values of total normal emissivity from 0.69 to 0.44 for alumina and from 0.62 to 0.44 for zirconia over the temperature range from 800° F to 2,000° F. These values are larger than values obtained in other investigations of these materials (refs. 7 to 9) but this difference is probably due to the method of application of the ceramic coatings.

The values shown in figure 19 from references 7 to 9 were obtained from slip-cast ceramic coatings which were applied to metal strips by use of a commercial frit, or an aqueous suspension of the powdered refractory. The test specimens were then cured to obtain a bond between the refractory and the base metal. The surfaces of the slip-cast ceramic coatings were much smoother than the surfaces of the flame-sprayed coatings and would be likely to have lower total emissivity values.

Values of total hemispherical emissivity for the flame-sprayed ceramics were not obtained by the methods used for pure metals because of the effect of radiation from the Inconel heater strip and the undetermined temperature drop through the ceramic. The fact that the ceramics have fairly rough surfaces and are electrical insulators indicates diffuse emission. Thus, it is believed that the values of total normal emissivity can be taken as those for total hemispherical emissivity with little error.

CONCLUDING REMARKS

This investigation indicates that one of the methods which may be used to produce materials having high emissivity is the oxidation of pure metals in air. For many metals this oxidation will produce a surface coating which will have a highly stable emissivity and be strongly adherent.

The results obtained from the test materials included in this investigation indicate that this type of oxide surface can be produced on type 347 stainless steel and Haynes alloys C, X, and 25. The measured values of total hemispherical emissivity are from 0.87 to 0.91 for type 347 stainless steel, from 0.90 to 0.96 for Haynes alloy C, from 0.85 to 0.88 for Haynes alloy X, and from 0.85 to 0.89 for Haynes alloy 25 over the temperature range from 600° F to 2,000° F.

Some metals form oxides at elevated temperatures which are unsuitable for application to radiant cooling because of the physical properties of the oxide produced. Haynes alloy B and tungsten are included in this group.

The total normal emissivity of the flame-sprayed ceramics tested are found to decrease with increases of temperature as shown by the values observed for alumina, from 0.69 to 0.44, and zirconia, from 0.62 to 0.44, over the temperature range of the investigation.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Field, Va., October 15, 1958.

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TABLE 1.- NOMINAL CHEMICAL COMPOSITION OF TEST SPECIMENS

	Percent
Type 347 stainless steel:	
Carbon	0.08 maximum
Chromium	17 to 19
Iron	68 to 73
Nickel	9 to 12
Niobium	0.80 maximum
Haynes alloy B:	
Carbon	0.12 maximum
Chromium	1.00 maximum
Iron	4 to 7
Manganese	1.00 maximum
Molybdenum	26 to 30
Nickel	60 to 67
Silicon	1.00 maximum
Haynes alloy C:	
Carbon	0.15 maximum
Chromium	15.5 to 17.5
Iron	4.5 to 7.0
Molybdenum	16 to 18
Nickel	52 to 60
Tungsten	3.75 to 5.25
Haynes alloy X:	
Carbon	0.05 to 0.15
Cobalt	0.5 to 2.5
Chromium	20.5 to 23
Iron	17 to 20
Manganese	1.00 maximum
Molybdenum	8 to 10
Nickel	42 to 52
Silicon	1.00 maximum
Tungsten	0.2 to 1.00
Haynes alloy 25:	
Carbon	0.05 to 0.15
Chromium	19 to 21
Cobalt	46 to 53
Iron	3.00 maximum
Manganese	1.00 to 2.00
Nickel	9 to 11
Phosphorous	0.04 maximum
Silicon	1.00 maximum
Sulfur	0.03 maximum
Tungsten	14 to 16

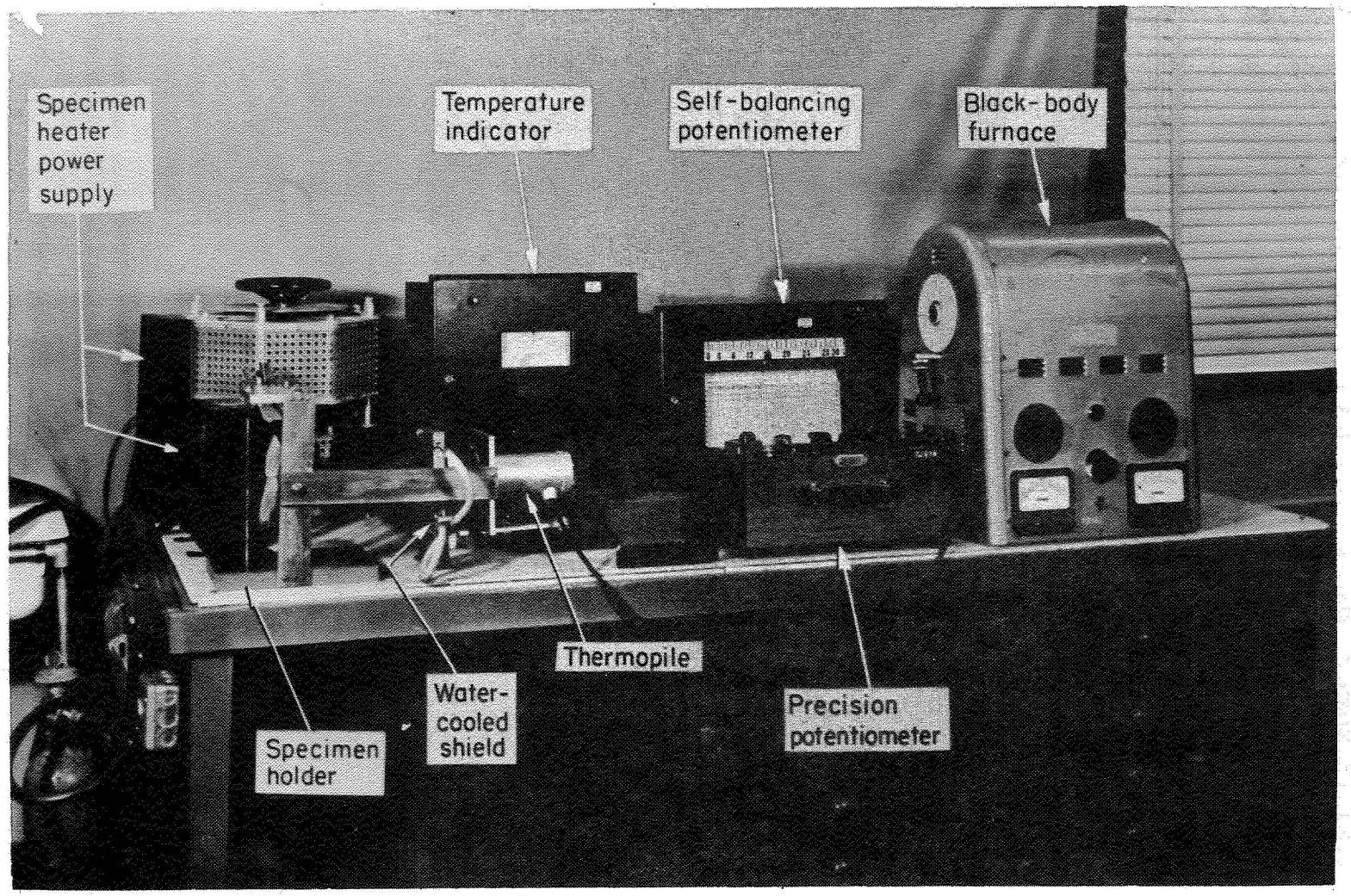

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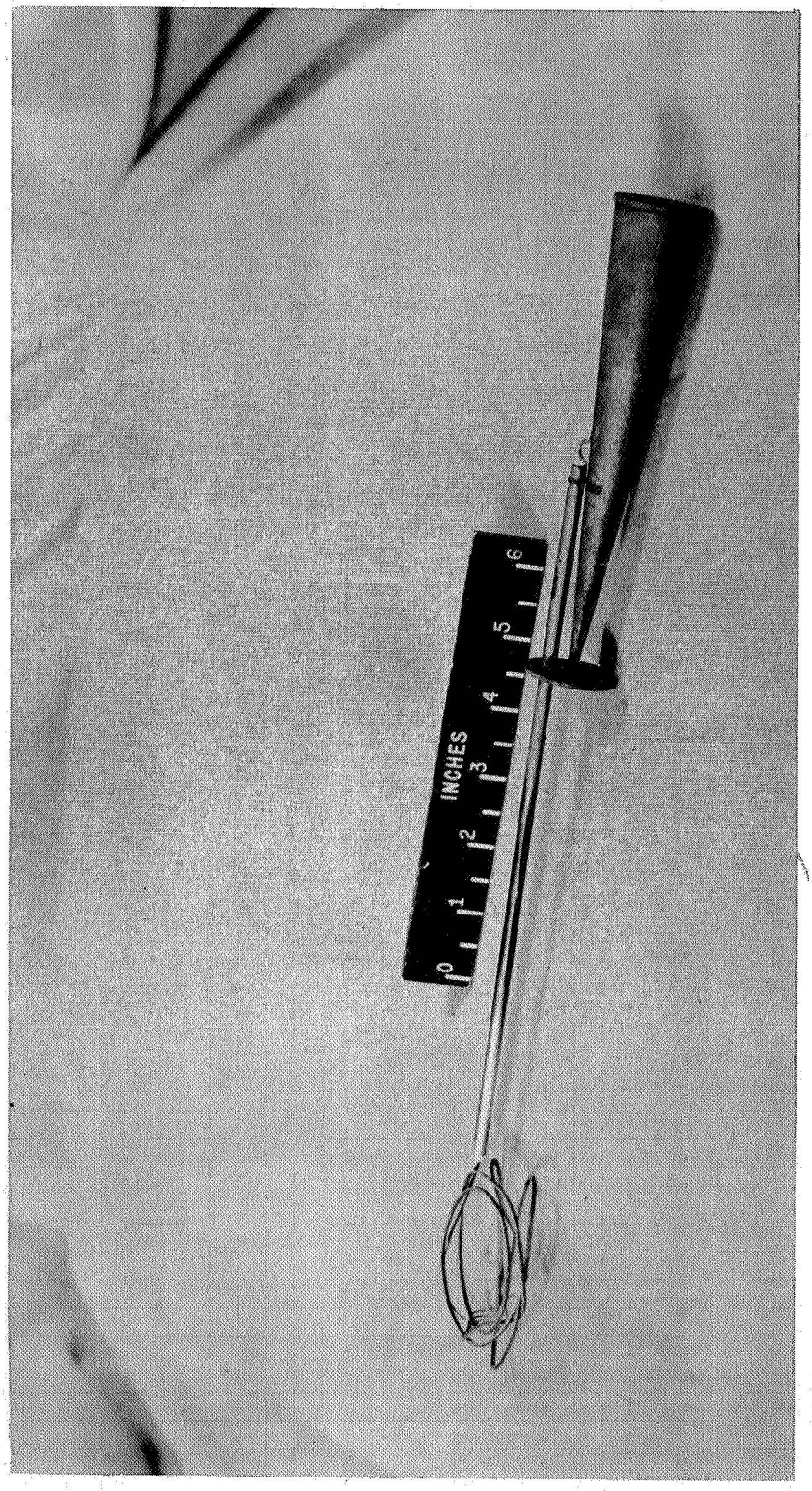
Figure 1.- General view of emissivity-measuring apparatus with identification of principal components.



L-96506

Figure 2.- Reference-black-body conical target with thermocouple.

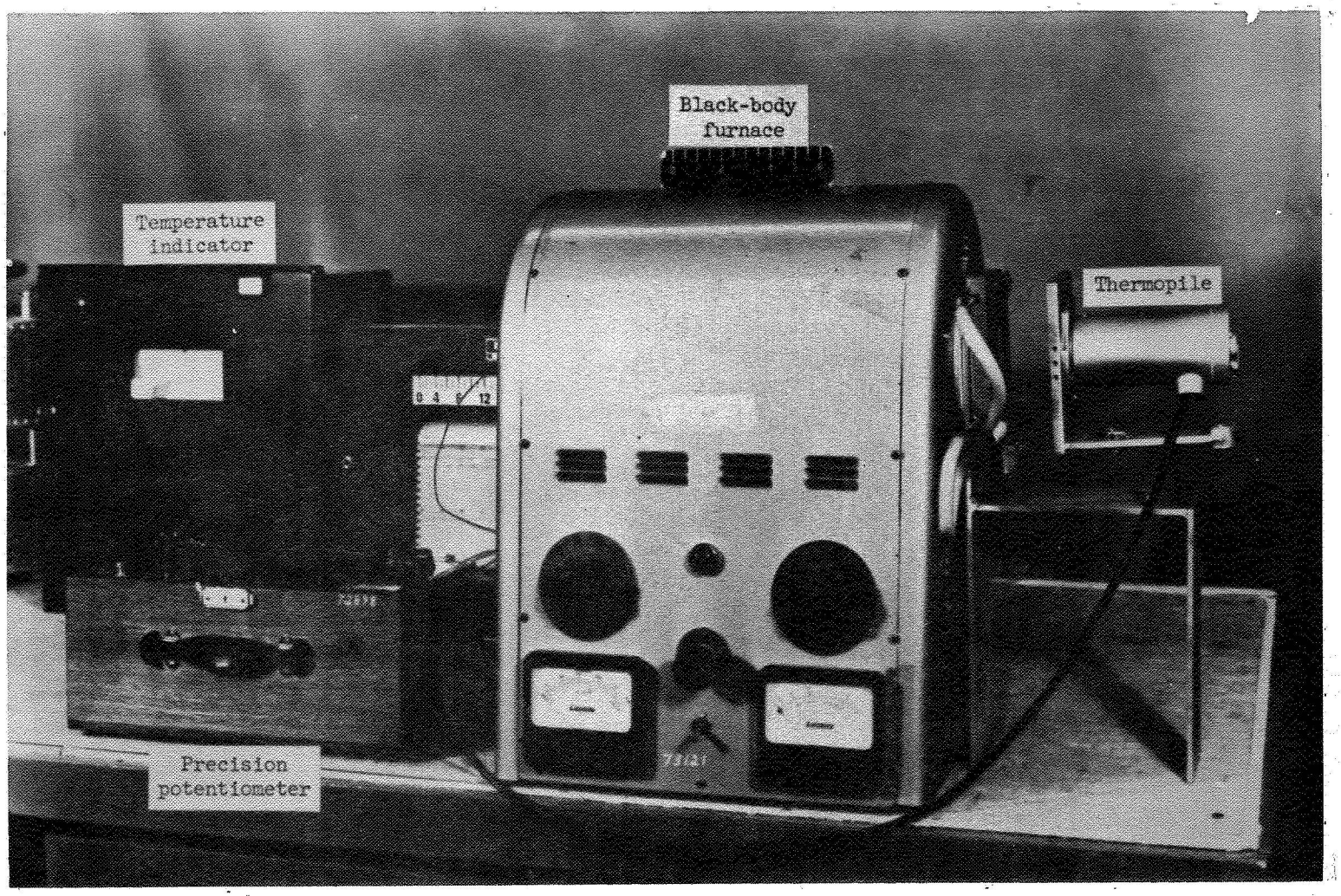


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Figure 3.- Reference-black-body furnace with thermopile and water-cooled shield in position for viewing black body, and precision potentiometer used with thermopile.

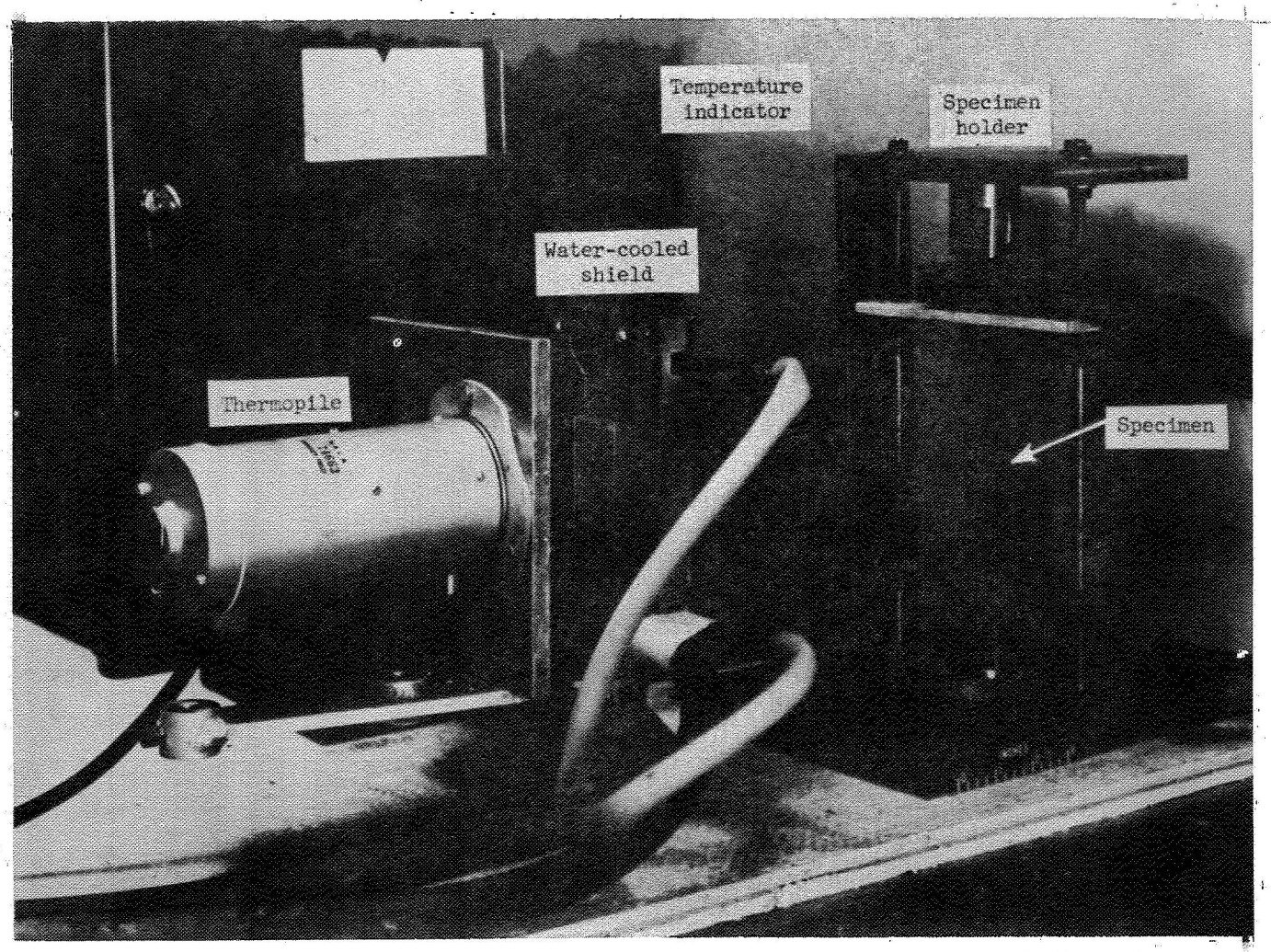

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Figure 4.- Pyrometer and water-cooled shield mounted on pivoted arm of test-specimen holder with test specimen installed.

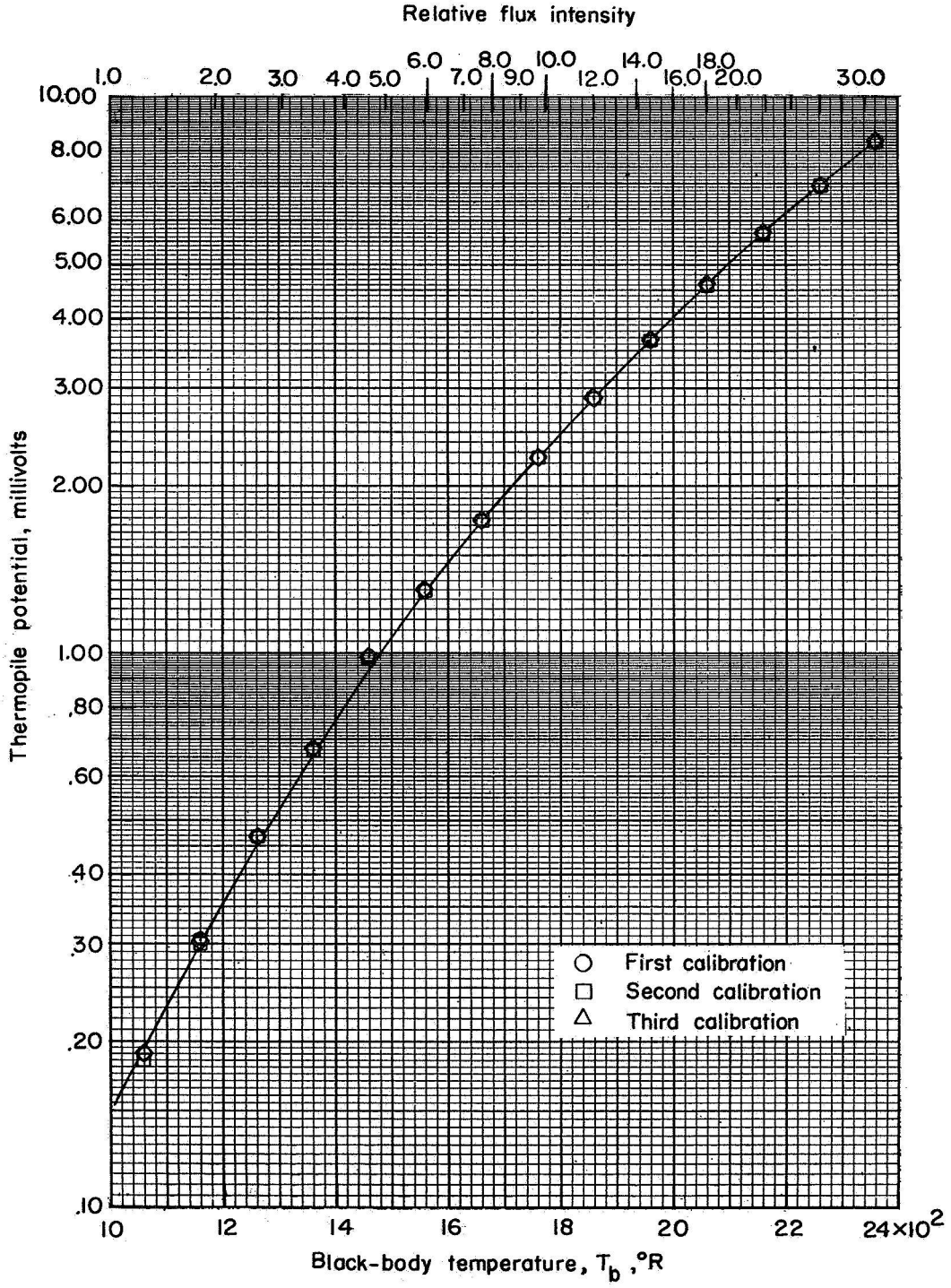
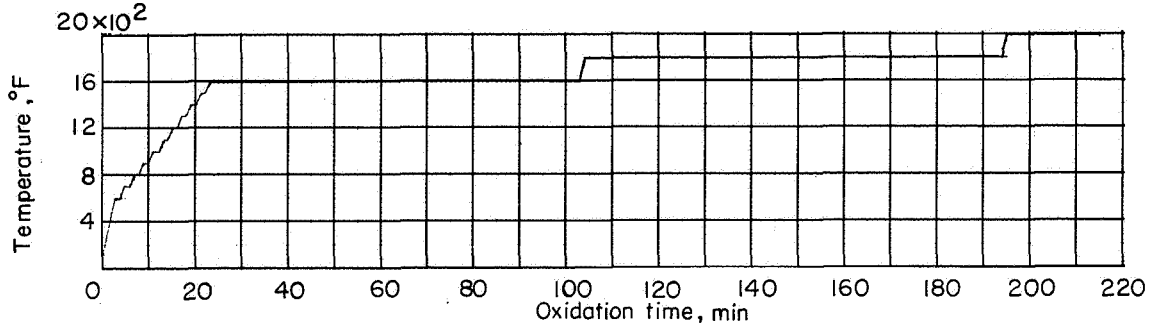
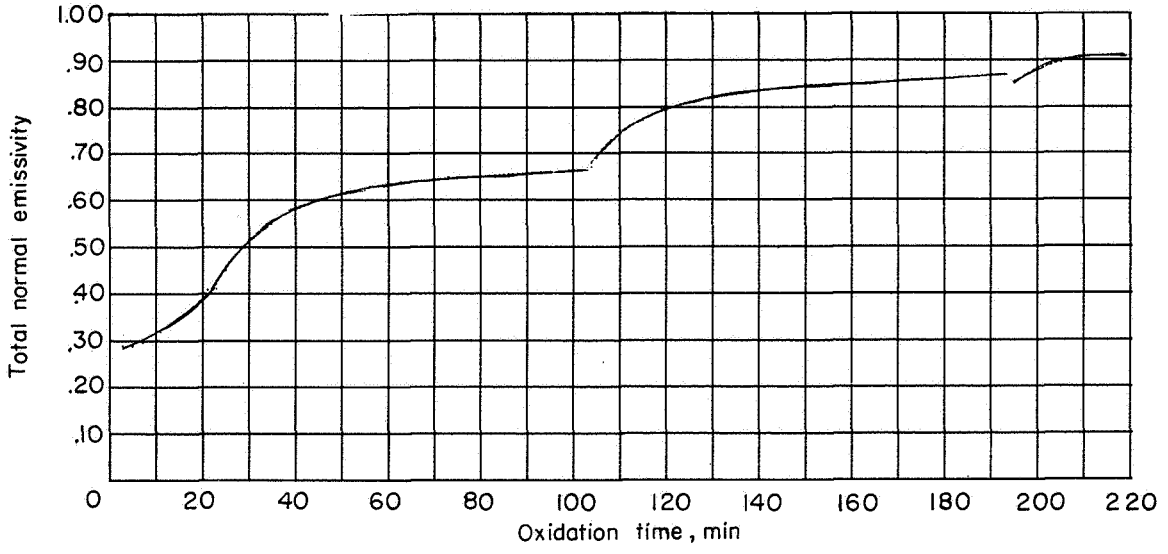


Figure 5.- Calibration of the thermopile radiation-flux measuring system.

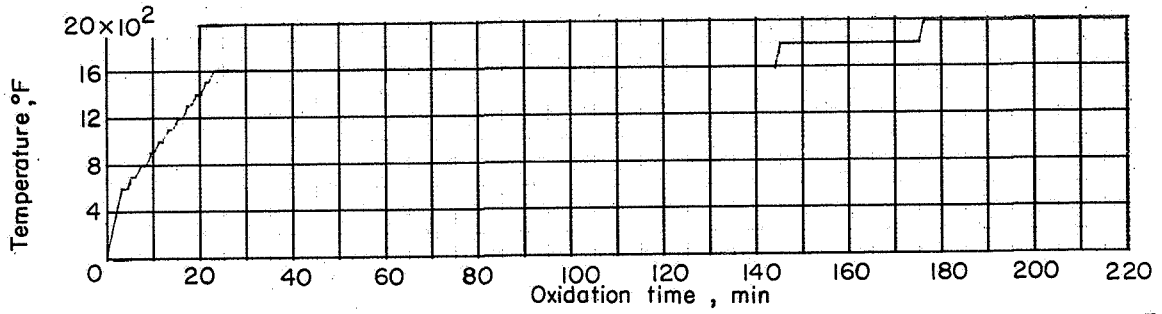


(a) Time history of temperature of specimen.

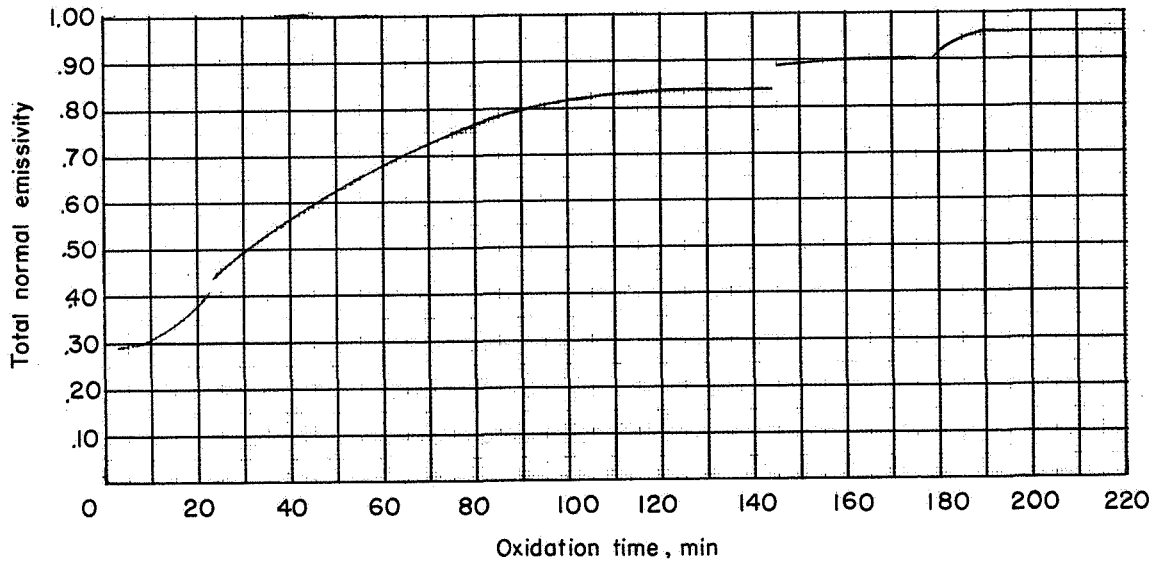


(b) Time history of total normal emissivity of specimen.

Figure 6.- Exploration of the stability of the total normal emissivity of type 347 stainless steel heated in quiescent air.

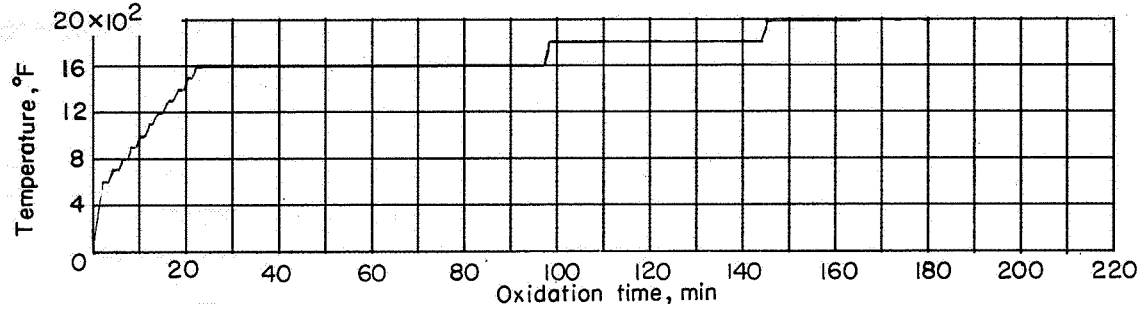


(a) Time history of temperature of specimen.

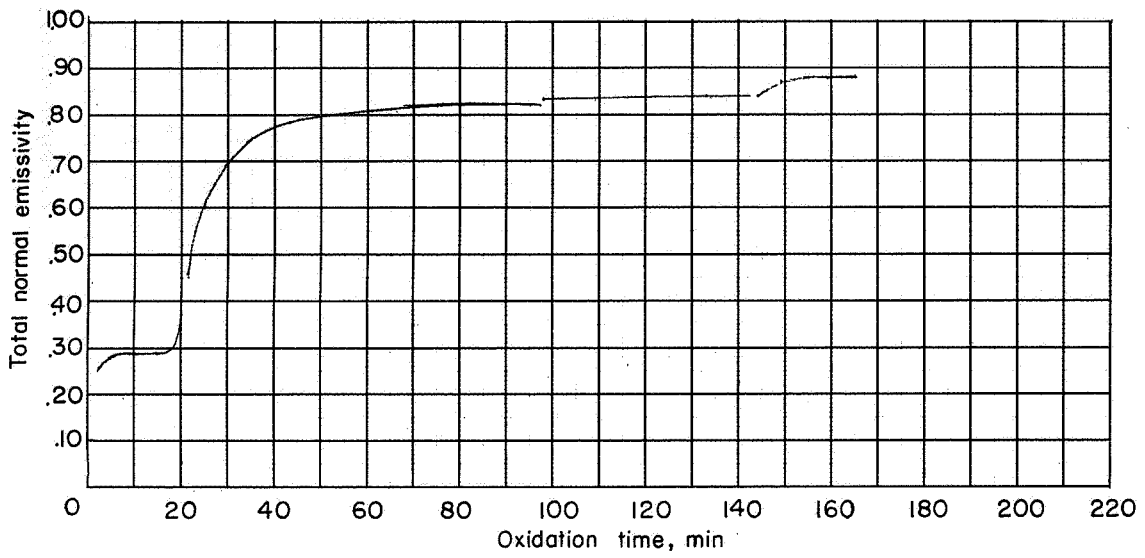


(b) Time history of total normal emissivity of specimen.

ure 7.- Exploration of the stability of the total normal emissivity of Haynes alloy C heated in quiescent air.

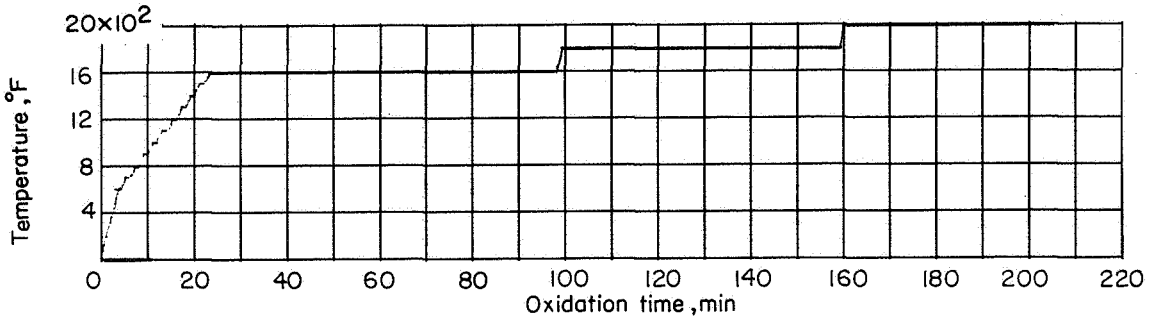


(a) Time history of temperature of specimen.

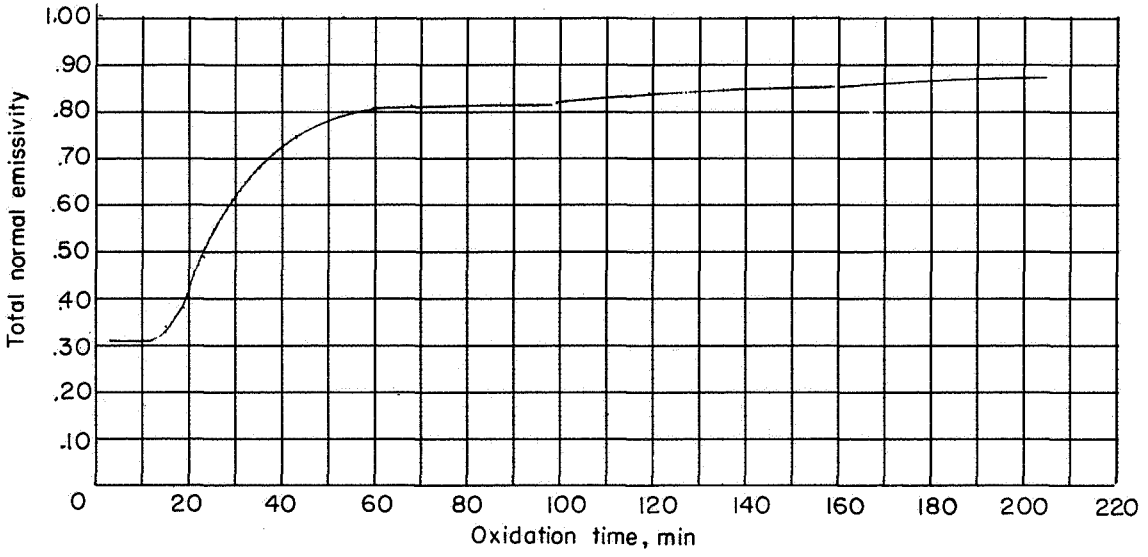


(b) Time history of total normal emissivity of specimen.

Figure 8.- Exploration of the stability of the total normal emissivity of Haynes alloy 25 heated in quiescent air.



(a) Time history of temperature of specimen.



(b) Time history of total normal emissivity of specimen.

Figure 9.- Exploration of the stability of the total normal emissivity of Haynes alloy X heated in quiescent air.

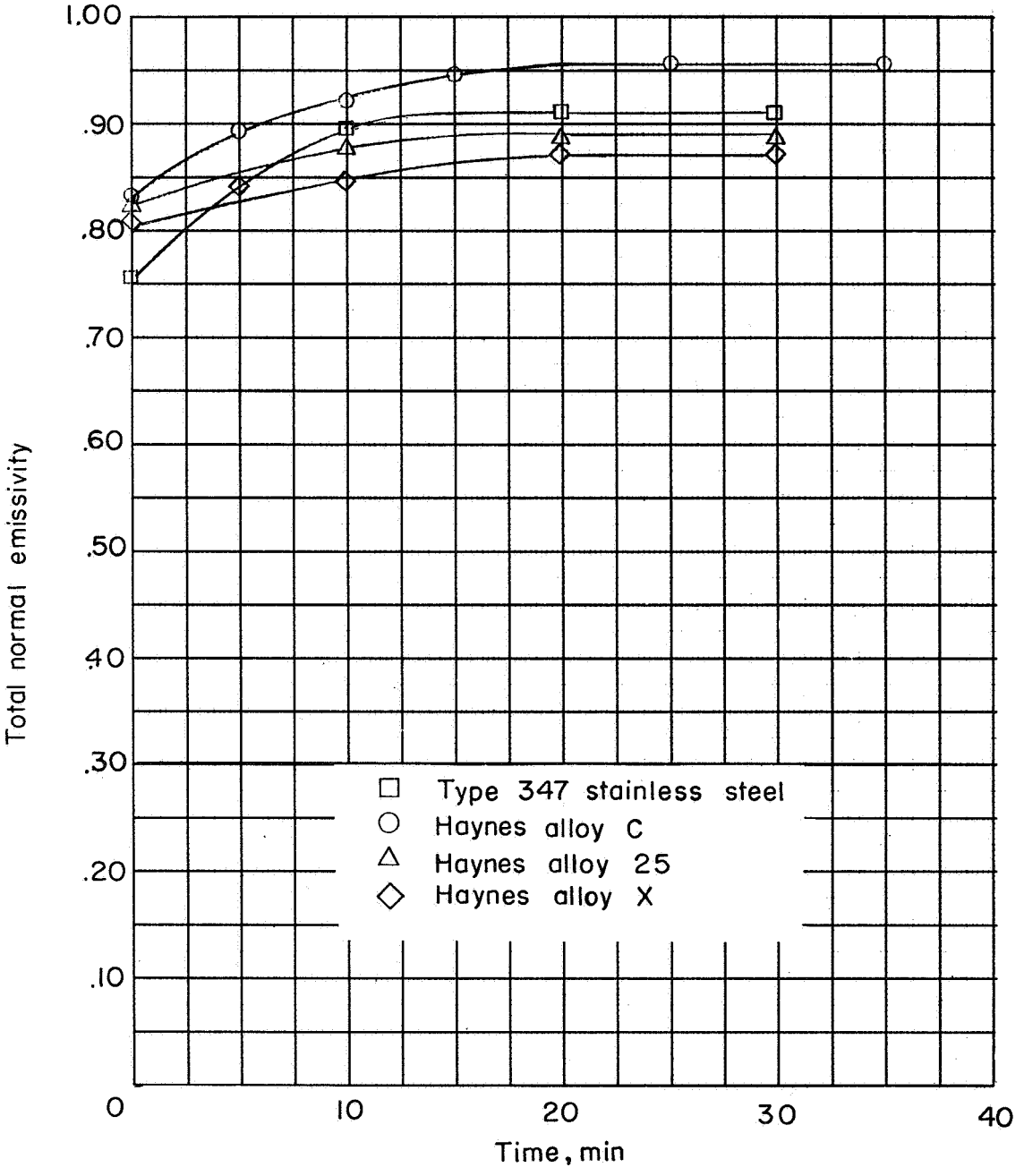


Figure 10.- Variation of total normal emissivity of test specimens with time of oxidation at 2,000° F in quiescent air.

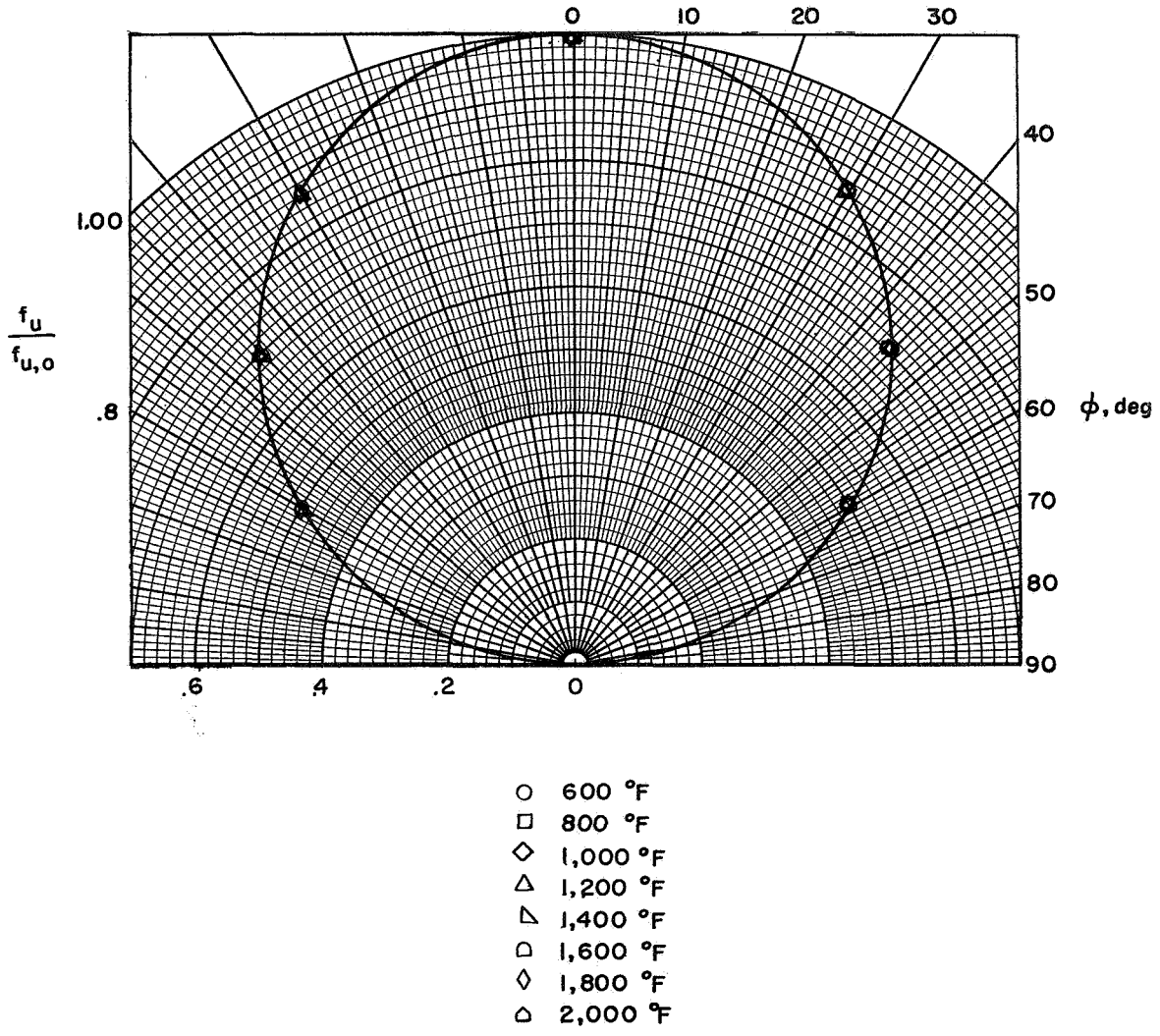


Figure 11.- Comparison of the emission of type 347 stainless steel oxidized 30 minutes at 2,000° F with the Lambert cosine law for diffuse emission at temperatures from 600° F to 2,000° F.

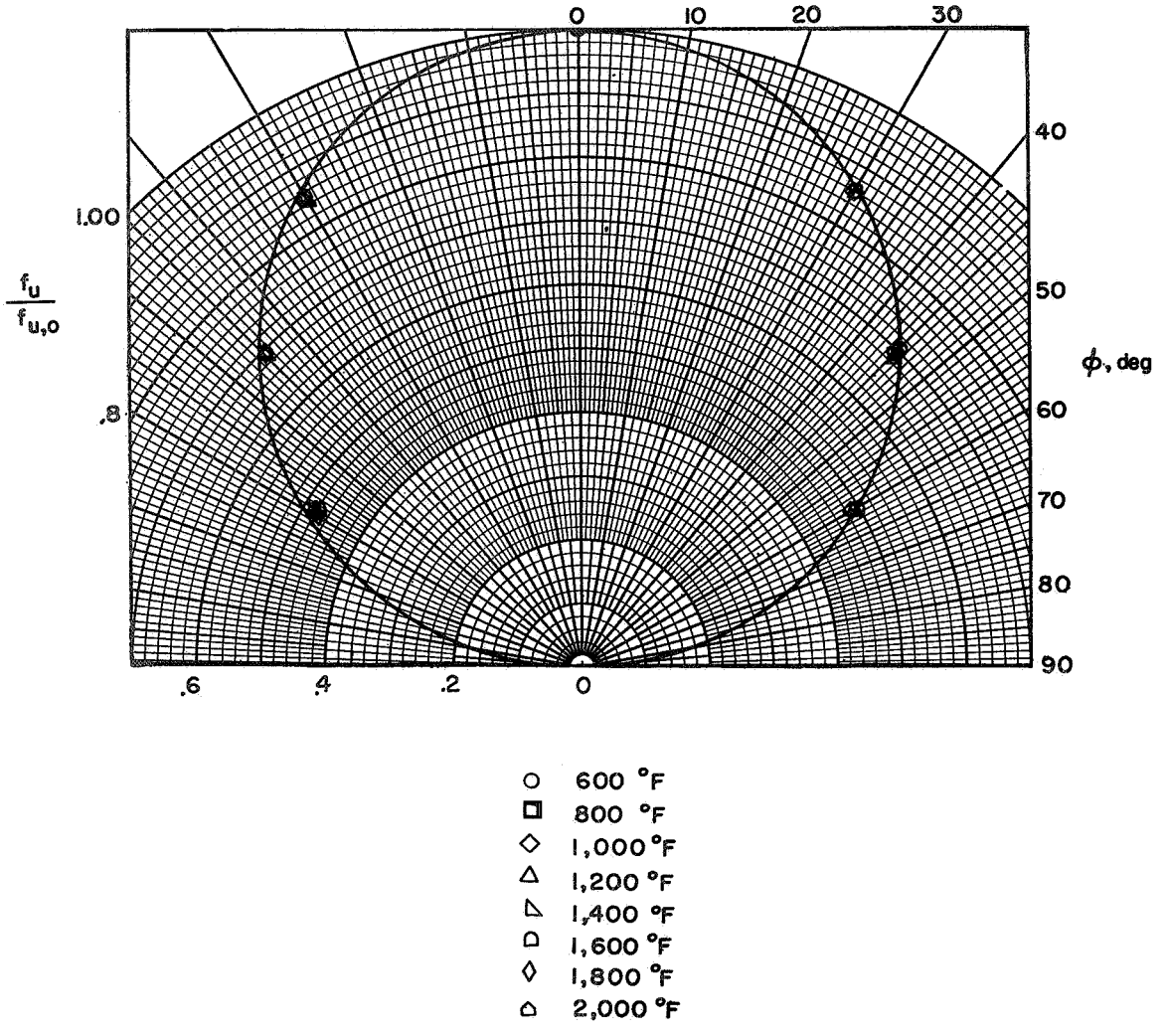


Figure 12.- Comparison of the emission of Haynes alloy C oxidized 35 minutes at 2,000° F with the Lambert cosine law for diffuse emission at temperatures from 600° F to 2,000° F.

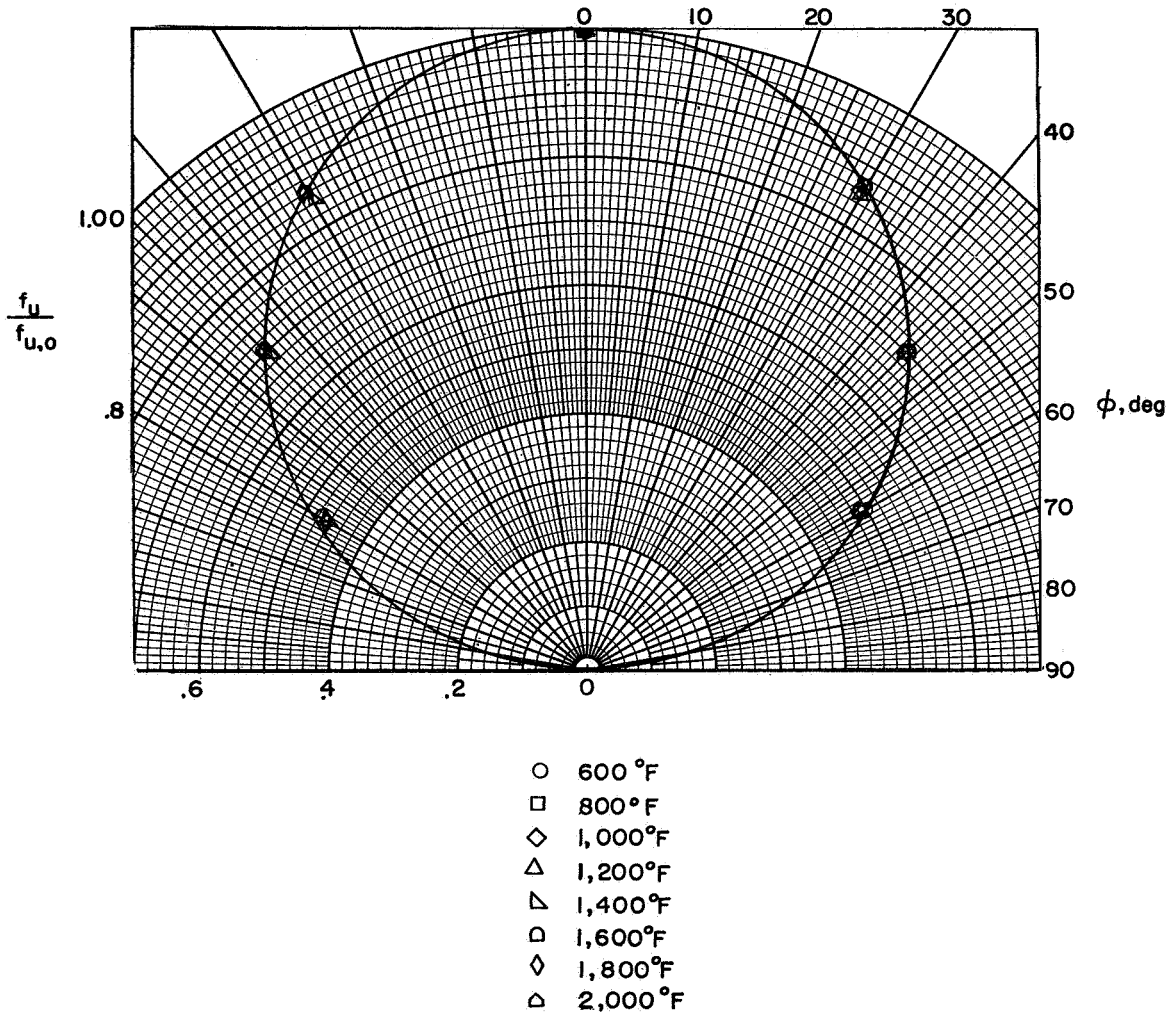


Figure 13 - Comparison of the emission of Haynes alloy 25 oxidized 30 minutes at 2,000° F with the Lambert cosine law for diffuse emission at temperatures from 600° F to 2,000° F.

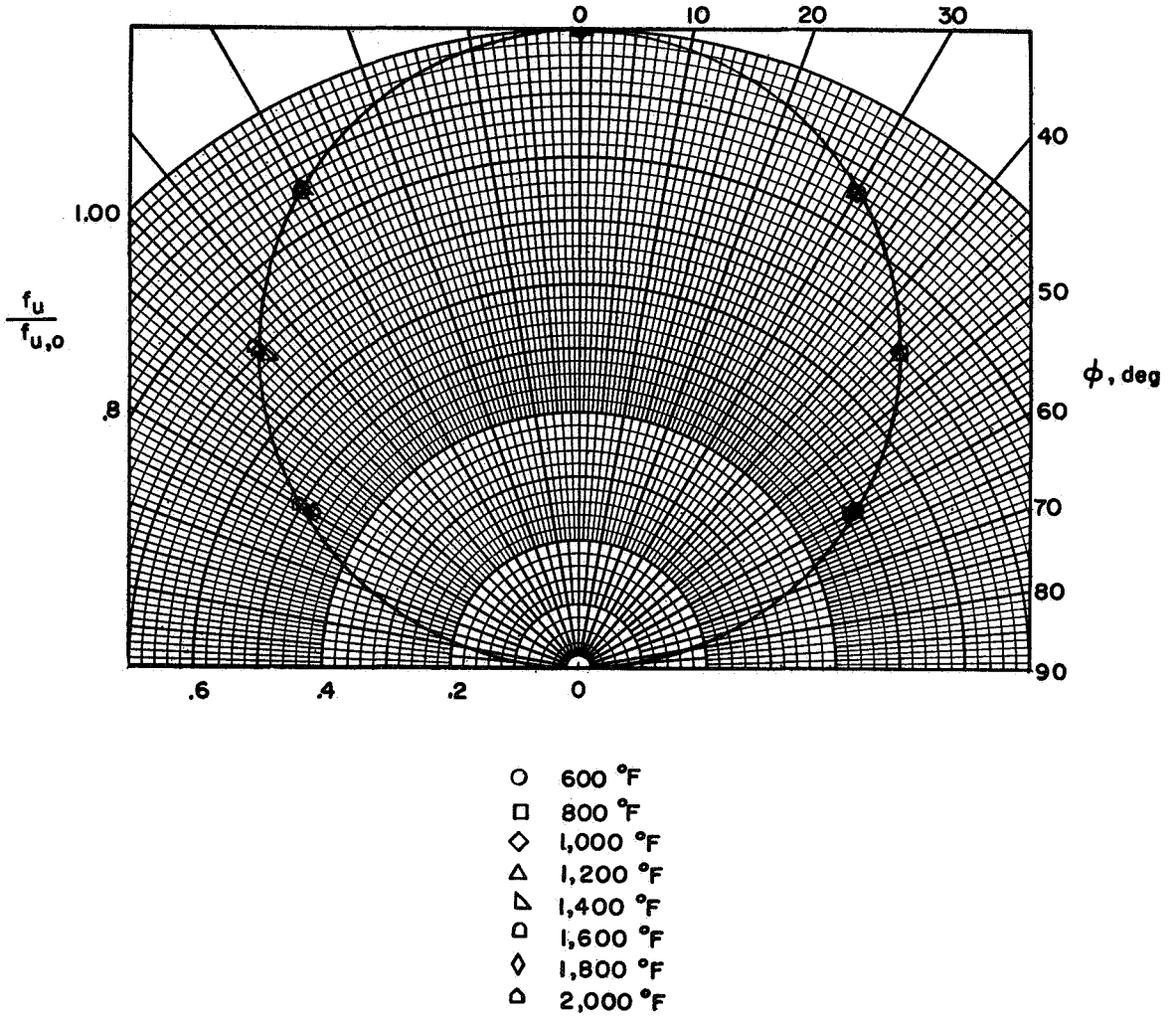
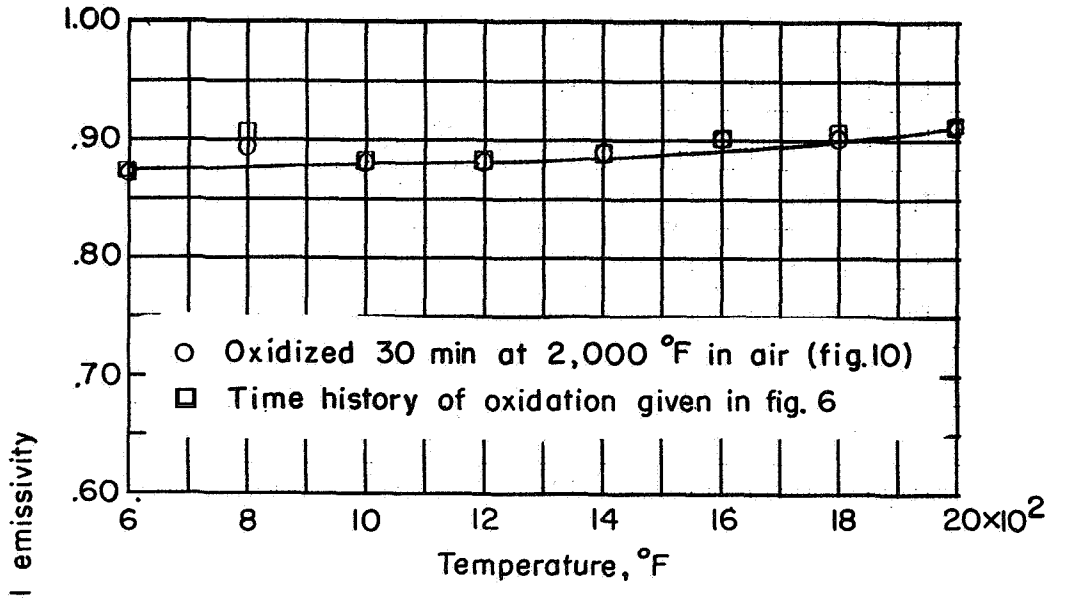
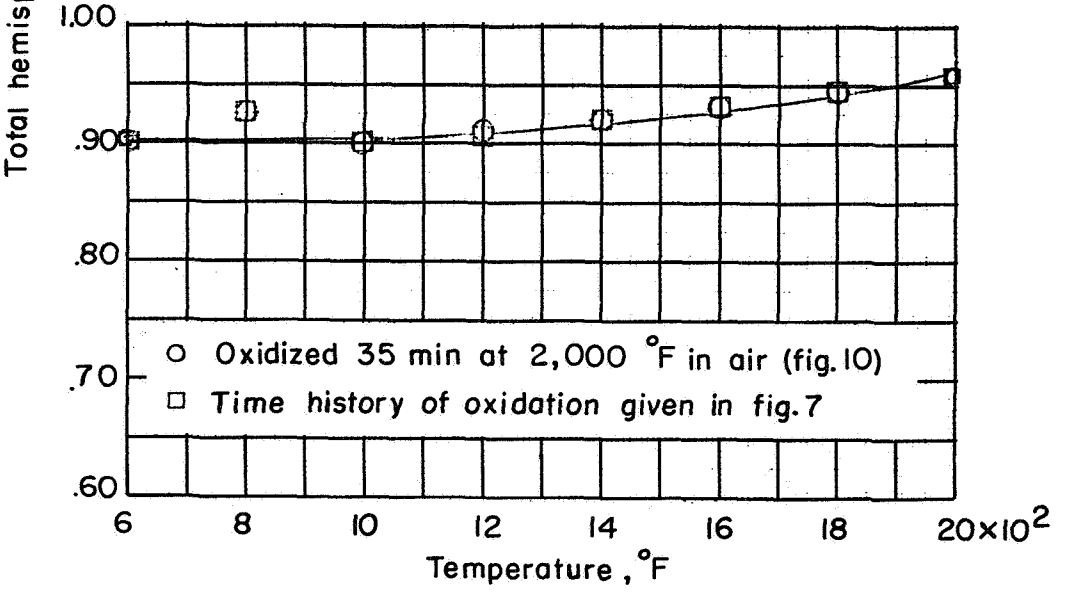


Figure 14.- Comparison of the emission of Haynes alloy X oxidized 30 minutes at 2,000° F with the Lambert cosine law for diffuse emission at temperatures from 600° F to 2,000° F.

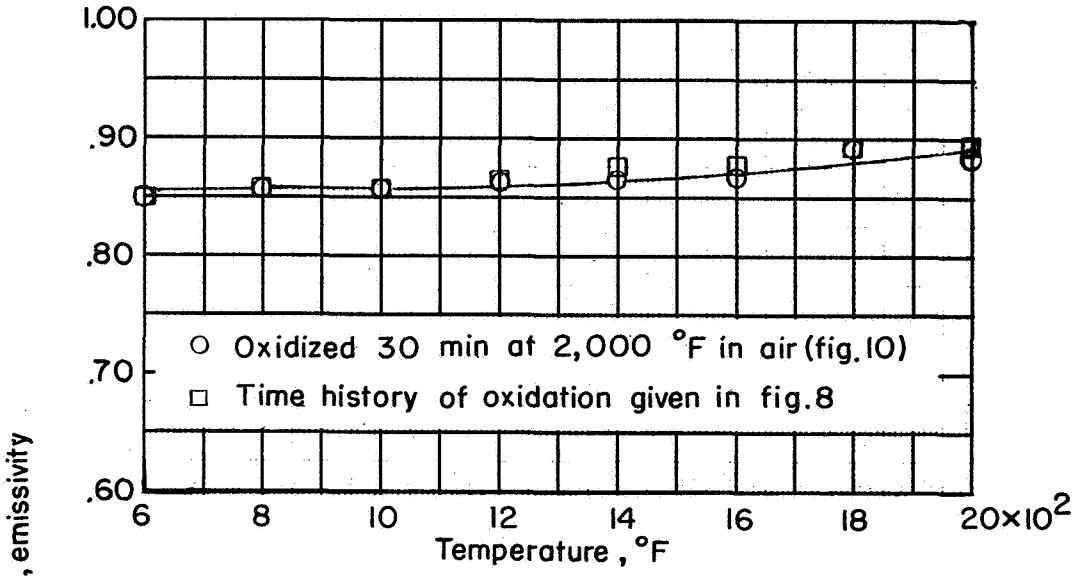


(a) Type 347 stainless steel.

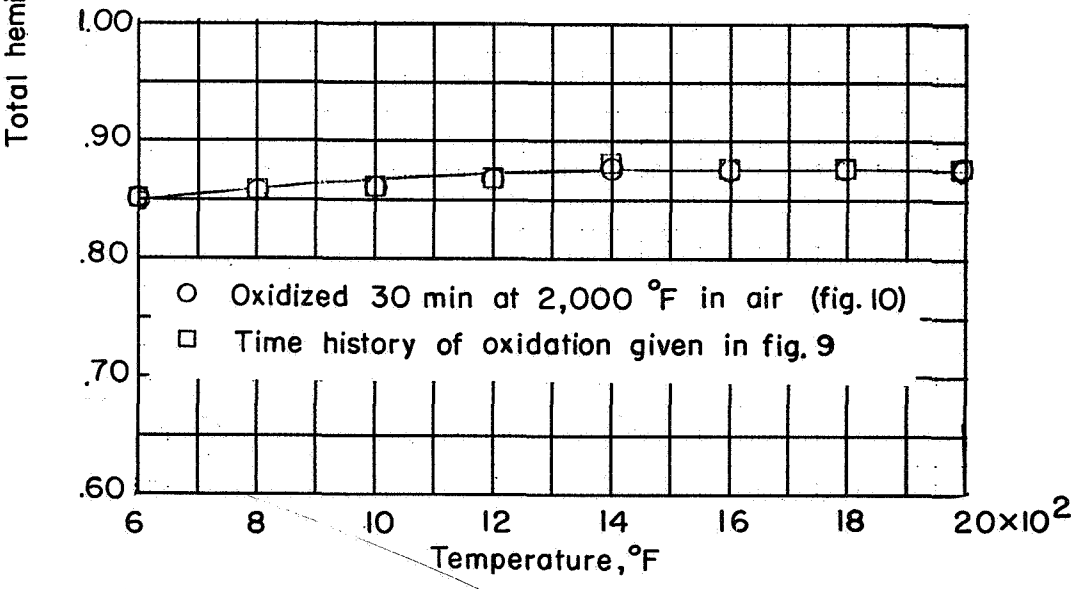


(b) Haynes alloy C.

Figure 15.- Total hemispherical emissivity of stably oxidized test specimens as a function of temperature.



(a) Haynes alloy 25.



(b) Haynes alloy X.

Figure 16.- Total hemispherical emissivity of stably oxidized test specimens as a function of temperature.

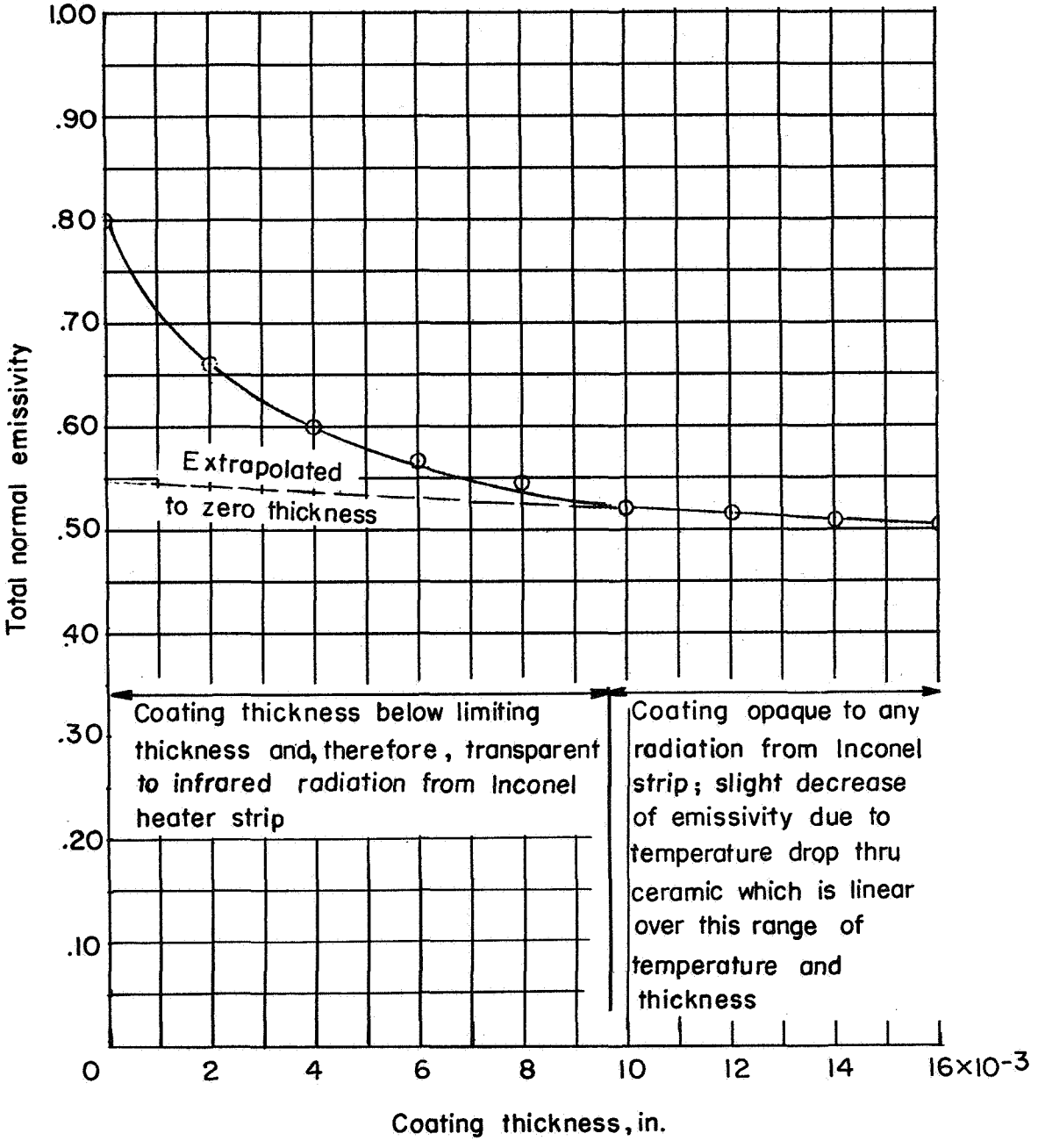


Figure 17.- Total normal emissivity as a function of coating thickness for flame-sprayed ceramic coating of zirconia at 1,200° F.

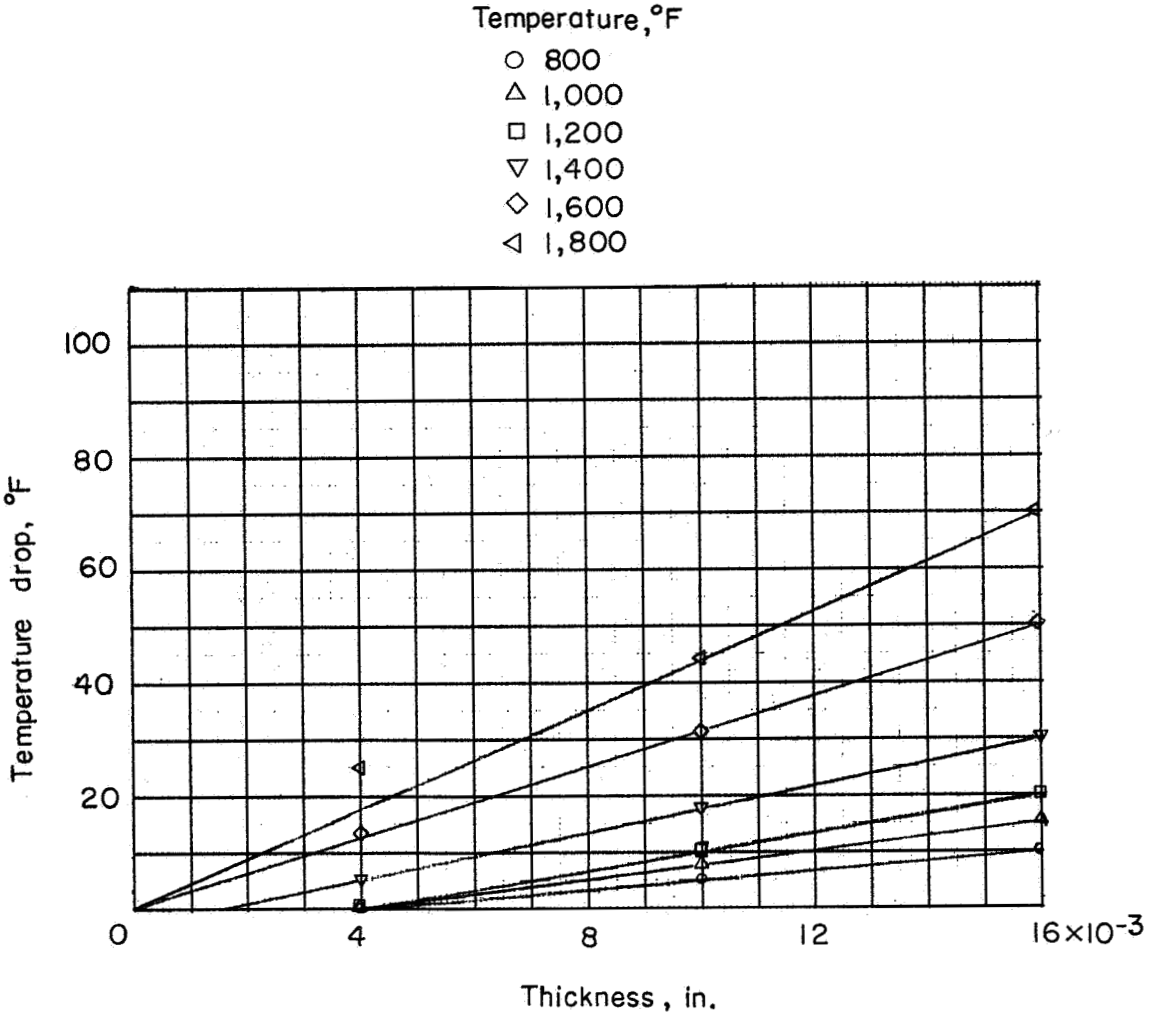


Figure 18.- Temperature drop through thin refractory coatings as a function of coating thickness.

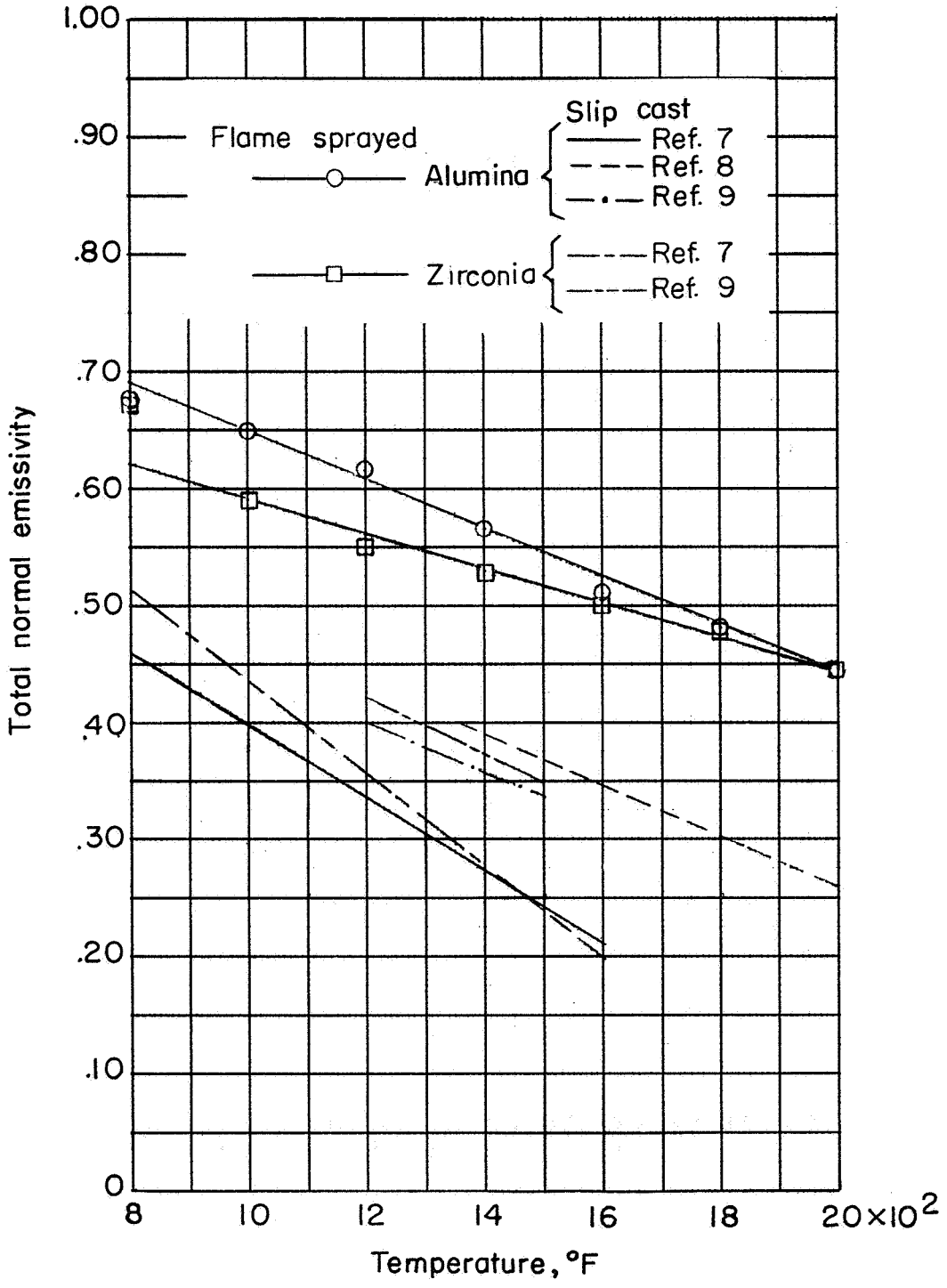


Figure 19.- Variation of total normal emissivity of various ceramic coatings as a function of temperature of heater strip.