

High temperature emissivity of high purity titanium and zirconium

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ABSTRACT

The spectral normal emissivity of high purity (99%) titanium and zirconium at temperatures above 1273 K was determined in high vacuum conditions ($<10^{-7}$ Torr) and for a very broad spectral range from 1 μm to 16 μm . The spectral normal emissivity was determined by comparing the radiative fluxes of the sample and a blackbody radiating cavity under the same conditions. The experimental setup not only avoids sample oxidization through high vacuum levels, but also prevents the sample contamination easily encountered by samples heated in crucibles. Samples were suspended inside a copper induction coil, where they could be electromagnetically heated. The spectral normal emissivities of titanium and zirconium are found to decrease with increasing wavelength and to increase slightly with increasing temperature, indicating no departure from typical metallic behavior. The maximum measurement uncertainty in emissivity was determined to be less than 4%. The broad spectral range of reported emissivity is used to determine total hemispherical emissivity. The measured spectral normal emissivities were compared to published values, although very little work has been done on these materials in the infrared.

KEY WORDS: emissivity; radiative surface properties; spectral normal emissivity;

1. INTRODUCTION

Thermal properties of high purity titanium and zirconium are of great importance in engineering processes. High purity zirconium is used as cladding for nuclear fuel rods due to its low thermal neutron absorption cross section. Commercial zirconium and titanium, exhibit a very high corrosion resistance which makes them useful in the chemical industry. Thermal management of fabricating processes such vacuum arc melting/re-melting has a tremendous significance to maximizing energy efficiency and reducing process cost by improving the efficiency of radiative heat transfer. Numerical simulation of radiation heat transfer processes requires accurate data for a material's emissivity in order to validate reliable models.

Relatively a small number of studies [1-7] have been reported on normal spectral emissivity of high purity zirconium and titanium, especially at elevated temperatures where metals are highly reactive and the tendency of oxides to form on their surfaces is great. The reported data are scattered and the spectral range is often very narrow and making inferences about hemispherical emissivity is not possible. Bradshaw [1] determined the emissivity of a zirconium in vacuum at a mean temperature of 1581 K using a pyrometer by comparing the radiative heat flux emitted from the sample and a small cavity drilled in the sample itself. The emissivity value determined was 0.426 at 0.652 μm . Aution and Scala Price [2] measured the spectral normal emissivity of single crystal zirconium at 1063 K and the average emissivity of basal and prismatic faces was found to decrease with increasing wavelength although peaks in emissivity were found between 2 and 3 μm and at 7 μm . Dmitriev et al. [3] determined the emissivity of zirconium at 1422 K

and observed that emissivity decreased as wavelength increased for a spectral range between 1 and 5 μm . Coffman et al. [4] measured normal spectral emissivity of zirconium specimens in vacuum for a spectral range from 0.4 to 4 μm at 1400 K, 1600 K, 1800 K and 2000 K. The reported emissivity data at a given temperature was seen to decrease with increasing wavelength and to decrease with temperature although some contradictory data was reported.

Bradshaw [1] have also determined the normal emissivity of titanium at the same pyrometer wavelength as zirconium measurement at temperatures between 1223 K and 1623 K and has found a very slight decrease in emissivity from 0.484 to 0.471 probably indicating an X-point above 0.652 μm . However, the uncertainty in measurement was not reported. Adams [5] determined the normal spectral emissivity of titanium with a reported error of $\pm 5\%$ for specimens under different heat treatments. The spectral range considered was from 1 μm to 15 μm and temperatures between 773 K and 1023 K. The emissivities measured in vacuum were quite large indicating a possible contamination/oxidization. Seemueller and Stark [6] determined the spectral normal emissivity of 99.5% purity titanium in high vacuum at 0.65 μm for temperatures from 1426 K up to melting point and the results showed a decrease of emissivity with increasing temperature and slightly higher than that reported in [1]. Walter and Wilford [7] measured normal emissivity of commercial titanium at 0.665 μm between 1050 K and 1400 K and observed a decrease in emissivity with increasing temperature from a value of 0.72 at 1050 K to 0.69 at 1400 K. The authors have also determined the total hemispherical emissivity which was seen to increase with increasing temperature.

Although there is some qualitative agreement among reported (mainly in visible range) data for both considered metals there is a substantial difference among them due to different conditions and samples used in the experiments and outdated equipments. Metals at high temperatures, just below their melting points, are highly reactive, thus inadequate vacuum levels together with interactions/reactions between the sample and the holder/heater can greatly influence the outcome. This present study uses an experimental setup which minimizes the sample contamination due to undesirable reactions/interactions and the effects of so called "hot" components. The sample is heated by a non-contact method and the sample temperature is monitored and controlled by a non-contact high accuracy ratio pyrometer.

The objective of this study is to determine the spectral normal emissivity of high purity zirconium and titanium (99%) in vacuum for a broader spectral range, using an experimental setup comprised of an FTIR spectrometer, a vacuum chamber equipped with a copper induction coil so the sample can be electromagnetically heated, and a high temperature blackbody cavity. The samples are suspended within the heating coils by a very thin wire, and temperatures are measured using a ratio pyrometer, leading to reduced possibility of sample contamination and/or sample-holder interaction. The FTIR spectrometer used in this experiment can rapidly scan spectra at high spectral resolution and broad spectral range. A vacuum level lower than 10^{-7} Torr is used to prevent sample oxidization, and achieved by coupling a turbo molecular and a roughing pump. The measurement temperatures considered here were 1401 K, 1514 K, 1650 K and 1686 K for zirconium and 1361 K, 1466 K, 1564 K and 1614 K for titanium, and the spectral range from 1 μm to 16 μm . The measurements were carried out by comparing the radiation heat fluxes from the sample and from the blackbody cavity, both being held at the same temperature.

2. EXPERIMENTAL SETUP

Figure 1 shows a schematic of the experimental system. The samples were suspended by a thin wire inside a copper induction coil, which is contained within a vacuum chamber. The sample surface temperature was continuously monitored through a vacuum chamber viewport by a high accuracy ($\pm 0.5\%$) Mikron ratio pyrometer. Radiative intensities from both the sample and from a high temperature blackbody cavity (for comparison) were coupled into a Perkin Elmer FTIR spectrometer (Spectrum GX). The optical path and the experimental apparatus is a modified version of previous experimental setups [8-10].

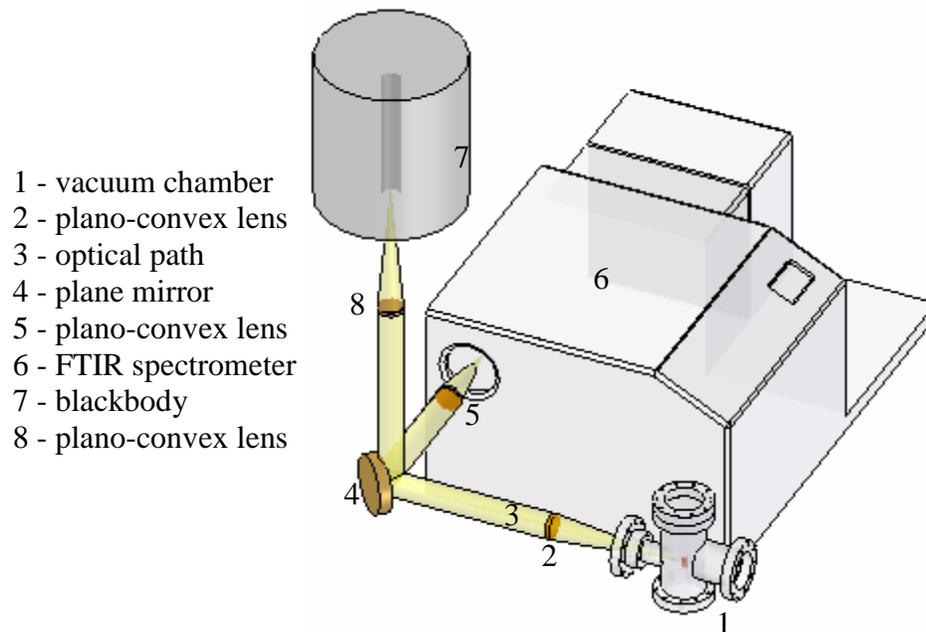


Fig. 1 Schematic of the experimental setup.

Radiative flux leaving the sample suspended inside the vacuum chamber (1) is collected through a zinc selenide side viewport by a plano-convex lens (2), which has a focal length of 254 mm and a diameter of 38.1 mm. The custom-made zinc selenide lens has a proprietary coating which ensures a transmissivity of more than 95% for the spectral range considered. The collected radiation is then collimated into the optical path (3) and directed toward a gold-coated plane mirror (4). The radiation reflected by the gold-coated plane mirror is directed toward the FTIR spectrometer external viewport. At the end of the optical path another plano-convex zinc selenide lens (5) with a focal length of 127 mm and a diameter of 38.1 mm is used to refocus the beam into the FTIR spectrometer (6). Radiative flux leaving the blackbody cavity is collected by another plano-convex zinc selenide lens (8) and collimated into the optical path. The blackbody cavity radiation flux can be directed toward the FTIR spectrometer (6) by adjusting the gold-coated plane mirror (4) position. Data collected were averaged over ten scans using 16 cm^{-1}

resolution. The blackbody-radiating cavity used in experiment was a high purity alumina furnace provided by Mellen Inc., highly insulated, with a maximum operating temperature of 1873 K. Its wall temperature was kept at the same temperature as the sample surface using a PID temperature controller. The blackbody furnace has four heating zones and their temperatures are monitored and regulated independently through the use of four high accuracy type R thermocouples.

The induction heating coils are an element of the earth-based electromagnetic levitator (EML) system developed at Auburn University [11, 12]. The EML can use one set of coils operated at a single frequency to both levitate and heat the sample. In the present work, levitation was not activated, and the coils were set only to heat the sample, which was suspended by a thin wire. The vacuum chamber used in the experiment is a key part of the EML. It has 4 viewports of 69.85 mm diameter and 4 viewports of 115.71 mm diameter. A viewport with a zinc selenide window, used to collect the sample radiation, is equipped with a shutter which helps prevent coating of the window due to sample evaporation during the time required to achieve a steady state. The shutter is opened only for a couple of seconds, just the time required for FTIR spectrometer detection. The optical path alignment is performed using two parallel diode lasers held on a special mount at opposite edges of the optical path, and the solid angle of 0.0049 sr is dictated by a 12 mm aperture inserted into the optical path inside the FTIR sample compartment. Future work with this apparatus will incorporate the levitation feature. One objective of the present work is to develop intensity and the temperature measurement techniques for the sample within the coils, without having to deal with the added complexity of levitation.

3. MEASUREMENTS

Zirconium and titanium samples of 6 mm diameter were used in the experiment. The samples were CNC machined from a 99.99% purity rod, resulting in a very smooth sample surface. The samples were electromagnetically heated until reached a steady state at desired temperatures. The samples were cooled to room temperature after each measurement and reheated three times so that data represent an average of three different runs. Their surface was visually inspected after all experiments, and no evidence of surface oxidation was observed. Radiative spectral-directional emissivity ϵ_λ is defined by:

$$\epsilon_\lambda(T, \lambda, \hat{n}) = \frac{I_\lambda(T, \lambda, \hat{n})}{I_{b\lambda}(T, \lambda)} \quad (1)$$

where I_λ is the emitted intensity within a vanishing solid angle leaving the sample in direction \hat{n} at a particular temperature T and wavelength λ , and $I_{b\lambda}$ is the spectral normal intensity emitted by a blackbody at the same wavelength and temperature. Measurements are performed over a small solid angle where the intensity is assumed to be constant and therefore the measured emissivity under a specified solid angle and wavelength can be evaluated as:

$$\varepsilon(T, \lambda, \theta, \varphi) \approx \frac{\int_{\theta_1}^{\theta_2} \int_{\varphi_1}^{\varphi_2} I_{\lambda}(T, \lambda, \theta, \varphi) \sin \theta d\varphi d\theta}{\int_{\theta_1}^{\theta_2} \int_{\varphi_1}^{\varphi_2} I_{b\lambda}(\lambda, T) \sin \theta d\varphi d\theta} \quad (2)$$

Because the intensity is assumed to be constant over the small solid angle considered, it can be taken outside the integral and the above equation can be simplified to Eq. 1. Consecutively, the measured spectral normal emissivity for a specific direction can be reduced to the ratio of the intensity emitted by the sample and the intensity emitted by the blackbody after the background noise is subtracted:

$$\varepsilon_{\lambda}(\lambda, T_s) = \frac{I_s(T_s, \lambda) - I_{b\lambda}(T_r, \lambda)}{I_{b\lambda}(T_b, \lambda) - I_{b\lambda}(T_r, \lambda)} \quad (3)$$

where $I_s(T_s, \lambda)$ is the intensity emitted by the sample surface at temperature T_s , $I_{b\lambda}(T_b, \lambda)$ is the intensity emitted by the blackbody cavity at temperature T_b (which is equal to the sample surface at temperature T_s), $I_{b\lambda}(T_r, \lambda)$ is the intensity emitted by the surroundings at room temperature, T_r , and spectral-normal emissivity is that component of the spectrally and directionally varying emissivity which is directed normal to the emitting surface. The emissivity is evaluated according to Eq. (2), taking into account the following assumptions:

- The solid angle over which the emission signal is collected is very small, and the spectral intensity is assumed to be constant within this solid angle.
 - The blackbody cavity is perfectly black, which means that the blackbody is isothermal and its aspect ratio of 13.33 and aperture size produce an effective emissivity of unity.
 - The sample and blackbody surfaces are isothermal during the radiation signal measurement.
- A heat transfer model was developed considering internal conduction and external radiation for spherical solid samples undergoing uniform induction heating around an equatorial band extending $+10^\circ$ (north and south) from the equator [13]. The model shows that the sample surface temperature varies within 2 K for the measurement temperature range. A maximum deviation of 0.25% between corrected and measured emissivity calculated for a change in sample surface temperature of 2 K and a change in blackbody emissivity of 1% was found, which indicated that the systematic errors associated with these assumptions are negligible relative to the maximum determined apparatus uncertainty, which is calculated below.

The uncertainty in the spectral normal emissivity value $\delta\varepsilon_{n\lambda}$ is defined as [14]:

$$\delta\varepsilon_{n\lambda} = \varepsilon_{n\lambda} \frac{\delta T}{\lambda T_s^2} \frac{c_2}{[\exp(-c_2 / \lambda T_s) - 1]} \quad (4)$$

where λ is the wavelength, T_s is the sample surface temperature, $\varepsilon_{n\lambda}$ is the spectral normal emissivity, and c_2 is the second radiation constant. The temperature uncertainty is derived from the uncertainty of the blackbody temperature, sample surface temperature, and the stability of the temperature control. According to Eq. (3) the relative uncertainty is inversely proportional to λT_s^2 , resulting in a maximum uncertainty at lower temperatures and shorter wavelengths. The uncertainty estimation procedure from Ref. [15] was used to determine the total estimated uncertainty as shown in Table I.

Parameter	Estimated $\pm 2\sigma$ confidence limits (%) ($^{\circ}\text{C}$)	Emissivity change at $\lambda=1 \mu\text{m}$
Blackbody temperature	0.3	0.0135
Sample surface temperature	0.5	0.0225
Stability of the temperature control	0.04	0.0018
Total uncertainty in emissivity $[\sum(\delta\mu_i)^2]^{1/2}$		0.0152
Total % uncertainty in emissivity ($\epsilon=0.531$, at $T=1088^{\circ}\text{C}$)		4%

Table I - Uncertainty Estimates of the Emissivity Measurement

The maximum uncertainty of emissivity was found to be less than 4% for the spectral and temperature ranges considered. As shown in Table I, the largest contribution to the uncertainty in emissivity measurements is the uncertainty in sample surface temperature measurements.

4. RESULTS AND DISCUSSION

Figure 2 shows the measured spectral-normal emissivity of zirconium at all four considered temperatures. The spectral-normal emissivity of zirconium is found to increase slightly with increasing temperature from 1359 K to 1678 K, and to decrease with increasing wavelength between 1 μm and 16 μm . The measured spectral-normal emissivity of high purity zirconium shows good agreement with characteristic metallic behavior reported by [16].

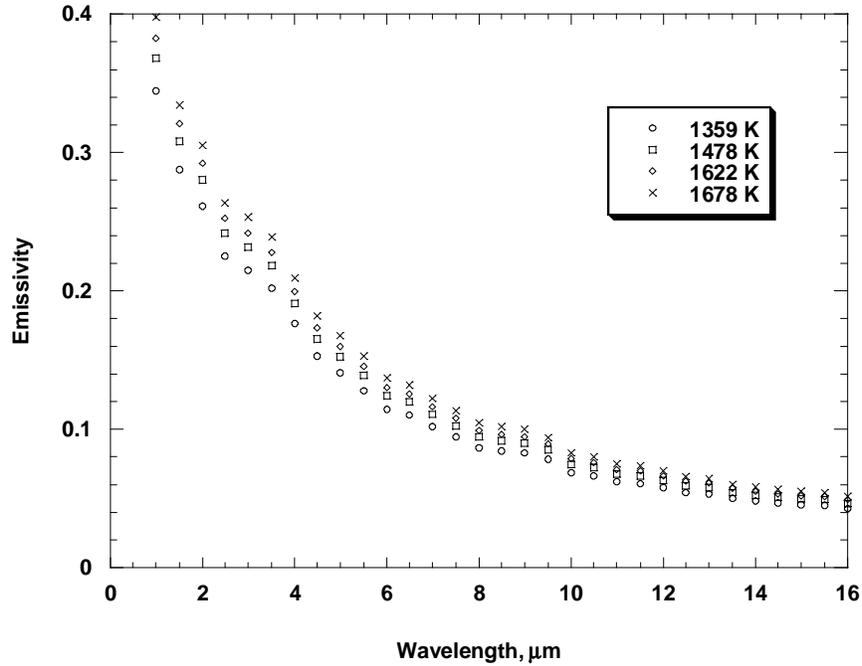


Fig. 2 Spectral-normal emissivity of zirconium.

Spectral-normal emissivity data from [4] are shown together with the present work in Fig. 3. Data reported by Coffman et al. [4] for specimen 2 at 1400 K, 1600 K and 2000 K are inconsistent with typical metallic behavior and show a decrease of emissivity with increasing temperature from 1400 K to 2000 K and an anomalous peak at 2000 K around 1 μm. Although the normal emissivity of zirconium from the present work was not determined for wavelengths shorter than 1 μm due to optical constraints, a qualitative agreement with data from [4] can be extrapolated at shorter wavelengths. Furthermore, for wavelengths above 1 μm, normal emissivity of zirconium reported in [4] is significantly higher than the normal emissivity of zirconium from the present work.

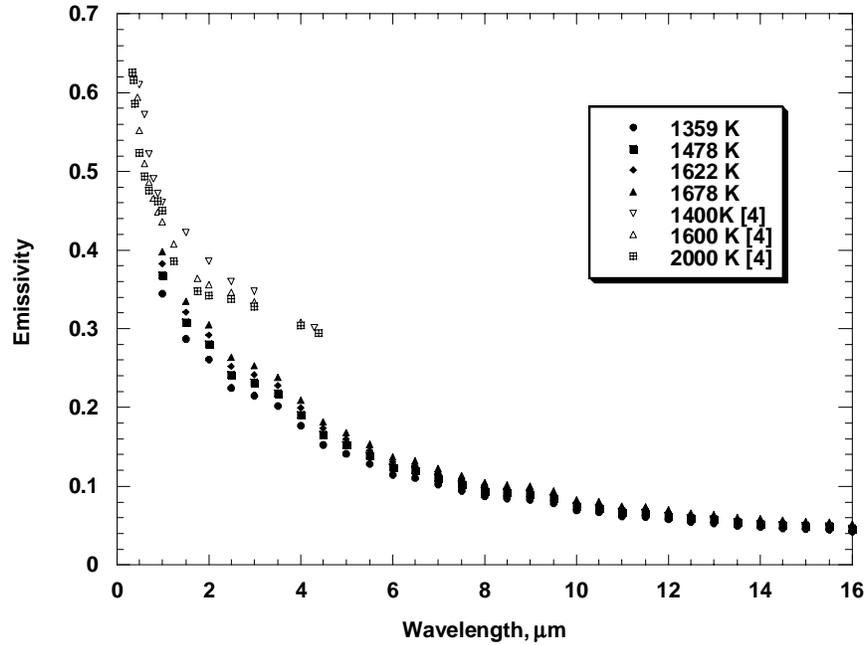


Fig. 3 Comparison of published values and present data for spectral-normal emissivity of zirconium.

This can be attributed to oxidation due to inadequate vacuum level. This is also suggested by the peak in emissivity which appears around $0.9 \mu\text{m}$ at a temperature of 2000 K. However, the authors reported that the sample surface became blackened during heating and the black deposit formed on sample's surface was removed by further heating.

The spectral normal emissivity of titanium from the present work is shown in Fig. 4.

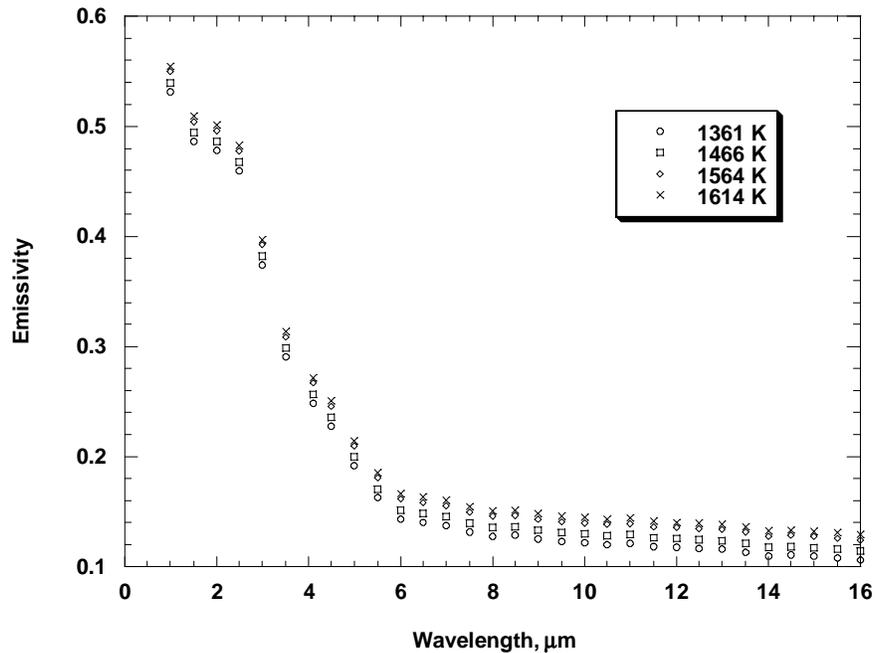


Fig. 4. Spectral-normal emissivity of titanium.

The spectral normal emissivity of titanium was found to increase slightly with increasing temperature from 1361 K to 1614 K, and to decrease with increasing wavelength from 1 μm and 16 μm .

It is important to note that the decrease in titanium normal emissivity is not monotonic at shorter wavelengths between 1 μm and 3.5 μm , although the surface oxidization was not observed upon cooling the sample. For a spectral range between 6 μm and 16 μm the normal emissivity of titanium decreases very slowly indicating agreement with the Hagen-Rubens relation [16]. The normal spectral emissivity of titanium from the present work is shown in Fig. 5, together with data reported by Adams [5].

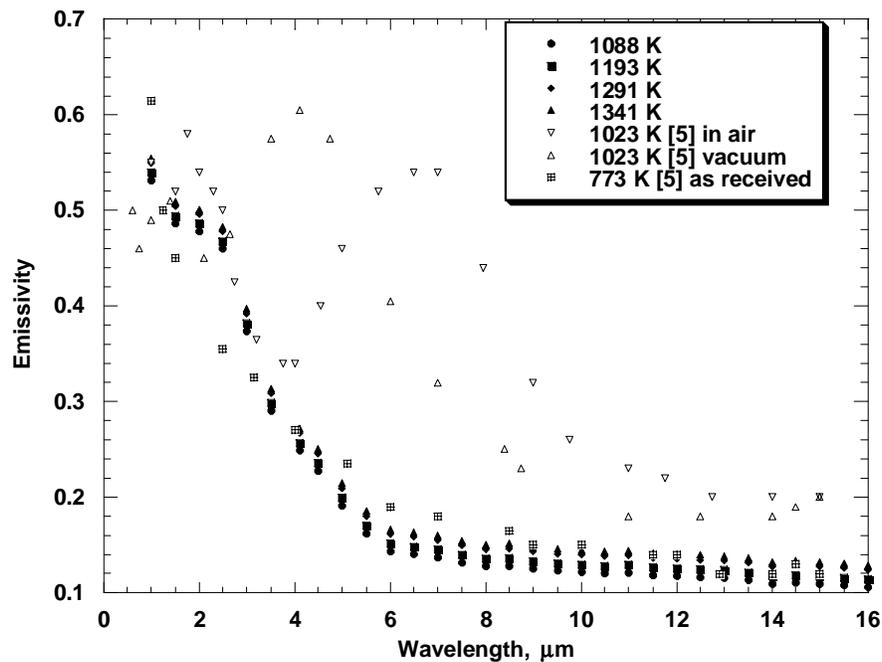


Fig. 5 Comparison of published values and present data for spectral-normal emissivity of titanium.

The as-received specimen normal spectral emissivity reported in [5] shows a qualitative agreement with data from present work, although the magnitude is higher and small peaks can be observed. This might suggest a sample surface oxidization or contamination. The measurements on the titanium sample performed in air at 1023 K in [5] exhibit a broad peak around 7 μm , indicating sample oxidization. Measurements performed in a vacuum at 1023 K in [5] show a broad peak in emissivity around 4 μm . The specimen was heated at 1073 K for 30 min. in a vacuum of 2.8×10^{-5} Torr before taking measurements. Both the broad peak developed around 4 μm and the high emissivity magnitude clearly indicate a departure from metallic behavior. This can be explained as due to inadequate vacuum level and/or contamination.

5. CONCLUSION

The spectral-directional emissivity of high purity (99%) zirconium and titanium, inductively heated in a vacuum at temperatures between 1401 K and 1686 K, is determined from

measurements of the radiative intensity leaving the sample. The spectral-normal emissivity of high purity zirconium is found to increase slightly with increasing temperature from 1401 K to 1686 K, and to decrease with wavelength between 1 μm to 16 μm , suggesting a behavior close to that of a pure metal. Spectral normal emissivity exhibits a monotonic decrease with increasing wavelength with no peaks or valleys, suggesting that the sample surface was uncontaminated by any oxide. The normal spectral emissivity of titanium is found to decrease with increasing wavelength and slightly increase with increasing temperature. The absence of any peaks or valleys in the reported spectral normal emissivities of high purity samples indicates that the non-contact method of heating and measuring sample's temperature in a high vacuum is a powerful tool which appears applicable to precision measurements on levitated molten samples.

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