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Heat Transfer Mechanisms in Porous Materials and Contemporary Problems in Thermophysical Properties Investigations: Analyses and Solutions

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ABSTRACT

This article is an overview of the topical problems in the investigation of thermophysical properties and the development of a database for porous materials. Determination of both apparent/measured and true thermophysical properties is discussed taking into account combined heat and mass transfer, latent heat effects during chemical and physical transformations, as well as structural changes. The approaches to the solution of these problems are demonstrated for a number of different classes of materials:

1. Industrial refractories, ceramics, highly porous insulation;
2. Moist materials and materials undergoing phase, chemical and structural transformations;
3. Materials semitransparent for heat radiation.

The approaches being used in the development of a thermophysical properties database consist in a combination of theoretical and experimental methods.

The analysis, generalization, and extrapolation of available reference data can be conducted based on the models for classical (conduction, heat radiation, gas convection) and additional (novel) mechanisms and processes affecting the apparent thermophysical properties. The novel heat transfer mechanisms include:

1. Heterogeneous heat and mass transfer processes occurring in pores existing at grain boundaries and in cracks, in particular, surface segregation and diffusion of impurities on pore surfaces and transport of gases produced from chemical reactions, evaporation, and sublimation.
2. Microstructure changes due to non-uniform thermal expansion of particles and grains. These changes are caused by the mismatch of thermal expansion coefficients of different phases in the material and anisotropic thermal expansion of crystals.

Keywords: construction materials, apparent thermophysical properties, heat transfer calculation, environmental conditions.

1. INTRODUCTION

Thermal physical properties of different materials is a determining factor in the energy efficiency and energy consumption playing the essential role in the reliable calculation of the building structure, engineering and operation of the heating, ventilation, and air conditioning (HVAC) equipment, and public utilities. Therefore, a comprehensive and reliable thermophysical properties database is substantially required. However, various energy codes, building and construction standards, and manufacturers' databases only contain the apparent thermal conductivity, a_{app}, values of construction materials in a limited range of temperature and environmental conditions (ASHRAE, 2001; EU Products data, 0001, 2007-2014; NRC-CNRC Model National Energy Code of Canada for Building, 1997; NIST, 2014).

The apparent (tested) thermal conductivity, λ_{app}, and diffusivity, a_{app}, are the basic parameters in Fourier equations and can be considered as a sum of the true, radiative, and heat-mass transfer components (Holm & Kuenzel, 2002; Kumaran et al., 2003; Litovsky & Kleiman, 2004; Mar, Litovsky, & Kleiman, 2008). Apparent properties can depend on boundary heat conditions because of the contribution of heat radiation and combined mass-heat transfer. The true thermal physical properties, λ_{true} and a_{true}, are intrinsic properties of the material composition, porosity, gas pressure, etc., and do not depend on the test method and boundary conditions.

In this article, an efficient way to develop the aforementioned database is outlined. The typical range of environmental conditions for applications of industrial

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materials that include the ambient temperature, T, and gas pressure, p, can be represented as follows: $-200°C < T < 2500°C$, 10^{-5} Pa $< p < 10^{8}$ Pa (Ya, Litovsky, & Shapiro, 1992; Litovsky, Shapiro, & Shavit, 1996; Litovsky, Gambaryan-Roisman, Shapiro, & Shavit, 1997, 2001; Litovsky & Kleiman, 2001; Litovsky, Horodetsky, & Kleiman, 2005; Litovsky, Kleiman, & Menn, 2001, 2002; Litovsky & Puchkelevich, 1982; Litovsky, Maurin, Puchkelevich, & Fedina, 1987, 1989; Litovsky, Korepanova, Birukova, Puchkelevich, & Fedina, 1990; Litovsky, Maurin, Korepanova, Puchkelevich, & Fedina, 1990). Development of a comprehensive thermophysical properties database for materials in this range of environmental parameters only using experimental investigations is very difficult or even impossible at this time. The difficulties related to thermophysical properties investigation of materials subject to chemical transformations, sintering, ablation of thermal insulation of spacecraft, taking into account thermal history and moisture transfer phenomena in porous materials make this task impossible.

Thus, two main problems can be identified in the development of a thermophysical properties database for solid and powder materials:

- Insufficient data for the apparent thermophysical properties in a wide range of environmental conditions: high temperature, different gas composition and pressure, moisture content.
- No data for the true thermophysical properties required for heat transfer calculations during phase and chemical transformations and combined heat radiation–conduction transfer.

Currently, a number of software packages are offered to conduct modeling of thermal transfer phenomena in the building structures (Holm & Kuenzel, 2002; Kazaragiozis, Kuenzel, Holm, & Desjarlaiis, 2001; Kumaran et al., 2003). However, the basic parameters of the combined heat transfer equations (heat radiation–conduction, gas convection–conduction, moisture transfer–heat conduction, the mathematical models of burning, chemical technology processes, ablation of space materials, etc.) are true thermal physical properties. A database for true thermal physical properties of gases and liquids can be found; however, there is no database for the thermophysical properties of solid materials and this problem is not discussed at most thermophysical and materials science conferences.

One of the main reasons is related to the difficulties of conducting the labor-intensive, long-term experimental investigations of apparent thermal conductivity at various combinations of the governing parameters. Thus, for instance, investigation of the moisture and temperature dependence of thermal conductivity for a particular specimen may take over a month. Testing of industrial refractories in the range of temperature, gases composition, and pressure typical for their applications is even more complicated, long, and expensive. Using such a low rate of data acquisition, the development of a comprehensive database of thermophysical properties to include many materials in different combinations of environmental conditions and other parameters is a task of paramount importance that would require an unreasonable amount of time and money to complete.

It would be reasonable to suggest that the development of an appropriate and reliable mathematical models of λ_{app} and λ_{cond} would provide a solution to this problem.

The main task of this article is to demonstrate our approaches and some examples to the fast development of a new generation of the database for λ_{app} and λ_{cond} of different solid materials.

2. GENERAL APPROACH

A methodology is suggested (Litovsky & Kleiman, 2004; Litovsky, Korepanova, et al., 1990; Litovsky & Puchkelevich, 1982; Litovsky et al., 1987, 1989), which allows solving this problem based on generalization and extrapolation of available experimental data.

The general scheme of the proposed approach is presented in Figure 1. The database development can be conducted by combining experimental and theoretical methods. Experimental studies would provide the data that will be necessary for the design and verification of theoretical models and determination of empirical correction coefficients that are difficult to be accurately calculated.

The theoretical methods based on physical models of heat transfer in porous media could be fundamental for calculation of all components of thermal conductivity. Experimental data, including available and reliable published information, should be used as the basis for extrapolation. This data contains “hidden” information about the real porous structure of a material and heat transfer mechanisms acting within the material. It can also be used for determination of appropriate empirical coefficients/corrections for the theoretical models of apparent thermal conductivity.

A comprehensive review of the models that can be used for calculation of the apparent thermal conductivity and its components, which we applied, can be found in Ya et al. (1992), Litovsky et al. (1996, 1997, 2001, 2005), and Litovsky and Kleiman (2001). In general, the apparent thermal conductivity, λ_{app}, depends on the solid phase thermal conductivity, λ_{solid}, of the porous structure, total porosity, $f(P)$, pores

thermal conductivity, λ_p, and parameter M determining the barrier heat resistance between particles:

$$\lambda_{app} = M \times \lambda_{solid} \times f(P, \lambda_p) + \lambda_{rad} + \lambda_{conv} \quad (1)$$

The parameter M can be calculated from the following relation (Litovsky, Gambaryan-Roisman, Shapiro, & Shavit, 1997):

$$M = \frac{\dfrac{R_\Pi}{1-\bar{a}^2} + \dfrac{R_b}{\bar{a}^2} + \dfrac{\Phi^2}{\Phi - 1}}{\left(\dfrac{R_\Pi}{1-\bar{a}^2} + \dfrac{\Phi}{\Phi - 1}\right)\left(\dfrac{R_b}{\bar{a}^2} + \Phi\right)}, \quad (2)$$

$$\Phi\bar{a}^2 = 1 - \frac{16}{\pi^2} \sum_{n=1,3,5,\ldots} \frac{I_1(n\pi b / L)}{n^2 I_1(n\pi r / L)} [I_1(n\pi r / L)$$

$$K_1(n\pi b / L) - K_1(n\pi r / L) I_1(n\pi b / L)]$$

In the above expression,

$$R_\Pi = \frac{\lambda_s}{\lambda_\Pi}\frac{\delta}{L} \text{ and } R_b = \frac{\lambda_s}{\lambda_b}\frac{\delta}{L} \quad (3)$$

are the non-dimensional contact thermal resistances and contact layer of intergrain material, respectively, where $\delta$is the crack thickness, L is the distance between microcracks, b and r are the effective radii of the contact area and microcrack or grain boundary, respectively, $\bar{a} = b / r$, λ_b is the thermal conductivity of the intergrain material, and I_1 and K_1 are the first-order modified Bessel functions of the first and second kind, respectively.

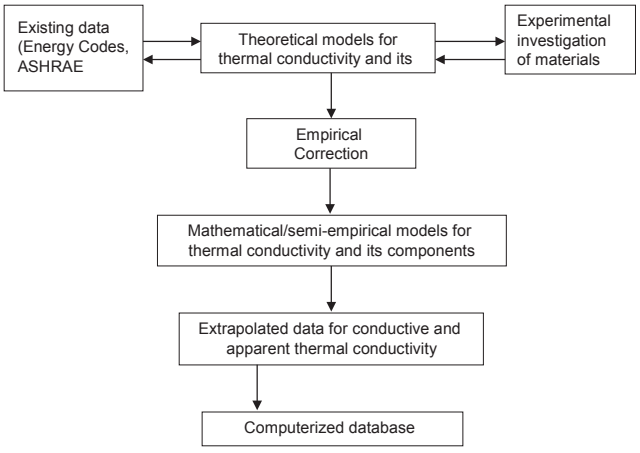

Figure 1. Block-diagram outlining the proposed approach for the development of a new database. Figure reproduced with permission from Mar et al. (2008).

The parameter M being a function of gas pressure allows explanation of a pronounced change of thermal conductivity at low temperature but does not explain thermal conductivity behavior in vacuum conditions, and especially at high temperatures (Ya et al., 1992; Litovsky et al., 1996, 1997, 2001, 2005; Litovsky & Kleiman, 2001). These variations cannot be explained based on classical heat transfer mechanisms in porous ceramics, such as heat conduction in solid and gas phases, radiation, and gas convection within the pores.

Therefore, additional mechanisms should be incorporated vis-a-vis the traditional mechanisms to explain the experimental data. Analyses and evaluation of changes of contact heat barrier resistance, actually, the M-parameter, are very important to explain and extrapolate the behavior of thermal conductivity (Figure 2).

The following two main groups of novel heat transfer mechanisms can be proposed:

- Heterogeneous heat and mass transfer processes occurring in pores existing at grain boundaries and in cracks, in particular, surface segregation and diffusion of impurities on pore surfaces, transport of gases produced from chemical reactions, evaporation, and sublimation (Ya et al., 1992; Litovsky et al., 1996, 1997, 2001; Litovsky & Kleiman, 2001).
- Microstructure changes due to non-uniform thermal expansion of particles and grains. These changes are caused by mismatch of thermal expansion coefficients of different phases in the material and anisotropic thermal expansion of crystals (Litovsky & Kleiman, 2001; Litovsky, Gambaryan-Roisman, Shapiro, & Shavit, 1999).

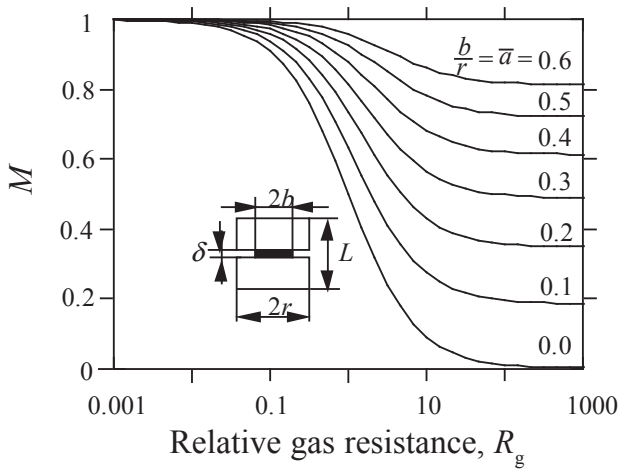

Figure 2. Dependence of contact heat barrier resistance parameter M on non-dimensional contact area and pores resistance. Figure reproduced with permission from Litovsky et al. (1997).

3. EXAMPLES OF EXPERIMENTAL DATA AND THEORETICAL ANALYSES OF THE APPARENT AND TRUE THERMAL PHYSICAL PROPERTIES

In this section, several examples of experimental data for the apparent thermal conductivity/diffusivity,

as well as calculation results for the apparent and true thermal conductivity for different materials and different environmental conditions, are shown.

Strong influence of the environmental factors, temperature, and gas pressure on the thermal conductivity and diffusivity properties can be observed in ceramics and industrial refractories.

Figure 3 shows thermal conductivity data collected for industrial chrome magnesite refractory brick used in vacuum steel production. In case of this multiphase material, the models describing the behavior of reversibly opening and closing microcracks can provide a satisfactory fit of experimental data.

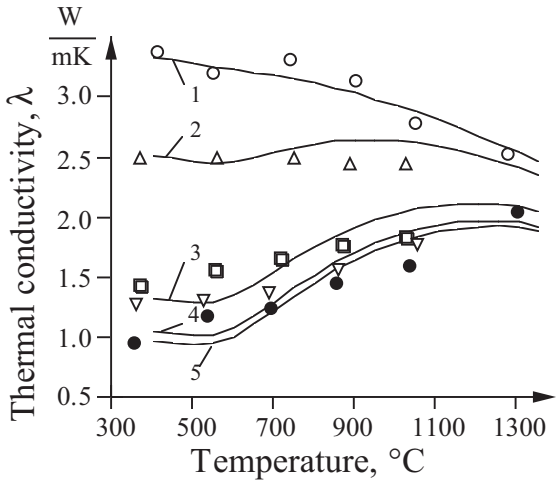

Figure 3. Thermal conductivity of chrome magnesite refractories. *Notes*: ○, 1–10^5 Pa; △, 2–$5{\cdot}10^3$ Pa; □, 3–$5{\cdot}10^2$ Pa; ▽, 4–10^2 Pa; ●, 5–10^{-2} Pa. Discrete points – experimental data. Solid lines – results of calculations by Equation (1). Figure reproduced with permission from Litovsky et al. (1997).

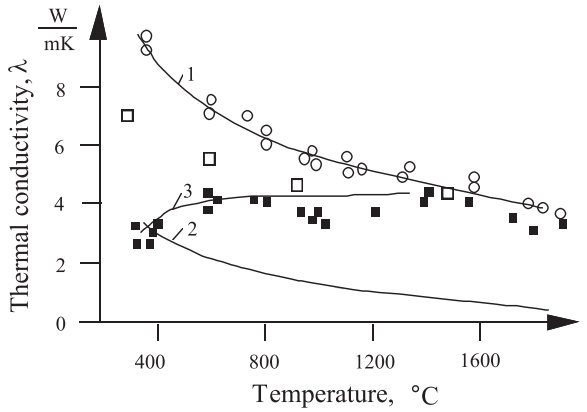

Figure 4. Thermal conductivity of ceramics based on Y_2O_3 with total porosity $\Pi = 7\%$. *Notes*: ○ – He, 10^5 Pa; □ – Ar, 10^5 Pa; ■ – Air, 10^{-2} Pa. Theoretical curves calculated from Equation (4): 1 – He, 10^5 Pa; 2 – Air, 10^{-2} Pa, $\lambda_\Pi = \lambda_{\Pi,g}$; 3 – Air, 10^{-2} Pa, $\lambda_\Pi = \lambda_{\Pi,g} + \lambda_{\Pi,s}$, with $\lambda_{\Pi,s}$ calculated by Equation (17). Figure reproduced with permission from Ya et al. (1992).

The results of experimental measurement and theoretical analysis of high purity Yttrium Oxide are presented in Figure 4. The segregated substance in this material is represented by oxygen vacancies existing in the crystal lattice.

Figure 5 shows the thermal conductivity behavior of highly porous alumina fiber insulation: apparent/tested, radiative/calculated, and conductive/calculated.

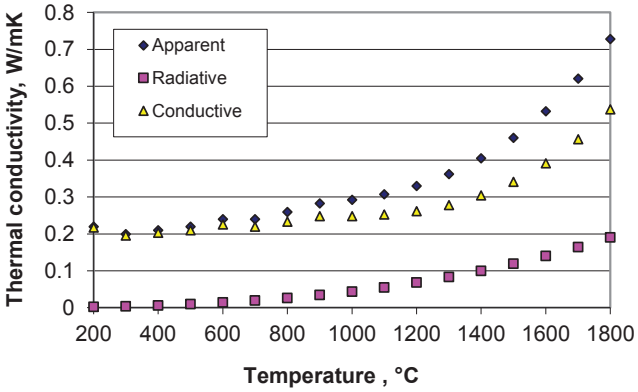

Figure 5. Apparent (tested), radiative (calculated), and true/conductive thermal conductivity of highly porous alumina–silica fiber insulation, Al_2O_3: 80%, porosity: 84%.

As can be seen from Figure 5, the radiative component constitutes about 25% of the apparent value in the temperature range of 1,500–1,800°C.

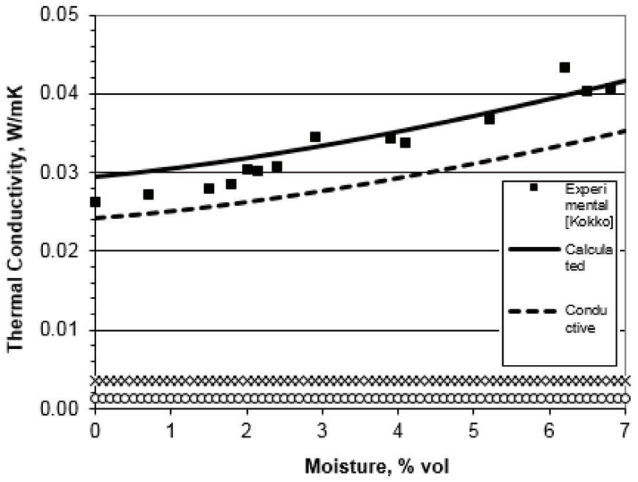

Figure 6. Thermal conductivity, apparent thermal conductivity, and its components of expanded polystyrene insulation determined for different moistures content. X, heat and mass transfer components (~0.004 W/mK); O, radiative component (~0.002 W/mK). Figure reproduced with permission from Mar et al. (2008).

The apparent/measured and true/conductive thermal conductivity of EPS insulation during phase and structural transformations is shown in Figures 6 and 7.

The calculated curves are in good agreement with available experimental data for the moist EPS material and its reference data at moisture content $w = 0$.

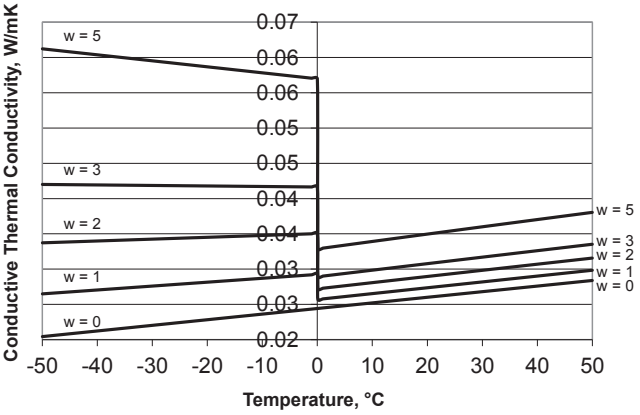

Figure 7. True/conductive thermal conductivity of EPS insulation with different moisture content vs. temperature. Figure reproduced with permission from Mar et al. (2008).

Similar considerations allow to develop semi-empirical models for calculation of thermal conductivity of refractories, insulation materials, pure oxide ceramics, and finally, to develop a comprehensive database for the apparent thermal conductivity of the materials (Litovsky, Korepanova, et al., 1990; Litovsky, Maurin, et al., 1990; Litovsky & Puchkelevich, 1982; Litovsky et al., 1987, 1989, 1999; Ojanen & Erkki, 2002).

4. CONCLUSIONS

Based on the conducted investigation and discussion, the following conclusions can be suggested:

- The proposed approach for development of a thermophysical properties database represents a combination of express test methods and physical/mathematical models of thermal conductivity.
- Theoretical models and approach for determination of the true thermal conductivity and diffusivity are suggested.

Future work should include comprehensive investigation and database development for different classes of materials, especially, regarding the true thermal conductivity.

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