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MEASUREMENT OF SPECTRAL EMISSIVITY AND THERMAL CONDUCTIVITY OF ZIRCONIA BY THERMAL RADIATION CALORIMETRY

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Abstract

The hemispherical total emissivity of partially stabilized zirconia has been obtained by a spectral analysis of the normal emission spectra between 400–850 K. Thermal conductivity was evaluated with this emissivity and temperature gradient in the sample. Effects of the scattering of the radiation in a ceramic sample are also investigated. In addition, specific heat capacity was measured by thermal radiation calorimetry. Current results are compared with those reported for tetragonal zirconia with the same yttria content and for monoclinic phase.

Keywords: Kirchhoff's law, Kramers–Krönig relations, thermal radiation, virtual mode equations

Introduction

Thermal radiation calorimetry (TRAC) has been originally developed to perform a simultaneous measurement of specific heat, thermal conductivity and diffusivity [1, 2]. A noble point in this calorimetry is that it is possible to obtain these thermophysical quantities independently of each other. Recently we have proposed a new method to evaluate the hemispherical total emissivity from a normal emission spectrum for silicate glasses [3]. It has been suggested that the effects of the radiation heat transfer on the emissivity may increase with temperature because of increasing radiation energy in the semitransparent frequency region of the material. This excess heat flow may also become an error source of the thermal conductivity.

In this paper, a spectral analysis proposed for silicate glasses is applied to a fine ceramic of partially stabilized zirconia. In case of a ceramic like a zirconia, the transmission occurs at lower frequency than silicate glasses. It is interesting to investigate the effect of the scattering of radiation in polycrystal and significant to obtain hemispherical emissivity, independently of specific heat, thermal conductivity and diffusivity.

Analytical method

Basic idea of this calorimetry comes from a consideration of heat exchange by radiation between the sample and the environment.

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Let us suppose that a disk shaped sample is heated on one face by infrared radiation in a vacuum chamber. At steady state, the radiant power (I_0-I_r) from the back surface of the sample is related to the thermal conductivity λ and the temperature gradient ($\mathrm{d}T/\mathrm{d}x$) in the sample as [2]

$$\lambda\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{\mathrm{T=T_0}}=\varepsilon(T_0)(I_0-I_r), \tag{1}$$

if we know the temperature T_0 of the back surface of the sample, T_r of the chamber and the total hemispherical emissivity $\varepsilon(T_0)$ of the sample. The radiant power from the back surface can be easily calculated based on the Stefan-Boltzmann's law $I=\sigma T^4$, where σ is the Stefan-Boltzmann's constant. If we assume that the temperature distribution in the sample is to be linear, we can obtain λ by

$$\lambda\frac{T_1-T_0}{d}=\varepsilon(T_0)\sigma(T_0^4-T_r^4) \tag{2}$$

knowing the surface temperatures, sample thickness d and the emissivity of the radiant surface. T_1 is the temperature of the front surface receiving the infrared radiation from the heater. There are two ways to evaluate the emissivity. One is to blacken the surface with a material whose emissivity is known. The other is to obtain the emissivity of the real surface of the sample. If we can do the latter, we have no need of blackening and calibration procedure for the emissivity of an artificial surface.

Fuchs, Kliewer and Pardee [4] have shown that the optical properties of an ionic crystal slab on a conductive substrate can be explicitly described by virtual mode equations, if we know the dielectric function $\xi(\nu)$ or complex refractive index of the crystal. According to them, the directional spectral emissivity $\varepsilon(\nu, \theta)$ for emission angle θ and frequency v is given by

$$\varepsilon(v,\theta)=1-\frac{1}{2}\left|\frac{2-L_\mathrm{p}}{L_\mathrm{p}}\right|^2-\frac{1}{2}\left|\frac{2-L_\mathrm{s}}{L_\mathrm{s}}\right|^2 \tag{3}$$

with $L_\mathrm{p}=1-i[\beta/\beta_0\xi(\nu)]\tan(\beta d)$ and $L_\mathrm{s}=1+i[\beta/\beta_0]\cot(\beta d)$, where $\beta=2\pi v\{\xi(v)-\sin^2\theta\}^{1/2}$ and $\beta_0=2\pi v\cos\theta$. Integrating the directional emissivity over a hemisphere and taking Planck's mean of it, we can obtain the hemispherical total emissivity $\varepsilon(T_0)$.

Optically, a dielectric function can be expressed by the real $n(v)$ and imaginary $k(v)$ parts of the complex refractive index $n_c(v)$ as $\sqrt{\xi(v)}=n_c(v)=n(v)+ik(v)$. These quantities can be calculated from a normal reflection spectrum using Kramers–Krönig relations. In order to obtain such dielectric function from a measured normal emission spectrum, we can refer the Kirchhoff's law for thermal radiation. That is, $T+R+E=1$, where T, R and E are respectively the reflectance, the transmittance and the emissivity for normal incidence of light.

If the sample is not transparent, the normal emission spectrum can be simply transformed to a normal reflection spectrum as $R=1-E$. However, a bulk sample become semitransparent slightly above the highest LO mode frequency of the material.

In this high frequency region, we have to estimate an empirical form for R based on the following facts: $R\approx0$ around the LO mode frequency and $R=[(n_\infty-1)/(n_\infty+1]^2$ at a high frequency limit, where n_∞ is a refractive index for visible light. In this work, we employed a harmonic oscillator model for simplicity of the estimation. Using these R, we can perform Kramers–Krönig transformation to obtain the complex refractive index. However, we have to make a correction for the imaginary part $k(v)$ in the high frequency region, since R in this region is mainly decided by the real part $n(v)$ of the refractive index only. In other words, R is not sensitive to $k(v)$ in this region. In case of small reflectance, the effect of the transmission–absorption can be related to the absorption constant $\alpha(v)=4\pi vk(v)$ as $T=\exp(-\alpha(v)L)=1-R-E$, where L is the optical path length ($L=2d$ for a metal backed sample). Consequently, we can obtain the dielectric function available for further analysis using virtual mode equations to calculate the hemispherical total emissivity.

Experimental and results

A fine ceramic of 5.3 mass% yttria stabilized tetragonal zirconia (YSTZ) was examined. Figure 1 shows a schematic setup for spectral thermal radiation calorimetry. A disk shaped sample of 24 mm in diameter and 5 mm in thickness was mounted over a flat heater of 5 cm square. The top surface of the sample was polished to optical grade for the spectral measurement. The other surfaces of the sample were coated with copper deposition. Only the bottom face of the sample was blackened with colloidal graphite for a good heating efficiency. Temperatures inside the sample were measured by thermocouples sheathed in a 0.5 mm ϕ inconel tube at two points separated by 3.86 mm along the disk axis.

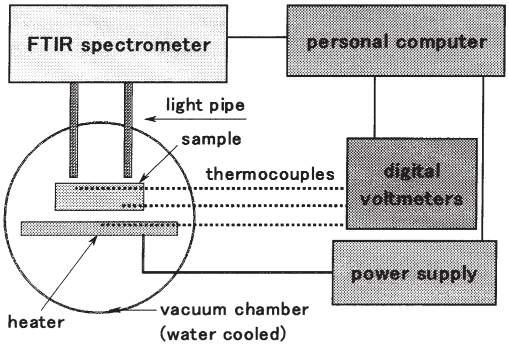

Fig. 1 Schematic of spectroscopic thermal radiation calorimetry

Starting from a normal emission spectrum, we have obtained the real part and the imaginary part of the refractive index and the hemispherical emission spectrum at each temperature. Examples of them at 523.1 K are illustrated in Fig. 2. The LO and TO mode frequency were respectively 700 and 400 cm^{-1}. The reflectivity ($1-E$) becomes zero around 800 cm^{-1}. The refractive index for visible light was taken as 2.25.

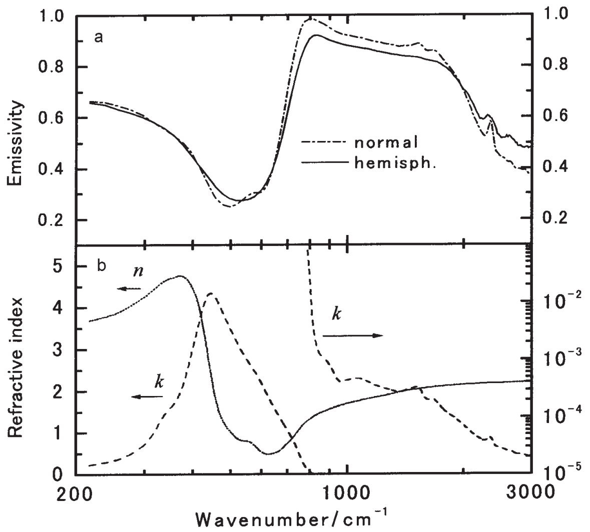

Fig. 2 IR spectra 5.3 mass% yttria stabilized zirconia; a – emissivity and b – refractive index

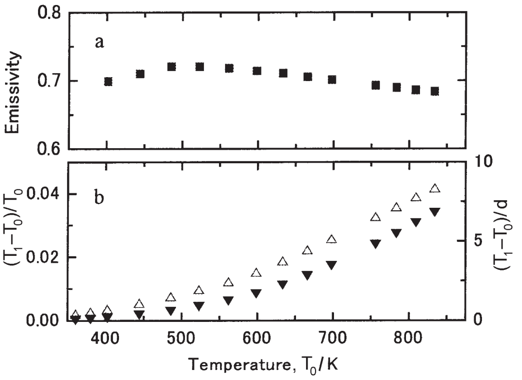

Fig. 3 Temperature variations of emissivity and temperature gradient; a – hemispherical total emissivity; b – temperature difference (Δ) between the surfaces and gradient (▼) in the sample with thickness 5 mm

The temperature variation of the total emissivity is shown by solid square symbols in Fig. 3a. The temperature gradient in the sample and difference between the surfaces normalized by surface temperature are shown in Fig. 3b. Based on these results, the thermal conductivity has been evaluated by Eq. (2). The solid symbols in Fig. 4a indicate λ by the present TRAC. The solid line is plotted after interpolation of the data obtained by a guarded hot plate method [5]. The broken and dotted lines indicate the calculated data after the results of a laser-flash method [6]. Only the data shown by the dotted line have been measured with a sample of 4 mass% YSTZ. Others are of 5.3 mass% YSTZ. Although the samples compared in Fig. 4a are slightly different in density and yttria concentration, these are in good agreement with each

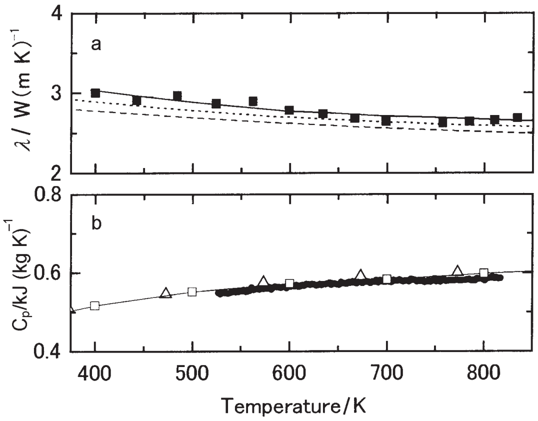

Fig. 4 Thermal conductivity and specific heat of different zirconia. a – (■) thermal conductivity by present TRAC, (–) by guarded hot plate method after [5], (····) and (- - -) by laser flash method after [6]; b – (●) specific heat by quasi-static TRAC, (Δ) by laser flash in [6], (□) by adiabatic method in [8]

other within the experimental errors less than 10%. From this result, the present method to evaluate hemispherical total emissivity and thermal conductivity can be regarded as reliable.

In the region where the sample is semitransparent, there may be excess heat flow by radiation in the sample. We can calculate this effect by analogy with the gray gas [3]. In case of a ceramic sample, however, it is better to investigate the effect of scattering of the radiation. We have measured the reflection spectrum of the metal-backed sample and that of the sample in free space at room temperature. However, we could not find any difference between them. This result implies that the radiation does not come out from inside the sample. Possible origin of this absorption will be attributed to the scattering of the radiation by the grain boundaries in a ceramic sample. Then we can suppose that the effect of the radiation heat transfer on the emissivity may be considerably small.

The schematic of the calorimeter for the heat capacity measurement has been illustrated elsewhere [7]. For the heat capacity measurement, temperature of the sample should be changed slowly and homogeneously. We have used one more heater over the sample. Since we could not measure the spectrum in this setup, both surfaces of the sample were blackened with colloidal graphite. From the heating and cooling processes, we can obtain the specific heat C_p at temperature T_s by [1].

$$C_p = \frac{A_s E_h (I_h - I'_h)}{M(\dot{T}_s - \dot{T}'_s)} \tag{4}$$

where prime indicate the cooling process, A_s the surface area and M the mass of the sample. I_h is the radiant power from heater. It should be noted effective emissivity E_h is the only one parameter that should be calibrated by the use of a standard material whose heat capacity is known. The term concerned with conductive heat losses through the wires supporting the sample and electrical leads disappears in this equation, since the difference between the both processes in this loss term can be neglected on a good approximation [1, 2]. This is the main advantage of this calorimetry. In Fig. 4b, we plot C_p by TRAC together with data in literature. The open squares indicate the results of pure zirconia in monoclinic phase [8]. Hasselman *et al*. have reported that the thermal diffusivity depends on the composition and the resulting difference in the crystal structure, but the specific heat does not [6]. As they suggested, there is no significant difference between the tetragonal zirconia and pure zirconia in specific heat as shown in Fig. 4b. This result also ensures TRAC is reliable.

Conclusions

Hemispherical total emissivity of partially stabilized zirconia has been obtained from normal emission spectrum between 400–850 K, independently of specific heat, thermal conductivity and diffusivity. With this emissivity, thermal conductivity at steady state has been evaluated. It is suggested that the scattering of radiation in a ceramic sample may compensate the effects of the radiation heat transfer on the values of the emissivity and thermal conductivity. Specific heat capacity has been measured by quasi-static TRAC. Current results are in good agreement with those in literature, ensuring reliability of spectral TRAC for thermal conductivity at steady state and quasi-static TRAC for specific heat.

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