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MEASUREMENTS OF TOTAL HEMISPHERICAL EMISSIVITY OF SEVERAL
STABLY OXIDIZED NICKEL-TITANIUM CARBIDE CEMENTED

HARD METALS FROM 600° F TO 1,600° F

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Langley Research Center
Langley Field, Va.

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SUMMARY

The total hemispherical emissivity of several nickel-titanium carbide cemented hard metals have been measured over a temperature range from 600° F to 1,600° F. A variety of cemented hard metals were obtained from the Kennametal Corporation. A brief discussion of the apparatus employed and the procedures used for this investigation is included.

The results of the tests of specimens in the as-received and polished states indicate a nearly constant emissivity for each material tested over the temperature range considered and only slight differences in emissivity values for the different materials. Values obtained on the stably oxidized specimens range from 0.90 to 0.94 at 600° F and 0.88 to 0.92 at 1,600° F for the as-received specimens and from 0.82 to 0.89 at 600° F and 0.85 to 0.87 at 1,600° F for the polished specimens.

The surface analysis of the oxidized materials as obtained by X-ray diffraction methods and metallographic techniques are presented as an aid to reproducing the surface on which these measurements were made.

INTRODUCTION

The surface temperatures encountered by hypersonic vehicles exceed the range for which adequate emissivity information is available. This investigation is concerned with the measurement of total hemispherical emissivity for several nickel-titanium carbide cemented hard metals and is a continuation of the program reported in references 1 and 2.

Preliminary tests of some of these nickel-titanium carbide cemented hard metals have indicated these materials may have application to leading edges and nose cones of high-speed aircraft. However, certain physical properties must be determined before a thorough evaluation can be made.

Since most clean metals have low emissivities, the surface must be coated with some material with a high emissivity for efficient radiant heat transfer. The use of stably oxidized surfaces for this coating has the advantages of ease of production and reproductibility. Thus, the subject of this investigation is the measurement of total hemispherical emissivity of these stably oxidized materials.

SYMBOLS

f	radiation flux, Btu/(sq ft)(sec)
T	absolute temperature, °R
ϵ	total hemispherical emissivity
ϕ	angle of incidence as measured from normal to surface

Subscripts:

b	black body
o	at $\phi = 0$ (normal to surface)
u	surface of unknown emissivity

APPARATUS

Emissivity Measurements

The apparatus used in this investigation is fully described in reference 1; therefore, only a brief description of the equipment needs to be repeated here to indicate the function of each component. The overall view of the equipment is shown in figure 1 and various components are shown in figures 2 to 5.

The total radiation pyrometer, together with its associated water-cooled shield and shutter assembly, is shown in figure 1 in position to view a radiating test specimen. This pyrometer is a commercially available unit which contains a thermopile of 10 chromel-constantan thermocouples connected in series. The hot junctions of the thermopile are flattened and blackened to allow for maximum absorption of incident radiation. An optical system for focusing radiation onto the thermopile hot junction consists of a calcium fluoride lens and an optical stop. Temperature-compensating resistors are connected in series and parallel

with the thermopile to assure an output independent of the cold junction temperature up to 250° F. The water-cooled shield and shutter was used to limit the temperature rise of the pyrometer housing only a few degrees above room temperature while viewing a radiating source.

The specimen holder and its associated power supply as shown in figure 2 were designed to allow a large variety of materials to be tested. The resistance heating of the test strip assures an easily controlled method of heating the strip and limits temperature gradients to a negligible value.

The black-body target cone is shown in figure 3. This target is a hollow cone of highly oxidized Inconel, which was 6 inches long and had a total apex angle of 8.6°. The associated black-body heater is a commercially available tube-type furnace heated by resistance elements. Figure 4 shows the pyrometer set in position to view the black-body target in place in the furnace.

The true surface temperature of the black-body and test specimens was measured by No. 30 (American wire gage) chromel-alumel thermocouples spot-welded to the surface. A self-balancing potentiometer calibrated to read directly in degrees Fahrenheit indicated the temperature. The thermoelectric electromotive force produced by the thermopile as a function of incident radiation was measured by a precision potentiometer.

Specimen Surface Analysis

The X-ray analysis of the stably oxidized specimen surfaces was performed with a diffractometer using Cu K- α radiation. Identification of the components was made with the aid of American Society for Testing Materials X-ray powder data cards. The photomicrographs of the specimen surfaces were made by using a standard metallograph and Eastman type M metallurgical plates.

PROCEDURES

Emissivity Measurement

The theory and procedures used in this investigation are discussed fully in reference 1 and only a brief repetition is considered to be necessary.

The measurement of total hemispherical emissivity may be performed by use of either the "filament-in-vacuum" method or the "reference-black-body" method. This investigation employed the latter as the most

convenient in obtaining information for a large variety of materials with the accuracy required for most engineering applications.

The emissivity is measured by this method by comparing the intensity of radiation emanating from a test specimen to that from a black body. When the areas viewed and the temperature of the test specimen and the black body are identical, the emissivity expression reduces to a simple ratio

$$\epsilon = \frac{f_{u,o}}{f_{b,o}}$$

For this investigation it was found to be more convenient to measure radiant flux intensities from the black body over the entire temperature range rather than alternate between the reference black body and test specimen at each temperature. The radiation detecting system was then considered to be calibrated and only an occasional check was necessary to determine any drift or change. The three calibrations of the system made during these tests are shown on figure 6 and indicate no appreciable difference from the first to the third calibrations.

This calibration curve is plotted in terms of thermopile electromotive force due to black-body radiation and the absolute temperature of the black body in degrees Rankine. Since only ratios of the radiant flux are necessary for calculation of the emissivity, the requirements upon the instrumentation are greatly lessened in that only relative values of flux intensity need to be measured. Therefore, an arbitrary scale of relative flux intensities is shown in figure 5 as a function of thermopile electromotive force.

The test specimens were fabricated by the manufacturer into strips 9 inches long, 1 inch wide, and approximately 1/8 inch thick by means of specialized powder metallurgical techniques. This technique consists of pressing the powdered metal and carbide components and presintering. Forming and shaping is conducted on these presintered forms and final sintering is then performed in vacuum furnaces at temperatures depending on the material. In this condition the materials have a roughness under 30 microinches root mean square. (See ref. 3.)

The initial test was made to determine the time of oxidation at 1,600° F necessary to insure a stably oxidized surface. After oxidation, the total normal emissivity of the stably oxidized surfaces was measured over the temperature range from 600° F to 1,600° F.

The investigation to determine any deviation from Lambert's cosine law for diffuse radiation was conducted on stably oxidized specimens. This test indicates whether the emitted radiation is diffuse (in which case the total hemispherical emissivity may be calculated as a direct

ratio of the relative flux intensities) or the surface emits nondiffusely (in which case double integration is required to determine the hemispherical emissivity as discussed in ref. 1).

Surface Analysis

Photomicrographs were made of the oxidized and unoxidized surfaces as an aid to reproducing these surfaces in the interest of engineering applications. These specimens were taken from the area of the test specimen viewed by the pyrometer during measurements of emissivity. The photographs of the oxidized specimens were made without metallographic preparation of the surface in order to indicate the degree of roughness and oxidation.

The unoxidized specimens were rough-surfaced with a high-speed 240 grit silicon carbide belt and a 320 grit carborundum stone lap flushed with water. Intermediate polishing was accomplished with 400 grit silicon carbide paper and 6 micron diamond paste on a wood lap with a filtered detergent used as a vehicle. Final polishing was performed with 3 micron and 1 micron diamond paste on a wood lap covered with photographic print paper emulsion side down. The photographs were made with a metallograph on Eastman type M metallurgical plates. The magnification and etch information is given under the photographs.

RESULTS AND DISCUSSION

Measurements of total hemispherical emissivity were made on two test specimens in the as-received condition, that is, with the surface finish resulting from the manufacturing process. The specimens were then polished to obtain a clean, bright surface and the measurements were repeated on these surfaces. The variations of emissivity measurements between the two specimens with the same surface condition were so nearly identical that an average of the measurements is plotted. The curves of figure 7 illustrate the variation of emissivity with time of oxidation for both as-received and polished test specimens. These curves indicate that slightly higher values of emissivity may be obtained for the as-received surface. The curves also show that both surfaces have stable values of emissivity after oxidation for approximately 10 minutes at a temperature of 1,600° F which is consistent with the oxidation-resistance characteristics of these materials, as reported by the manufacturer. (See ref. 3.)

The curves of figure 8 show the values of emissivity for both the as-received and polished stably oxidized test specimens. These curves

show higher values of emissivity for the as-received surface over the entire temperature range. The measured values ranged from 0.90 to 0.94 at 600° F and from 0.88 to 0.92 at 1,600° F for the as-received specimens. The polished specimens had measured values ranging from 0.82 to 0.89 at 600° F to 0.85 to 0.87 at 1,600° F. A slight variation of emissivity may result between different specimens of the same material in the as-received condition and is probably due to the variations in surface finish. The results obtained during this investigation indicate that this variation of emissivity for the as-received specimens is unlikely to exceed 2 percent for any particular material. The variation for the polished specimens was found to be less than 1 percent. Further, the values of emissivity are nearly constant for any particular material and exhibit only slight differences of emissivity for the various materials. This result is believed to be due to the similar chemical compositions, the grain size, and surface oxidation of these materials. The results obtained from this investigation indicate that these nickel-titanium carbide cemented hard metals, when stably oxidized, have a high stable total hemispherical emissivity which will materially increase the radiative heat transfer of these materials.

Other nickel-titanium carbide cermets which contain cobalt as the metal phase in place of nickel (Kennametal designations K6, K11, and K92) were tested. During oxidation at 1,600° F the oxide formed on these materials was a thick coating of a porous oxide which did not achieve a stable emissivity. The material K-175B which contained a large percentage of molybdenum oxidized in a similar manner. Since these materials are unsuitable for use at elevated temperatures, due to the nature of the oxide coating formed, further tests were not conducted.

The results of the investigation which was made to determine the adherence to Lambert's cosine law of the nickel-titanium carbide stably oxidized specimens over the temperature range from 600° F to 1,600° F and angles of incidence from 0° to 60° are shown in figures 9 to 14. In these figures perfectly diffuse radiation is shown by the circles and the experimental test points are indicated. These data indicate that the radiation for the stably oxidized test specimens was essentially diffuse over the range of temperatures and angles considered. Thus, the total normal emissivity may be taken as values of total hemispherical emissivity as discussed in reference 1.

The X-ray diffraction analysis of the oxidized surfaces is shown on table I together with the nominal chemical composition of the materials, as received from the manufacturer. These data indicate that the oxides formed are very similar in composition. Although no quantitative analysis of the oxide coating was made, there is an indication of increasing emissivity with an increasing nickel content or a decreasing percent of titanium carbide. The total hemispherical emissivity of a surface varies

with surface oxidation and roughness as well as temperature. Thus, the values reported are characteristic of a particular surface. The photomicrographs in figures 15 to 18 show variations in the surface microstructure of an oxidized specimen and the oxide structure on different test specimens. The photomicrographs of the test specimens also indicate a nonhomogeneity of the structure of these materials as indicated by the voids which are present. These varying surface conditions probably explain the differences in emissivity for surfaces of nearly identical chemical composition.

CONCLUDING REMARKS

The values of total hemispherical emissivity obtained for the titanium carbide cermets tested indicated that somewhat higher values of emissivity may be achieved by oxidation of the material in its as-received condition rather than by preliminary polishing. For the stably oxidized as-received test specimens, the emissivity values range from 0.90 to 0.94 at 600° F and from 0.88 to 0.92 at 1,600° F. For the specimens which were brightly polished prior to oxidation, the emissivity values range from 0.82 to 0.89 at 600° F and from 0.85 to 0.87 at 1,600° F. Although a variation of emissivity may result, due to differences in the surface finish of the as-received metals, this variation is unlikely to exceed 2 percent for any specific material.

Results obtained on materials which contain only nickel, titanium carbide, and columbium carbide indicate that the emissivity of the stably oxidized surface possibly increases with an increase in nickel content, although the differences of emissivity for the materials tested is so slight as to be inconclusive.

Materials tested which contain cobalt as a metal phase in place of nickel, or a high percentage of molybdenum, possess characteristics which prevent the formation of stable oxide coatings with desirable physical properties.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Field, Va., February 17, 1959.

REFERENCES

1. O'Sullivan, William J., Jr., and Wade, William R.: Theory and Apparatus for Measurement of Emissivity for Radiative Cooling of Hypersonic Aircraft With Data for Inconel and Inconel X. NACA TN 4121, 1957.
2. Wade, William R.: Measurements of Total Hemispherical Emissivity of Various Oxidized Metals at High Temperature. NACA TN 4206, 1958.
3. Anon.: Engineering Properties of Kentanium. Kennametal, Inc. (Latrobe, Pa.), July 1, 1955.

TABLE I

NOMINAL CHEMICAL COMPOSITION OF KENNAMETAL HARD METALS
AND THE OXIDES FORMED AT 1,600° F

Material	Percentage composition	Surface analysis after oxidation
K150A	Nickel, 10 percent; titanium carbide, 80 percent; columbium carbide, 10 percent ¹	NiO; TiC; and TiO ₂
K151A	Nickel, 20 percent; titanium carbide, 70 percent; columbium carbide, 10 percent ¹	NiO; TiC; and TiO ₂
K152B	Nickel, 30 percent; titanium carbide, 65 percent; columbium carbide, 5 percent ¹	NiO; TiC; and TiO ₂
K153B	Nickel, 40 percent; titanium carbide, 54 percent; columbium carbide, 6 percent ¹	NiO; TiC; and TiO ₂
K163B1	Nickel, 33.3 percent; molybdenum, 6.7 percent; titanium carbide, 54 percent; columbium carbide, 6 percent ¹	NiO; TiC; TiO ₂ ; Ta ₂ O ₅ ; and C
K184B	Nickel, 40 percent; molybdenum, 4 percent; aluminum, 3 percent; chromium, 3 percent; titanium carbide, 40 percent; columbium carbide, 10 percent ¹	NiO; TiC; TiO ₂ ; Al ₂ O ₃ ; Ta ₂ O ₅ ; and Cr ₂ O ₃

¹Added as a solid solution of columbium carbide, tantalum carbide, and titanium carbide containing about 90 percent columbium carbide.

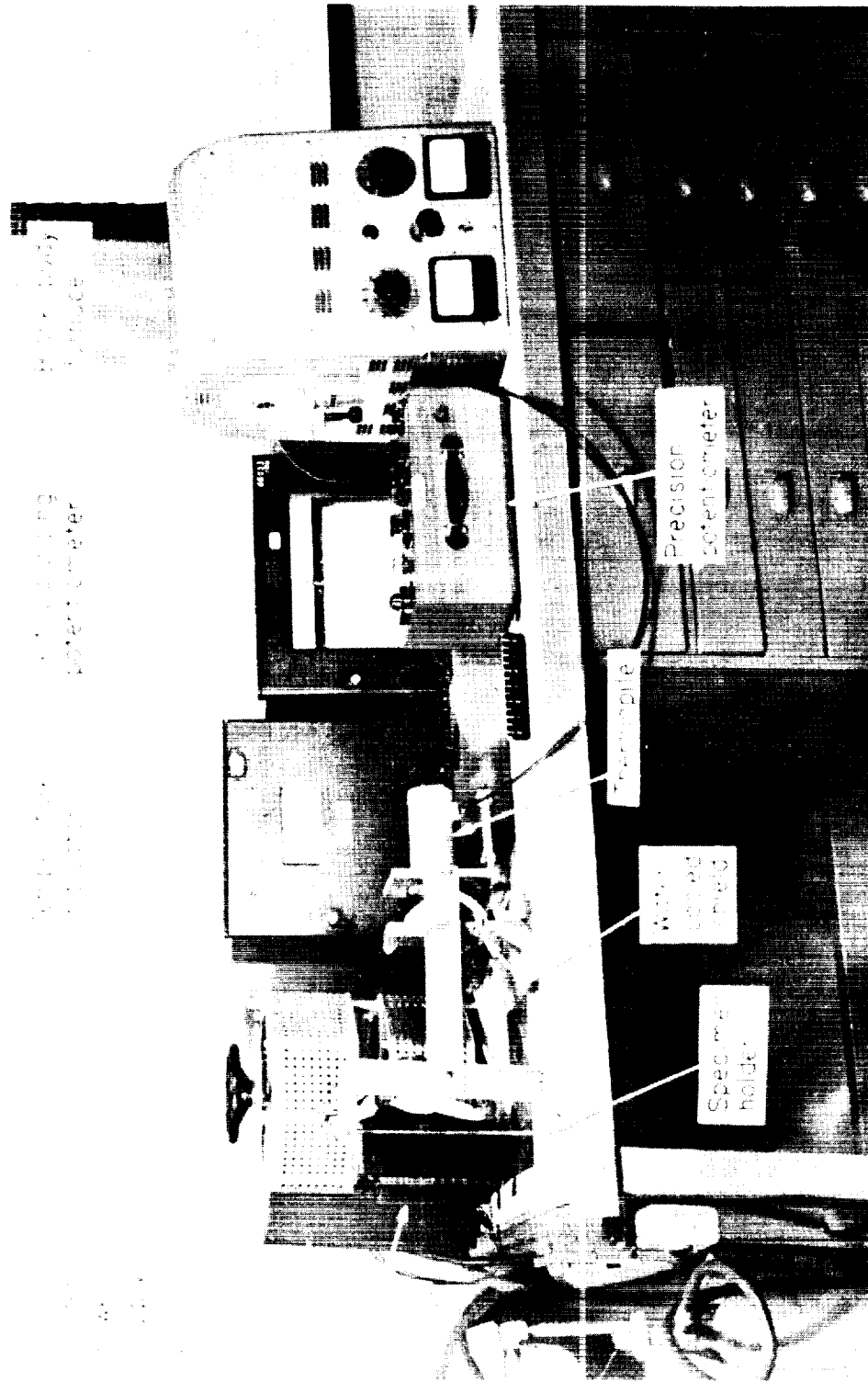
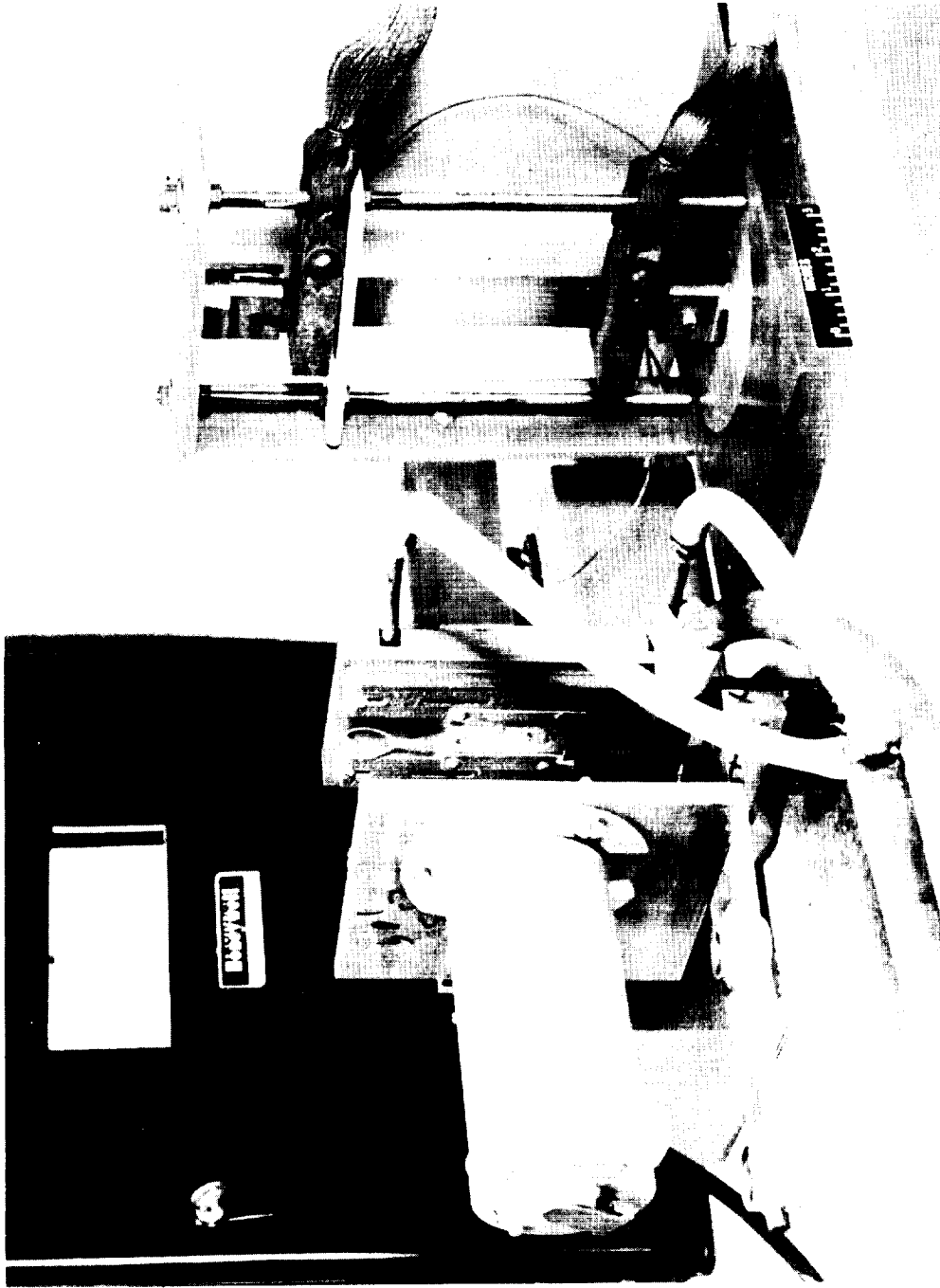
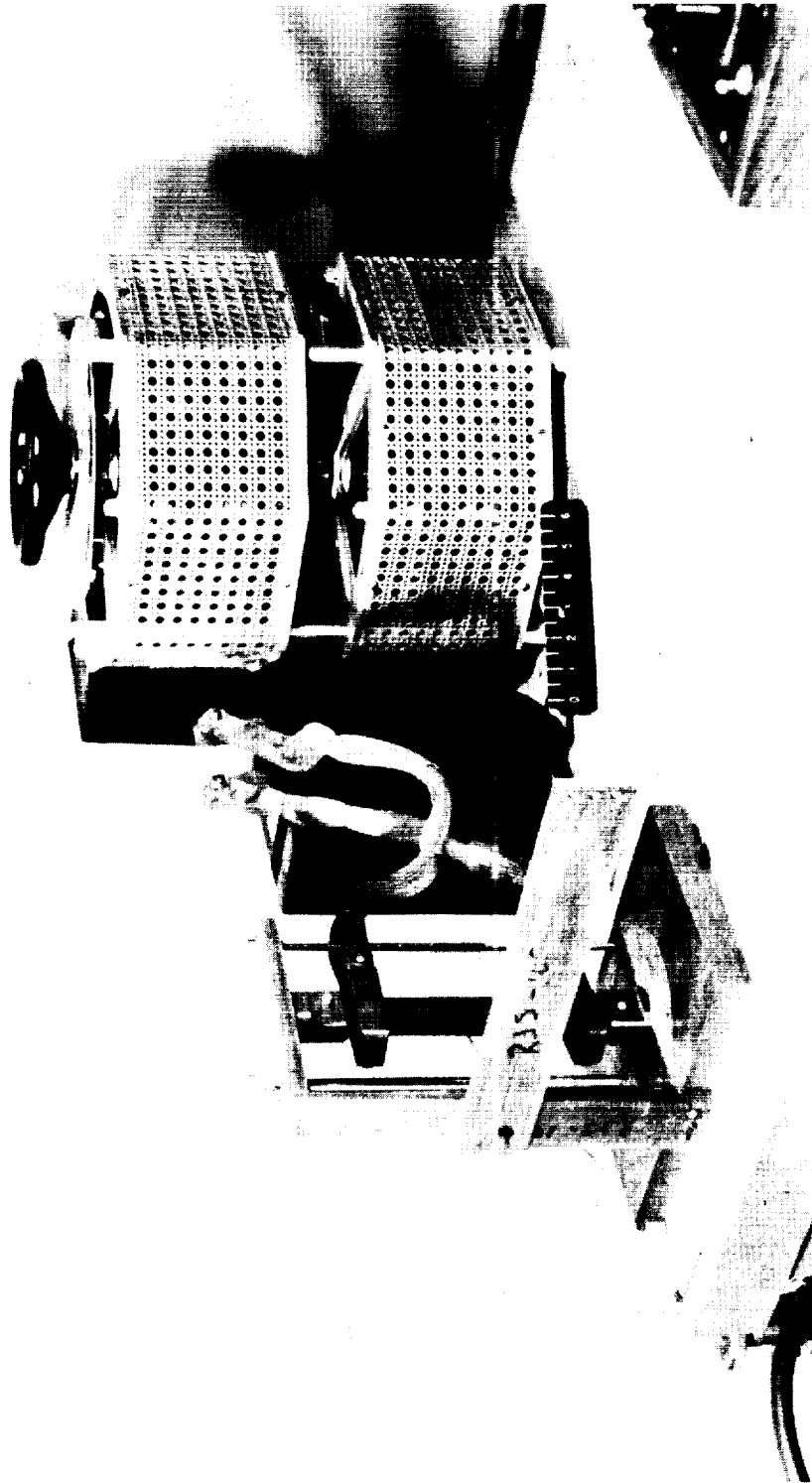


Figure 1.- General view of emissivity measuring apparatus with identification of principal components.

L-96503.2



L-97037
Figure 2.- Pyrometer and water-cooled shield mounted on pivoted arm of test-specimen holder with
test specimen in place.



I-96504
Figure 3.- Test specimen holder with specimen in place and the electrical power supply for heating test specimens.

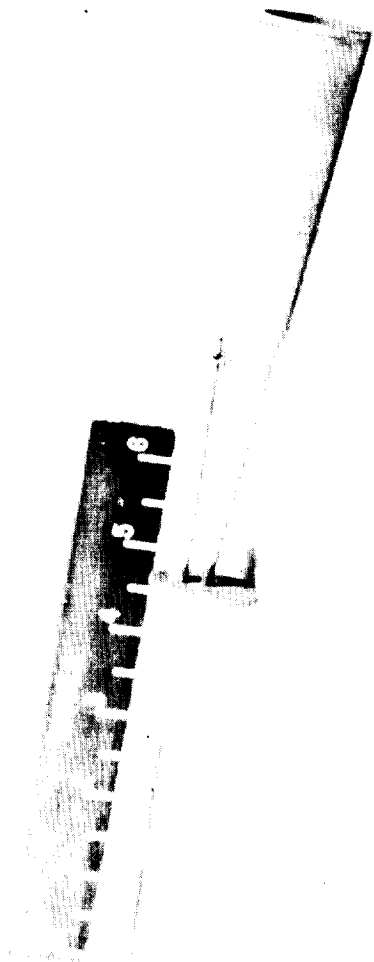
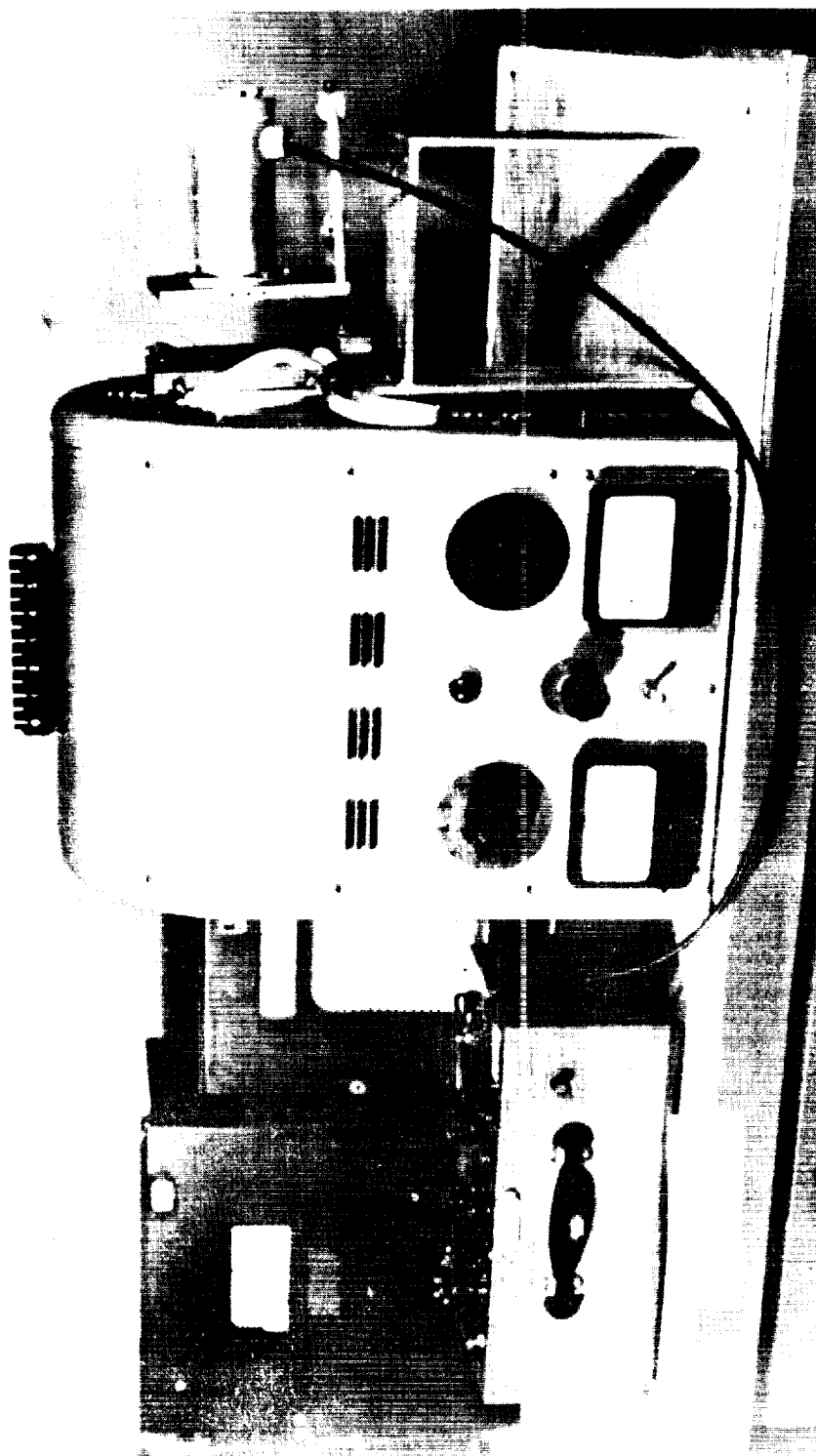


Figure 4.- Reference black-body conical target with thermocouple installed. L-96506



L-96505.2
Figure 5.- Reference black-body furnace with thermopile and water-cooled shield in position for viewing black body, and precision potentiometer used with thermopile.

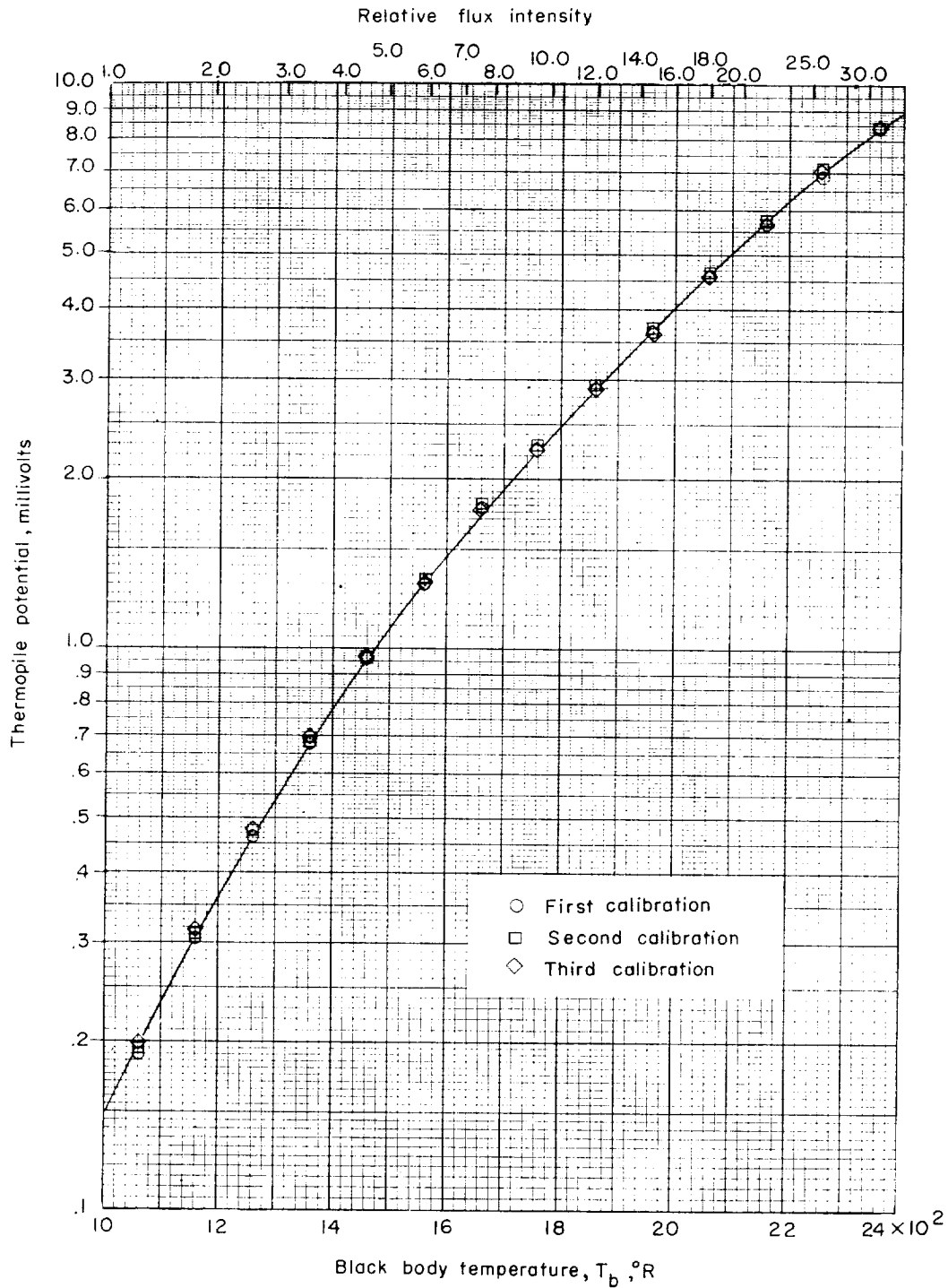
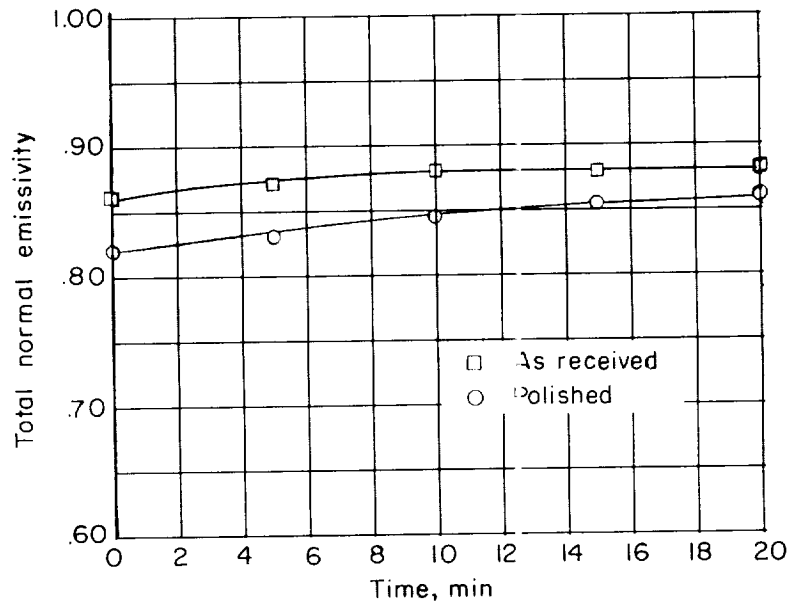
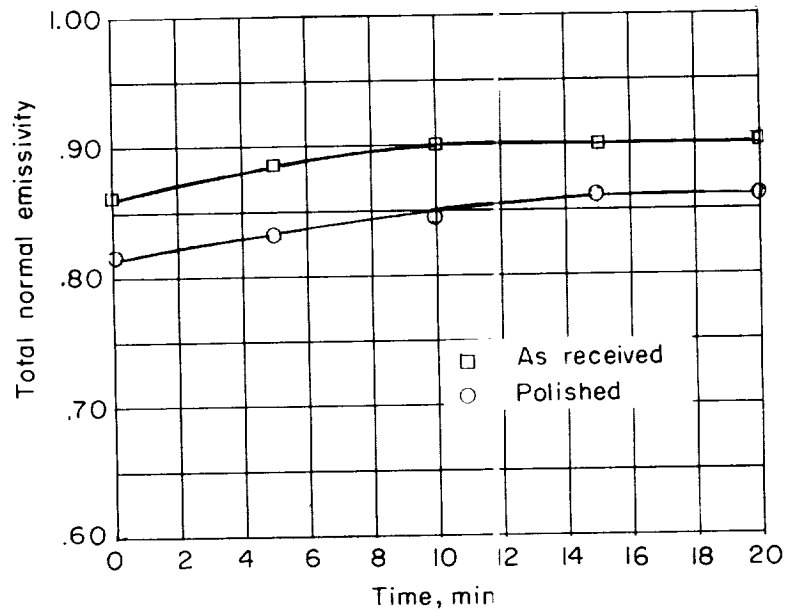


Figure 6.- Calibration of the thermopile radiation-flux measuring system.

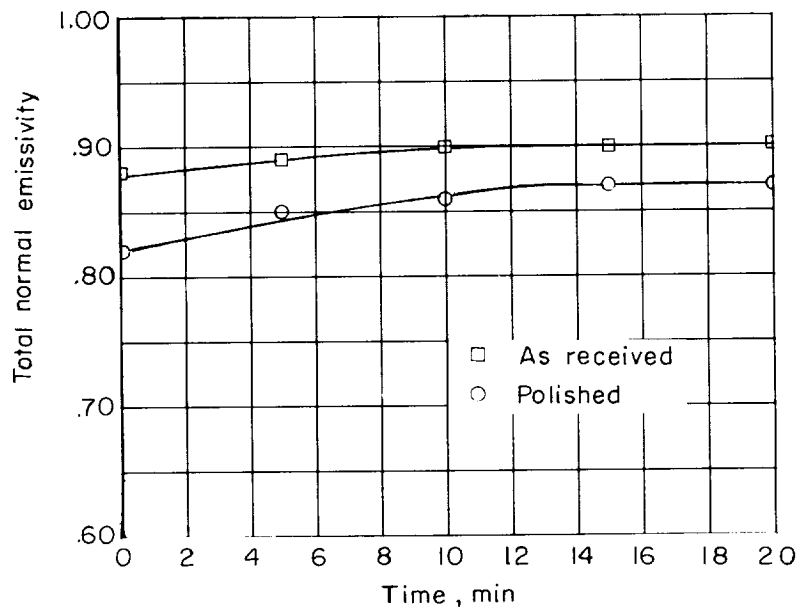


(a) K150A.

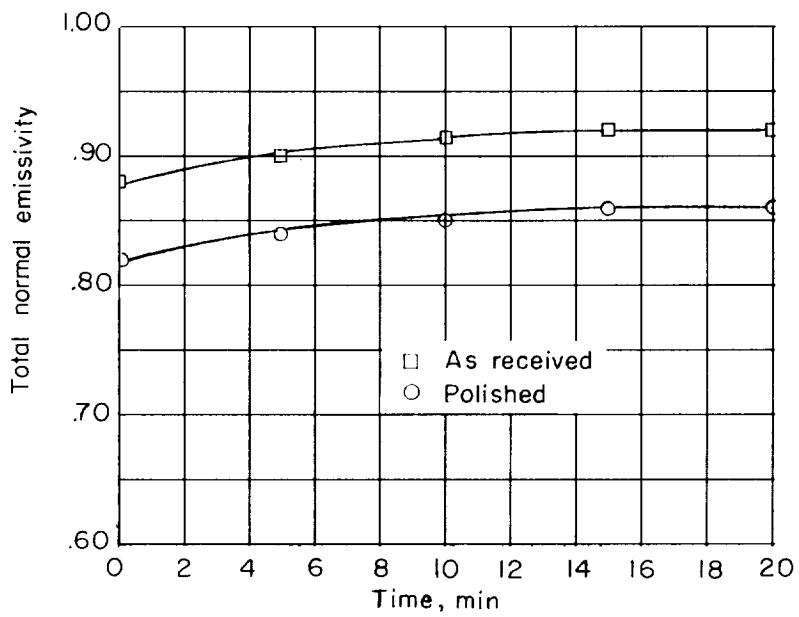


(b) K151A.

Figure 7.- Variation of total normal emissivity with time of oxidation at 1,600° F in quiescent air.

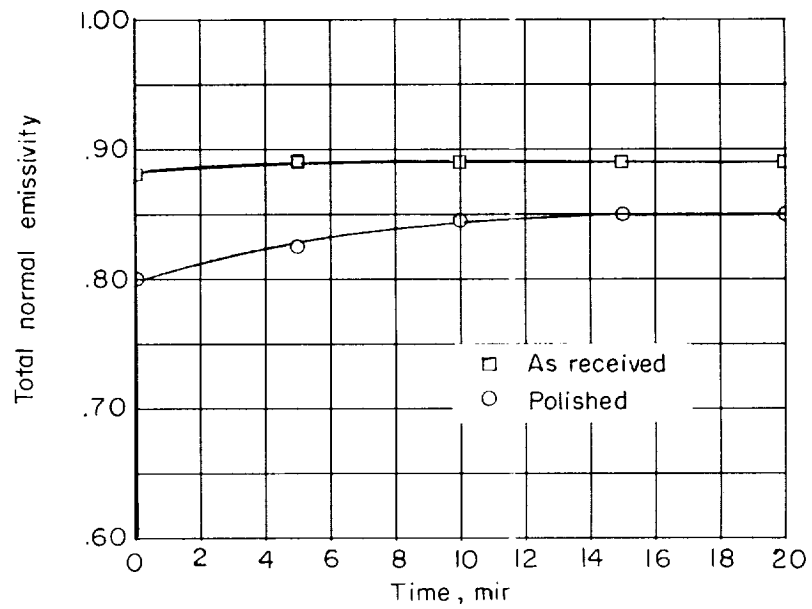


(c) K152B.

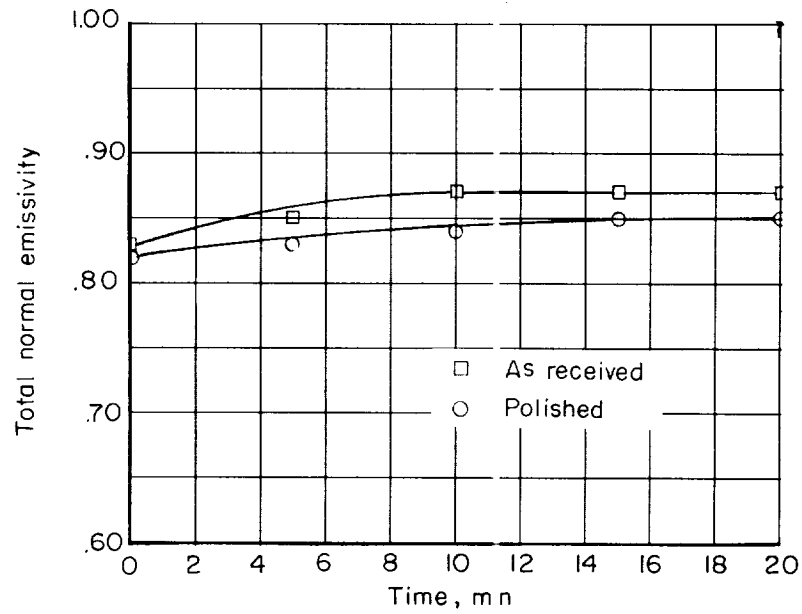


(d) K153B.

Figure 7.- Continued.

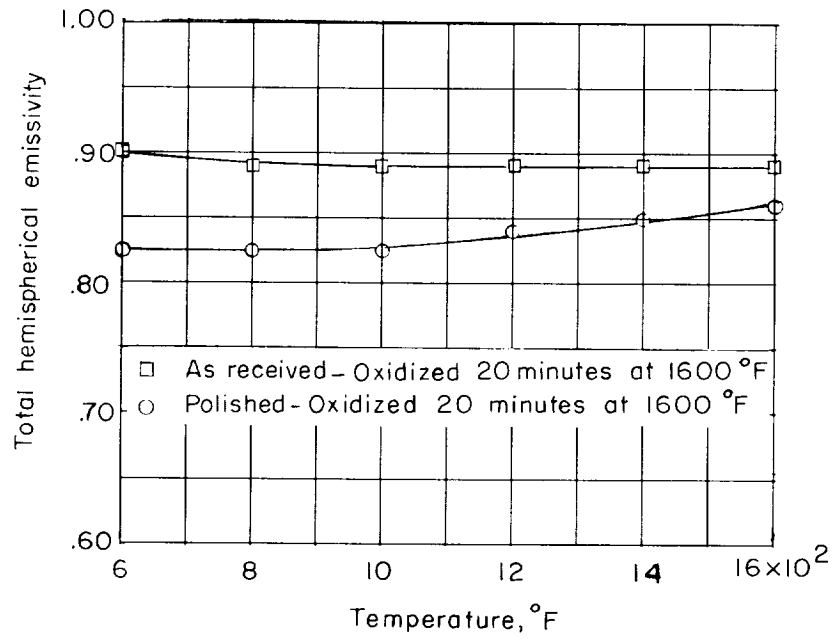


(e) K163B1.

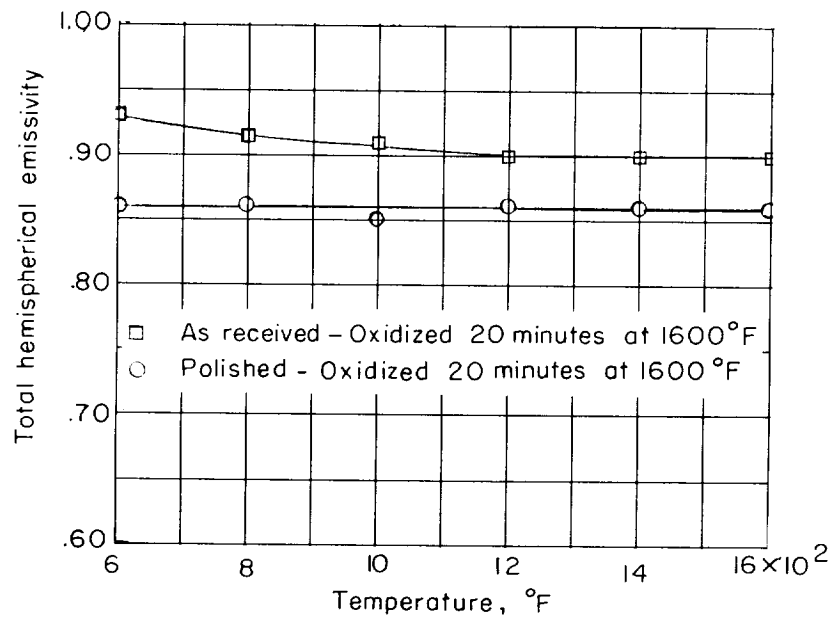


(f) K184B.

Figure 7.- Concluded.

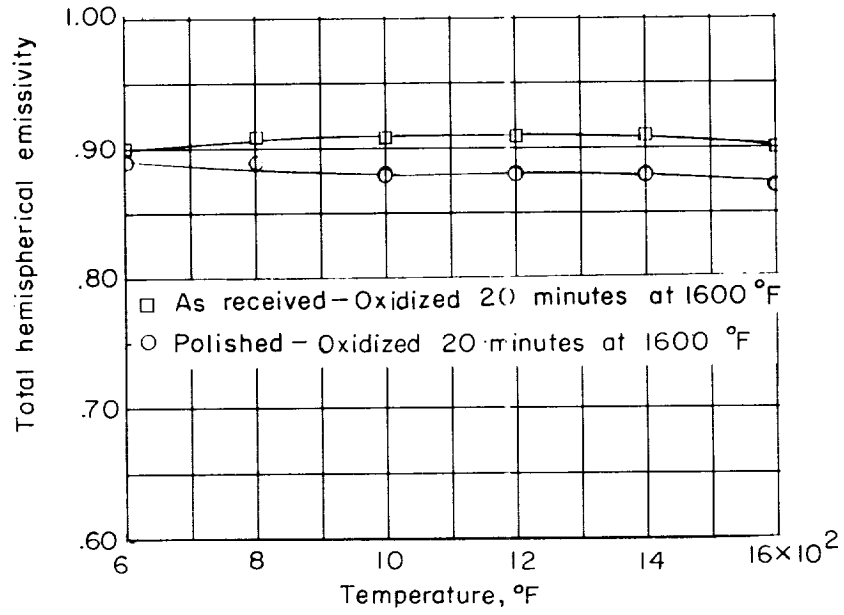


(a) K150A.

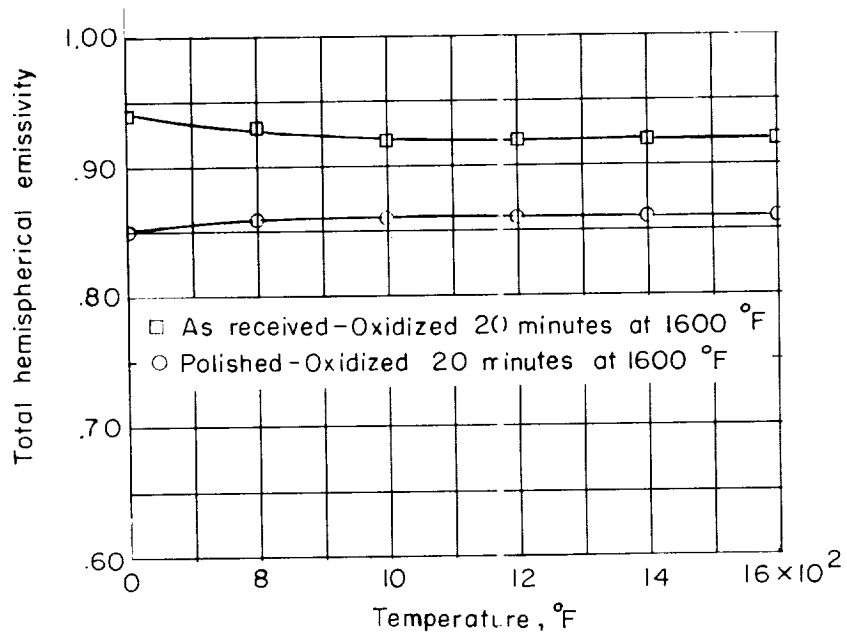


(b) K151A.

Figure 8.- Total hemispherical emissivity as a function of temperature.

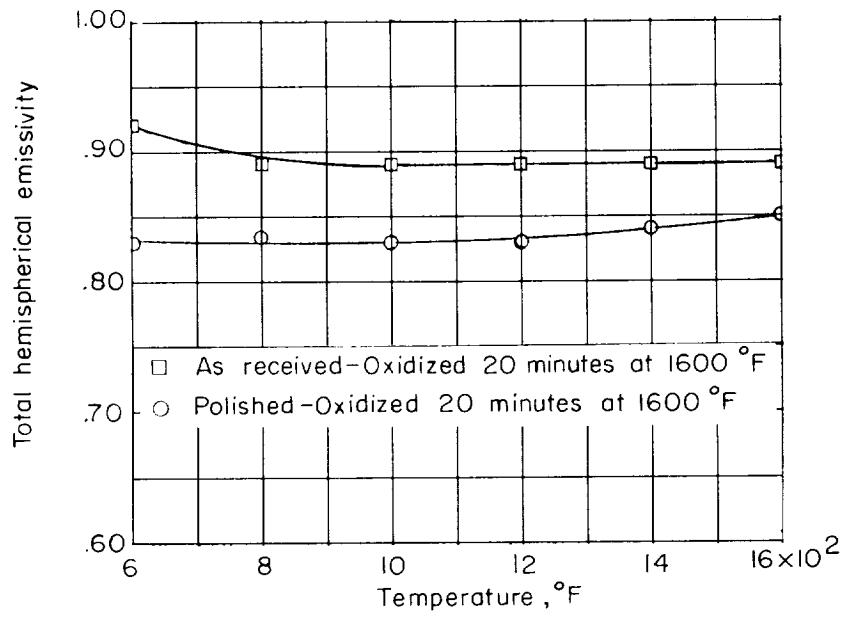


(c) K152B.

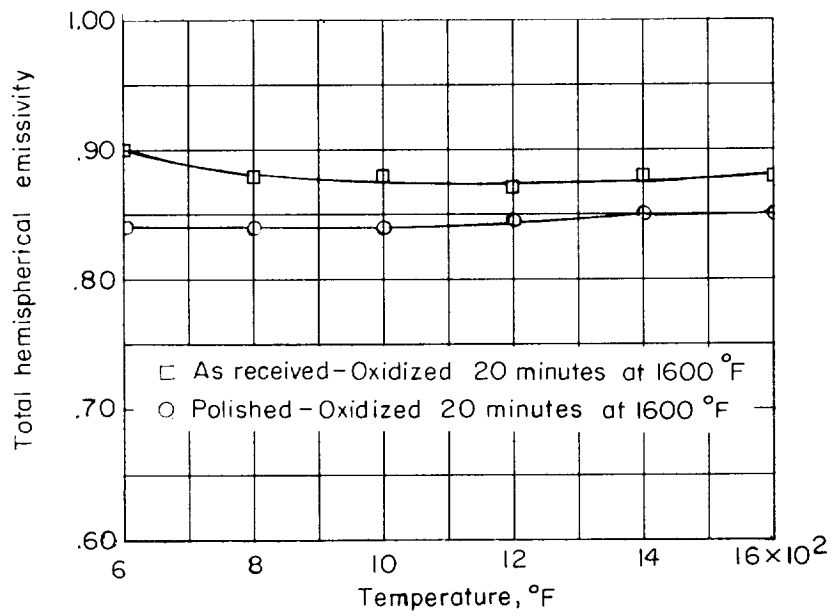


(d) K153B.

Figure 8.- Continued.



(e) K163B1.



(f) K184B.

Figure 8.- Concluded.

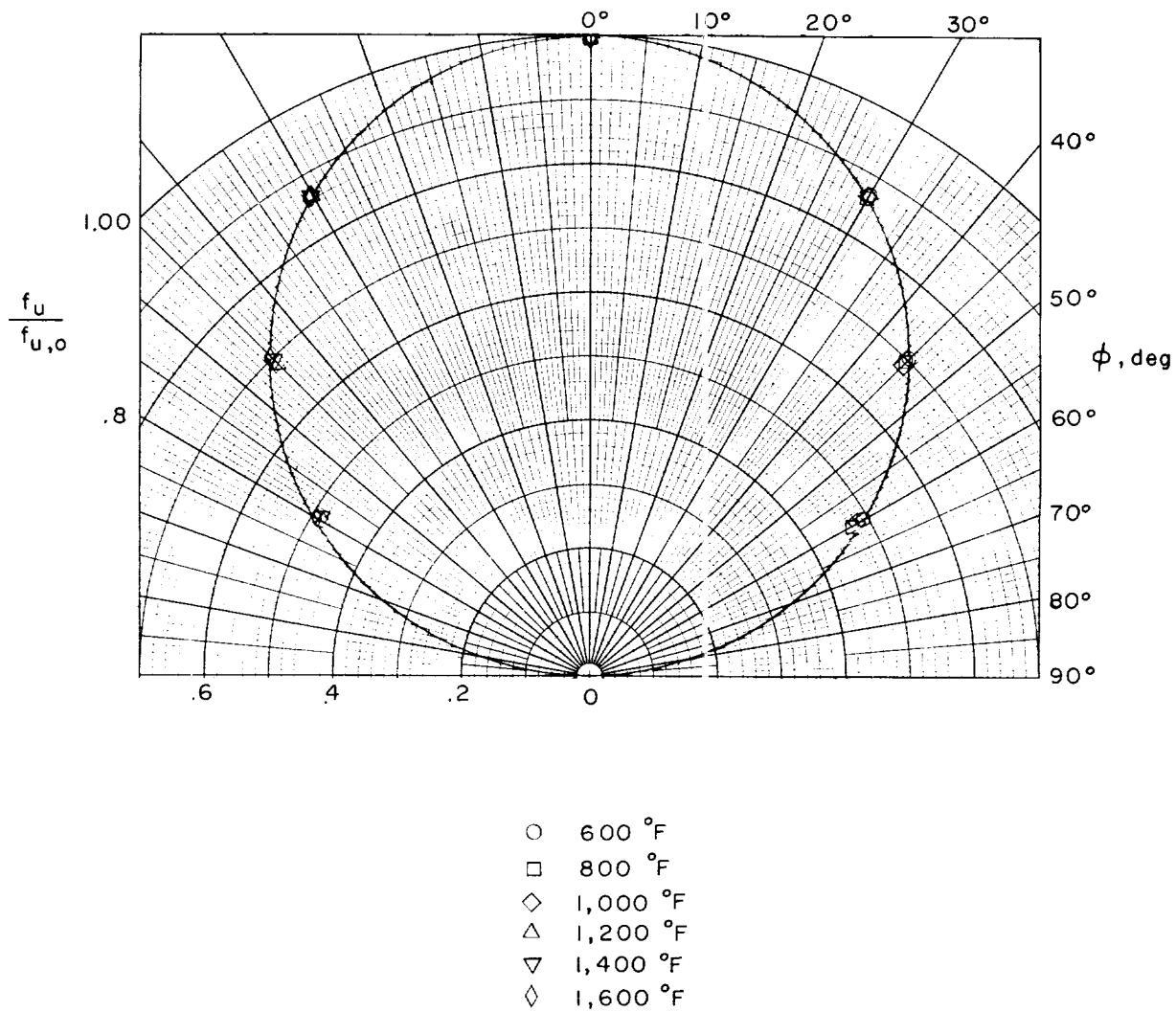


Figure 9.- Comparison of the emission of K150A oxidized 20 minutes at 1,600° F with Lambert's cosine law of diffuse emission.

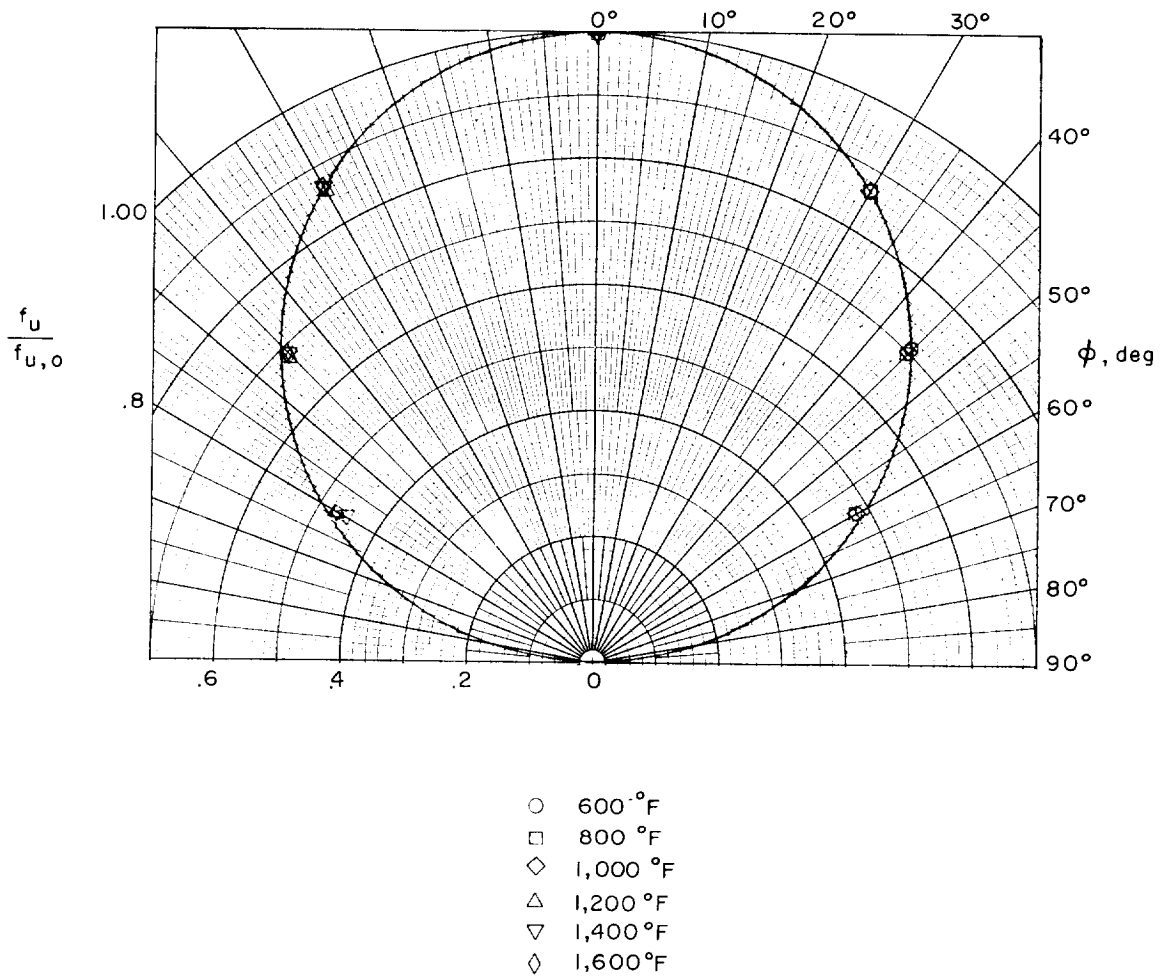


Figure 10.- Comparison of the emission of K151A oxidized 20 minutes at 1,600° F with Lambert's cosine law of diffuse emission.

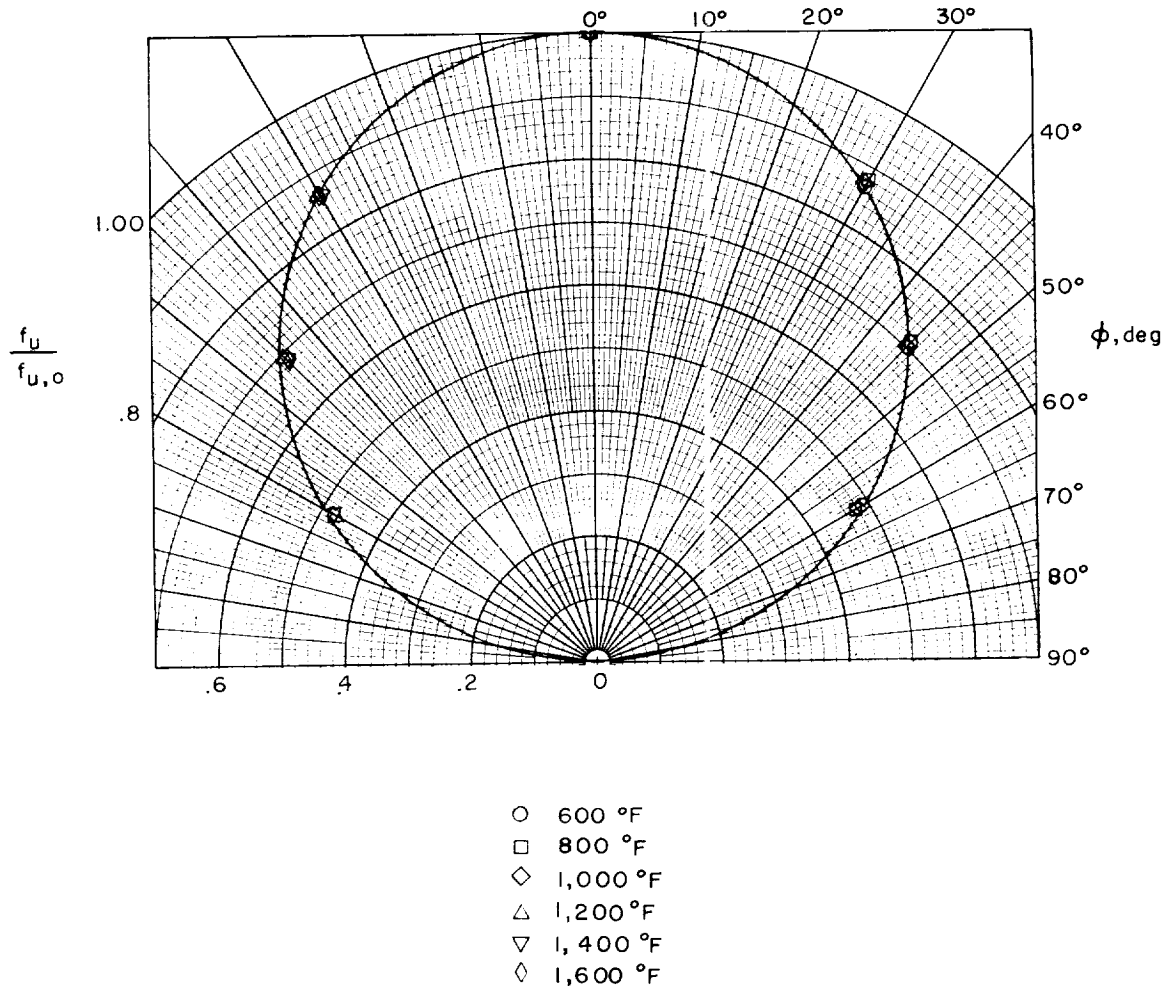


Figure 11.- Comparison of the emission of K152B oxidized 20 minutes at 1,600° F with Lambert's cosine law of diffuse emission.

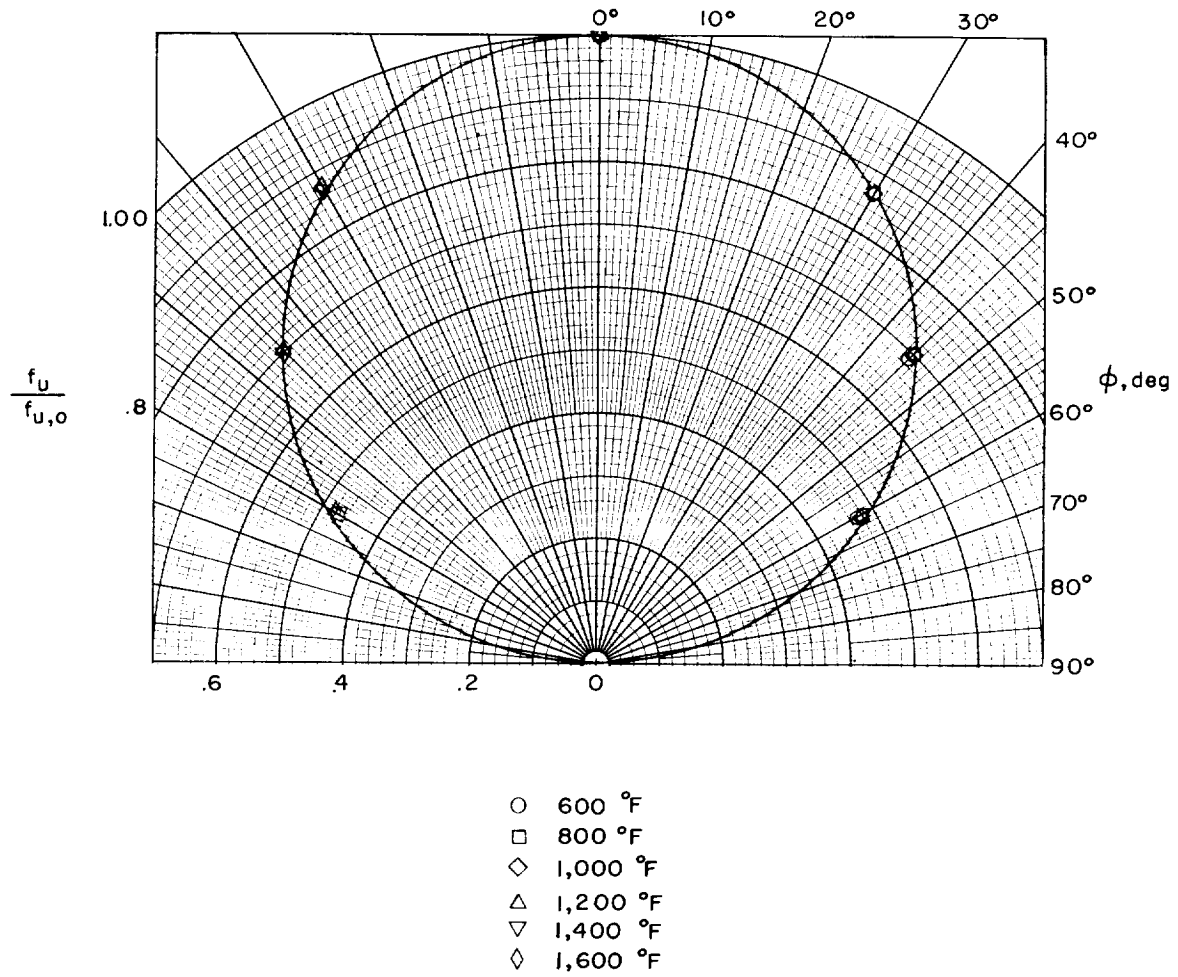


Figure 12.- Comparison of the emission of K153B oxidized 20 minutes at 1,600° F with Lambert's cosine law of diffuse emission.

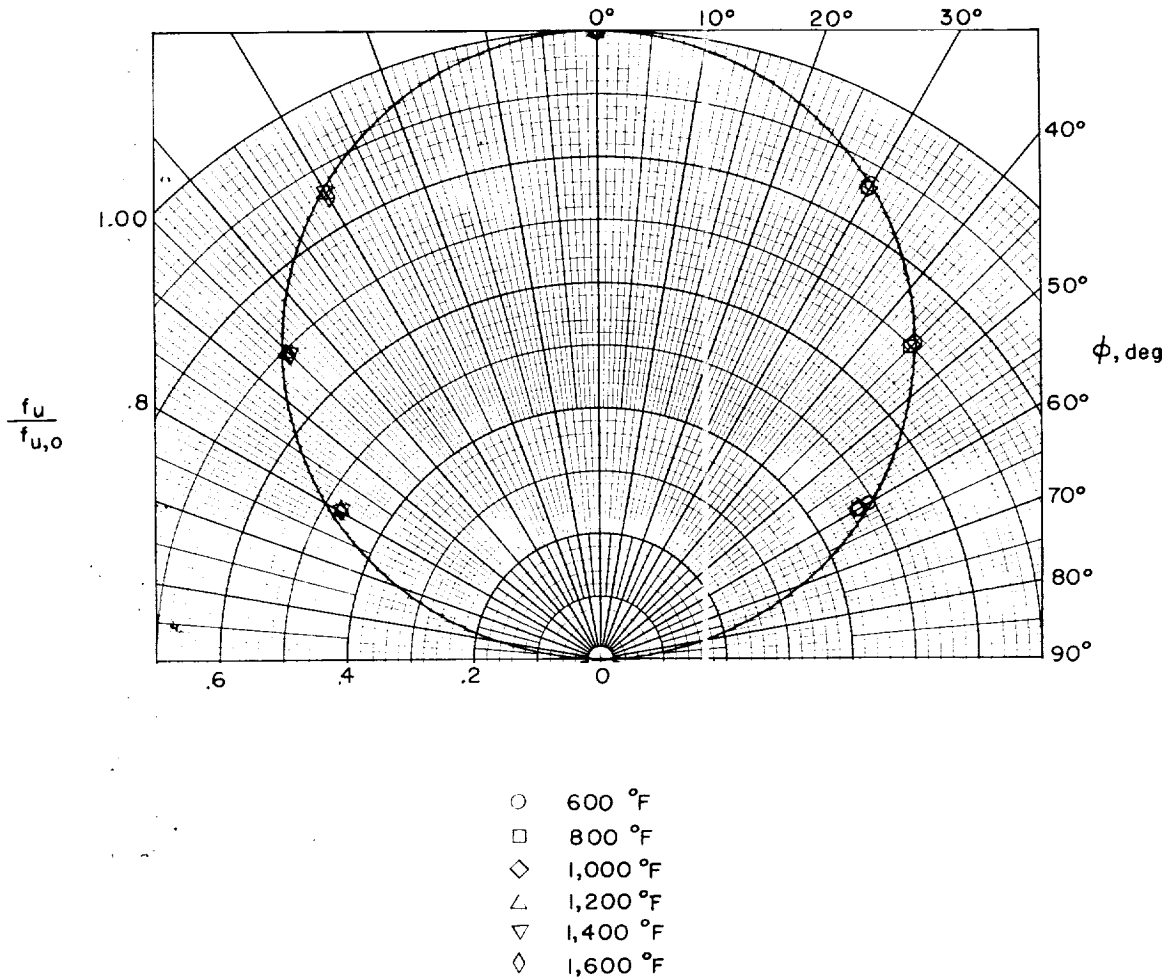


Figure 13.- Comparison of the emission of K163B1 oxidized 20 minutes at 1,600° F with Lambert's cosine law of diffuse emission.

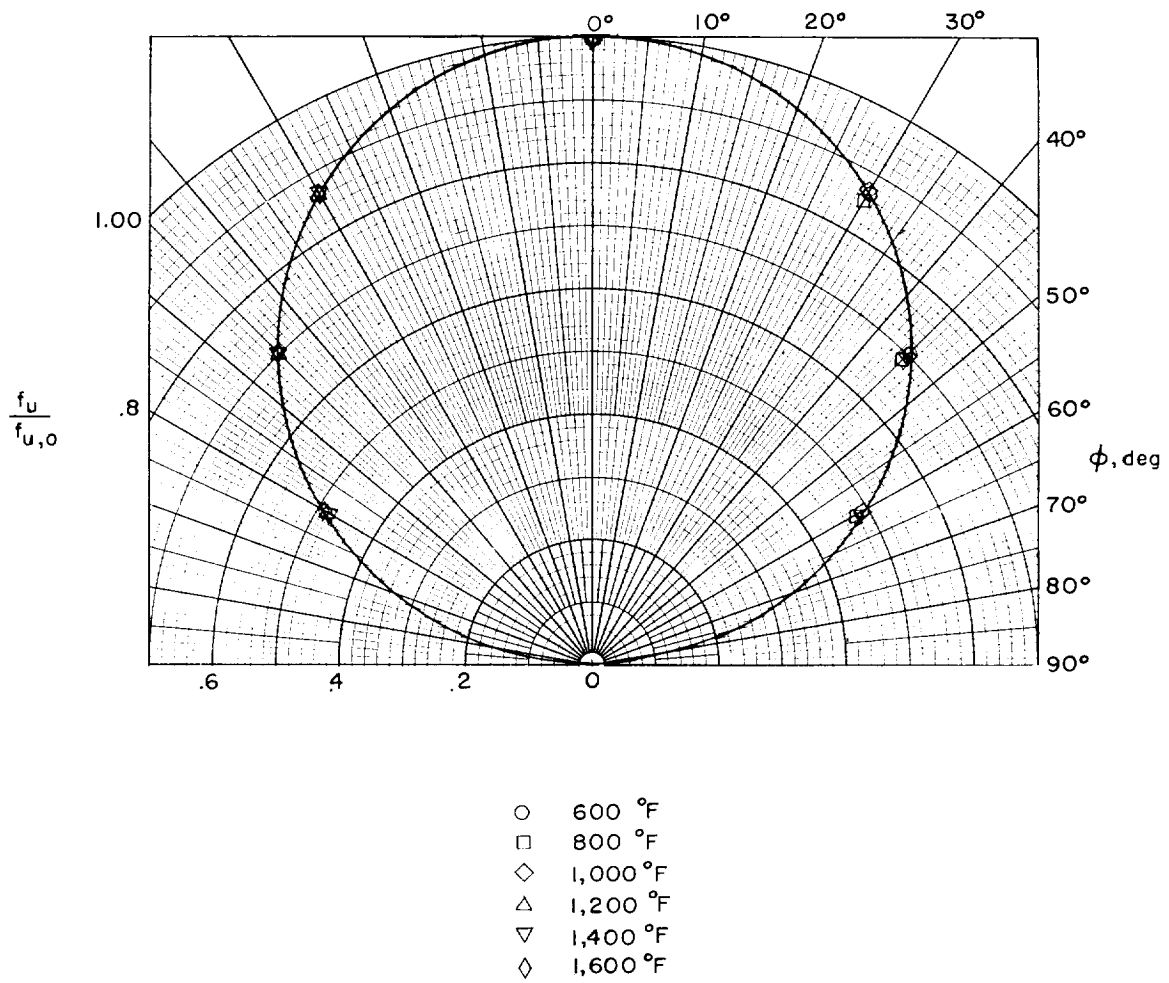
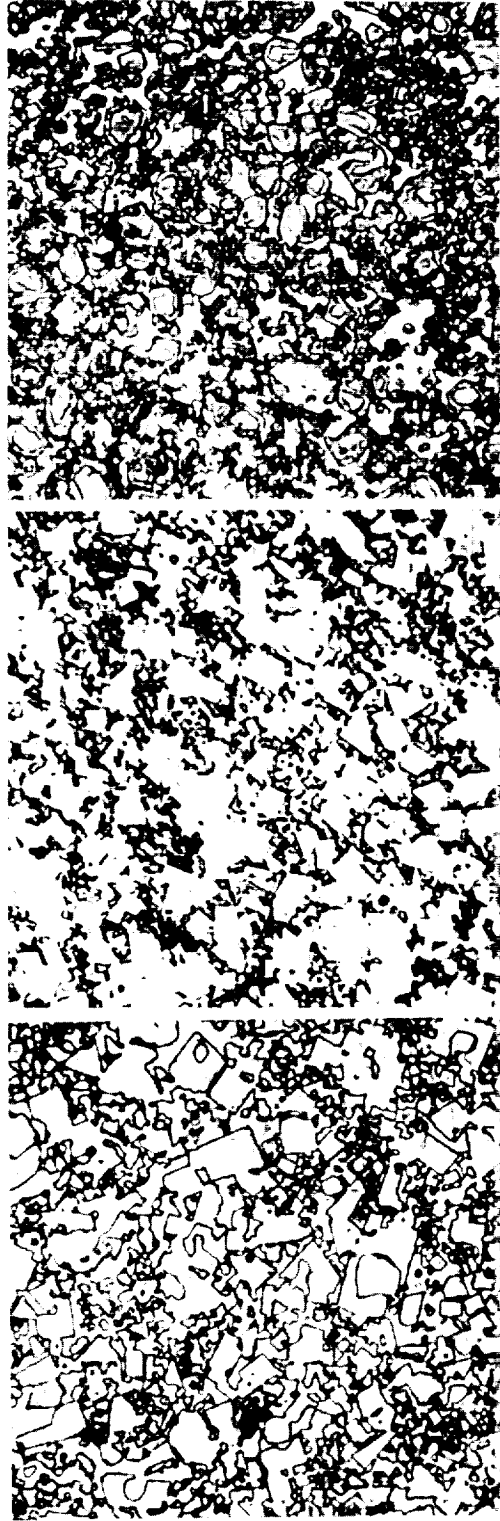


Figure 14.- Comparison of the emission of K184B oxidized 20 minutes at 1,600° F with Lambert's cosine law of diffuse emission.

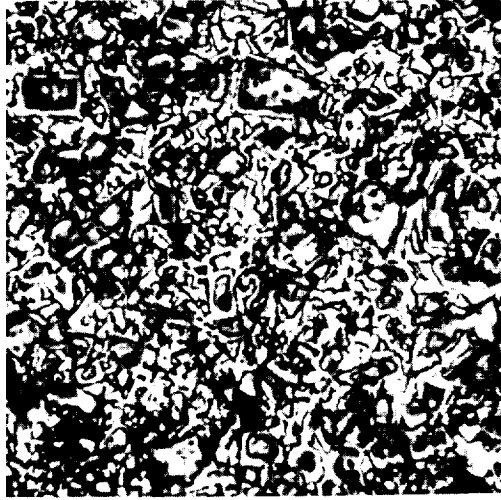


Material : K - 153 B
 Etchant : electrolytic
 Potassium hydroxide
 Magnification : X 1000

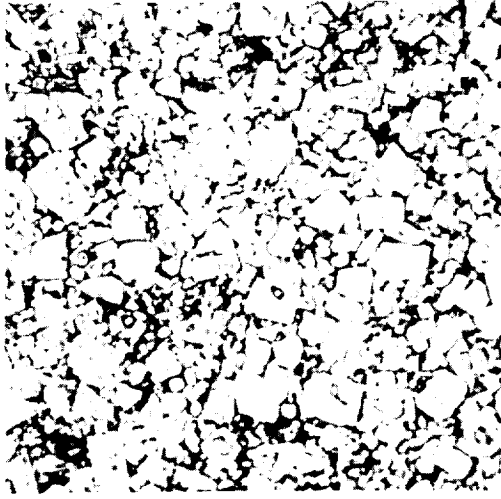
Material : K - 163 B 1
 Etchant : ferric chloride
 Potassium ferri cyanide
 Magnification : X 1000

Material : K - 184 B
 Etchant : electrolytic
 Potassium hydroxide
 Magnification : X 1000

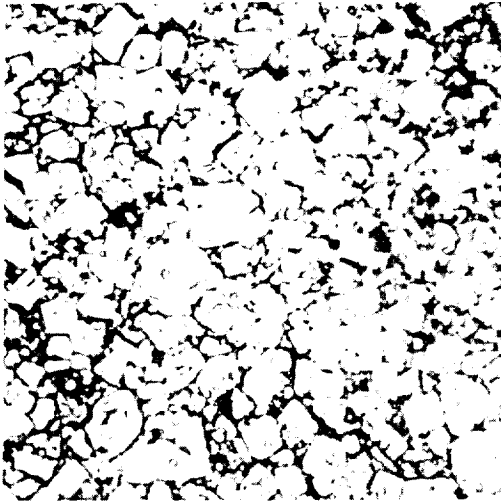
Figure 15.- Photomicrographs showing surface microstructure of polished test specimens.
 I-59-225



Material : K-152 B
Etchant : Electrolytic
Potassium hydroxide
Magnification : X 1000

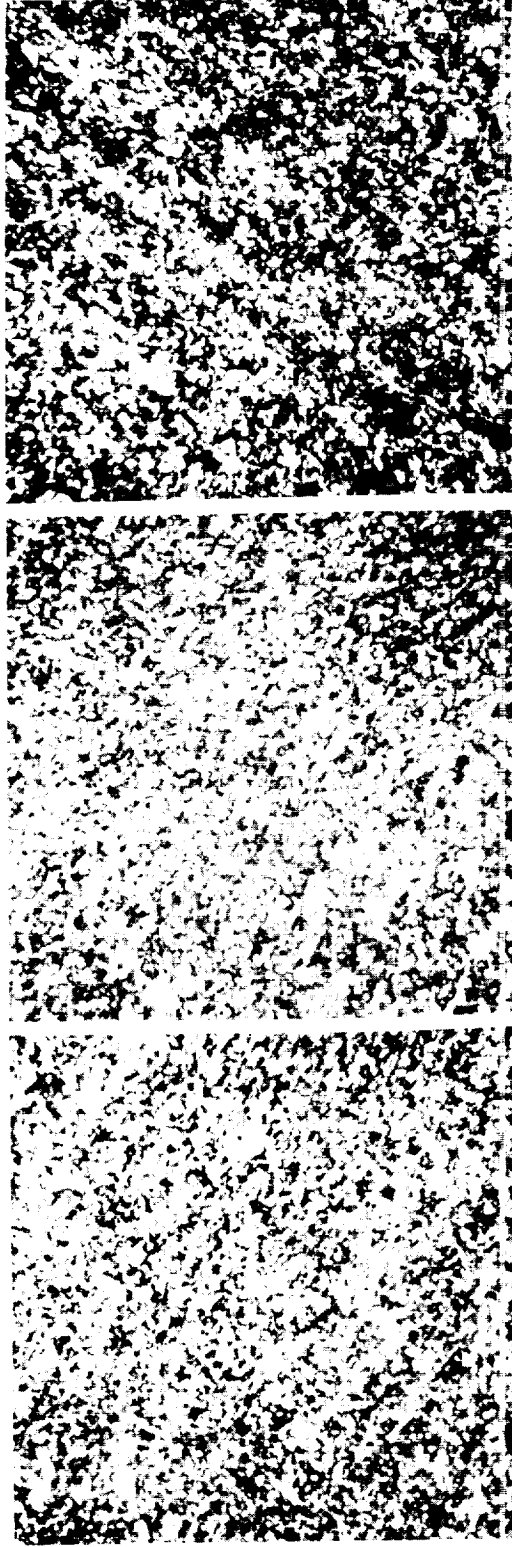


Material : K-151 A
Etchant : Electrolytic
Potassium hydroxide
Magnification : X 1000



Material : K-150 A
Etchant : Electrolytic
Potassium hydroxide
Magnification : X 1000

Figure 16.- Photomicrographs showing surface microstructure of polished test specimens.
L-59-226

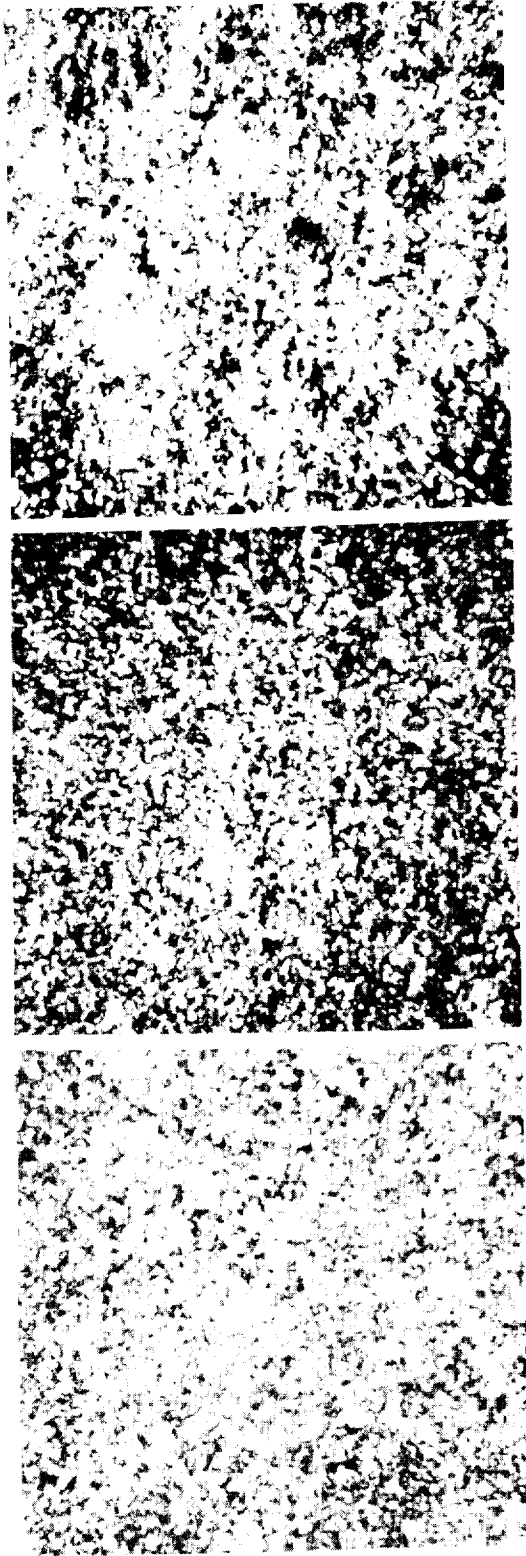


Material: K-152 B
No polish or etch
Magnification: X 250

Material: K-151 A
No polish or etch
Magnification: X 250

Material: K-150 A
No polish or etch
Magnification: X 250

Figure 17.- Photomicrographs showing surface condition of the stably oxidized test specimens.
L-59-227



Material : K-153 B
No polish or etch
Magnification : X 250

Material : K-163 B I
No polish or etch
Magnification : X 250

Material : K-184 B
No polish or etch
Magnification : X 250

L-59-228
Figure 18.- Photomicrographs showing surface condition of the stably oxidized test specimens.

