

MEASUREMENT AND PREDICTION OF THE THERMAL CONDUCTIVITY OF POWDERS AT HIGH TEMPERATURES

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Abstract

An equation for the prediction of the thermal conductivity of powder beds up to high temperatures is suggested by the authors. The predicted values by the equation are compared with the values of the thermal conductivity of alumina powder, magnesia powder and zirconia powder reported in the literature, and are found to be consistent. The predicted values by the equation are also compared with the measured values of the thermal conductivity of calcium hydroxyapatite powder, at various temperatures, up to 500°C by the laser-heated method.

I. Introduction

The temperatures used during the Selective Laser Sintering process are ordinarily near the fusion points of the powders. The data of the thermal conductivities of powder beds at high temperatures are therefore of importance to this process. For the prediction of the thermal conductivity of powder beds up to high temperatures, a number of equations are found in the literature. The present authors adopted and changed a model (Zehner-Schlünder's model) [1], checked it with the data in the literature, and checked with the data they measured by the laser-heated method [2,3]. They found the consistency of the predicted values with the measured values to be within $\pm 30\%$ relative error.

The measurement of the thermal conductivities of hydroxyapatite powder bed from room temperature up to 500°C was done by the use of the laser-heated method by the authors. A description of the equipment used the authors to collect the high temperature data of the thermal conductivities of powder beds, including diagrams about the construction of the apparatus, was given in an earlier article [2]. The authors have also made preparation for the future use of this apparatus for the measurement of the thermal conductivities of powder beds in vacuum and in other gaseous environments.

II. Predictive Model

A. The Model and Its Derivation. There are some equations in the literature for the prediction of the thermal conductivity of powder beds. Besides Yagi-Kunii's equation [4], Zehner-Schlünder's equation [1] has been noticed to be a comparatively good one [5]. Schlünder's equation [6] considered conduction only. Later, with the cooperation of Zehner, Schotte's equation [7] was adopted for the consideration of the radiation effect. In the derivation of Zehner-Schlünder's equation, the present authors found some mistakes in the original article [1]. We rederived the equations, and suggested the consideration of the radiation by the direct addition of the Damköhler's term to give

$$\frac{k}{k_s} = (1 - \sqrt{1 - \varepsilon}) \left(1 + \frac{\varepsilon k_R}{k_s} \right) + \sqrt{1 - \varepsilon} \left[(1 - \phi) \left(\frac{2}{1 - \frac{Bk_s}{k_s}} \left(\frac{B}{\left(1 - \frac{Bk_s}{k_s}\right)^2} \left(1 - \frac{k_s}{k_s}\right) \ln \frac{k_s}{Bk_s} - \frac{B+1}{2} - \frac{B-1}{1 - \frac{Bk_s}{k_s}} \right) + \frac{k_R}{k_s} \right) + \phi \frac{k_s}{k_s} \right] \quad (1)$$

Free fluid
Core heat transfer (incomplete solid contact)
(Complete solid contact)

where,

k = effective thermal conductivity of the powder bed, W/m-K;

k_g = thermal conductivity of the gas inside the pores of powder bed, W/m-K;

k_s = thermal conductivity of the skeletal solid, W/m-K;

ε = porosity of the powder bed;

k_R = thermal conductivity part of the powder bed owing to radiation, denoted by the Damköler's equation below, W/m-K;

ϕ = flattened surface fraction of particle in contact with another particle; $\phi = 0$ when there is no contact for the particles; $\phi = 1$ when there is complete particle contact; and

B = deformation parameter of the particle.

In the heat transfer through powder, the part transferred by the free fluid, or diffusion and molecular conduction, is $1 - \sqrt{1 - \varepsilon}$, and the other part, or $\sqrt{1 - \varepsilon}$, is for conduction through solid and the fluid entrained in the solid particle interstices. The right-hand side of the above equation is separated into three main parts. The first part is due to the thermal transport done by free fluid, including the conduction part and the radiation part as well. The second and third parts of the above equation are for the heat transfer done by the solid and the fluid entrained in the solid particle interstices. The second part of the above equation is for incomplete solid contact, including heat transfer by conduction and radiation. The third part is for complete solid contact by the conduction of heat only. Heat transfer by convection is not considered here.

For the deformation parameter, B , it has the following relationship to the cylindrical radius, r , and the z -coordinate of the z -axis in the cylindrical coordinate system.

$$r^2 + \frac{z^2}{[B - (B - 1)z]^2} = 1. \quad (2)$$

We may see that when $B=0$, it is the z -axis; when $B=1$, the particle surface is that of a sphere; and, when $B \rightarrow \infty$, $r^2 = 1$, or it is a cylinder. So, for $B < 1$, it is a prolonged needle, and for $B > 1$, it is a barrel-like body.

The k_R term, or thermal conductivity part of the powder bed owing to radiation, is calculated by the Damköler's equation [8]. For the prediction of the thermal conductivity of powder beds at high temperatures, the heat transfer effect due to radiation should be considered. Damköler [8] first proposed the following simple relationship to account for the radiation effect of heat transfer through a powder bed.

$$k_R \Delta T = \xi s d_p e \sigma (T_b^4 - T_1^4) = \xi s d_p e \sigma (T_b^2 + T_1^2)(T_b + T_1)(T_b - T_1) \quad (3)$$

or: $k_R = \xi s d_p e \sigma (T_b^2 + T_1^2)(T_b + T_1) \approx 4 \xi s d_p e \sigma T_b^3. \quad (4)$

where,

k_R = the thermal conductivity contributed by radiation, W/m-K,

ξ = the area fraction occupied by the canals for the radiation per total unit area,

s = a numerical factor of about 1,

d_p = the diameter of the powder particle m,

e = emissivity,

σ = Stefan-Boltzmann constant = 5.67×10^{-8} W/m²-K⁴,

T_b = the temperature of the powder bed, and

T_1 = the temperature of the surrounding, assumed to be near to T_b

Damköhler suggested that ξs might take the value of 0.3, but he also mentioned that for definite powder beds, one might just measure ξs . In an example in his writing, Damköhler put $\xi s e = 1/3$.

B. Comparison of the Predicted Values by the Proposed Equation with the Measured Data Reported in the Literature. We found in the *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology* [9] some high temperature data of the thermal conductivity of powder beds. The numerical data were for alumina (Al₂O₃) powder, magnesia (MgO) powder, and Zirconia (ZrO₂) powder, and they included the temperature, porosity and the particle diameter in the data as well. We also found the thermal conductivity of the alumina, magnesia and zirconia in solid form at the various temperatures (some by interpolations). In calculating, we found the predicted values and the reported values in the literature match in the range of differences of $\pm 30\%$. It has been noted that the predicted values of the thermal conductivity of the powder bed (e.g. alumina powder, $\epsilon = 0.71$) by our equation is much better than by Yagi-Kunii's equation, and also a little better than by Zehner-Schlünder's equation. The following is a graph showing the result.

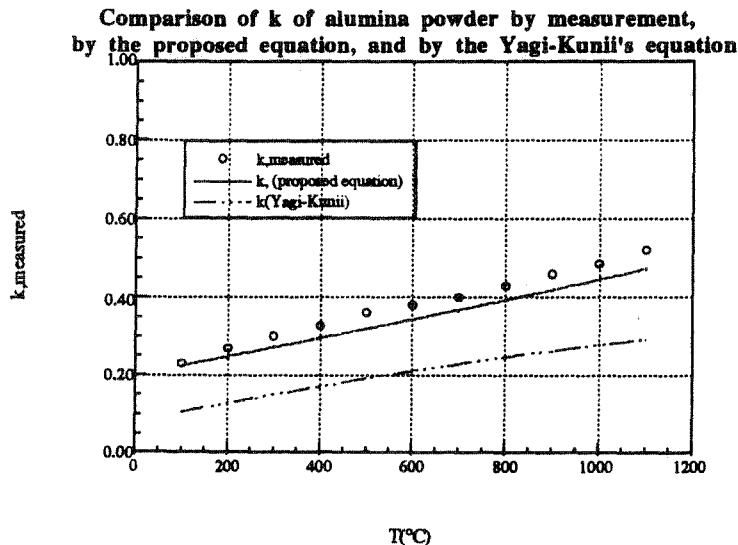


Figure 1. Comparison of k of alumina powder ($\epsilon=0.71$) (reported) with the predicted values by the authors' equation and Yagi-Kunii's equation.

The following are the graphs showing the comparisons of the predicted values with the reported values of the thermal conductivity of the various powder (alumina, magnesia, and zirconia) beds.

**k(calculated)/kg compared with k(measured)/kg,
alumina powder, $\epsilon=0.71; 0.632; 0.572;$
 $0.564; 0.52; 0.51; 0.42$**

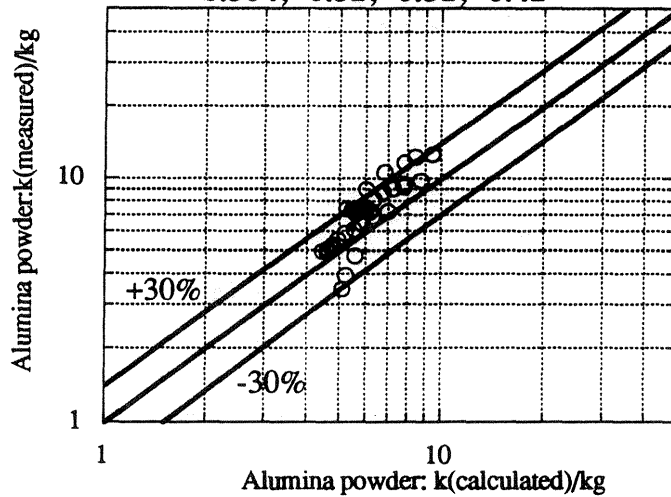


Figure 2. The comparison of the predicted values (calculated values) with the reported values (measured values) of alumina powder beds of various porosities (ϵ).

**k(calculated)/kg compared with k(measured)/kg,
MgO powder, $\epsilon=0.57; 0.525; 0.42$**

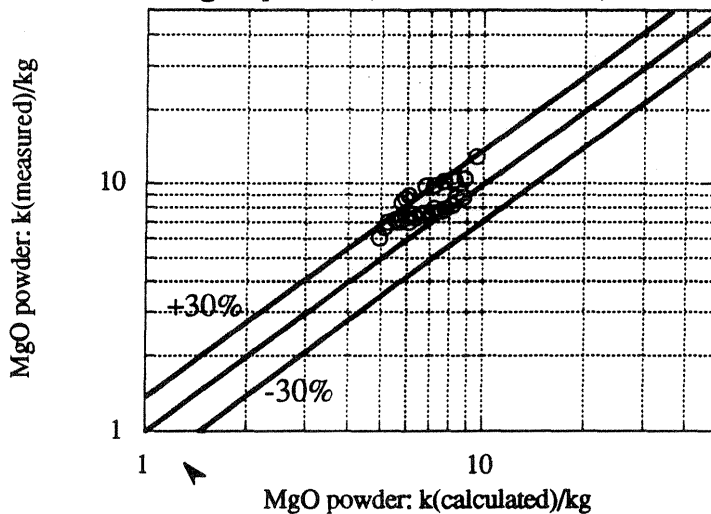


Figure 3. The comparison of the predicted values (calculated values) with the reported values (measured values) of magnesia powder beds of various porosities (ϵ).

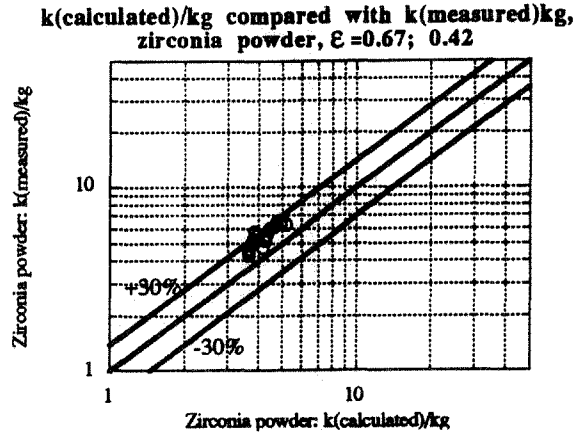


Figure 4. The comparison of the predicted values (calculated values) with the reported values (measured values) of magnesia powder beds of various porosities (ϵ).

III. Comparison of the Model with Experimental Data for Hydroxyapatite

The authors measured the thermal conductivity of hydroxyapatite powder from room temperature up to 500°C, by the laser-heated method. To obtain the k of a powder bed by the apparatus used by the authors, one must know first the heat capacity of the powder as the measurements by the apparatus only give the thermal diffusivities at the various temperatures. In literature, we found only few references on the heat capacities of hydroxyapatite. [10, 11, 12] In all the cases in the literature, hydroxyapatite samples were preheated to around 1000°C for long hours. Thus, as Kijima and Tsutsumi [10] conceded that the samples that they tested were actually oxyhydroxyapatite. We used the Differential Scanning Calorimeter (Perkin-Elmer DSC-7) for the measurement of the heat capacities of the hydroxyapatite powder (Monsanto Company), starting from room temperature and ending at 500°C, with slow speed for the increase of temperature. The result of our measurement of the heat capacity of hydroxyapatite is shown in the following graph.

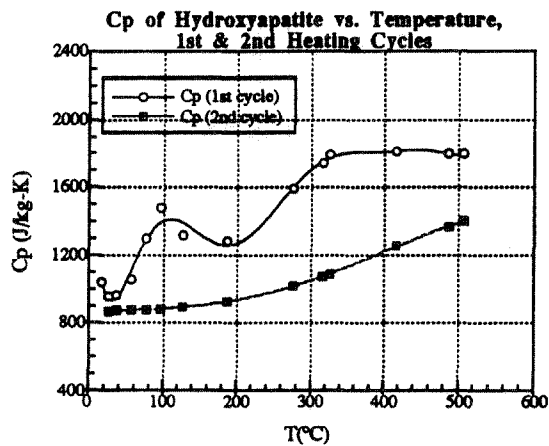


Figure 5. Graph of Cp of hydroxyapatite vs. temperature, 2 heating cycles compared

As the hydroxyapatite powder (Monsanto Company) contained a definite amount of water moisture, it may be seen that around 100°C that was an increase of heat capacity. The second curve in the above graph shows the measured C_p vs. temperature curve of the hydroxyapatite powder which went through a heating cycle from room temperature to 500°C once and cooled down again to room temperature to start for another cycle of the measurement. In heating the powders repeatedly at high temperatures, we found for the second cycle the heat capacities of the powders are lowered and the curve became smoother, with no peak value around 100°C. This was probably owing to the loss of water and change in the chemical structure of hydroxyapatite.

The density of the sample powder bed that we used for the measurement is 0.4004 gm/cm³. From the relationship of $k = \rho \times C_p \times \alpha$, by measuring the thermal diffusivity, α , we obtained the thermal conductivity of the hydroxyapatite powder bed vs. temperature, from room temperature up to 500°C in 10°C increments, which is shown in Figure 6 below. (C_p of the first cycle was used in the calculations.)

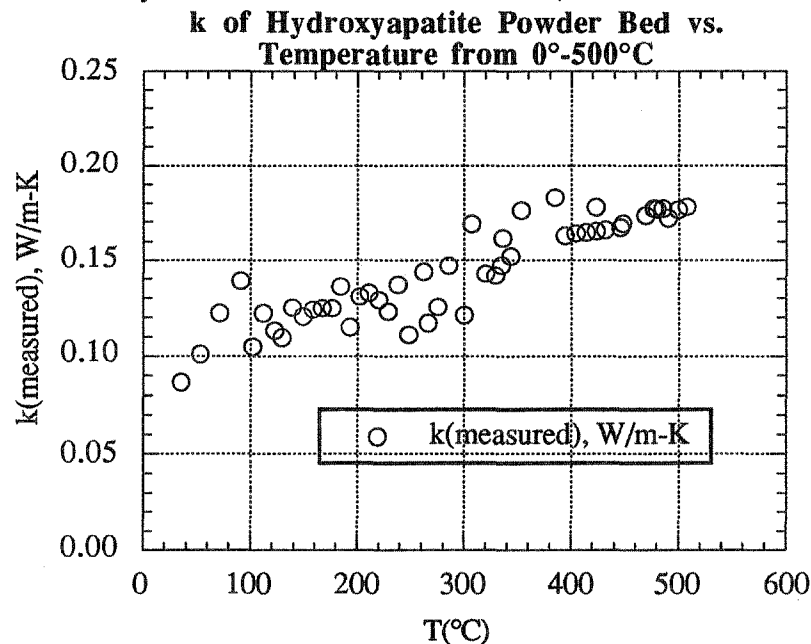


Figure 6. k of hydroxyapatite powder bed vs. temperature, from 0°-500°C

For the application of the above equation to the hydroxyapatite powder bed, we use the following relationship for the calculation of the thermal conductivity of air, k_g , inside the pores of the powder at the various temperatures.

$$k_g = (0.0000586 + 0.00000017639T) \times 418.4 \quad \text{W/m-K} \quad (5)$$

In the above equation, T is the temperature in °C. This equation was taken from the Chemical Engineers' Handbook. [13]

For the value of k_s , the thermal diffusivity vs temperature graph of Tsuyoshi Kijima and Masayuki Tsutsumi [10] is referred to by the present authors. Kijima and Tsutsumi heated hydroxyapatite using the range of 1050°-1450°C, with each sample heated for 3 hours. They found that the thermal diffusivity vs. temperature curves for the different sample nearly fell into coincidence. The Figure 8 of their article is reproduced below for reference.

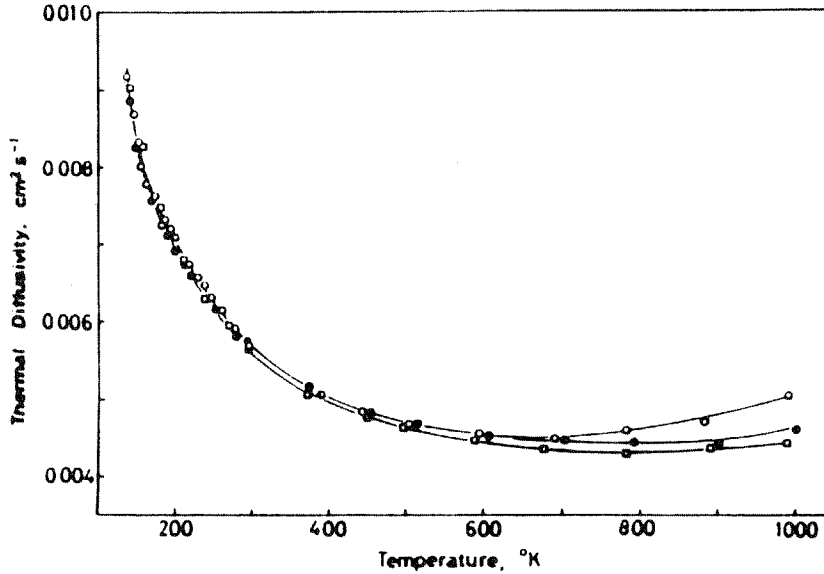


Figure 7. Thermal diffusivity vs. temperature for hydroxyapatite [10] sintered at 1050° (sample S-1, □), 1100° (sample S-2, •), and 1150°C (sample S-3, O).

We assume that hydroxyapatite heated up to 500°C would also have its diffusivity vs. temperature curve of about the same form. With the use of C_p vs. temperature curve of our own measurement (Figure 5 of this article, 1st cycle) again, and the average solid density of hydroxyapatite of 2.4625 gm/cm³, from the relationship of $k_s = \rho_s \times C_p \times \alpha$, we calculated the k_s vs. temperature values for solid hydroxyapatite. We presumed ϵ to be 0.8374 from knowledge of the bulk and solid densities of hydroxyapatite.

We have for porosity, ϵ ,

$$\epsilon = \frac{\rho_s - \rho_b}{\rho_s} = \frac{2.4625 - 0.4004}{2.4625} = 0.8374.$$

In the above equation, ρ_b is the bulk density of the powder bed.

As the melting point of hydroxyapatite is well above 1000°C, the deformation parameter, B , is assumed to be 1, i.e. the particles are all spherical; and the flattened surface fraction, ϕ , is taken to be zero, i.e. there are no flattened surfaces.

Following Damköhler's suggestion [8], we assumed $\xi_{se} = 0.3$, as we have not yet measured emissivity values to calculate the ξ_s . For the particle size, d_p , we got a size distribution report of the hydroxyapatite powder from Monsanto Company, the producer of the powder. As radiation is related to a surface area controlling phenomenon, we calculated the mean diameter of the particle by an equation according to the following [14].

$$d_p = D_{20} = \left(\frac{\sum N_i D_i^2}{\sum N_i} \right)^{1/2} \quad (6)$$

Through calculation, we got the $d_p = 15.091 \mu\text{m}$.

In substituting the above values into our proposed equation, we found the equation gives predicted values for the thermal conductivity of the powder bed quite well. The following graph shows the nearness of the predicted values by the equation to the measured values of the k of the powder bed. The Yagi-Kunii's equation for the case of the

hydroxyapatite powder bed is shown on the same graph. It may be seen that the proposed equation or ours gives much better predictions than the Yagi-Kunii's equation. The proposed equation of ours gives also a little better predictions than the Zehner-Schlünder's equation.

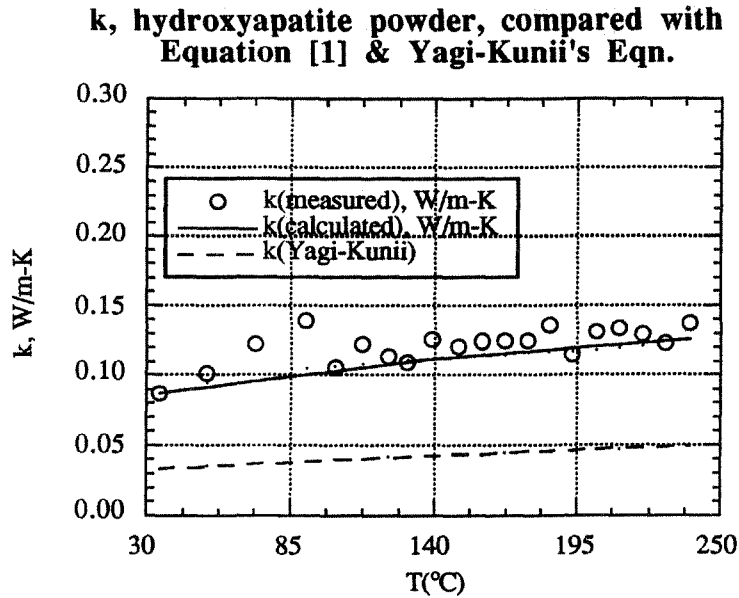


Figure 8. The measured data of the thermal conductivity of hydroxyapatite powder bed compared with the predicted value of the proposed equation of the authors and the Yagi-Kunii's equation.

In the following graph, the measured values of k/k_g are compared with the values predicted by Equation [1]. It may be seen that the predicted values and the measured values match one another quite well.

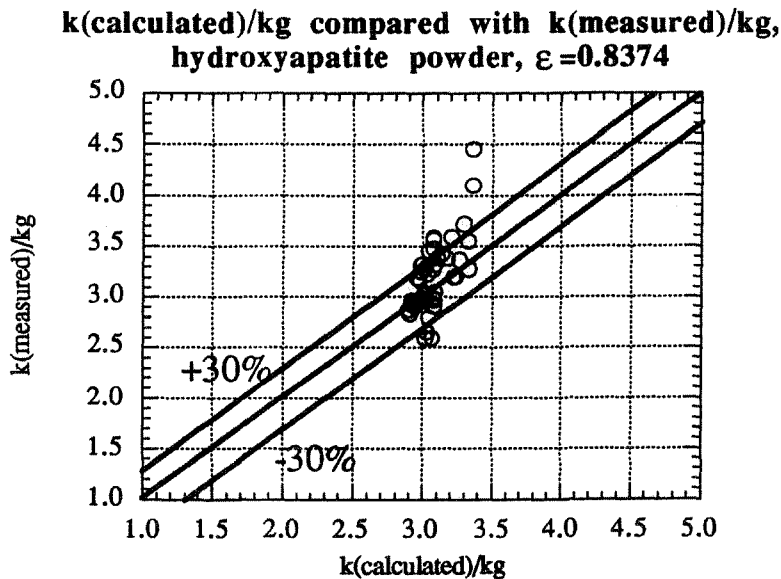


Figure 9. $k(\text{calculated})/k_g$ compared with $k(\text{measured})/k_g$ for the hydroxyapatite powder bed.

IV. Conclusion

We used a new equation to predict the thermal conductivity of powder beds from room temperature up to high temperatures. The new equation proved to be predicting the thermal conductivity of powder beds to within $\pm 30\%$ of the values reported in literature and the measured values of the thermal conductivity of hydroxyapatite powder from room temperature up to 500°C.

Acknowledgments

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