# Adaptation of the modified pulse method for determination of thermal diffusivity of solids in the vicinity of the second-order phase transition points

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**Abstract**   The paper presents the adaptation of the modified pulse method for investigating temperature characteristics of thermal diffusivity in the vicinity of the second-order phase transition points. The principle of the adaptation consists in the modified in relation to the original method, development of the characteristics of temperature changes between boundary surfaces of a flat-parallel specimen after the laser shot onto its front surface. The application of this adaptation was illustrated with investigation into thermal diffusivity of nickel (99.9% wt) in the temperature range of 20–380°C. In all cases the measurement error was less than 3%, and the averaging interval for the measured values of thermal diffusivity was not greater than 1.2 K.

**Keywords:** Thermal properties; Flash methods; Thermal diffusivity; Nickel

## Nomenclature

$a$    –   thermal diffusivity, m$^2$/s
$c_p$    –   specific heat ($p = const$), J/kgK

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$E$     –     voltage, V
$g$     –     thickness of the superficial layer of the specimen in which the surface heat source is generated after a laser pulse interaction with the surface of the specimen, m
$k$     –     thermoelectric power, $\mu$V/K
$K$     –     voltage amplification, V/V
$l$     –     thickness of the investigated specimen, m
$Q$     –     average surface energy density supplied to the specimen during interaction of a laser pulse with the surface of the specimen, J/m$^2$
$t$     –     time, s
$t_i$     –     discrete value of time, s
$T$     –     temperature, K, °C
$x$     –     Cartesian coordinate, m

**Greek symbols**

$\delta$     –     relative error
$\rho$     –     density, kg/m$^3$
$\tau$     –     characteristic time, s
$\Delta E$     –     difference of the voltage, V
$\Delta T$     –     difference of the temperature, K
$\Delta t_\tau$     –     time interval within which characteristic time $\tau$ is determined, s
$\Theta(x,t)$     –     temperature surplus of the specimen at distance $x$ from the front surface at moment $t$ in relation to $T_0$ , K
$\Delta\Theta(t)$     –     theoretically determined temperature difference between boundary surfaces of the specimen at moment $t$, K
$\Delta\Theta'(t)$     –     experimentally determined temperature difference between boundary surfaces of the specimen at moment $t$, K

**Subscripts**

$0$     –     reference temperature
$\infty$     –     infinity
$A$     –     alternating voltage
$C$     –     Cuire point
$t$     –     thermocouple
$th$     –     thermoelectric
$1,2$     –     no. of surfaces

# 1   Introduction

In the investigations of thermal diffusivity, $a(T)$, changes in the immediate vicinity of phase transition, as anywhere where that physical quantity undergoes huge changes in a function of temperature, the temperature range of averaging the experimentally determined value, $a(T)|_{T_1}^{T_2}$, is of considerable importance. If the temperature change interval, $\Delta T = T_2 - T_1$, is big,

there is a high probability that during the measurement of thermal diffusivity, $a(T)$ the information about the real character of the changes within $\Delta T$ can be lost owing to the averaging of the results in the function of temperature. Therefore, from the metrological point of view, the temperature change interval should be as small as possible. On the other hand, it should be big enough to grasp the character and values of the temperature change in function of time, on the basis of which the thermal diffusivity value is determined.

In currently most frequently used pulse methods for thermal diffusivity, the interval is usually reported to be $\Delta T =$ 2–15 K [1,4–6], and in the Ångström method [1–3] the interval $\Delta T <$ 5 K. It happens quite often that the publications do not give the value of $\Delta T$ or its value is misinterpreted. This relates mostly to the classical pulse method [4], when it is assumed that $\Delta T = \Theta_\infty$ is a temperature rise on the rear surface of the investigated specimen.

It seems that, considering the potential of the methods for thermal diffusivity of solids in the close vicinity of phase transition points, the adapted and modified pulse method offers the best potential possibilities. The first version of this method has been described in [5–9]. This paper presents adaptation of the primary version of the pulse method for thermal diffusivity determination, which allows significant reduction of $\Delta T$.

## 2 Description of the method

Evaluation of the thermal diffusivity by means of the modified pulse method is based on:

- theoretical determination of temperature distribution inside a non-opaque specimen as well as the temperature difference between its two side surfaces. In this case one dimensional model approximating real heat transfer in the 'specimen-surroundings' system is assumed;

- recording the temperature difference between the front and the rear surface of the specimen, as a result of the one dimensional process of temperature equalization in the specimen;

- identification of the curve, which is the theoretical solution of the problem, best fitting into the results of the experiment. The optimization parameter is the thermal diffusivity. The value of the thermal diffusivity corresponding to the best fitting is taken as the right one.

Boundary conditions in the heat transfer model on which thermal diffusivity is determined in this method are shown in Fig. 1. They are identical with the boundary conditions in the Parker method [4]. Initial condition $\Theta(x, t = 0)$ has a form of a rectangular temperature pulse generated in the near-surface layer of one of the boundary surfaces of the specimen

$$\Theta(x,0) = \left\{ \begin{array}{ll} = Q/(\rho\,c_p g) & \text{for} \quad 0 \le x \le g\,, \\ = 0 & \text{for} \quad g < x \le l\,, \end{array} \right. \tag{1}$$

where $\Theta\,(x,\,0) = T(x,\,0) - T_0$ is the initial temperature distribution of the specimen, $g$ is the effective thickness of the specimen's layer in which the surface heat source is generated with temperature equal to $Q/(\rho\,c_p g)$ due to the absorption of the laser pulse energy with the surface density $Q$, and $l$ is the thickness of the specimen.
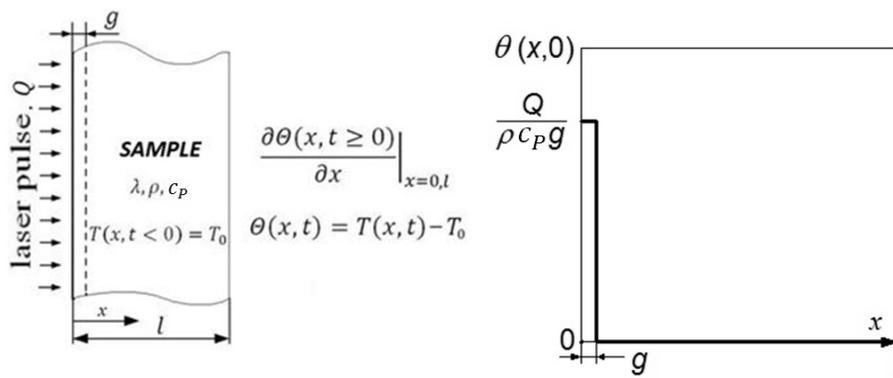


Figure 1. Heat transfer model used for thermal diffusivity of solids determined with the classical and the modified pulse methods.

Carslaw and Jaeger [3] give the general solution of the unsteady heat conduction equation in the one-dimentional and adiabatic specimen with the initial condition $\Theta\,(x,\,0)$ in the following form:

$$\Theta(x,t) = \frac{1}{l} \int_0^l \Theta(x',0)dx' +$$

$$+ \frac{2}{l} \sum_{n=1}^{\infty} \exp\left(-\frac{n^2\pi^2}{l^2}at\right) \cos\frac{n\pi x}{l} \int_0^l \Theta(x',0) \cos\frac{n\pi x'}{l}dx'\,, \tag{2}$$

taking into account (1) and that $g << l$, it can be written as

$$\Theta\,(x,t) = \Theta_\infty \left[ 1 + 2 \sum_{n=1}^{\infty} \cos\,\left(\frac{n\,\pi\,x}{l}\right)\,\exp\,\left(-n^2\frac{t}{\tau}\right) \right]\,, \qquad (3)$$

where $\Theta_\infty = Q/\left(\rho\,c_p l\right)$ is the increase of the specimen temperature after the transient process equalization of the heat transfer inside the adiabatic specimen, and $\tau$ is the characteristic time

$$\tau = \frac{l^2}{\pi^2\,a}\,. \qquad (4)$$

The temperature difference on the boundary surfaces of the investigated specimen $(x = 0$ and $x = l)$, on the basis of (3) is equal to

$$\Delta\Theta(t) = \Theta(0,t) - \Theta(l,t) = 4\Theta_\infty \sum_{n=1}^{\infty} \exp\left[-(2n-1)^2\frac{t}{\tau}\right]\,. \qquad (5)$$

For $n = 1$ it takes the form

$$\Delta\Theta_{n=1}(t) = \left[\Theta_{n=1}(0,t) - \Theta_{n=1}(l,t)\right] = 4\Theta_\infty \exp\left(-\frac{t}{\tau}\right)\,. \qquad (6)$$

Temperature changes on the boundary surfaces of the specimen $\Theta_1(t) = \Theta(0,t)$ and $\Theta_2(t) = \Theta(l,t)$ and their difference $\Delta\Theta(t)$ with the values characteristic of those changes are shown in Fig. 2.

The keynote of the adaptation of the modified pulse method for thermal diffusivity of solids strongly dependent on temperature was the following:

- using for that purpose only part of the change course $\Delta\Theta\,(t)$, given by (5), which is obtained assuming that $n = 1$ (Fig.3). Thus, the basic dependence used in the adaptation of this method for $a\,(T)$ is dependence $\Delta\Theta_{n=1}(t)$, given by (6);

- in the basic version of the modified pulse method, the correctness criterion for the determination of $a\,(T)$ was the minimum value of the sum of discrete values of temperature modules, in the interval of $0.2\tau \leq t_i \leq 3.5\,\tau$ (step by step), between the values – theoretical $\Delta\Theta\,(t_i)$ and experimental $\Delta\Theta'\,(t_i)$. In the adaptation of the method, the correctness criterion for the determination of $a\,(T)$ is the same as in the basic version, but it is used in the narrower interval of $\tau \leq t_i \leq 3.5\,\tau$.
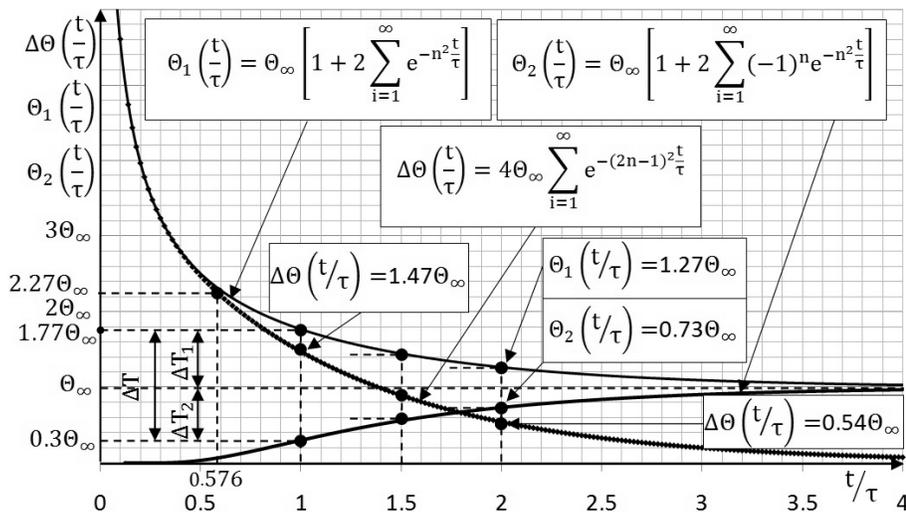
Figure 2. Temperature changes on the boundary surfaces of the investigated specimen and the difference between them with the values characteristic of those changes.

Thus the value $a(T)$ in the fundamental version of the method is defined as the average value of this quantity in the temperature range from $T_0$ to $T_0 + 4\Theta_\infty$, and after the adaptation, and assuming that the lower limit of the averaging range is $\tau$, the averaging range is from $T_0 + 0.3\Theta_\infty$ to $T_0 + 1.77\Theta_\infty$ (Figs.2 and 3). The lower limit of the averaging range for $a(T)$ may be even narrower here.

If the expression (5) is replaced by (6), then the error

$$\delta\left(\frac{t}{\tau}\right) = 1 - \frac{\Delta\Theta_{n=1}(t/\tau)}{\Delta\Theta(t/\tau)} \tag{7}$$

depends on the value of coordinate $t/\tau$, which is shown in Fig. 4. For example, from (7) we can obtain consecutively: for $t/\tau = 0.576$ we have $\delta = 10^{-2}$, for $t/\tau = 1$ we have $\delta = 4 \times 10^{-4}$, and for $t/\tau = 2$ we have $\delta = 10^{-7}$. Temperature changes on the boundary surfaces of the specimen $\Delta\Theta_1(t/\tau) = \Theta_1(t/\tau) - \Theta_\infty$ and $\Delta\Theta_2(t/\tau) = |\Theta_\infty - \Theta_2(t/\tau)|$ as referred to value $\Theta_\infty$ and the difference between them are shown in Fig. 5.

The result of logarithming dependence (6) is the following expression:

$$\ln\left[\Delta\Theta_{n=1}(t)\right] = \ln 4\Theta_\infty - \frac{t}{\tau}, \tag{8}$$
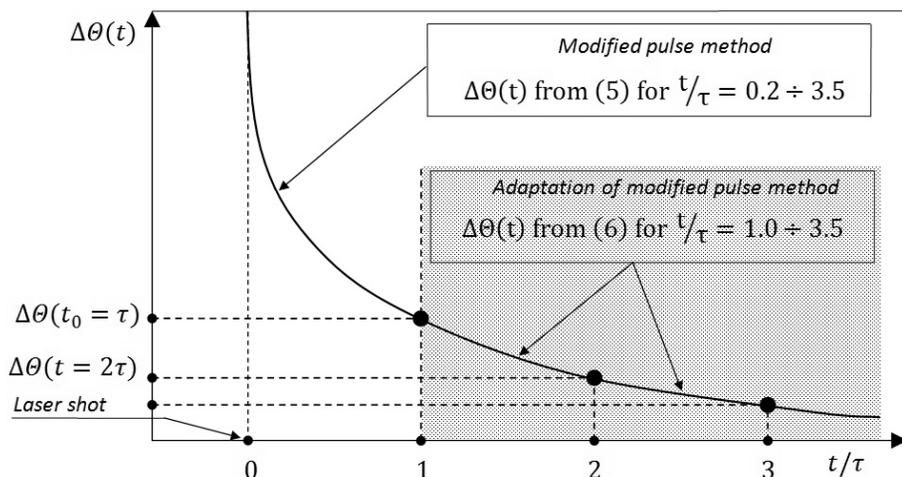
Figure 3. The course of changes of the temperature difference $\Delta\Theta(t)$ between the boundary surfaces of the specimen, used for the determination of thermal diffusivity with the modified pulse method, and the section of this course $\Delta\Theta_{n=1}(t)$ used after the adaptation of the method.
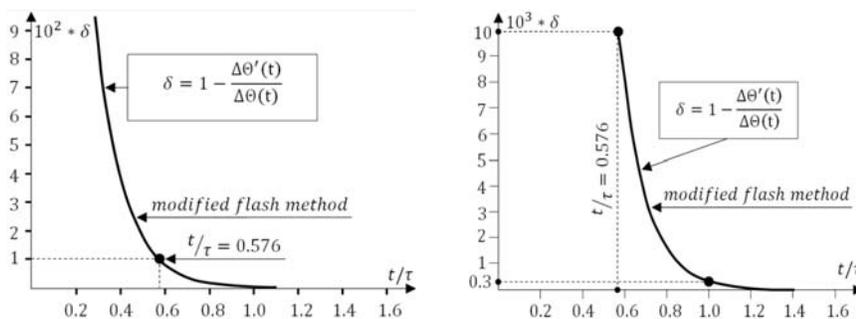


Figure 4. Error $\delta\left(t/\tau\right)$ on account of replacing expression (5) for the change of the temperature difference $\Delta\Theta(t)$ on the boundary surfaces of the specimen with its approximated form (6).

which allows extracting, directly from experimentally determined course $\Delta\Theta'(x, t)$, the corresponding part $\Delta\Theta'_{n=1}(t)$ and determining characteristic time $\tau$. For that purpose, assuming that $t \geq \tau$, on the curve $y = \ln[\Delta\Theta'(t)]$ closed interval $t_1 \geq \tau \leq t \leq t_2 \cong 2\tau$ is selected. In this interval, using the least square method, the equation of the line is determined (8), its directional coefficient $(-\tau^{-1})$ and the value of temperature rise $\Theta_\infty$ of the

specimen after the transitional process has settled. They are equal respectively to

$$\tau = (t_2 - t_1) \left[ \ln \frac{\Delta \Theta'_{n=1}(t_1)}{\Delta \Theta'_{n=1}(t_2)} \right]^{-1} , \qquad (9)$$

and

$$\Theta_\infty = 0.25 \lim_{t \to t_0 = 0} \left[ \Delta \Theta'(t) \right] . \qquad (10)$$

The known thickness of the specimen, $l$, and the experimentally determined value of the characteristic time, $\tau$, allows calculating from (4) the searched value of thermal diffusivity of the material the specimen has been made of

$$a(T) = \frac{l^2}{\pi^2 \tau} . \qquad (11)$$

The choice of the value $t_1$ and $\Delta t_\tau = t_2 - t_1$, from dependence (9), and thereby having a determinative influence on the thermal diffusivity value $a(t)$ determined from (11) should be optimized.

Significant components to include in the optimization process are the following:

- selection of a feasibly large value of $t_1/\tau$ for the purpose of minimizing the error given by dependence (7), and of narrowing the temperature averaging interval $\Delta T = T_2 - T_1$ of thermal diffusivity $a(T)|_{T_1}^{T_2}$;

- measuring signals values $\Delta \Theta(t_1)$ and $\Delta \Theta(t_2)$ were high and the fluctuations related to thermal noise and action of external electromagnetic fields affected them only negligibly. Therefore, value $t/\tau$ should be very small;

- in order to eliminate the effect of the supply voltage on the measurement of $a(T)$, time interval $\Delta t_\tau = t_2 - t_1$, in which $\tau$ was determined (the least square method) was adopted as corresponding to period $T_A = 20$ ms of the mains alternating current (50 Hz), or its multiple.

During the experiment, the temperature averaging interval of the thermal diffusivity value (11), determined on the basis of curve $\Delta \Theta(t)$ can be influenced in two ways:

- by shifting the interval $(t_2 - t_1)$ for determining characteristic time, $\tau$, to the right on the time axis,
- by laser-generated area density $Q$ of the radiation pulse falling on the specimen.
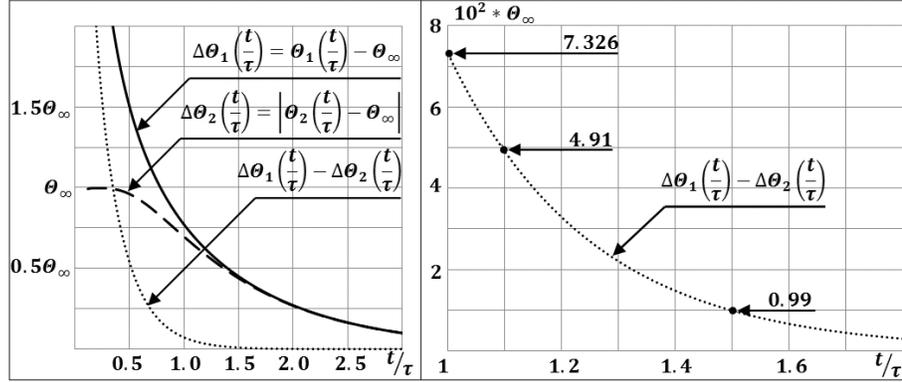
Figure 5. Temperature changes on the boundary surfaces of the specimen $\Delta\Theta_1(t/\tau)$ and $\Delta\Theta_2(t/\tau)$ referred to $\Theta_\infty$, and their difference.

In both cases there are constraints depending on, among others:

- resolving power of the difference signal $\Delta\Theta'(t)$ detection system,
- measuring signal noise levels,
- heat loss from both surfaces of the specimen.

Figures 2 and 5 show the resultant temperature averaging interval of the thermal diffusivity value, $a(T)$, and the time interval for determining characteristic time $\tau$. The temperature range within which thermal diffusivity values are averaged is

$$\left[\bar{T} - \Delta T_2\right] \div \left[\bar{T} + \Delta T_1\right] \,, \tag{12}$$

where $\bar{T} = T_0 + \Theta_\infty$ is the average value of the specimen's temperature after the transition period, and differences $\Delta T_1$, $\Delta T_2$ are equal to $\Delta T_1 = [T_0 + \Theta_1(t)] - \bar{T} = \Theta_1(t) - \Theta_\infty$ and $\Delta T_2 = \bar{T} - [T_0 + \Theta_1(t)] = \Theta_\infty - \Theta_2(t)$, respectively. If possible, $\Delta T = T_1 - T_2 = \Delta T_1 + \Delta T_2$ should be selected with a view to satisfy condition $\Delta T_1 = \Delta T_2 = 0.5\Delta T$ (Figs. 2 and 5). Then

$$\bar{T} \pm 0.5\Delta T = (T_0 + \Theta_\infty) \pm 0.5\Delta T \,. \tag{13}$$

For example, for $t/\tau = 1$, from dependence (3) $T_1 = T_0 + 1.77\Theta_\infty$ and $T_2 = T_0 + 0.3\Theta_\infty$, and the temperature averaging interval of thermal diffusivity is $\Delta T = T_1 - T_2 = 1.47\Theta_\infty$. Because in this case $\Delta T_1 \cong \Delta T_2$ to an accuracy of $\sim 7.3 \times 10^{-2}\Theta_\infty$ (Figs. 2 and 5), then

$$\bar{T} \pm 0.5\Delta T \cong \bar{T} \pm 0.74\Theta_\infty \,.$$

If $t/\tau \geq 1.5$, then $\Delta T = 0.89\Theta_\infty$. Because in this case $\Delta T_1 = \Delta T_2$ to an accuracy of $\sim 10^{-2}\Theta_\infty$ (Fig. 5), then

$$\bar{T} \pm 0.5\Delta T = \bar{T} \pm 0.445\Theta_\infty \ ,$$

and $t/\tau \geq 2.0$ then $\Delta T = 0.54 \times 10^{-2}\Theta_\infty$ and

$$\bar{T} \pm 0.5\Delta T = \bar{T} \pm 0.27\Theta_\infty \ .$$

The average temperature value is $\bar{T} = T_0 + \Theta_\infty$.

Metrological advantage of the modified pulse method and its adaptation lies in the fact that the lower limit $t_1$ of time interval $t_1$–$t_2$, within which characteristic time $\tau$ is determined and the thermal diffusivity, can be shifted towards much smaller values than $t/\tau = 1$. In practice it is assumed that $1 \leq t_1/\tau \leq 2$.

## 3    Experimental verification

The method was verified on a pure nickel (99.9% wt) sample. The temperature range for the thermal diffusivity measurement with the adapted pulse method was assumed to be 20 ºC $\leq T \leq$ 380 ºC, and the sample temperature in the immediate vicinity of the Curie point was adjusted discretely, every $\Delta T \approx 0.5$ K.

Thermal diffusivity results analysis is of significant importance for the presented method. The analysis was conducted following the procedure presented below.

- Thermal diffusivity was determined using Eq. (11). The thickness of the sample, $l$, was measured with a micrometer screw gauge and the characteristic time $\tau$ was determined using the experimentally traced $\Delta\Theta'(t)$ and the Eq. (9). From the metrological point of view, three factors play an instrumental role in determining thermal diffusivity using the modified pulse method: the measurement of the stabilized temperature, $T_0$, of the sample immediately before the laser shot onto its front surface, temperature variations at its edges $\Theta_1(t)$ and $\Theta_2(t)$, and the difference between them, $\Delta\Theta(t) = \Theta_1(t) - \Theta_2(t)$, as the result of the shot.

- The temperature $T_0$, $\Theta_2(t)$ and $\Delta\Theta(t)$ was measured with the use of thermocouples. In the case of $T_0$ and $\Theta_2(t)$ the thermocouple used

was of the Fe-CuNi type. The temperature difference $\Delta\Theta(t)$ at the edge surfaces of the sample was measured using a differential thermocouple made up by connecting in series of two conductors: conductor CuNi – the front face of the sample, and the rear face of the sample – conductor CuNi. The schematic of the measuring procedure is shown in Fig. 6. The measurement of $T_0$ and $\Theta_2(t)$ could be readily performed because the $k(T)$ characteristics of Fe-CuNi thermocouple is known. The characteristics $k_t(T)$ of thermocouple 'CuNi – the material of the investigated sample' is unknown as a rule. It is impossible to determine the values of $a(T)$ averaging the interval $\Delta T$ when the characteristics $k_t(T)$ is not known. Since in both cases the thermoelectric voltage in the assumed temperature change intervals are linear functions of $\Theta_2(t)$ and $\Delta\Theta(t)$, when $E_2(t)$ and $\Delta E(t)$ were measured simultaneously, the problem was solved (Fig. 6). For both cases, once the temperature in the sample stabilized, we obtained

$$\Delta E_{n=1}(t=0) = K\,\Delta E_{n=1,th}(t=0) =$$
$$= K\,k_t\Delta\Theta_{n=1}(t=0) = 4K\,k_t\Theta_\infty \ , \tag{14}$$

$$E_2(t \to \infty) = \ KE_{th,2}(t \to \infty) = K\,k\,\Theta_\infty \ , \tag{15}$$

where $\Delta E_{n+1}(t=0)$ is the is the voltage difference on the opposite surfaces of the sample at $t=0$, $E_2$ is the voltage on the rear surface of the sample, $k$ and $k_t$ denotes the thermoelectric power of thermocouple Fe-CuNi and Cu-Ni, respectively (Fig, 6).
Having disposed $\Theta_\infty$ from expressions (14) and (15), we obtained:

$$k_t = 0.25\ k\frac{\Delta E_{n=1}(t=0)}{E_2(t \to \infty)} \ . \tag{16}$$

During the measurements (Fig.6), signals $E_{th,2}(t)$ and $\Delta E_{th}(t)$ were amplified, and the gain in both cases was $K = 1000$. Sample data and calculation results for $k_t$ of thermocouple 'CuNi – material of the investigated sample' for selected temperatures are shown in Tab. 1.

- To eliminate the impact of the supply voltage on the measurement results, time interval $\Delta t_\tau = t_2 - t_1$ in relationship (9) within which $\tau$ was determined using the least squares method, was assumed to be equal to two periods $\Delta t_\tau = 2\,T_A = 40$ ms of the alternating voltage (50 Hz). The procedure was as follows:

$$\Delta E_{th}(t) = k_t \Delta \Theta(t) =$$

$$= k_t[\Theta(0,l) - \Theta(l,t)] =$$

$$= k_t[\Theta_1(t) - \Theta_2(t)]$$

$$E_{th,2}(t) = k\Theta(l,t) = k\Theta_2(t)$$
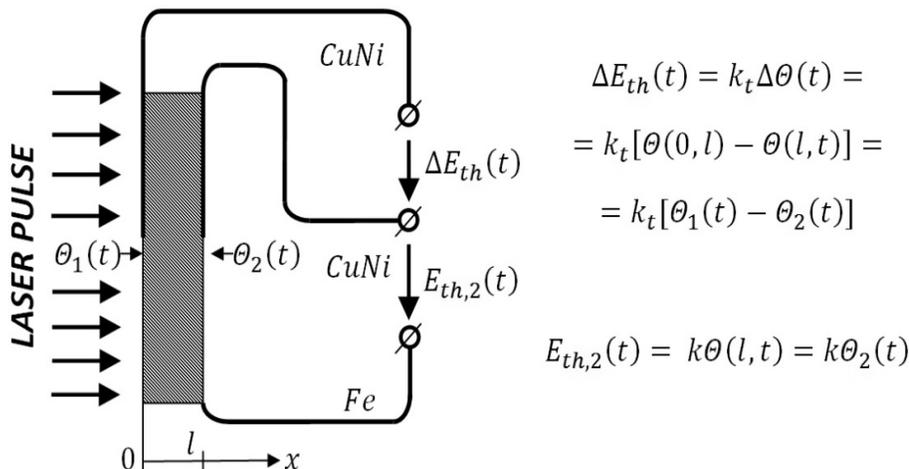
Figure 6. Principle of the sample temperature measurement, $\Theta_2(t)$, and the difference of the temperature $\Delta\Theta(t)$ between the extreme surfaces of the sample: $k_t$ – the thermoelectric power of the thermocouple 'CuNi - the material of the investigated sample'; $k$ – the known thermoelectric power of the thermocouple 'Fe–CuNi'.

Table 1. Data and calculation results of $k_t$ of 'CuNi–Ni' for selected temperature values.

| $T$ [°C] | $K$ [V/V] | $k$ [$\mu$ V/K] | $E_{2,\infty}$ [$\mu$V] | $\ln K\Delta E_{n=1}(t=0)$ | $\Delta E_{n=1}(t=0)$ [$\mu$V] | $k_t$ [$\mu$V/K] |
|---|---|---|---|---|---|---|
| 360.3 | 1000 | 55 | 38.0 | $-2.4$ | 95.0 | 34.4 |
| 373.2 | 1000 | 55 | 41.0 | $-2.2$ | 95.0 | 31.9 |

- on the basis of $\Delta\Theta'(t)$, the mean value of the characteristic time, $\overline{\tau}$, was predetermined using the modified pulse method;

- then, having assumed that $\Delta t_\tau = 2T_A = 40$ ms and for the same run $\Delta\Theta'(t)$, from relationship (9) the local change of $\tau(t)$ as a function of time was determined, starting from $t = t_1 = 0.58\overline{\tau}$ through $t = t_1 = 2\overline{\tau} - 40$ ms (Fig. 7);

- the criterion for the correctness of eliminating the mains hum from signal $\Delta E'_R(t)$ is the constant function $\tau(t = t_1) = idem$ within the interval $\overline{\tau} \leq t = t_1 \leq 2\overline{\tau} - 40$ ms. The use of the procedure described above was illustrated by determining the value of $\tau(t = t_1)$ for two selected temperature values (Fig. 8).
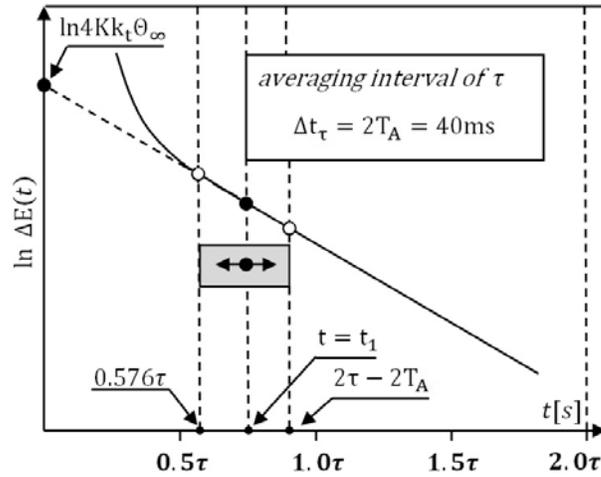
Figure 7. Method for determining the changes of the mean characteristic time $\tau(t_1)$ in the interval $(t_2 - t_1) = 40$ ms.
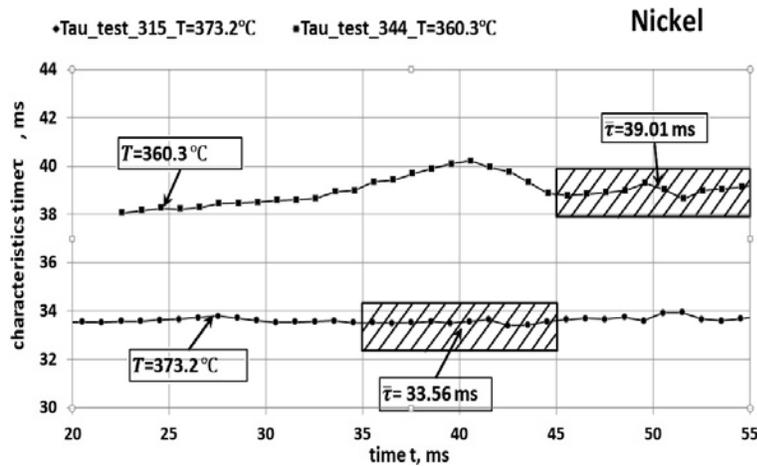


Figure 8. Method for determining characteristic time, $\tau$, for two temperature values $T = 360.3\ °C > T_C$ and $T = 373.2\ °C > T_C$, and when $\Delta t_\tau = 40$ ms.

For $T = 360.3\,°$C and $\Delta t_\tau = 40$  ms, the maximum of function $\tau(t)$ seems to be connected directly with the temperature change from $T_0$ to $T_{1,\max}$ of $Q/\rho c_p c$ in the near-surface layer of the sample (Fig. 9) following the laser shot onto that surface. In consequence, the value of the thermal diffusivity of this layer changes discretely until $a(T = T_{1,\max})$. From that

point, as a result of heat conduction through the sample, its temperature decreases together with its thermal diffusivity until value $a(T_1 = T_0 + \Theta_\infty)$ is reached. Temperature $T_1 = T_0 + \Theta_\infty$ corresponds to the stabilized heat transfer state in the sample $(0 \to 1 \to 2)$. When the temperature of the front face of the sample changes from $(0 \to 1 \to 2)$, at the rear surface at the same time the temperature changes form $(0 \to 2)$, i.e., in the range $T_0$–$T_0 + \Theta_\infty$. This range notes much smaller change of $a(T)$. Additionally, we have to remember that the higher the decrease in the value of $a(T)$, the more intense reduction in transient heat transfer. As $a(T)$ is strongly dependent on temperature in the material of the sample, the distribution of temperature difference $\Delta\Theta_{n=1}(t) = 4\Theta_\infty \exp(-t/\tau)$ decreases for the boundary value of $t = t_1 \geq 0.576\tau$ and may be disturbed at large temperature differences between the sample's extreme surfaces. But if it is possible to dislocate the averaging interval $\Delta t_\tau$ on the time axis far beyond this boundary value, then it is possible to eliminate the influence of that disturbance on the measurement result of $a(T)$. A horizontal segment of the characteristics of $\tau(t)$ should be obtained, as given by the results in Fig. 8. For $T = 373.2\,°$C (cooling) and $\Delta t_\tau = 40$ ms, the procedure is similar to that for $T = 360.3\,°$C. But considering that the steeper the slope of characteristics $a(T)$, the more intense the process of transient heat transfer in the investigate sample, and concluding from the run of the characteristics $\tau(t = t_1)$ (Fig. 9) that in the material the sample is made of the dependence of $a(T)$ on temperature is poor, it follows that even at a large temperature difference between the extreme surfaces of the sample, the process of decrease in the temperature difference $\Delta\Theta_{n=1}(t) = 4\Theta_\infty \exp(-t/\tau)$ above the boundary value of $t \geq 0.576\tau$ may by subject to only a slight disturbance.

Examples of the results of the study of thermal diffusivity of Ni (99.9% wt) for the same two temperature values are shown in Figs. 10 and 11. The summary of the thermal diffusivity results for Ni (99.9% wt) obtained using the modified pulse method during the cooling of the sample together with their analytical approximation are shown in Fig. 12. Figure 13 presents the results of own studies of thermal diffusivity of Ni (99.9% wt) with the source data [10,11].

Discrete values of $a(T)$, from CINDAS database [10] were determined using the Ångström method. The relationship $a(T) = \lambda(T)[\rho(T)c_p(T)]^{-1}$ together with data from the database [11] helped to create another characteristics of $a(T)$. The temperature of phase transition $T_C$ (Curie point) of nickel has different values depending on the data sources. In our case
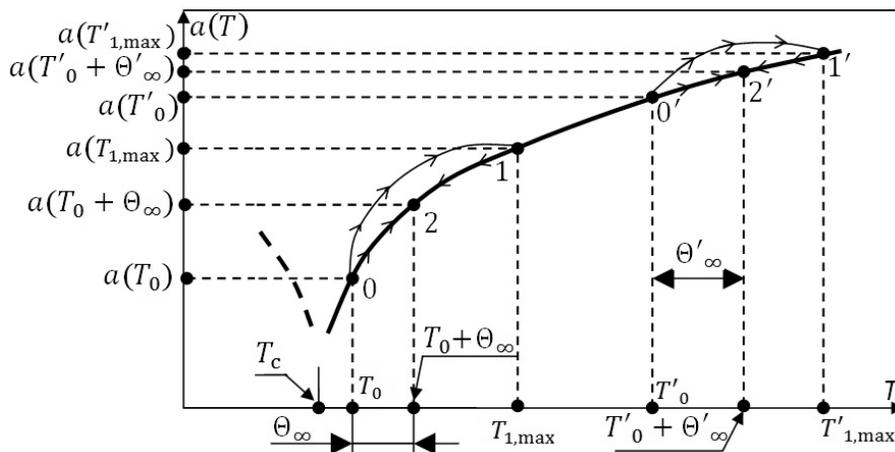
Figure 9. Relative positions of $T_0$, and $\Theta_\infty$, $T'_0$, $T_C$ and $\Theta'_\infty$, and the corresponding values of $a(T)$.
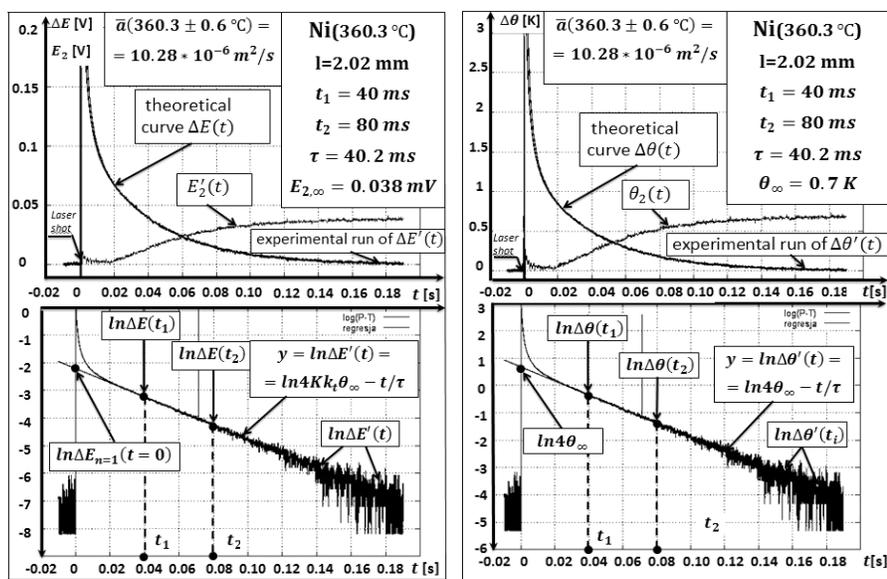


Figure 10. Thermal diffusivity results for Ni (99.9% wt) at the temperature of $T = 360.3\ ^\circ$C, and runs of the temperature changes $\Theta_2(t)$ and $\Delta\Theta(t)$.

the temperature of phase transition was estimated to be equal to $T_C \cong 359.8\,^\circ$C ($\cong 632$ K).
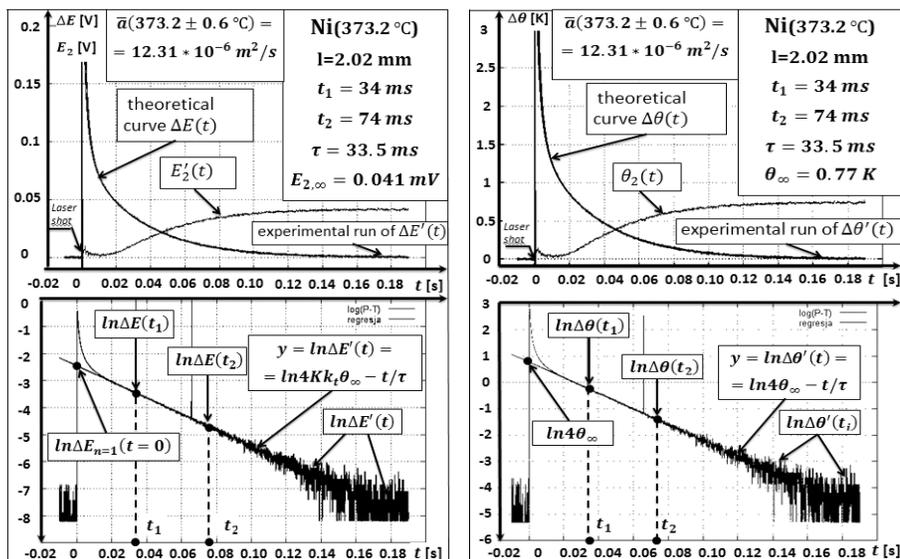
Figure 11. Thermal diffusivity results for Ni (99.9% wt) at the temperature of $T = 373.2$ °C, and runs of the temperature changes $\Theta_2(t)$ and $\Delta\Theta(t)$.
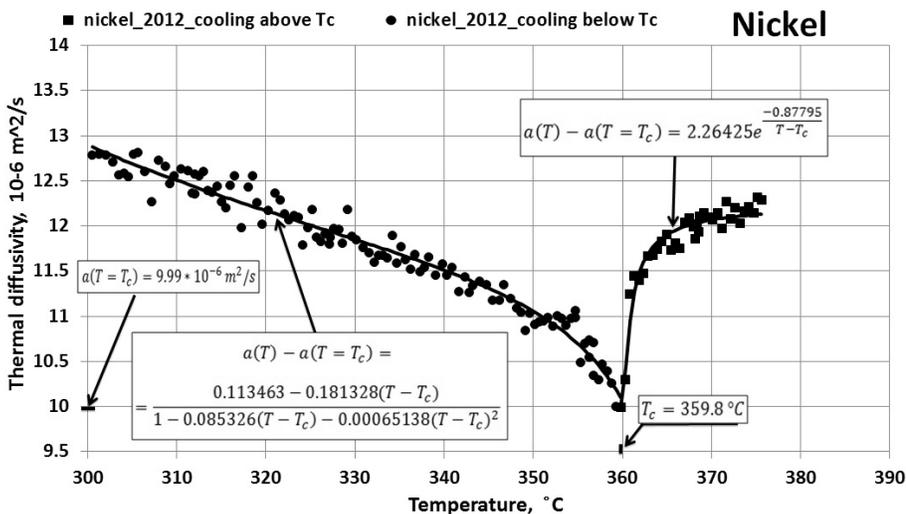


Figure 12. Thermal diffusivity results for Ni (99.9% wt) obtained using the modified pulse method during the heating and cooling of the sample for $\Delta t_\tau = t_2 - t_1 = 40$ ms.
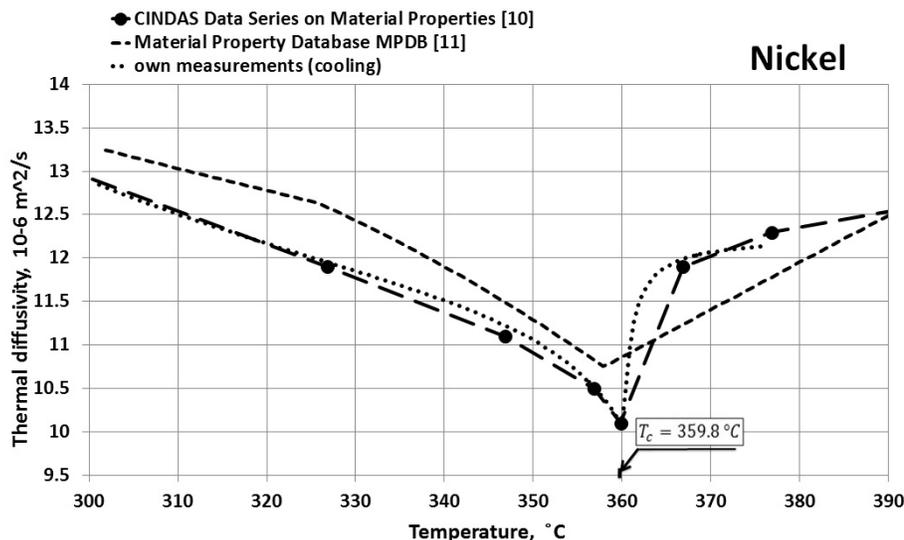
Figure 13. Thermal diffusivity results for Ni with the phase transition taken into account.

The error made while measuring thermal diffusivity using the modified pulse method was estimated on the basis of relationship (11) and is

$$\left| \frac{\Delta a}{a} \right| = 2 \left| \frac{\Delta l}{l} \right| + \left| \frac{\Delta \tau}{\tau} \right| , \qquad (17)$$

where $\Delta l$ is the sample thickness measurement error, and $\Delta \tau$ is the characteristic time measurement error.

In relationship (17), $|\Delta \tau / \tau|$ is the sum of errors

$$\left| \frac{\Delta \tau}{\tau} \right| = \left| \frac{\Delta \tau'}{\tau} \right| + \left| \frac{\Delta \tau_l}{\tau} \right| , \qquad (18)$$

where $\Delta \tau'$ is the the mean square error of determining characteristic time $\tau'$ in the time interval $t_1 - t_2$, and $\Delta \tau_l$ is the error of determining the characteristic time $\tau$ connected with the heat loss from both faces of the sample.

The total error made while measuring thermal diffusivity using the modified pulse method, calculated from relationship (11), was estimated to be less than 3%. The sample thickness measurement error depends on the thickness of the sample and was estimated to be equal to $2 \left| \Delta l / l \right| \cong 0.99 \times 10^{-2}$, where $l = 2.02$ mm and $\Delta l = 10^{-2}$mm. The error component $|\Delta \tau / \tau|$ made when the characteristic time, $\tau$, is measured is defined as a sum of

- component $|\Delta\tau'/\tau|$, related to the fluctuations of the signal in the time interval $t_1$–$t_2$. It is determined through numerical processing of signal $\Delta\Theta'(t)$, recorded in the memory of the data acquisition and processing system. This error was always less than $|\Delta\tau'/\tau| \leq 0.25{\times}10^{-2}$;

- and the other error component $|\Delta\tau_l/\tau|$ for determining the characteristic time, $\tau$, made because of heat loss from both surfaces of the sample. On the basis of [12] it was estimated to be less than $10^{-2}$.

## 4   Summary and conclusions

The paper presents the adaptation of the modified pulse method to investigations of thermal diffusivity of solids characterized by large changes of that parameter as a function of time, and especially in the immediate vicinity of the Curie points. The method was tested on a pure nickel (99.9% wt) sample. The adaptation has a number of advantages, including:

- accurate determination and narrowing of the temperature averaging range of thermal diffusivity $\bar{a}(T) = a(T)|_{T1}^{T2}$ calculated using this method in relation to the methods used so far. The tests conducted on the nickel sample proved that narrowing the interval to $\Delta T = T_2 - T_1 \leq 1$ K is feasible;

- making the measurement result of $\bar{a}(T) = a(T)|_{T1}^{T2}$ independent from the initial phase of temperature changes at the edges of the sample. The initial phase of temperature changes at the front face, if its diffusivity depends strongly on temperature, has a significant effect on the half-time $t_{0.5}$, and on the value of this quantity determined using the classical method (the Parker method [4]) from the relationship $a = 1.368\ l^2(\pi^2 t_{0.5})^{-1}$, where half-time $t_{0.5}$ corresponds to increase of temperature value to $0.5_{infty}$);

- simultaneously recording signals $E_2(t)$ and $\Delta E(t)$, proportional to the temperature changes at the rear face of the sample $\Theta_2(t)$ and the temperature difference at its edges $\Delta\Theta(t)$ plus the known value of $k_{Fe-CuNi}$ allowed determining ordinarily unknown factor $k_{CuNi-sample}$ of the thermocouple 'CuNi – the material of the investigated sample'. The known value of $k_{CuNi-sample}$ allows determining the course of temperature changes $\Theta_1(t)$ and $\Delta\Theta(t)$.

Obtained characteristics of $\bar{a}(T) = a(T)\big|_{T1}^{T2}$ in the immediate vicinity of the Curie point indicated that the largest changes in $\bar{a}(T)$ occurred while the sample was cooled, just before the minimum value of $\bar{a}(T)$ was reached. The temperature change of 1 K caused 12% change of $\bar{a}(T)$. It was noted that the values and character of the discrete changes of the results for $\bar{a}(T_i)$ of nickel in the CINDAS database [10] are, with the accuracy to 2%, in agreement with the determined based on the own studies results (Figs.12 and 13) characteristics of $\bar{a}(T)$. In the case of MPDB database [11], the differences are large and amount to max. $\pm 8\%$.

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