# THE MEASUREMENT OF THE THERMAL PROPERTIES AND ABSORPTANCES OF POWDERS NEAR THEIR MELTING TEMPERATURES

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## Abstract

A new technique, using a laser as the heating source, has been adopted to measure the heat capacities, thermal diffusivities, thermal conductivities, and absorptances of powders (especially polymer powders) near their melting temperatures. This makes use of an unsteady state process. The data of the thermal conductivities obtained through this technique below 100°C are in concord with the values obtained through the other techniques, which predicts well for the use of this technique for still higher temperatures, up to the melting temperatures of the powders to be investigated.

## Introduction

In the SLS process, a thin layer of powder is spread over a base and a computer-program-controlled laser scans and selectively sinters the layer. This process is continued until the part is generated. The unsintered powder part is brushed off after the entire job. Knowledge of the thermal properties, especially heat capacities, thermal diffusivities, thermal conductivities, and absorptances of powders, is essential to the study of many technical processes, including Selective Laser Sintering (SLS). This paper reviews the ways for measuring the thermal conductivities and thermal diffusivities of powders found in the literature and shows the data of the thermal diffusivities and thermal conductivities of some powders at temperatures below 100°C obtained through a method adopted agreed well with the values obtained through other methods. And this predicts well for the effective use of this technique for still higher temperatures, up to the melting temperatures of the powders.

## Literature Review

The heat capacities and the thermal conductivities of the material powders at various temperatures during the sintering process have a strong influence to the process of fabrication and the quality of the product, and should certainly be precisely investigated.

1. The Measurement of the Heat Capacities of Powders.

The specific heats of all the powders found are quite the same as those of the corresponding solids. This is because of the mass of the gas phase in the powder relative to that of the solid phase. A Differential scanning calorimeter (DSC) , DSC-7 made by the Perkin-Elmer Company, has been used [1] to measure the heat capacities at various temperatures between 0°C and 100°C for all of the powders used. The heat capacities of the powders were found to be function of temperature. The specific heats of all the powders investigated increase as the testing temperature is raised. This method has been used to measure the heat capacities of four kinds of PVC powders, ABS, two kinds of nylons, a glass supplied by the Potters Industries, two waxes supplied by the BFGoddrich Company and tin [2].

2. The Measurement of Thermal Conductivities of Powders.

For the investigation of the thermal conductivities of solids, especially those of the powders, the following methods are possible to be used, and have been used by some investigators.

(1) Steady-State Methods

(a) Plate (or Disk) Method. C.H. Lees first reported a method in 1908 for measuring the thermal conductivity of a solid by supplying heat at the top of the sample rod at a constant rate Q by an electric heater, and extracting heat at the bottom by the heat sink. The two thermocouples measure the steady-state temperatures $T_1$ and $T_2$. In this arrangement, the thermal conductivity, k, at an average temperature of $\frac{1}{2}(T_1 + T_2)$ is computed from

$$k = \frac{QL}{A(T_1 - T_2)} \qquad (1)$$

For the measurement of the thermal conductivities of poor conductors such as semiconductors, and of powders, the sample is put in the form of a plate or a disk, with the specimen length to width ratio being greatly reduced to a small fraction, because the smaller the length to width ratio, the smaller is the ratio of lateral heat losses to the heat flow through the specimen, and the shorter is the equilibrium time. And the k is also given by the above equation. The rate of heat flow into the specimen may be determined by measuring the power input to a guarded electrical heater [3-5], by measuring the heat flow out of the specimen with a guarded water-flow calorimeter [6] at the low temperature end, by a boil-off calorimeter [7-10] , or by a heat flow meter[11]. (The heater or the calorimeter is guarded by a guard cylinder or ring for the prevention of heat losses.) A double plate apparatus was also used by C.H. Lees in which the heat was generated in a thin plate heater sandwiched between two identical plates of the sample material. Half of the heat then flows out through each plate. Such an apparatus is used for the measurement of the thermal conductivities from 300°K up to 1800°K of poorly conducting solids or powders. For the application of this method, a definite temperature difference must be obtained, which sometimes reaches to 90 Centigrade degrees, and the surface of the higher temperature one is deformed, and the thermal conductivity measured will have less accuracy.

(b) Cylindrical Method. Callendar and Nicolson first reported this cylindrical heat flow method under steady-state conditions [12]. A heater placed along the axis of the cylinder produces a radial flow of heat Q and the temperatures $T_1$ at a radius $r_1$ and $T_2$. at $r_2$ are measured. The thermal conductivity is given by

$$k = \frac{Q \ln(r_2/r_1)}{2\pi L(T_1 - T_2)} \qquad (2)$$

where L is the length of the cylinder. The guard rings at the extremities of the cylinder prevent heat loss out of the ends.

(c) Spherical and Ellipsoidal Methods. The heater is a small sphere embedded in the center of the sample [13] and the thermocouples are at temperatures $T_1$ at a radius $r_1$ and $T_2$. at $r_2$. The thermal conductivity is determined from the following equation.

$$k = \frac{Q\,(r_2-r_1)}{4\pi r_1 r_2(T_1 - T_2)} \qquad (3)$$

Sometimes a prolate ellipsoid method is used instead of the spherical form [14]. The cylinder, sphere, and ellipsoid methods are generally used for determining k of poorly conducting solids at temperatures from 300°K up to 2500°K. The advantage of these methods is supposed to be that heat losses by radiation transfer are small, but this is often offset by difficulty in fabricating the sample forms. The temperature differences used in these methods are all comparatively large, which influence the measurements in their accuracy.

(2) Time-Dependent (Non-steady-State) Methods

(a) Transient Hot Wire Method. The line heat source method was originally developed by Stalhane and Pyk [15]. This method is also now used for the measurements on loose-filled materials such as powders [16]. In this method, a long thin heater wire which serves as a line heat source was embedded in a large specimen initially at uniform temperature. The heater is then turned on, which produces constant heat, $q_l$. $q_l$ is the power per unit length. The temperature at a point in the specimen is recorded as a function of time. The thermal conductivity is given by the expression

$$k = \frac{q_l}{4\pi(T_2 - T_1)} \ln\frac{t_2}{t_1} \qquad (4)$$

where $(T_2 - T_1)$ is the temperature difference at two times $t_1$ and $t_2$.

(b) Thermal Probe Method [17]. This method uses the same principle as the transient hot line method, but is more practical, in which the heat source is enclosed inside a probe for protection and easy insertion into a specimen. The use of this method for testing the thermal conductivities of dry brick powder, dry dune sand, dry cement, mica powder [18], and other powders [19] has been reported.

(c) Transient Hot Strip Method [20]. In this method, a metal foil works both as a continuous plane heat source and a sensor of the temperature changes in the foil itself. The platinum strip is embedded inside the sample material [21]. A constant current is passed through the strip and the voltage increase at the end of the strip is recorded by a digital microvoltmeter. In order to obtain a constant current throughout the experiment, a stabilizing circuit is used. As the constant current passes through the strip, heat is generated and the temperature of the strip is raised. There is a transfer of heat from the strip to the sample material surrounding it. As the strip is thin and it might be assumed that the strip is surrounded by an infinite solid, a solution of the heat transfer equation may be found in the book by Carslaw and Jaeger [22]. The change in the temperature of the strip is dependent on the heat flow between the strip and the surroundings, the thermal conductivity of the sample material, and the time of the passing of the constant current. As the resistivity of the metal strip increases when the temperature of the strip is raised, the electrical resistance of the strip and the voltage difference across the two ends of the strip all increase. So the voltage difference change may be used to show the temperature of the strip at various times from the start of the experiment. From the voltage vs. time curve of the circuit, one may calculate the thermal conductivity of the sample powder surrounding the strip, with known values of temperature coefficient of resistivity (TCR), the geometrical dimensions of the strip, the starting electrical resistance of the strip, the constant electrical current, the bulk density of the sample bed, and the heat capacity of the sample powder.

(d) The Water Baths Method [23, 24]. The thermal conductivities of powders are measured by an unsteady state method with two water baths of small temperature differences. The kinds of powders that have been investigated by this method include polycarbonate powder, four kinds of PVC powders, ABS powder, two kinds of Nylon powders, a purple wax, two kinds of glass powders, tin powder, and nickel powder. The range of the temperatures investigated, limited by the boiling point of water, was mainly from 30-90°C, i.e. below the sintering temperatures of the powders. As the temperatures used during the SLS process are not limited to the ambient temperatures, a new technique must be adopted in the pursuance of the further study for the higher temperatures.

## Experimental Technique

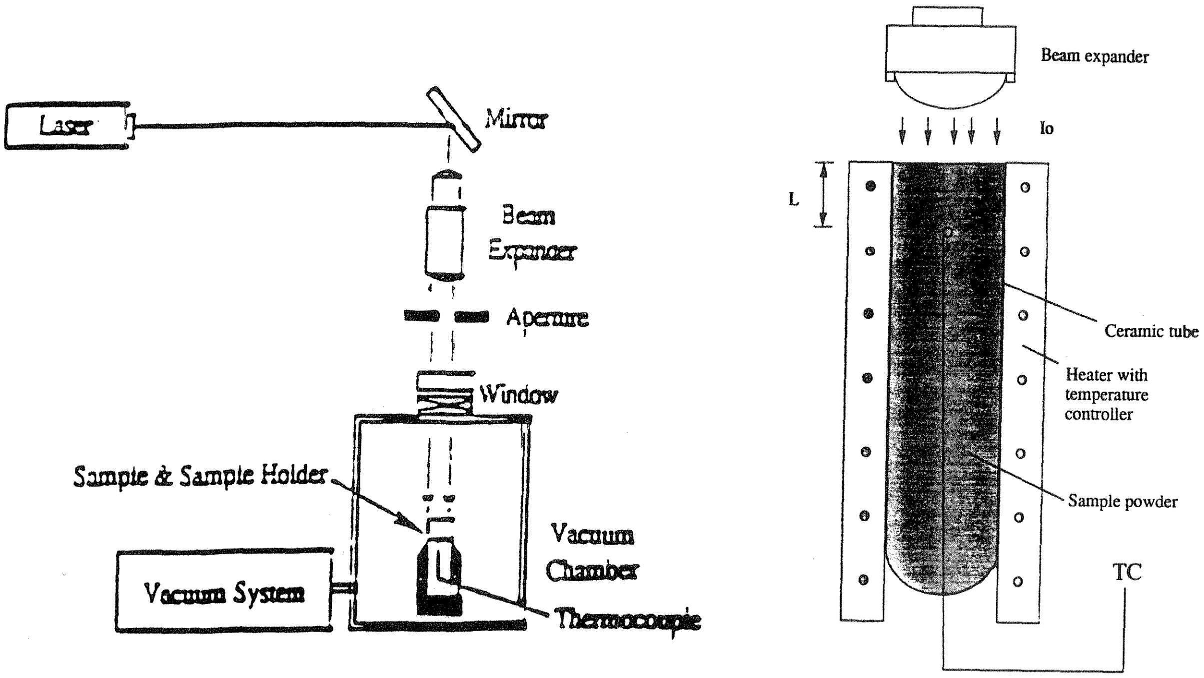
For the measurement of the thermal diffusivities, thermal conductivities, and optical absorptances of the powder materials to be used for the fabrication up to their sintering temperatures, the following setup is used.

The method used here is a transient state one. This is owing to the fact that the steady-state experiments ordinarily use high temperature differences with long time of baking to reach the steady state, which will cause deformation of the powder surface and inaccuracy in the data obtained.

The technique developed by Ikeda et al. using laser as the heat source for the measurement of the thermal properties of the powders to be used is adopted [25]. As laser irradiation is the process used in the SLS fabrication, the use of laser as the heating source for the measurement of the thermal variables is certainly the best one to be chosen.

The experimental setup according to the Japanese workers is shown in Figure 1(a).

The Japanese workers used the finite slab configuration of the sample of theirs. For the convenience of doing experiments with powder samples, we used the semi-infinite bed configuration as shown in Figure 1(b). The principle of the experiment is to consider the heat transfer in the sample a one-dimensional conduction problem as in Figure 2.



(a) (b)

Figure 1. (a) The laser optical/thermal property measurement system; (b) the laser and the powder sample.

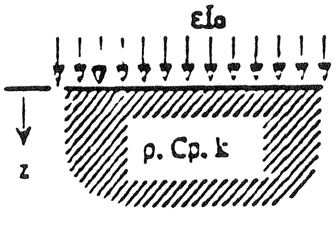


Figure 2. The 1-D conduction in a semi-infinite bed

The solution for this heat transfer problem is given as follows:

$$\Delta T(z,t) = \frac{2\varepsilon I_o}{k}\sqrt{\alpha t}\, ierfc\left[\frac{z}{2\sqrt{\alpha t}}\right] \qquad (5)$$

An example of the temperature rise curve (an explanatory one) is shown in Figure 3 to illustrate the principle for this method of measurement.

By defining the temperature rise ratio R as:

$$R = \frac{\Delta T\,(L,\,2t_1)}{\Delta T(L,t_1)} \qquad (6)$$

and with the Fourier number $Fo = \alpha t_1/L^2$, we may see from Equation (6) and Equation (5) that the relation between R and the Fourier number is independent of the material properties.

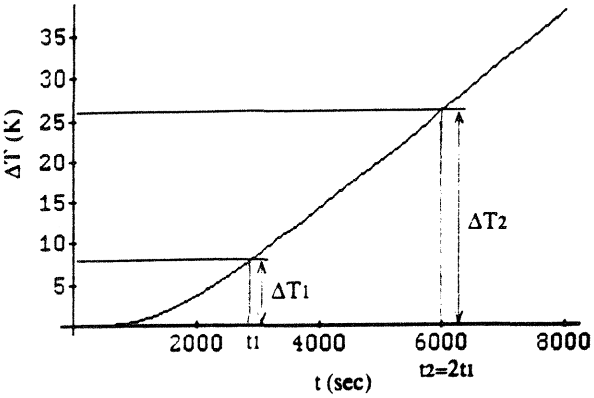


Figure 3. The temperature rise at z = L

The R vs. Fo relation for this case is shown in Figure 4. The curve is just a little lower than that for the finite-slab case.

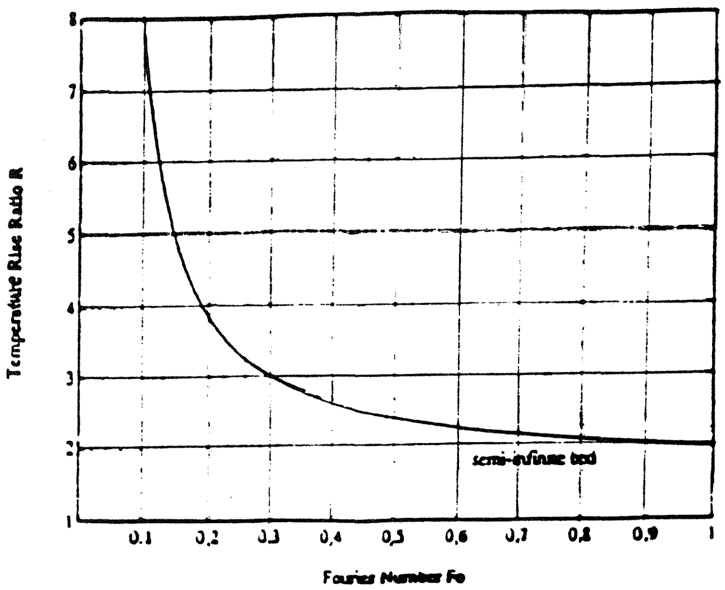


Figure 4. The R vs. Fo relations for semi-infinite bed configurations

When the heat loss to the environment is considered, one is to use the heat loss parameter a. When there is no heat loss, a =0, that will be the case of an experiment done in vacuum and at room temperature. For higher values of a, the R vs. Fo curves are a little lower than the no heat loss one. Their relationship for the finite-slab case is illustrated in Figure 5.

To determine the heat loss parameter a, as a is specific for the equipment, environment and the surface condition of the sample, etc., it is essential to do this by using a sample of which the thermal diffusivity is known beforehand, and if possible, just use a =0 for the case of doing the experiment in vacuum and at room temperature.

The thermal diffusivity of the sample may be found by measuring R from the temperature rise curve of the sample and finding the corresponding Fo value from Figure 4 and the following relationship:

$$\alpha = \frac{FoL^2}{t_1} \qquad (7)$$

The thermal conductivity of the sample may be obtained by the multiplication of the thermal diffusivity α by the bulk density and the heat capacity of the sample powder.

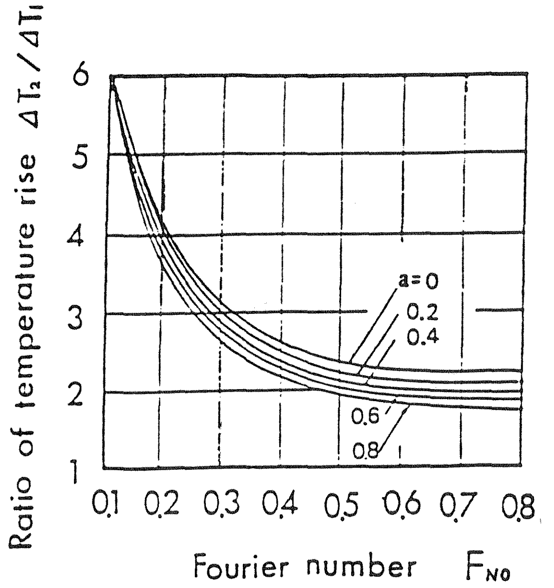


Figure 5. Relationships between the ratio of temperature rise and the Fourier number for various heat loss parameters in the finite-slab case.

For the surface absorptance, ε, one may use the following procedure:

(1) Measure the temperature rise of the sample powder vs. time. (2) Next, use the laser of the same power to irradiate the same sample covered by a thin layer of a material of which the surface absorptance is know beforehand, and measure the temperature rise vs. time curve once again. Owing to the following relationship,

$$Cp = \frac{\varepsilon I_0 A(t_2 - t_1)}{m(\Delta T_2 - \Delta T_1)} = \frac{\varepsilon_k I_0 A(t_2 - t_1)'}{m(\Delta T_2 - \Delta T_1)'} , \qquad (8)$$

one may calculate the surface absorptance of the sample, without knowing the quantity $I_0A$.

## Experimental Results and Analysis

Experiments are carried out using long tubes of powder samples (as shown in Figure 1) and the semi-infinite solution Eqn. (5). Nickel and Tin powders have been tested. A graph of a run of this experiment on nickel powder (porosity: 0.641) is shown in Figure 6.

In this run, the thermocouple was placed 1 cm below the surface of the powder bed. The starting bed temperature (room temperature) was 22°C. Take $t_1$ to be 120 sec; $2t_1 = 240$ sec. It may be found that $R = \frac{(\Delta T)_2}{(\Delta T)_1} = \frac{18}{5} = 3.6$. Fo is found from the graph of the relationship between R and Fo to be 0.23, assuming $a = 0.2$.

$$\alpha = \frac{Fo\,L^2}{t_1} = \frac{0.23 \times 1^2}{120} = 0.00192\,\frac{cm^2}{sec} = 1.92 \times 10^{-7}\frac{m^2}{sec} .$$

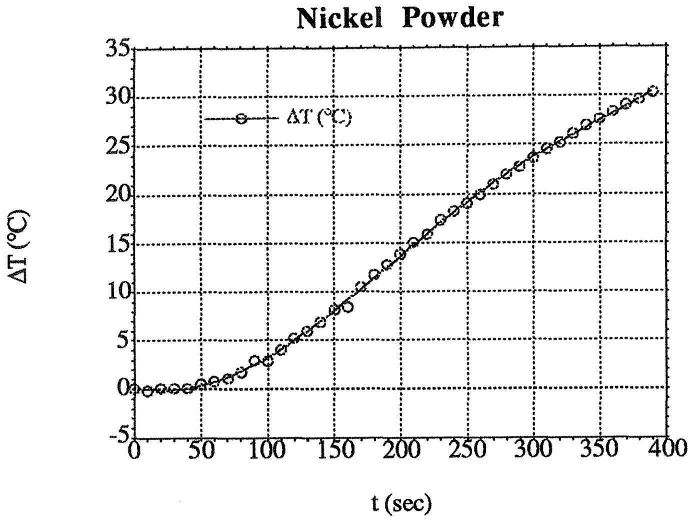


Figure 6. The temperature rise curve of nickel powder

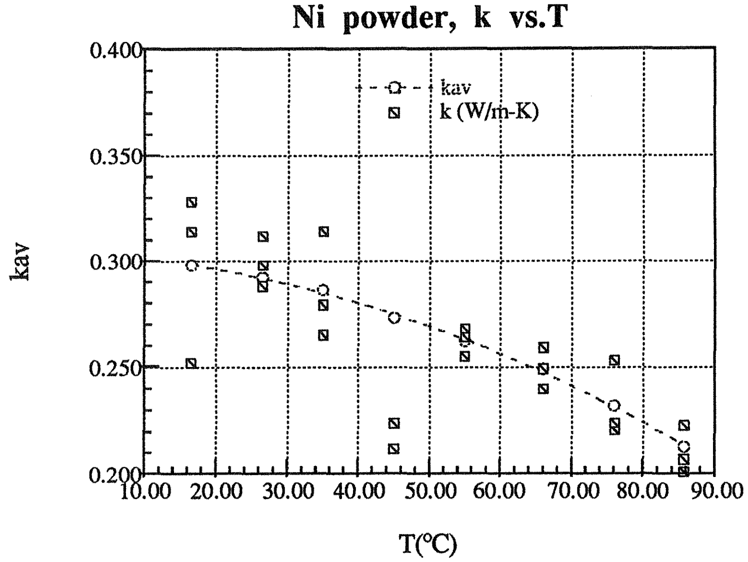


Figure 7. k of nickel powder (porosity:0.612) vs. temperatures graph. (Water baths method)

As $\rho = 3191.5 \frac{\text{kg}}{\text{m}^3}$ which is the bulk density of the powder used, and Cp of nickel is 443.5 $\frac{\text{Joules}}{\text{kg-K}}$, the thermal conductivity of the nickel powder is 0.272 W/m-K.

The k of nickel powder (porosity: 0.612) tested by the water baths method at various temperatures below 100°C are shown in Figure 7.

So the thermal conductivity of nickel powder found by the laser beam irradiation method is consistent with the values obtained by the water-baths method.

A graph of a run of this experiment on tin powder (porosity: 0.355) is shown below in Figure 8.

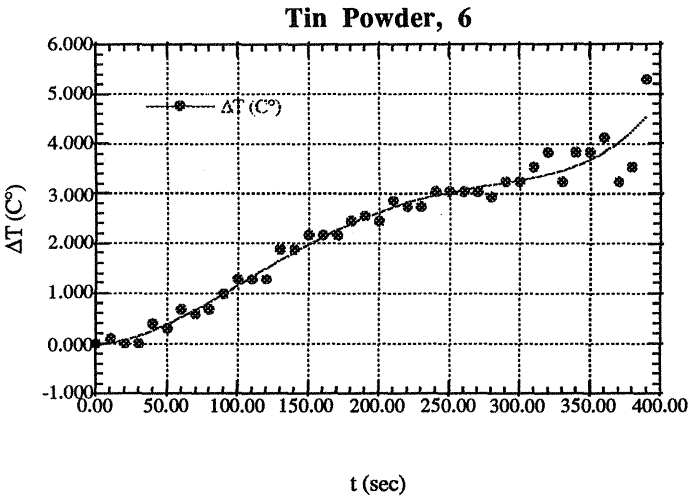


Figure 8. A temperature rise curve of tin powder

In this run, the thermocouple was placed 1 cm below the surface of the powder bed. The starting bed temperature (room temperature) was 25°C. Take $t_1$ to be 100 sec; $2t_1 = 200$ sec. It may be found that $R = \frac{(\Delta T)_2}{(\Delta T)_1} = \frac{2.7}{1.2} = 2.25$. Fo is found from the graph of the relationship between R and Fo to be 0.72, assuming a = 0.2.

$$\alpha = \frac{\text{Fo}\, L^2}{t_1} = \frac{0.72 \times 1^2}{100} = 0.0072 \ \frac{\text{cm}^2}{\text{sec}} = 7.2 \ \times 10^{-7} \frac{\text{m}^2}{\text{sec}}$$

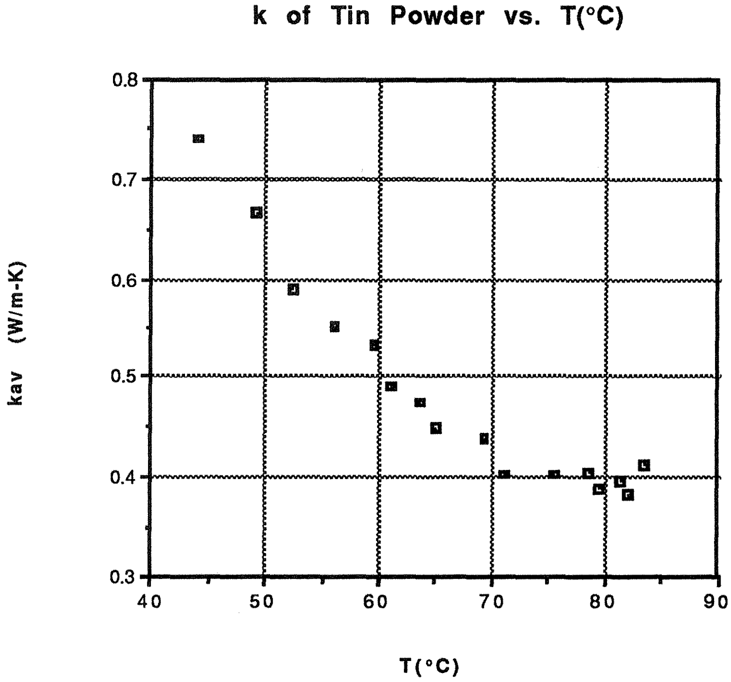


Figure 9. k of tin powder (porosity:0.417) vs. temperatures graph. (Water baths method)

As $\rho = 4704.5 \ \frac{\text{kg}}{\text{m}^3}$ which is the bulk density of the powder used, and Cp of tin is 230 $\frac{\text{Joules}}{\text{kg-K}}$, the thermal conductivity of the tin powder is 0.780 W/m-K.

The k of tin powder (porosity: 0.417) tested by the water baths method at various temperatures below 100°C are shown in the following graph.

So the thermal conductivity of tin powder found by the laser beam irradiation method is again consistent with the values obtained by the water-baths method.

## Conclusion

As the water-baths method used by the authors for the investigation of the thermal properties of powders below 100°C must be changed for the investigation at higher temperatures, the new method adopted by the authors shows near results for thermal conductivity tests of the nickel and tin powder samples below 100°C to those obtained by the water-baths method. And this predicts well for the validity of this method for the investigation of the properties of powders near the sintering temperatures of the powders.

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