Melting Points, Spectral Reflectivity and Emissivity

of Semitransparent Ceramic Materials[1]

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ABSTRACT

A new method based on multiwavelength optical probing and multiwavelength pyroreflectometry of open sample surface to measure spectral optical properties of semitransparent ceramic materials at their melting point and to determine their true melting temperatures has been developed.

With the method developed spectral optical properties (reflectivity, emissivity, transmittance) of Nd_2O_3, Gd_2O_3, Er_2O_3 and Ho_2O_3 for seven wavelengths in spectral range 0,4-1,1 μm at their melting points have been measured for the first time. It is shown that the method developed has high precision in determining the true melting temperatures for semitransparent ceramic materials. In open surface pyrometry this method is used for the first time.

KEY WORDS: ceramics; emissivity; melting point; pyrometry; pyroreflectometry; radiance temperature; reflectivity; semitransparent materials; true temperature.

1. INTRODUCTION

Some of refractory oxide ceramics relate to the class of semitransparent volume scattering materials [1]. In spite of wide application of these materials in laser and solar technologies and advanced technique their thermal radiation properties at the melting point are poorly presented in literature. This is due to complexity of investigation of the semitransparent materials at high temperatures. The task becomes more difficult when advanced methods of measuring thermal radiation properties with one side sample heating [2,3] are used. For example, in laser heating some of oxide ceramic materials their reflectivity and emissivity are not physical constants that can be related to the sample surface temperature.

Also open surface pyrometry (without blackbody model) is used to make the temperature measurement in these methods. In this case pyrometer measures the temperature which is not the surface radiance temperature of the semitransparent sample due to volume nature of its thermal emission. Therefore the temperature measured by a pyrometer for semitransparent sample was called as the effective temperature [1]. According to this definition the effective temperature "…corresponds to the temperature of a blackbody whose radiation at the wavelength of the pyrometer has the same intensity as the radiation reaching the pyrometer from a layer of infinite optical thickness adjoining the surface of the sample being studied" [1]. So the authors consider that an individual approach must be made for every semitransparent ceramic sample and the heating and measurement conditions must be taken correspondingly.

But we would like to suggest another way of solving this problem. Our objective is to present a new method to measure thermal radiation properties at the melting point

of semitransparent ceramic materials and their true melting temperature on the basis of open sample surface pyrometry. Moreover the method developed does not need the individual approach for every material being studied.

2. **METHOD**

2.3. Opaque materials

In our earlier publication [4] a method for measuring spectral reflectivity and emissivity of opaque materials near their high temperature phase transformations was developed and described in detail. Here we propose to extend the capacities of the method for measuring thermal radiation properties of semitransparent ceramic materials at their melting point. The essence of the method is as follows (Fig.1.).

The sample placed at the focal zone of an imaging furnace is heated to temperatures above its melting point. Then the sample is rapidly covered by the integrating sphere and the sample is allowed to cool. A multichannel commutator starts the recording system and turns on the flash-lamps at desired time. The flash-lamps placed into integrating sphere produce a diffuse irradiation of the cooling sample at the moment of the phase transition of interest through the lower aperture in the sphere wall.

The phase transition is manifested by a peak in the radiance temperature versus time function at different wavelengths and by a plateau in the true temperature versus time function (Fig.2). The peak is probed by the pulse light of the flash-lamps. The reflected portions of the polychromatic light incident on the sample and temperature signals are measured by means of multiwavelength high speed micropyrometer that operates in the spectral range 0,4-1,1 μm. If accept the opacity assumption for studied sample surface then the method enables one to measure spectral reflectivity and

emissivity of refractory materials at their high temperature phase transitions including melting.

2.2. Semitransparent materials.

In order to extend the capacities of the method to the semitransparent materials we don't accept the assumption of sample surface opacity for all the wavelengths of the probing light flux. Then multiwavelength pulse light probing the sample surface heated by concentrated light flux with simultaneous application of multiwavelength pyrometry enables one to measure the N spectral reflectivities, the N emissivity values, the N radiance temperatures and to determine the N true temperatures at different wavelengths (N is the number of pyrometer channels).

At the phase transition point all the N true temperatures have equal values if the sample investigated is opaque. For example, at melting point all the N true temperatures take the meaning of melting temperature. If studied sample is semitransparent then true temperatures determined with opacity assumption at N wavelengths have different values and it is very difficult task to obtain the melting temperature.

However, we have found that the effective temperatures at the melting point of the semitransparent ceramics increase with wavelength from 0,4 μm to 1,1 μm.

This fact means that absorptance increases with increasing the wavelength. But if the opacity assumption is accepted for the wavelengths - 0,848, 0,904, 0,966 μm the calculation of true temperature gives the same values for the melting point of the semitransparent ceramic material. So we consider that the opacity assumption for semitransparent ceramics may be accepted at above mentioned wavelengths.

Thus the measured spectral range 0,4-1,1 μm by a multiwavelength pyrometer is divided in the opacity and transparent regions. Therefore one can write the following equations using Wien's approximation

for transparent region

$$\rho^*_\lambda + \tau^*_\lambda + \varepsilon^*_\lambda = 1 \tag{1}$$

$$k \quad \begin{cases} T^{-1} - T^{-1}_{ef,1} = \lambda_1 C_2^{-1} \ln[1 - \rho^*_{\lambda,1} - \tau^*_{\lambda,1}], \\ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ T^{-1} - T^{-1}_{ef,i} = \lambda_i C_2^{-1} \ln[1 - \rho^*_{\lambda,i} - \tau^*_{\lambda,i}], \\ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ T^{-1} - T^{-1}_{ef,k} = \lambda_k C_2^{-1} \ln[1 - \rho^*_{\lambda,k} - \tau^*_{\lambda,k}] \end{cases} \tag{2}$$

and for opacity region

$$\rho_\lambda + \varepsilon_\lambda = 1 \tag{3}$$

$$m \quad \begin{cases} T^{-1} - T^{-1}_{r,k+1} = \lambda_{k+1} C_2^{-1} \ln[1 - \rho_{\lambda,k+1}], \\ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ T^{-1} - T^{-1}_{r,j} = \lambda_j C_2^{-1} \ln[1 - \rho_{\lambda,j}], \\ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ T^{-1} - T^{-1}_{r,n} = \lambda_n C_2^{-1} \ln[1 - \rho_{\lambda,n}] \end{cases} \tag{4}$$

Here $k + m = n$ - is the number of channels of multiwavelength pyrometer; $\rho^*_{\lambda,i}$ is the effective spectral directional-hemispherical reflectance at i-st channel for semitransparent sample; $\tau^*_{\lambda,i}$ is the effective spectral directional hemispherical transmittance; ε^*_λ is the effective spectral directional emittance; ε_λ is the spectral directional emissivity; $T_{ef,i}$ is the effective temperature of the semitransparent sample; T is the true sample surface temperature; λ_i is the wavelength at i-st channel of a multiwavelength pyrometer; $\rho_{\lambda,j}$ is the spectral directional-hemispherical reflectivity of the sample at j-st channel; $T_{r,j}$ is the

radiance temperature of the sample surface at j channel; C_2 is the second Planck's radiation constant.

Multiwavelength optical probing the sample surface and using a multiwavelength pyrometer for temperature and reflectivity measurements at different wavelengths gives a lot of information which is enough to solve these equation systems. Here $T_{ef,i}, \rho^*_{\lambda,i} (i = 1 \div k)$ and $\rho_{\lambda,j}, T_{r,j} (j = k+1 \div n)$ - are measured $\lambda_i, \lambda_j, C_2$ - are known and $T, \tau^*_{\lambda,i}$ - are unknown and determined from this set of equations.

Such a manner of pyroreflectometry is used for the first time so let us test its reliability for semitransparent ceramics.

3. RESULTS

The materials used in this investigations were Nd_2O_3, Er_2O_3, Gd_2O_3, Ho_2O_3. The purity of these oxides was more than 99, 95%. Reflectivity and emissivity measurements were performed in liquid state of these materials at the melting points. Sources of uncertainty in reflectivity and emissivity measurements were presented in our earlier publication [4]. Overall uncertainty in spectral optical properties measured by this method doesn't exceed $\pm 2\%$. The uncertainty in determining the true melting temperatures is not more than ±10 K.

Measured spectral optical properties for Nd_2O_3 at its melting point are summarized in Table I. It is shown that Nd_2O_3 is transparent at 0,579 and 0,644 μm and opaque from 0,713 μm to 0,966 μm in the studied spectral range. Spectral optical properties of Gd_2O_3 at its melting point are presented in Table II. Here the transparent region is widened up to 0,713 μm and opacity region is within 0,789-0,966 μm.

Measured spectral optical properties for Er_2O_3 and Ho_2O_3 at their melting points are given in Table III and Table IV respectively. Also in all the Tables the true melting temperatures are calculated for different wavelengths and given the recommended melting temperatures. The data on spectral optical properties of these oxides with taking into account of their semitransparancy at the melting point have been obtained for the first time.

Therefore in order to estimate the reliability of the method developed the true melting temperatures of studied oxides determined with their measured spectral optical properties and the melting-point radiance temperatures at different wavelengths are compared with available literature data on the melting temperatures of these materials. This comparison is given in Table V.

4. DISCUSSION

It is shown (Table V) that our results on the melting temperatures of the ceramics investigated are in good agreement with the results of Foex [5] and Lopato [6]. Concerning the results of Noguchi [7] one can say that his values for all the refractory oxides are more lower than values obtained by other investigators. Noguchi measured melting temperatures on the open sample surface heated at focal zone of solar furnace. In order to determine the true melting temperature he was simultaneously measuring the radiance temperature and spectral reflectivity at 0,65 μm. For obtaining the spectral emissivity Noguchi accepted the opacity condition of the sample surface at 0,65 μm. As mentioned above (Table I-IV) this condition is not right at 0,65 μm for these oxide ceramic materials at their melting point. Also Noguchi measured only specular

component of the reflectivity at the melting point. These methodics errors of the experiment led to the lowered values of the melting temperatures.

Bober et al [2] measured the melting temperature only for Nd_2O_3 with an integrating - sphere laser reflectometer. He used the opacity condition at 0,63 μm for open sample surface (flat disk) at the melting point of Nd_2O_3. From Table I it can be seen that Nd_2O_3 is transparent up to 0,644 μm so opacity condition at 0,63 μm accepted in [8] is not right for Nd_2O_3 at its melting point.

As mentioned above the agreement of our results with the values obtained by Foex [5] and by Lopato [6] is very well though our method differs from theirs. Both Foex [5] and Lopato [6] used the model of absolute black body in the solar furnace to measure the melting temperatures of the refractory oxides. Measurements were performed on thick melt layer occuring inside the rotating black body. Such experimental conditions enable one to create the optical thick layer of the melt and to measure properly the true melting temperatures of these semitransparent materials.

Therefore good agreement of our results with the results obtained by quite different methods confirms the reliability of our method developed for measuring spectral optical properties of semitransparent ceramic materials at their melting point.

5. CONCLUSIONS

A new original method based on multiwavelength optical probing and multiwavelength pyroreflectometry of open sample surface to measure spectral optical properties of semitransparent ceramic materials at their melting point and to determine their true melting temperatures has been developed. The main features of this method are as follows : a) diffuse multiwavelength probing the open sample surface at the melting

point with using of multiwavelength pyroreflectometer for simultaneous reflectivity and temperature measurements at different wavelengths; b) finding transparent and opacity regions for each semitransparent material at its melting point; c) determining the spectral optical properties and true temperatures at different wavelengths at the melting point for semitransparent materials.

With the method developed spectral optical properties (reflectivity, emissivity, transmittance) of Nd_2O_3, Gd_2O_3, Er_2O_3 and Ho_2O_3 for seven wavelengths in spectral range 0,4-1,1 μm at the melting points have been measured for the first time. Also the method proposes the reliable procedure of determining the true melting temperatures of semitransparent ceramic materials with high precision. In open surface pyrometry this method is used for the first time.

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Table I. Measured Spectral Optical Properties of Nd_2O_3 at its Melting Point

λ, μm	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.25	0.25	0.20	0.18	0.18	0.16	0.14
$\tau(\lambda)$	0.31	0.29	0	0	0	0	0
$\varepsilon(\lambda)$	0.44	0.46	0.80	0.82	0.82	0.84	0.86
$\mathbf{T_r}$**, K**	2365	2352	2480	2497	2489	2493	2497
$\mathbf{T_m}$**, K**	2565	2561	2567	2567	2563	2563	2562
$T_m = 2564 \pm 10K$							

Table II. Measured Spectral Optical Properties of Gd_2O_3 at its Melting Point

λ, μm	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.196	0.200	0.192	0.220	0.126	0.120	0.100
$\tau(\lambda)$	0.351	0.317	0.068	0	0	0	0
$\varepsilon(\lambda)$	0.453	0.483	0.740	0.780	0.874	0.880	0.900
$\mathbf{T_r}$**, K**	2457	2453	2565	2572	2605	2610	2620
$\mathbf{T_m}$**, K**	2666	2666	2667	2665	2660	2666	2669
$T_m = 2666 \pm 10K$							

Table III. Measured Spectral Optical Properties of Er_2O_3 at its Melting Point

λ, μm	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.190	0.190	0.187	0.185	0.166	0.132	0.130
$\tau(\lambda)$	0.410	0.395	0.093	0.055	0	0	0
$\varepsilon(\lambda)$	0.400	0.415	0.720	0.760	0.834	0.868	0.870
$\mathbf{T_r}$**, K**	2445	2430	2573	2582	2617	2620	2620
$\mathbf{T_m}$**, K**	2687	2687	2685	2686	2692	2682	2685
$T_m = 2686 \pm 10K$							

Table IV. Measured Spectral Optical Properties of Ho_2O_3 at its Melting Point

λ, μm	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.220	0.220	0.220	0.219	0.210	0.180	0.150
$\tau(\lambda)$	0.390	0.370	0.120	0.026	0	0	0
$\varepsilon(\lambda)$	0.390	0.410	0.660	0.755	0.790	0.820	0.850
$\mathbf{T_r}$**, K**	2419	2409	2525	2560	2572	2575	2590
$\mathbf{T_m}$**, K**	2663	2665	2663	2665	2667	2660	2665
$T_m = 2664 \pm 10K$							

Table V. Melting temperatures (K) of some semitransparent ceramics as reported in literature.

Investigator	Nd_2O_3	Gd_2O_3	Er_2O_3	Ho_2O_3	note
Foex (1965)	2583±10	2668±10	2673±10	2669±10	model of absolute black body was used;
Noguchi (1967)	2506±20	2603±20	2617±20	2603±20	open surface, only specular component of reflectivity for opaque body was measured;
Lopato (1974)	2593±25	2653±25	2663±25	2663±25	model of absolute black body was used;
Bober (1980)	2540±25	-	-	-	open surface, diffuse component of reflectivity for opaque body was measured;

Present work	2564±10	2666±10	2686±10	2664±10	open surface, semitransparent nature of these materials was taken into account for the first time.

FIGURE CAPTIONS

Fig.1. Schematic diagram of the experimental setup.

Fig.2. Typical behaviour of radiance T_r and true temperatures T versus time function during sample cooling near phase transition point (1, 2, 3 are master pulses to start flash-lamps; a, b, c are the reflected portions of the pulse light of flash-lamps incident on the sample at different time moments near phase transition).