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Effect of the addition of microencapsulated phase change material to epoxy resin on the thermal diffusivity of the resulting structure

Łukasz Omen[1*], Andrzej J. Panas[1,2], Przemysław Wajdzik[1], Robert Szczepaniak[3]

[1] Faculty of Mechatronics, Armament and Aerospace, Military University of Technology, ul. Gen. Sylwestra Kaliskiego 2, 00-908 Warszawa, Poland
[2] Air Force Institute of Technology, ul. Księcia Bolesława 6, 01-494 Warszawa, Poland
[3] Polish Air Force University, Faculty of Aviation, ul. Dywizjonu 303 no 35, 08-521 Dęblin, Poland
* Corresponding author's e-mail: lukasz.omen@wat.edu.pl

ABSTRACT

This work concerns the study of the effect of adding microgranules containing a phase change material (PCM) on the thermal diffusivity value of the resulting composite structure. Two commercially available epoxy resins were applied as the composite matrix material: pure epoxy resin and epoxy resin with a filler in the form of metal powder. The dispersed phase was the BASF Micronal DS5038 X microgranulate, i.e. a bed of polymer spherical shells containing PCM filling. The tests were carried out using the modified Ångström method in a symmetrical bilateral harmonic excitation of the temperature of outer sides of assembled two tested disc-shaped samples. The temperature range of measurements covered the interval from 273.15 K to 308.15 K, i.e. most of the typical working range of microgranules. In selected measurement cases, the tests were extended to temperatures from 263.15 K to 348.15 K. The results obtained for the four structures studied were compared and analyzed to illustrate the quantitative effects of structure modification and to document the qualitative effects of the observed phase changes that occurred both on heating and cooling.

Keywords: epoxy composites, dispersed composites structures, thermal diffusivity, temperature oscillation method, phase change material filling.

INTRODUCTION

Composite materials and structures are used in a wide variety of technical and industrial applications [1, 2]. A particular groups of composite materials and structures are those characterized by the occurrence of a phase transition of the first kind [3] with the reaching of the temperature threshold of the phase transition. This phase change and the associated thermal effects enable them to be used in a variety of thermal energy storage systems (e.g. passive cooling systems for electrical/electronic systems [4], in the construction industry to increase the thermal capacity of building bulkheads [5, 6, 7] or as a thermal shock protection material [8]). A useful structure, characterized by low production costs and good heat accumulation properties (e.g. a relatively high value for the latent heat of the solid-liquid transition), are microcapsules containing phase change material (PCM) [9, 10]. The widespread use of microcapsules translates into a significant number of papers devoted to the study of material structures doped with PCM microcapsules. The relevant literature also contains results of selected thermophysical properties of structures with spherical PCM inclusions. The authors of the articles focus their attention especially on the study of specific heat at constant pressure [11, 12, 13]. The leading research method is the differential scanning calorimetry [14]. The results of the studies of specific heat are typical for phase transition

materials of the first type [15]. However, there is a lack of work that presents high-resolution thermal diffusivity results including the phase transition region. In this context, the work attempts to add to the state of the art. In addition to the work, inspired by the results published in [16], it was also decided to check the effect of another additive, metallic microparticles - on the possibility of shaping thermal diffusivity values.

It is natural to take this course of action because as applications for phase-change materials structures increase, so do the material requirements for their physical and chemical properties. Among these, thermophysical properties occupy an important place. The thermophysical parameter that combines the above-mentioned quantities is thermal diffusivity. This is because it expresses the ratio of heat transport properties to heat accumulation properties. In the context of materials research, the analysis of thermal diffusivity values allows the influence of modifiers introduced into existing structures to form their functional properties to be identified. Such analyses require the use of transient methods [17, 18] typically used in thermal diffusivity studies. Among the wide range of methods and techniques for measuring thermal diffusivity, the temperature oscillation method deserves attention [19, 20]. This is because it is characterized by a high temperature resolution of measurement compared to other test methods [21, 22].

MEASUREMENT METHOD AND PROCEDURES

Thermal diffusivity tests were performed using a modified temperature oscillation method [21, 22]. Compared to the original method [19], the solution is sought in a flat, infinite plate of thickness l [20, 21]. Measurements are conducted at a regular heating regime of the 2nd and 3rd kind [18, 21, 23]. The reader will find a detailed description of the method in [19–22]. In the measurement system of two symmetrically assembled samples (Fig. 1), the temperature response signal in the symmetry plane (point 2 in Fig.) is compared with the signal of harmonic temperature changes excitation on the external surfaces (points 1 and/or 3 in Fig. 1). The comparison results in determining the amplitude reduction

$$\psi(x) = \sqrt{\frac{\cosh 2kx + \cos 2kx}{\sinh\ 2kl + \cos 2kl}} \tag{1}$$

where: ψ – amplitude reduction (-); k – temperature wave coefficient (m^{-1}); l – thickness (m); x – linear coordinate (m); t – temperature (K).

And phase shift of the response signal

$$\varphi(x) = \arg\left[\frac{\cosh kx(1+i)}{\cosh kl(1+i)}\right] \tag{2}$$

where:

$$k = \sqrt{\frac{\pi f}{a}} = \sqrt{\frac{\pi}{a\tau_\Omega}} \tag{3}$$

where: φ – phase shift (-), x is the spatial coordinate of the temperature reading of the thermal response along the model object and f is the frequency of temperature oscillation [21, 24].

By solving the nonlinear Equation 1 taking into account (3) one can obtain the so-called amplitude value of the sought thermal diffusivity a_ψ. The phase value of thermal diffusivity a_φ can be obtained by solving the nonlinear Equation 2 taking into account (3). If the model requirements are met, both values should be equal. Any differences can be used to determine the measurement error. As a rule, the upper limit for the sought diffusivity value is the phase value, and the lower limit is the amplitude value.

EXPERIMENTAL STUDIES

Research stand

The diffusivity tests were performed on a test bench consisting of a PC controller, a National Instruments SCXI data acquisition system, a Lauda RL 6CP low-temperature thermostat, and

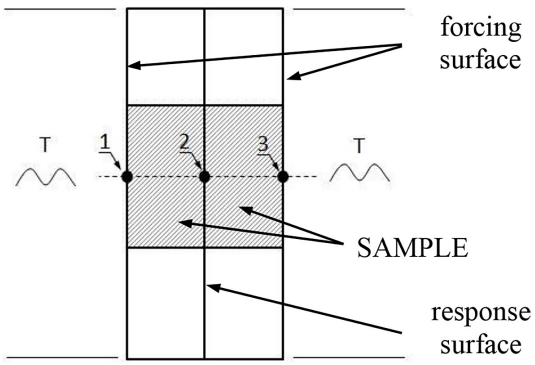

Figure 1. Diagram of a thermal forcing: 1, 3 – points of the forcing signal, 2 – points of the response signal

an Amrel PPS 1322 power supply supplying two Peltier elements. A set of K-type thermocouples with a diameter of 0.05 mm was used to measure the temperature. A more detailed characterization of the system is presented in [21], while the system configuration is shown in [24] and [25].

Sample preparation

Four types of composite samples were tested. The base component (matrix material) was Diall's pure epoxy resin and mishmash of Diall's epoxy resin and metallic powder. Sample A was made from a base component of pure epoxy resin. Sample B was made from a metal powder epoxy resin base. Sample C was made as a mixture of pure resin with microcapsules filled with phase-change material in polymer coatings under the trade name Micronal DS5038X [26]. The fourth sample D was made as a mixture of resin with metallic powder and Micronal DS5038X microcapsules. For the production of samples C and D, the same amount of mixture components by weight was measured. It is worth noting that the material of sample B and the material component of sample D is a manufacturer's commercial product with unknown characteristics of the metallic powder used. At this stage of the research, it was decided to abandon attempts to precisely determine the type of additive and only referred to the information about the expected higher thermal conductivity of the material. It can be assumed with great probability that the additive is aluminum alloy powder.

The specifics of the research required that the matrix material used to produce the samples be prepared within a single batch of production. Only then was it possible to investigate the influence of the addition of metallic powder and microcapsules with phase change material on the thermal diffusivity of the final product. Due to the nature of the measurements carried out, samples were made in pairs as bipartite samples. The samples were prepared in silicone moulds. After filling moulds the samples were left to solidify for a period of 24 hours. The finished bipartite (L and R parts) samples are presented in Fig. 2. The basic parameters of the samples are presented in Table 1.

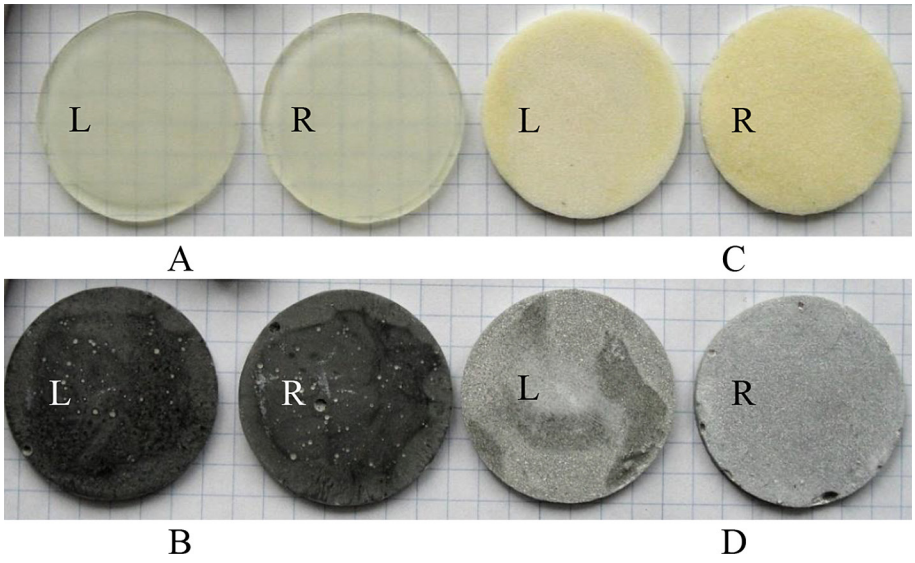

Figure 2. Photographs of bipartite samples: epoxy resin (A), epoxy resin with metallic powder (B), epoxy resin and Micronal microgranulate (C) and epoxy resin with metallic powder and Micronal microgranulate (D)

Table 1. Basic parameters of the tested samples

Sample	Density ρ [g·cm^{-3}]	Thickness/ [mm]	
		Sample L	Sample R
A	1.0527	2.24	2.27
B	1.0634	2.18	2.14
C	0.7204	2.20	2.20
D	0.8003	2.00	2.10

RESULTS

As a direct result of the measurement recordings of temperature changes over time were collected. Crucial ones are forcing temperature oscillation (Fig. 1, points 1 and 3) and temperature response (Fig. 1, point 2). The measurement data was usually collected at frequency 1 Hz or 4 Hz. Example recordings of temperature change signals for the case of testing sample A in Figure 3. Raw data processing is performed in two stages. In the first stage, the oscillation parameters are determined: amplitude, phase, mean oscillation level and its rate of change (linear trend). Nonlinear approximation is used using the Levenberg-Marquart procedure. Then, after calculating the relative amplitude changes and determining the phase delay, the appropriate system of nonlinear equations is solved. As mentioned before processing of the acquired data lead to two values of thermal diffusivity: amplitude a_ψ and phase a_φ. For the present study, the direct result of the study is the effective thermal diffusivity value in the form of geometric mean of the amplitude and the phase value.

Typically, measurements are performed both while cooling the set of test samples, as is the case with the data in Figure 3, and while heating them. Typical results of the thermal diffusivity tests currently discussed are presented in Figures 4 and 5. In both cases, the heating and cooling results are presented superimposed to illustrate repeatability. Small differences can

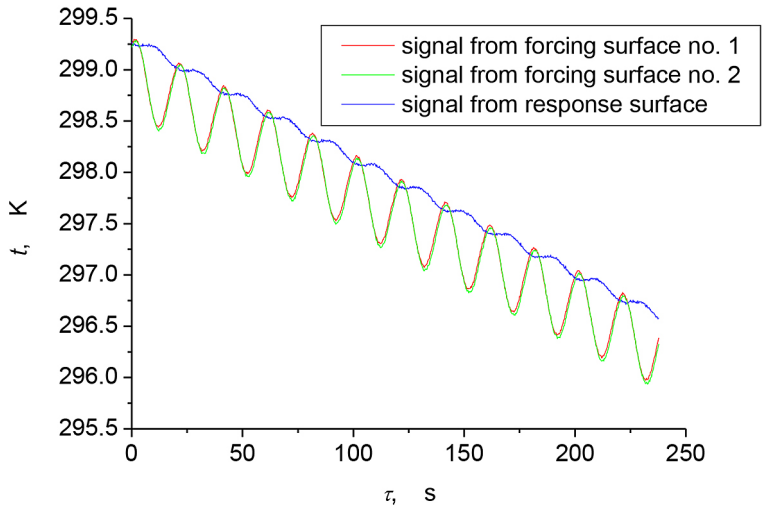

Figure 3. Fragment of the measurement signals recorded during the sample A study. The temperature forcing signals are: (period of oscillation (s)) $\tau_\Omega = 20$ s, (excitation amplitude (K)) $A_w < 0.5$ K, the temperature response amplitude (response amplitude (K)) $A_r < 0.05$ K

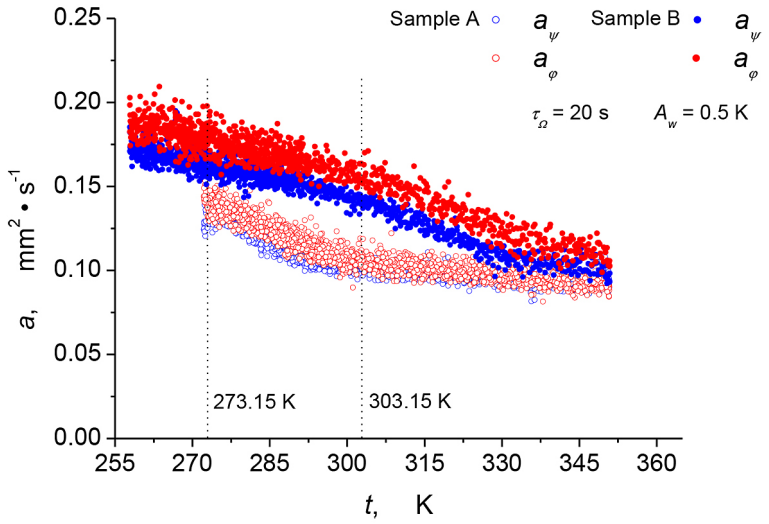

Figure 4. Thermal diffusivity test results for samples A and B; $\tau_\Omega = 20$ s, $A_w = 0.5$ K

be noticed only for the phase change around 268.15 K for the tests of samples containing granules with PCM material (Fig. 5). The PCM phase solidification transition peak is shifted slightly towards a lower temperature compared to the melting peak. It is also characteristic that in the low-temperature transition the peaks of the amplitude data (down) and phase data (up) are opposite, unlike in the main transition with a peak around 297.15 K.

As for general trends the analysis of the obtained results reveals a decrease in amplitude and phase values of diffusivity with increasing temperature. This is an expected and typical effect for most polymeric materials. In addition, a typical dependence of the phase values over the amplitude values was observed for all samples tested.

A detailed analysis of the results obtained for samples A and B shows the qualitatively different nature of the course of the calculated thermal diffusivity values as a function of temperature. Furthermore, the results document an excess of the a_ψ (thermal diffusivity calculated from the amplitude reduction ($m^2 \cdot s^{-1}$)) and a_φ (thermal diffusivity calculated from the phase shift ($m^2 \cdot s^{-1}$)) values for sample B relative to the results obtained for sample A in the temperature range from 273.15 K to 353.15 K. A maximum percentage excess of both the amplitude and phase thermal diffusivity values of 30% was recorded for a temperature of about 303.15 K. The explanation for the observed effect is the influence of the addition of metallic powder as a dispersion filler used in sample B.

An in-depth analysis of the results presented in Figure 5 documents the lack of significant quantitative changes due to the presence of metallic powder within the epoxy resin matrix and Micronal microcapsules (changes within individual samples do not exceed 10%). However, more importantly, the addition of Micronal microcapsules became apparent in the temperature courses of changes in the thermal diffusivity values of samples C and D in the form of a reciprocal divergence of a_ψ and a_φ values for a temperature of approximately 270.65 ± 0.5 K and a concerted decrease in a_ψ and a_φ values for a temperature range of approximately 288.15 K to approximately 298.15 K. The behaviour of the results clearly indicates the occurrence of two phase transformations (Ist P.C. (phase change) and IInd P.C.). The difference in the nature of changes in amplitude and phase thermal diffusivity values could indicate a difference in the nature of the phase transition. However, the results of microcalorimetric studies of microencapsulated phase change material, for example those presented in [27], provide a basis for classifying these phase transitions as first-order transitions. It is worth mentioning that this was confirmed by our own DSC studies of both microcapsules and structures with their addition. The reasons for the analyzed divergences of the courses should be sought in the deviations of the phenomena from the adopted model of the measurement method. The diffusivity values obtained for the structure in the area beyond the phase transition are in fact effective values. In the area of phase transitions, however, they take on the character of effective properties. Using the standard data conversion procedure [22] for calculating the geometric mean value of thermal diffusivity using the relationship:

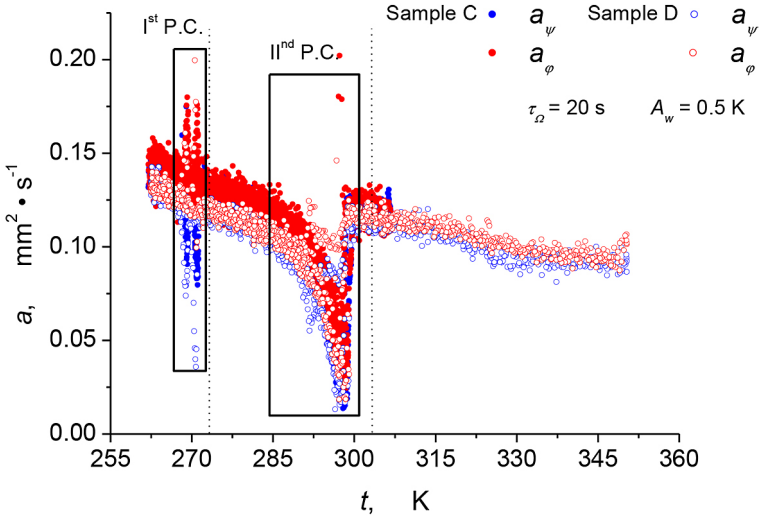

Figure 5. Thermal diffusivity test results for samples C and D; τ_Ω = 20 s, A_w = 0.5 K

$$a_{geom} = \sqrt{a_{\psi} \cdot a_{\varphi}} \quad (4)$$

The geometric mean value was determined for two arbitrarily selected temperature points: 273.15 K and 303.15 K. The temperature control points were selected so that they were equidistant from the temperature end point of the phase transition: Ist P.C. and IInd P.C. Results of the calculations are presented in Fig. 6 and Table 2. The results shown in Table 2 represent the averaged result for the L and R parts comprising the sample of the structure under study. As mentioned above for the samples B, C and D these are effective thermal diffusivity values.

In an analysis of the data, the expected increase in the thermal diffusivity values is noticeable when the addition of metallic powder is introduced. However, it is interesting to compare the thermal diffusivity values at 273.15 K and 303.15 K obtained in the tests of samples A and C. At 273.15 K, the addition of phase change-filled microcapsules results in a nearly 25% decrease in geometric mean thermal diffusivity relative to the value determined for sample A. This may be due to the introduction of a phase with lower effective thermal conductivity and to an increase in the thermal resistance of heat conduction in the sample structure. Determining the exact cause is difficult due to the complex relationship between thermal diffusivity and thermal conductivity for non-homogeneous structures. The problem is beyond the scope of current research. The situation is different for a temperature of 303.15 K, which exceeds the value of the end of the IInd PhC transformation. The sample with the addition of microcapsules records an increase of almost 15% in the geometric mean value of the thermal diffusivity compared to the results recorded for sample A. Phenomenologically, this effect can be related to the transition of the entire phase change material to the liquid phase. Furthermore, a decrease in the thermal diffusivity value determined for sample

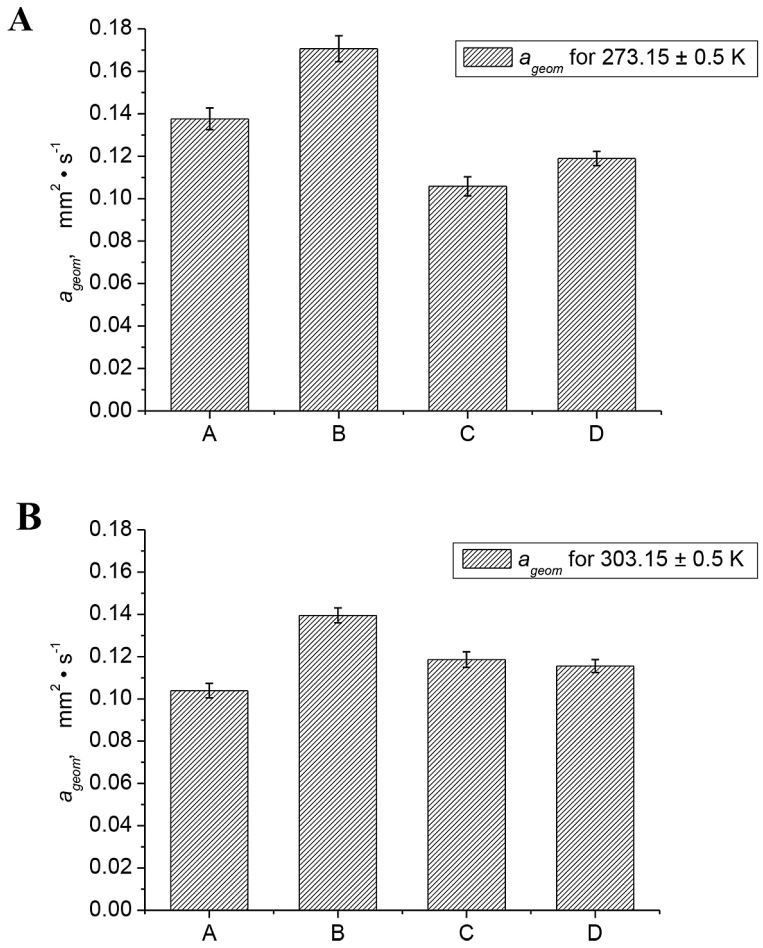

Figure 6. Geometric mean values of the thermal diffusivity of the tested series of samples for temperature 273.15 ± 0.5 K (A) and 303.15 ± 0.5 K (B)

Table 2. Data of a_{geom} (geometric mean of the amplitude and the phase thermal diffusivity ($m^2 \cdot s^{-1}$)), RD –relative difference, STD – standard deviation

Sample	a_{geom}	STD	RD	t
	[$mm^2 \cdot s^{-1}$]	[$mm^2 \cdot s^{-1}$]	[%]	[K]
A	0.1376	0.0051	3.71	273.15
B	0.1706	0.0061	3.58	
C	0.1058	0.0044	4.16	
D	0.1189	0.0034	2.86	
A	0.1039	0.0034	3.27	303.15
B	0.1395	0.0036	2.58	
C	0.1186	0.0037	3.12	
D	0.1155	0.0030	2.60	

D at 303.15 K was revealed, relative to the value recorded for the same sample at 273.15 K. The reason for this effect has not explained. To complement the data for the temperature control points, in addition to the geometric mean value of the thermal diffusivity a_{geom}, the standard deviation (STD) value and the relative difference between the a_{geom} and the STD (RD) value were also presented.

CONCLUSION

As part of the completed thermal diffusivity tests, a set of four temperature courses of changes in the calculated thermal diffusivity values were determined for four composite structures made on the basis of epoxy resin. The influence of metallic and phase-change microadditives on the effective - resultant thermal diffusivity value was then determined. A detailed analysis of the test data indicates an increase in the thermal diffusivity of the structure in the resin matrix due to the addition of metallic powder. The introduction of phase-change material microcapsules into the resin starting material manifests itself in the presented runs by a countersimilar divergence of amplitude and phase diffusivity values at: 270.65 ± 0.5 K and a concordant decrease in a_{ψ} and a_{φ} values for the temperature range from about 288.15 K to about 298.15 K. Furthermore, the phase-change additive only causes an increase in the thermal diffusivity values when the phase-transformation temperature of the phase-change material occurring in the range from approximately 288.15 K to approximately 298.15 K is exceeded. For lower temperatures, the addition of microcapsules results in a decrease in the value of the determined parameter. Analysis of the test data also documented a decrease in the thermal diffusivity determined for sample D at 303.15 K, compared to the value recorded for the same sample at 273.15 K. The reason for this effect has not been explained and requires further research.

As a result, the work confirmed the effectiveness of the thermal diffusivity measurement procedures used, which enabled the determination of high-resolution and reliable thermal diffusivity results by using a temperature oscillation method that complements the existing range of thermal analysis methods and techniques. On the other hand, the analysis of the obtained results opens the field for discussion concerning the interpretation of thermal diffusivity test results for the case of inhomogeneous structures, in particular structures exhibiting phase transformations.

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