JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 6, No. 4, Oct.–Dec. 1992

Normal Spectral Emittance of W-Re-HfC and W-Re-ThO_2 Alloys

Bang-Hung Tsao* and Mysore L. Ramalingam†
UES, Inc., Dayton, Ohio 45432
N. O. Moraga‡
Universidad De Santiago De Chile, Santiago, Chile
and
D. L. Jacobson§
Arizona State University, Tempe, Arizona 85287

A photon counting pyrometer was used effectively in determining the normal spectral emittance of tungsten, rhenium alloys at 1500–2500 K. These tungsten, rhenium alloys were then compounded with thoria and hafnium carbide separately, and the normal spectral emittance for these combinations of alloying systems were generated in the same temperature regime. Although spectral emittance could be a strong function of several variables, such as surface roughness, wavelength of interference filters, in addition to alloying content, our investigation was centered around the effects of alloying thoria and hafnium carbide on the normal spectral emittance of tungsten, rhenium alloys. The normal spectral emittance of W-Re-ThO_2 and W-Re-HfC decreased with respect to the temperature. Addition of HfC-ThO_2 apparently raises the emittance compared to that obtained with the previous results for W-Re alloys. HfC exhibited a stronger dependence of emittance on temperature, compared to ThO_2. Reproducible data were also generated with a maximum deviation of 1.5%. The effect of cavity size indicated that normal spectral emittance could be used between 1500 and 2500 K to correct the difference between the cavity and ideal blackbody temperatures when the length-to-diameter ratios were larger than eight.

Nomenclature

C_2	=	Planck's second constant
L	=	cavity length to diameter ratio
Ra	=	arithmetic average roughness
T_h	=	temperature of the hohlraum
T_s	=	temperature of the surface
ε	=	emittance
ε_a	=	effective emittance of cavity
ε_λ	=	normal spectral emittance
λ	=	pyrometric effective wavelength

Introduction

THERMIONIC energy conversion is a process of converting heat energy to electrical energy. Refractory alloys used in this process are operated at very high temperatures to make the conversion efficiency high. An accurate energy balance at these high temperatures requires accurate knowledge of the spectral emittance of the particular surface being heated. A knowledge of its variation with temperature in the operating range of a thermionic energy converter, helps in designing a converter.

The original concept of a photon counter to improve the accuracy of temperature measurement at high temperatures is attributed to Storms and Mueller[1] whose photon counting pyrometer was capable of measuring temperatures in the range 1400–2200 K within 2 K of the International Practical Temperature Scale. Bice and Jacobson[2] then used this photon counter and the "Integral Method" to compare the radiative intensities emanating from an isothermal enclosure and the selective surface around it, and eventually arrived at the normal spectral emittance of the surface. The normal spectral emittance of several tungsten, rhenium alloys were determined by Ramalingam and Jacobson[3] and these results were complemented by those of Moraga et al.[4] whose investigation extended to total hemispherical emissivities.

Petrov et al.[5] determined the total emittance of molybdenum and found it increased with increase in temperature. Gubareff et al.[6] explained the existence of the well-known results for metals that the derivative of spectral emittance with respect to temperature changes sign as the wavelength goes up. Sadykov[7] later presented results on the variation of spectral emittance with temperature that exhibited distinctly different trends below and above $\lambda = 0.72$ μm.

Thoria and hafnium carbide particles tend to segregate on grain boundaries and limit grain boundary migration, thus resulting in small grains for the same annealing situation.[8,9] The effect of this preferential segregation on the normal spectral emittances of tungsten, rhenium alloys is the major topic of investigation for this article.

Experimental Procedures

The W-Re-ThO_2 and W-Re-HfC alloys were prepared by powder metallurgical techniques. The W-Re-ThO_2 samples were sintered from tungsten, rhenium, and thoria powders. The alloys were fabricated at a pressure of 200 MPa and a temperature of 2500 K, then swaged to the desired diameter. The process was carried out in a reducing atmosphere of ultrahigh purity hydrogen. The sintered W-Re-HfC alloys underwent arc melting. After fabrication, all the samples were subjected to electronmicroprobe analysis to ensure homogeneity in chemical composition. These materials were ground and sliced by a diamond-tipped wheel to 9.31-mm diameter and 2.72-mm thickness. Hohlraums, each of 0.7-mm diameter and 7-mm depth were machined by electrical discharge machining. All the samples were chemically polished to obtain

Received July 11, 1991; revision received Sept. 27, 1991; accepted for publication Oct. 1, 1991.

*Research Scientist, Scientific and Engineering Services Division.

†Senior Scientist, Scientific and Engineering Services Division. Senior Member AIAA.

‡Engineering Faculty.

§Professor, Chemical, Bio, and Materials Engineering Department. Member AIAA.

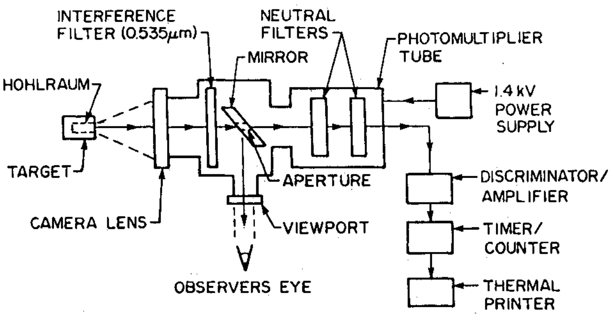

Fig. 1 Schematic of photon-counting pyrometer and its accessories.

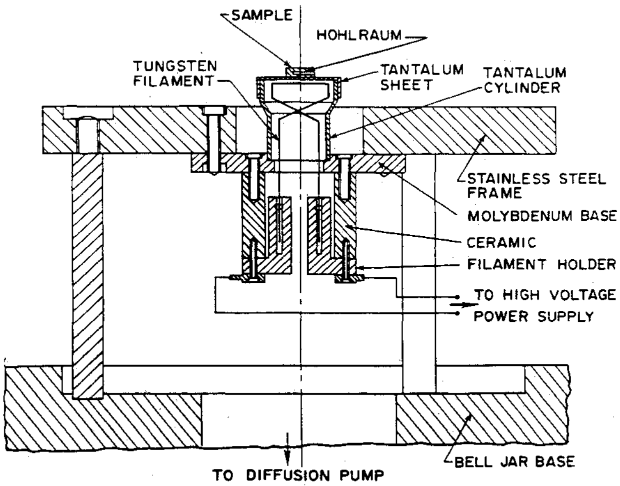

Fig. 2 Cross-sectional view of the sample holder and associated components.

smooth surfaces. An optical microscope was used for preliminary metallographic studies. Microstructures were examined and photographed for future comparison and analysis. Finally the samples were annealed and outgassed at 2500 K in a vacuum of 1.3×10^{-5} Pa for an hour before testing.

Each specimen was heated by electron bombardment using a 0.05-cm-diam tungsten wire wound in the form of a flat spiral filament. The brightness (surface) and holhraum temperatures of the specimen were measured by a very accurate photon counting pyrometer ($\lambda = 0.535\ \mu$m) and/or micro-optical pyrometer ($\lambda = 0.65\ \mu$m), at a distance of approximately 40-cm from the sample. Figure 1 represents a schematic diagram of the photon-counting pyrometer and its accessories, including the recording instrument. Figure 2 represents a cross-sectional view of the sample holder and associated components.

The principle of operation of the photon-counting pyrometer is as follows: only thermal radiation corresponding to a wavelength of 0.535 μm is allowed to pass through the interference filter and then through a 0.1-mm-diam aperature in a nickel mirror, before entering two neutral density filters and reaching the photomultiplier tube. A discriminator processes the electrical pulses that were converted from the incident thermal radiation in the photomultiplier. The output signal was fed into a frequency counter and time-measuring system. An interface displayed the photon counts that were recorded in a thermal printer at the desired time-steps, ranging from 1 s to 1 h. The photon counter was calibrated at Los Alamos National Laboratory, and it was found to be accurate to within 2 K in a temperature range of 1400–2500 K.

The normal spectral emittance at a pyrometric effective wavelength of 0.535 μm and/or 0.65 μm was obtained from steady-state measurements of the brightness T_s and hohlraum T_h temperatures and Wein's approximation, in the form

$$\varepsilon_\lambda = \exp[C_2(1/T_h - 1/T_s)/\lambda] \qquad (1)$$

The optical temperature measurements were made on either side of the hohlraum in a horizontal plane so as to minimize the effects of the temperature gradient across the thickness of the specimen.

Experimental Results and Discussion

As far as the general behavior of normal spectral emittances with temperature was concerned, all the alloys exhibited a decreasing trend in normal spectral emittance with temperature, which was expected because sustained annealing makes the surface smoother than at lower temperatures. Normal spectral emittance characteristics of W-Re-ThO_2 alloys corresponding to a pyrometric effective wavelength of 0.535 μm are shown in Fig. 3. A common trend exhibited by these data is that the normal spectral emittance of W-Re-ThO_2 alloys decreases linearly as the temperature is increased. This behavior is consistent with that previously reported for tungsten and all other alloying elements used, when the wavelength was between 0.3 and 1 μm.

The effect of the additive thoria on the normal spectral emittance for sintered tungsten, rhenium is illustrated in Fig. 3. Close inspection of the data revealed the following characteristics: a) the temperature has a stronger effect on the normal spectral emittance of the thoriated tungsten, rhenium alloys; and b) the general trend is that the addition of thoria increases the normal spectral emittance of W-Re alloys in the temperature range of 1500–2500 K with the exception of W-23Re in the temperature range of 2100–2500 K. It is well known that grain boundary and surface segregation are thermodynamically favorable under these conditions. Impurities, including contaminations of any type, cause deviations of surface properties from those of an optically smooth pure metal surface. The common example is the presence of a thin layer of an oxide on the metal. As dielectrics ThO_2 particles have generally high values of emittance. There is reason to believe that the addition of thoria enhances the optical properties, thereby yielding higher values of spectral emittance. Adding ThO_2 prevents grain boundary migration and consequently reduces the smoothing effect associated with the formation of larger grains and fewer grain boundaries.

The experimental results of W-Re-0.35HfC alloys for normal spectral emittance at pyrometric effective wavelengths of 0.535 and 0.64 μm are shown in Figs. 4 and 5. These figures show that the normal spectral emittance at $\lambda = 0.535\ \mu$m decreases with increasing temperature, which is quite similar to the results for the W-Re-ThO_2 alloys.

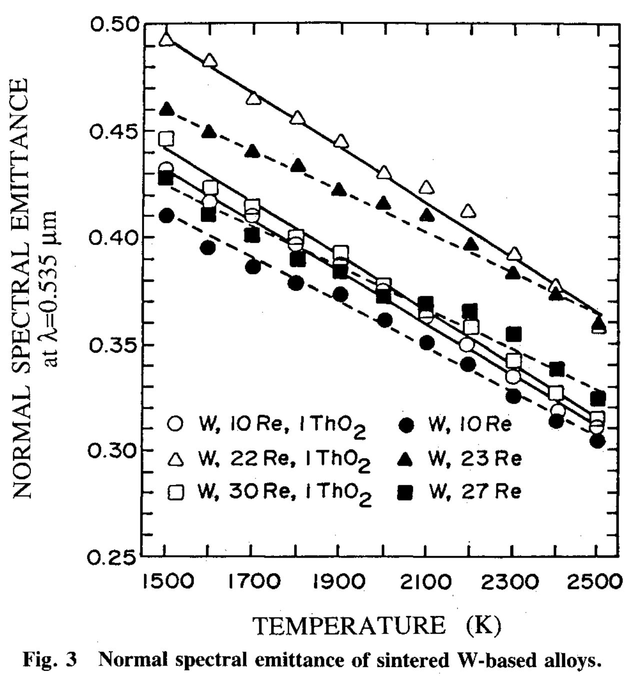

Fig. 3 Normal spectral emittance of sintered W-based alloys.

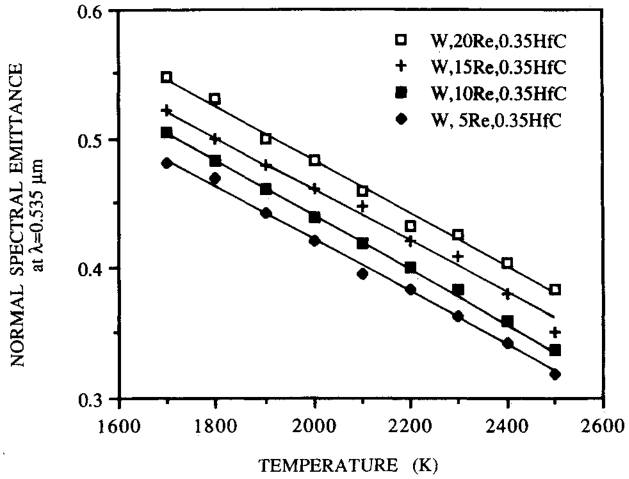

Fig. 4 Temperature dependence of the normal spectral emittance at λ = 0.535 μm for W-Re-0.35HfC alloys.

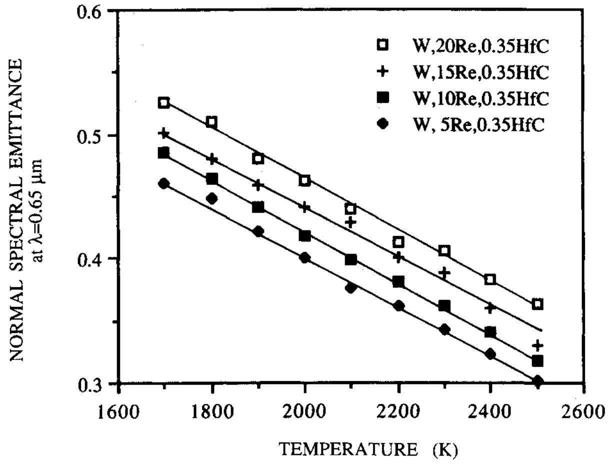

Fig. 5 Temperature dependence of the normal spectral emittance at λ = 0.65 μm for W-Re-0.35HfC alloys.

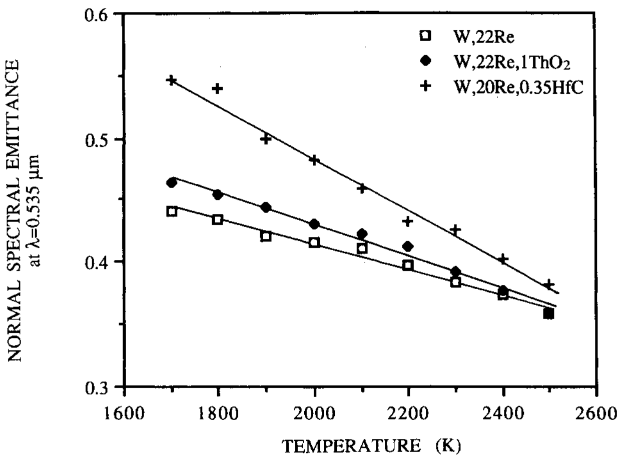

Fig. 6 Temperature dependence of the normal spectral emittance at λ = 0.535 μm for W alloys containing 20 or 22% Re.

However, the values of normal spectral emittance at λ = 0.65 μm were always lower than those for 0.535 μm throughout the experimental temperature range. Such behavior is, in general, in good agreement with that for normal metals as well as ultralloys.[10,11] The Hagen-Reubens emissivity relation predicts that emissivity is a function of $\lambda^{-1/2}$. A decrease in emittance with increasing wavelength in Figs. 4 and 5 is in accordance with the Hagen-Rubens relation. Other wavelengths were not considered because calibrated interference filters were not available. Another important feature shown in Figs. 4 and 5 is that the addition of rhenium increases the emittance of W-Re-ThO_2. The influence of rhenium content on the sintered tungsten alloy wire in electrical lamps and the electronic industries has been studied.[12] At room temperature the resistivity of a 0.2-mm-diam wire made of tungsten containing rhenium was found to increase with an increase in the rhenium content. As mentioned earlier, the material that has the higher electrical conductivity exhibits lower emittance.

As shown in Fig. 6, the emittance at 0.535 μm for the W-20Re-0.35HfC alloy decreases from 0.54 to 0.38, while the temperature increases from 1700 to 2500 K. However, the previous results for normal spectral emittance of similar sintered alloys indicated values ranging from 0.44 to 0.36 for the W-22Re alloy and from 0.38 to 0.36 for the W-22Re-1ThO_2 alloy. The arc-melted alloys containing HfC exhibited higher normal spectral emittance than the comparable alloys from earlier investigations. The addition of ThO_2 causes greater negative rates of decrement with respect to temperature, but HfC amplifies this effect appreciably. Similar results for these dispersoids might be expected for W-Re alloys with compositions other than those investigated.

The influence of surface roughness on the normal spectral emittance was studied for two of the cast alloys. Grinding papers were used to increase the roughness of the smooth surface from 0.1 to 1.1 μm. The value of the roughness was obtained with a surface profile measuring instrument. This instrument has the capability of measuring the roughness between 50 and 65,000 nm with a vertical resolution of 0.1 nm. In general, the standard measurement of the surface roughness adopted was the arithmetic average roughness *Ra* (ANSI b46.1-1973). This parameter physically represents the arithmetic average deviation of the ordinates of profile height increment of the surface from the centerline of that surface. In the past, the rms roughness was used and those values were approximately 11% larger than the calculated arithmetic average. A total of 240 different values of the heights of the irregularities were measured in two perpendicular directions at equal intervals before evaluating the averaged arithmetic roughness.

The results shown in Figs. 7 and 8 indicate that the normal spectral emittance increases as the arithmetic average roughness increases. The magnitude of the increments was independent of the temperature for W-3Ta and approximately

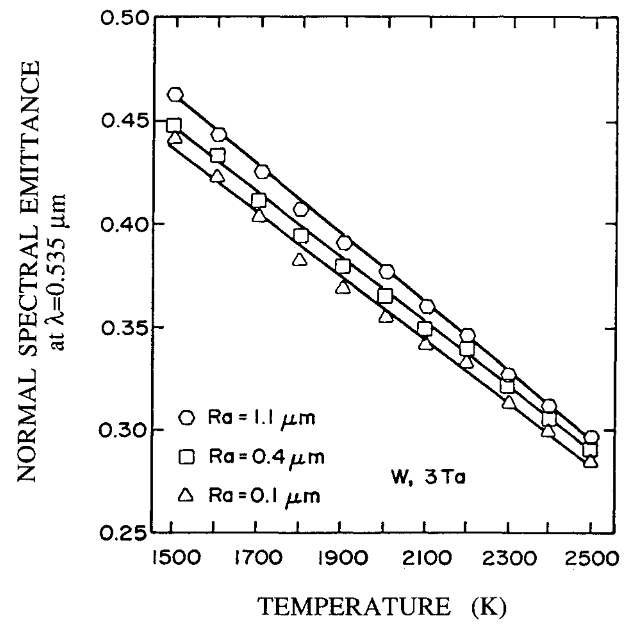

Fig. 7 Effect of surface roughness on normal spectral emittance of W-3Ta.

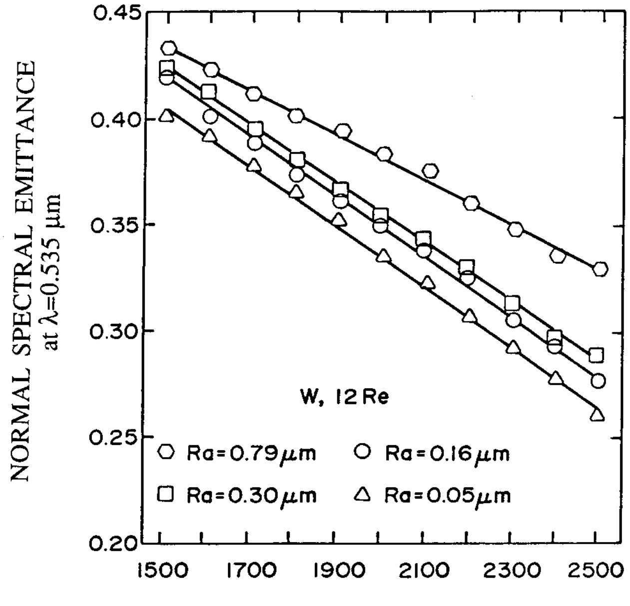

Fig. 8 Effect of surface roughness on normal spectral emittance of W-12Re.

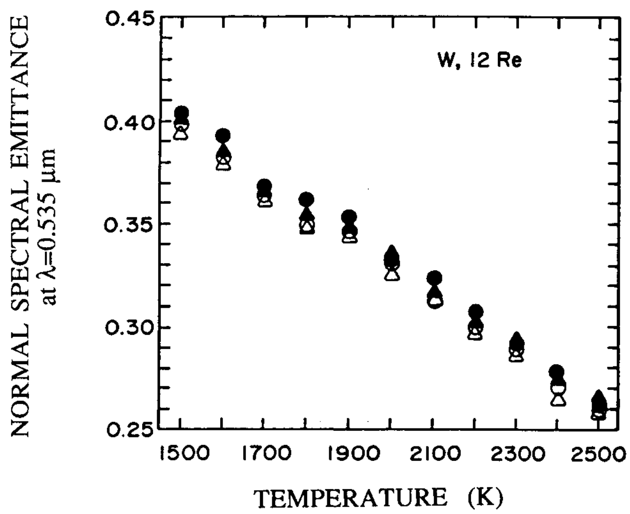

Fig. 9 Reproducibility of normal spectral emittance results of W-12Re.

equal to 5.5% when the roughness increased from 0.1 to 1.1 μm. In the case of W-12Re similar variations of the surface roughness results in increments of normal spectral emittances that were between 6.8% at 1500 K and 26% at 2500 K. As a result of the roughness, one can expect multiple reflections within the pores that simulate the trapping of incident radiation, thereby increasing the emittance of the surface.

One criterion used to check the quality of the data was to examine the reproducibility of the experimental results. Figure 9 shows four sets of the normal spectral emittance data corresponding to the W-12Re sample. It is noted that the results of the measurements performed during the progressive heating cycle from 1500 to 2500 K, denoted by open symbols, are a little bit lower than those collected during the reverse cycle. However, the 1.5% maximum difference on normal spectral emittance measurement suggests that these were minor effects. The accuracy in the measurement of temperature using optical methods depends on the correct design of the cavity used to simulate a blackbody. The exponential relation between temperature and normal spectral emissivity prescribed by either Planck or Wien laws suggests that this is the property that is more sensible to uncertainties in temperature measurements. Therefore, some experiments were designed to test the effect of the size of the cavity on the normal spectral emissivity.

Five circular cylindrical cavities with length-to-diameter ratios L equal to 2.8, 4, 5, 7.2, and 10 were drilled, in a radial inward direction, on the sides of a disk-shaped rhenium sample. The effect of temperature on the normal spectral emissivity of rhenium at a characteristic wavelength of 0.535 μm was studied, in the temperature range 1500–2550 K, using the data of each cavity and the respective values of the brightness temperatures. Every set of data corresponding to each of the cavities was obtained after the specimen was allowed to cool down under vacuum, rotated to focus the photon counting pyrometer in the center of the bottom wall of the desired cavity, and preheated for 1 h at 2500 K in order to remove oxides and impurities from its surface. The results of this series of experiments are illustrated in Figs. 10 and 11 where the normal spectral emissivity is plotted first as a function of temperature and then in terms of the cavity length to diameter ratio. Figure 10 shows that the size of the cavity has a strong effect on the measurement of the normal spectral emissivity. The magnitude of the deviations between the values obtained with a cavity having a dimensionless length equal to 2.8 and those corresponding to $L = 10$ range from 14.2% at 1500 K to 29.7% when the temperature is 2500 K. This figure also illustrates that the use of shorter cavities results in higher values of normal spectral emissivity with lower degree of temperature dependence.

Normal spectral emissivity at $\lambda = 0.535$ μm of rhenium obtained using circular cylindrical cavities of five different sizes are shown in Fig. 11 at three different temperature levels. The experimental data are also compared with those values predicted by Eq. (2)

$$\varepsilon_a = 1 - \frac{1 - \varepsilon}{1 + L^2} \tag{2}$$

and with those obtained from the model proposed by Quinn.[13] The trends exhibited by the experimental results (represented by full lines in this figure) indicate that the normal spectral emissivity decreases very fast initially, as the nondimensional length increases from 2.8 to 7.2 and then, it tends to attain an asymptotic value that is almost independent of the size of the cavity when $L = 10$. The second observation is that the use of the theoretical model for the effective emissivity of the cavity proposed by Quinn[14] to correct the values of the normal

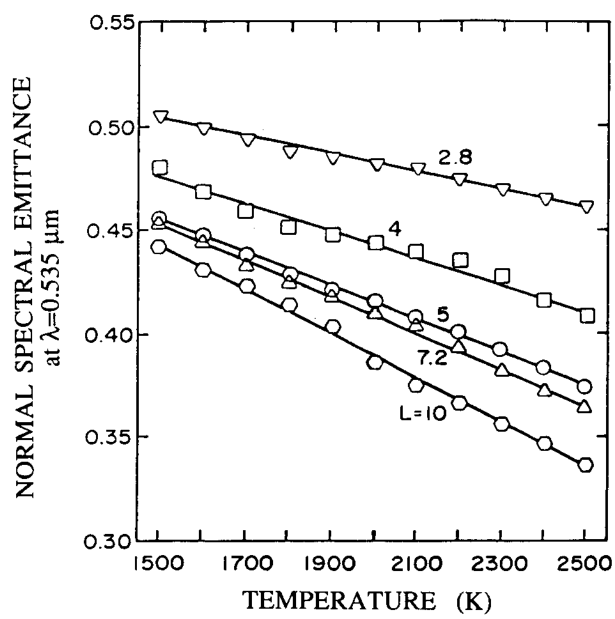

Fig. 10 Influence of cavity size on normal spectral emittance of rhenium at $\lambda = 0.535$ μm.

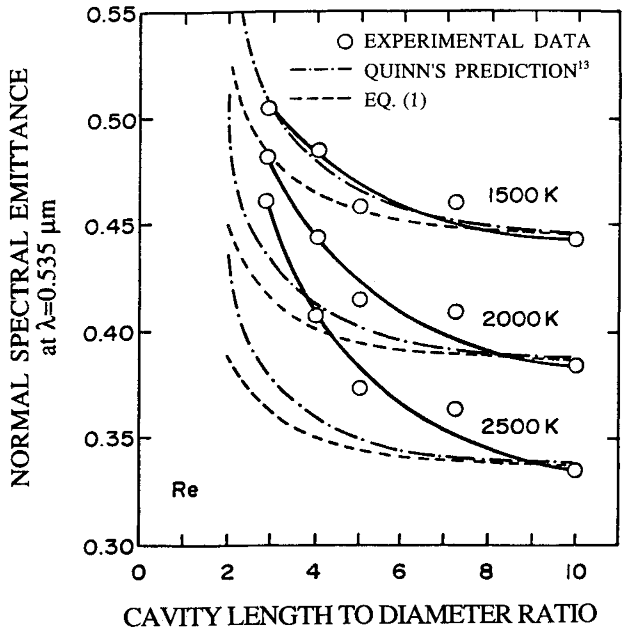

Fig. 11 Variation of the normal spectral emittance of rhenium with cavity size.

spectral emissivity is accurate at 1500 K for all the cavity sizes tested. At higher temperatures, the agreement of this model with present data is good only as the dimensionless length of the cavity is larger than eight. It is also interesting to notice that the simple model obtained when only one reflection on the cavity is considered (Quinn's model incorporates a second-order correction to evaluate two reflections), represented by Eq. (2), can be successfully used between 1500 and 2500 K to correct the difference between the cavity and ideal blackbody temperatures when the length-to-diameter ratios are larger than eight.

Conclusion

The normal spectral emittance at $\lambda = 0.535\ \mu m$ and/or 0.65 μm decreased linearly with respect to temperature for each of the W-Re-ThO_2 alloys and the W-Re-0.35HfC alloys investigated in this study. Addition of HfC-ThO_2 apparently raises the emittance in general compared to that obtained with the previous results for W-Re alloys. HfC exhibits a stronger dependence on temperature compared to ThO_2. These thermal emission properties of W-Re-ThO_2 and W-Re-0.35HfC alloys should be useful resources for designing future space power systems. Furthermore, they increase the basic scientific knowledge of the elevated temperature properties of refractory ultralloys.

Acknowledgments

The research activity was sponsored by the USAF-AFOSR and executed at the Thermionics Laboratory at Arizona State University. The authors thank Lisa Beljan for preparing the manuscript.

References

[1]Storms, E. K., and Mueller, B. A., "Very Accurate Pyrometer for General Laboratory Use," NBS Special Publication, 561, *Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases*, 1979, pp. 143–152.

[2]Bice, V. C., and Jacobson, D. L., "Emissivity Data for Metals at High Temperature," AIAA Paper 85-0987, Williamsburg, VA, June 19–21, 1985.

[3]Ramalingam, M. L., and Jacobson, D. L., "Effect of Temperature on the Emissivity of Sintered Tungsten, Rhenium Alloys," *High Temperature Science*, Vol. 23, No. 1, 1987, pp. 53–66.

[4]Moraga, N. O., Jacobson, D. L., and Morris, J. F., "Fracture Resistant Ultralloys for Space Power Systems: Nuclear Thermionic Conversion Implications of W, 27Re," *Engineering Fracture Mechanics*, Vol. 34, No. 3, 1989, pp. 553–565.

[5]Petrov, V. A., Chekovskoi, Y., and Sheinblin, A. E., "Experimental Determination of the Integral Emissivity of Metals and Alloys at High Temperatures," *High Temperature Science*, Vol. 1, 1963, pp. 19–23.

[6]Gubareff, G. G., Janssen, J. E., and Torburg, R. H., "Thermal Radiation Properties Survey," Honeywell Research Center, Minneapolis, MN, 1960.

[7]Sadykov, B. S., "Temperature Dependence of the Radiation Power of Metals," *High Temperature Science*, Vol. 3, 1965, pp. 352–356.

[8]Ramalingam, M. L., and Jacobson, D. L., "Elevated Temperature Softening of Progressively Annealed and Sintered W-Re Alloys," *Journal of the Less Common Metals*, Vol. 123, 1986, pp. 153–167.

[9]Tsao, B. H., Tang, M. T., and Jacobson, D. L. "Normal Spectral Emissivity and Electron Emission Studies of W-Re-HfC Alloys at Elevated Temperatures," The Minerals, Metals and Materials Society Annual Meeting, Las Vegas, NV, Feb. 1989.

[10]Siegel, R., and Howell, J. R., *Thermal Radiation Heat Transfer*, Hemisphere Publishers, Washington, DC, 1981, Chap. 5, pp. 122–159.

[11]Moraga, N. O., and Jacobson, D. L., "An Accurate Method for the Normal Spectral Emissivities of Refractory Alloys," AIAA 22nd Thermophysics Conf., CP87-1584, Honolulu, HI, June 8–10, 1987.

[12]Pugh, J. W., Amra L. H., and Hurd, D. T., "Properties of Tungsten-Rhenium Lamp Wire," *Transactions of the American Society for Metals*, Vol. 55, 1962, pp. 451–461.

[13]Quinn, T. J., *Temperature*, London Academic Press, Inc., 1983, Chap. 7, pp. 284–359.

[14]Quinn, T. J., "The Calculation of the Emissivity of Cylindrical Cavities Giving Near Black-Body Radiation," *British Journal Applied Physics*, Vol. 18, 1967, pp. 1105–1113.