Thermophysical Investigation of Structural Relaxation

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This paper presents a method for investigating structural relaxation by the measurements of specific heat, thermal diffusivity, and thermal conductivity. The relaxation effects are demonstrated on a composite based on carbon. A model for the investigated material is suggested. The material consists of regions which are in equilibrium state and regions which are in nonequilibrium state. The transition to the equilibrium state is manifested by reduction in the anharmonic effects and by chemical reactions. The contradictory behavior of the thermal diffusivity above room temperature is discussed.

KEY WORDS: anharmonic effects; composites; specific heat; structural relaxation; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The properties of materials are dependent on their composition and on the deviation from the equilibrium state resulting from technological treatment. The thermodynamic state of the materials changes by heat treatment. Structural relaxation is a phenomenon related to the transition of materials from a specific nonequilibrium state to a less nonequilibrium state [1–3]. Generally, the state of the material is characterized by the Gibbs energy. The deviation, known as excess Gibbs energy, decreases with time and in limit it vanishes. This phenomenon is known as "ageing" in material sciences.

A method for the study of the structural relaxation is presented in this paper. The method utilizes the measurements of the specific heat as a thermodynamic parameter and of thermal diffusivity and thermal conductivity as transport parameters. The measurements were performed in various temperature regimes.

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2. EXPERIMENT

2.1. Material Characterization

The composite consists of five components. The matrix is created by polyorganosiloxane (35%) and it plays the role of binder. Anorganic oxides (10% MgO) and graphite (14.5%) create the filler. Glass fibers (40%) form a skeleton. Calcium stearate (0.5%) has been added to the mixture. The network of the skeleton is formed by curing of the organo-silanol. The finished product has characteristics similar to those of silicate materials.
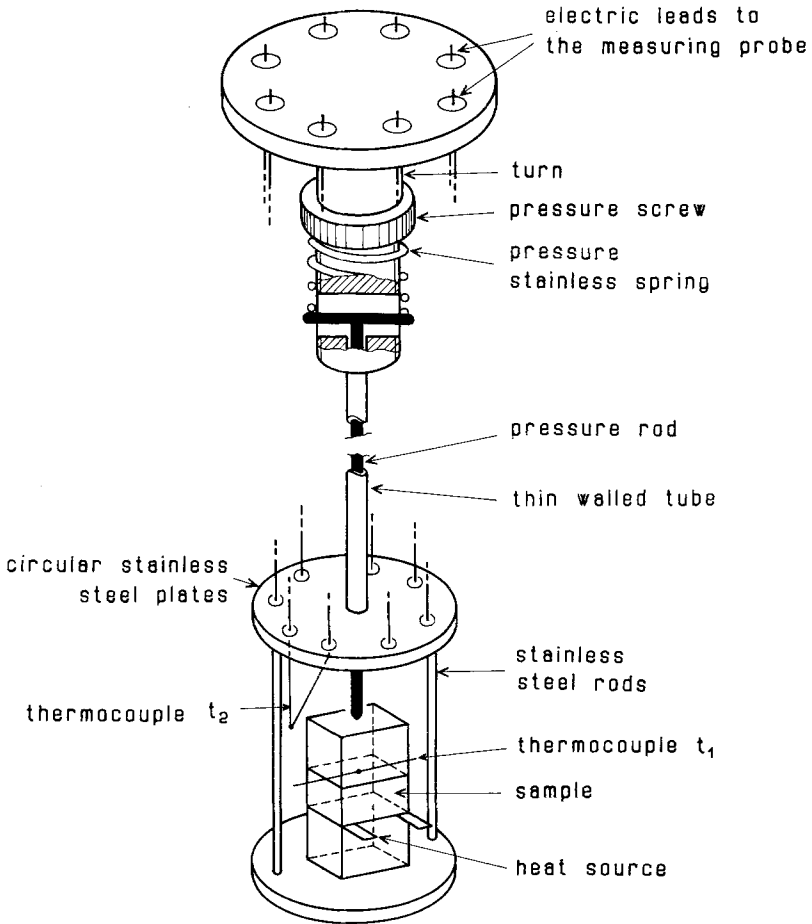

Fig. 1. Sample holder for measurements by the pulse method. t_1 and t_2 are thermocouples for measuring temperature response and sample temperature, respectively.

2.2. Characterization of the Experimental Method

A pulse method with a plane heat source was used for measurement of specific heat (c), thermal diffusivity (a), and thermal conductivity (λ) [4, 5]. The principle of the method is based on measuring the temperature response to the heat pulse. A schematic of the sample holder is shown in Fig. 1. Constant pressure on the sample is maintained at various temperatures by the "pressure stainless spring." The desired pressure on the sample is exerted by the "pressure screw." The sample holder is mounted into the furnace [5]. The heat source was made of nickel foil (thickness, 20 μm) by the photolitographic technique [2]. The current leads to the heat source were made of copper wires (diameter, 0.2 mm; length, 40 mm). The manganine wires (diameter, 0.05 mm; length, 40 mm) were used as voltage leads to the heat source. The width and the output energy of the heat pulse were 2 s and $10^5 \, J \cdot m^{-2}$, respectively. A chromel–alumel thermocouple (diameter, 20 μm) was used for measurement of the temperature response to the heat pulse. Thermal contacts were improved by using silicon paste. All the measurements were performed in vacuum. The measurement parameters were optimized from the point of view of minimal measurement error [5, 6]. The characteristic parameters of the sample are given in Fig. 2.

The combinations of various isotherms with the heating or cooling of the sample were used for the determination of the thermophysical parameters in the temperature range 20–400°C. The temperature regimes were controled by the computer automatically during the experiment. The chosen temperature regime corresponds to the real conditions of the material used in practical applications.
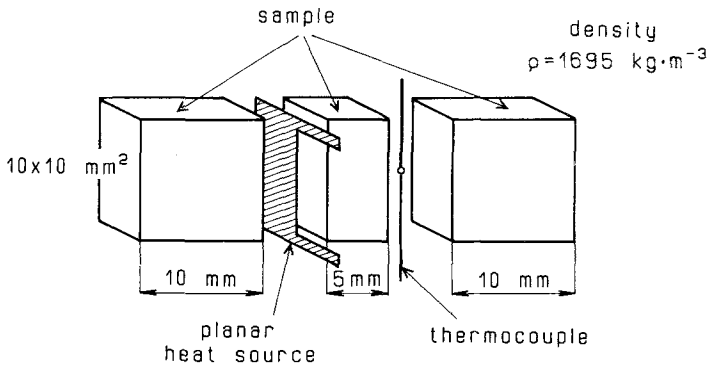

Fig. 2. Experimental arrangement for measurements of thermophysical properties by the pulse method.

3. EXPERIMENTAL RESULTS

Time dependence of temperature, specific heat, and thermal diffusivity is shown in Fig. 3. The different sequences of the temperature regimes are labeled $S_1 \cdots S_{13}$. The same notation of sequences is used throughout this paper to make the orientation easier. The mean values of the thermophysical parameters were calculated from the sequences of the data sets corresponding to the isotherms of 25, 250, and 400°C, respectively. The scatter of the measured data for the specific heat and thermal diffusivity decreased in the course of heat treatment at the 400°C isotherm (Fig. 3). This can be seen more clearly in Figs. 4, 5, and 6, where specific heat, thermal diffusivity, and thermal conductivity are plotted against the actual sequence of the temperature regime. Every next sequence in the 400°C isotherm lowers the scattering. The data analysis shows no significant influence of the heat treatment on the mean values of the specific heat, the thermal diffusivity, and the thermal conductivity at 400°C.

The mean values of the specific heat and the thermal diffusivity at 250°C were affected by the heat treatment. A similar behavior is shown by the mean values of the specific heat (Fig. 4), the thermal diffusivity (Fig. 5), and the thermal conductivity (Fig. 6) calculated from the sequences of the
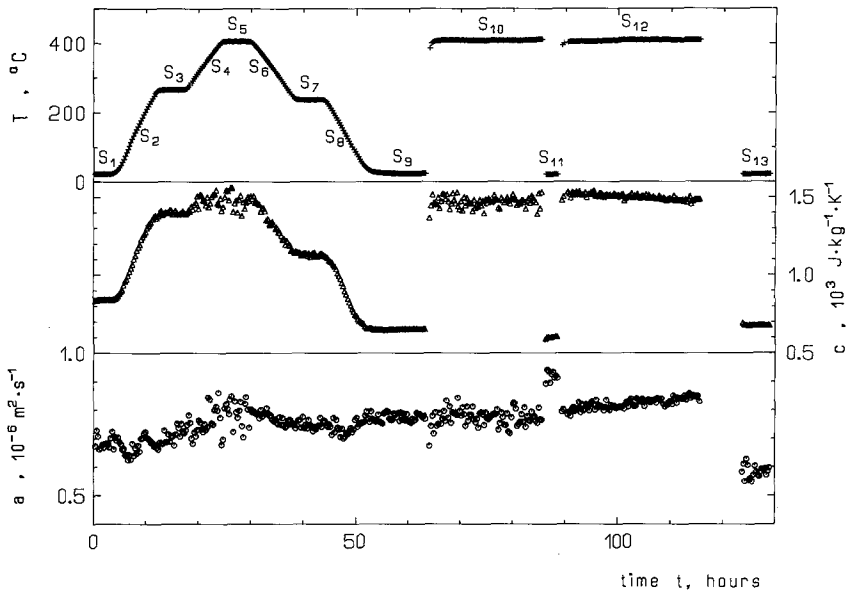

Fig. 3. Temperature regimes and measured parameters (temperature, T; specific heat, c; thermal diffusivity, a) of the composite.
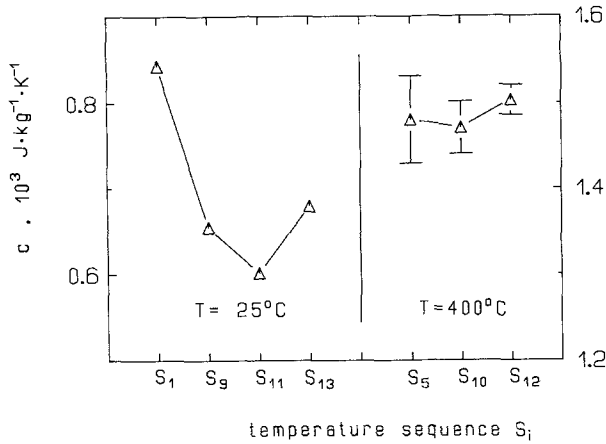
Fig. 4. Specific heat of the composite in different thermodynamic
states at 25 and 400°C.

data sets corresponding to the isotherm at the room temperatures. The
specific heat values decrease systematically (Fig. 3), except the last value
corresponding to the sequence S_{13} does not follow this tendency. The
change in the specific heat was 32% of its initial value. The thermal
diffusivity values have a tendency to increase, with the exception of the last
value (isotherm S_{13}). The change in thermal diffusivity was 35% of its
initial value. The mean values of the thermophysical parameters measured
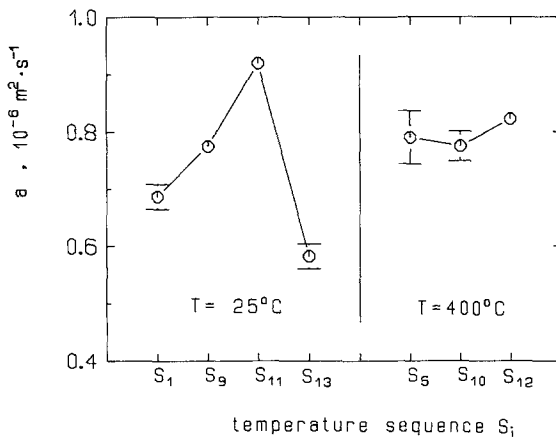at all isotherms are shown in Table I.

Fig. 5. Thermal diffusivity of the composite in different
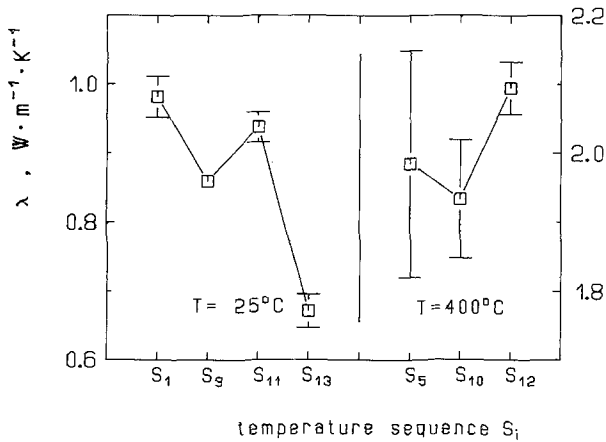thermodynamic states at 25 and 400°C.

Fig. 6. Thermal conductivity of the composite in different thermodynamic states at 25 and 400°C.

4. DISCUSSION

The structure of the investigated material is complicated. Figure 7 shows a schematic representation of the structure of the material. The specimen consists of the regions which are near equilibrium state and of the regions which are in nonequilibrium state. The latter usually has a disordered structure. Real atomic potential in the disordered structure has a complicated form in comparison to the crystals. A double-well potential

Table I. Mean Values of the Thermophysical Parameters at Different Temperature Isotherms

| S_i	T (°C)	a ($10^{-6}\,m^2 \cdot s^{-1}$)	c ($10^3\,J \cdot kg^{-1} \cdot K^{-1}$)	λ ($W \cdot m^{-1} \cdot K^{-1}$)
S_1	23.1	0.687 ± 0.021	0.842 ± 0.003	0.981 ± 0.030
S_3	266.3	0.705 ± 0.022	1.402 ± 0.011	1.676 ± 0.054
S_5	406.5	0.788 ± 0.047	1.478 ± 0.057	1.978 ± 0.177
S_7	237.7	0.747 ± 0.014	1.133 ± 0.009	1.436 ± 0.033
S_9	24.5	0.774 ± 0.011	0.654 ± 0.001	0.859 ± 0.012
S_{10}	409.2	0.775 ± 0.025	1.471 ± 0.031	1.934 ± 0.085
S_{11}	21.5	0.922 ± 0.015	0.602 ± 0.002	0.943 ± 0.015
S_{12}	408.9	0.822 ± 0.016	1.502 ± 0.018	2.095 ± 0.038
S_{13}	22.0	0.582 ± 0.021	0.679 ± 0.004	0.671 ± 0.024

non-equilibrium state

equilibrium state
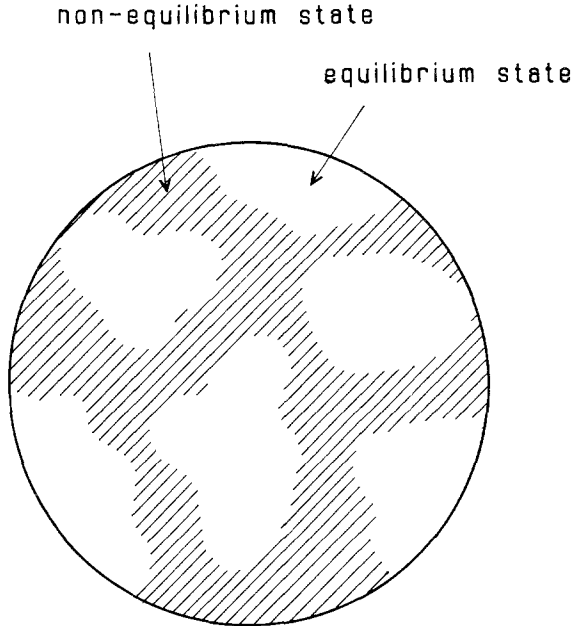
Fig. 7. Model of the composite.

model including also anharmonic effects can be used for describing the studied processes [7]. Tunneling exists at low temperatures, anharmonic effects play an important role at medium temperatures, and chemical reactions together with reorientation jumps contribute at higher temperatures. The chemical reactions are accompanied by the scatter in the specific heat data as well as in the thermal diffusivity data because heat pulse energy is changed through random absorption or emission of the reaction energy, and this changes the temperature response to the heat pulse. The specific heat data show that the chemical reactions were initiated just below 400°C (Fig. 3). Scatter in the data diminished through annealing. The sequence of the data set S_{12} does not show any scatter in the specific heat values. A similar feature is shown by the thermal diffusivity data at these temperatures (Fig. 3). Thermal diffusivity depends on the acoustic velocity and the free path of the phonons. The scatter in the thermal diffusivity in the sequences S_1, S_2 is caused by the removal of the microstresses from the material.

Structural relaxations influence specific heat and thermal diffusivity through anharmonicity of the interatomic potential [3, 8]. The form of the atomic potential is simplified through structural relaxations and it becomes less anharmonic. The contribution of the anharmonicity to the specific heat

decreases. This is demonstrated in Fig. 4, where specific heat values of the investigated material in various stages of the structural relaxation are plotted. High anharmonic interatomic potential causes strong phonon–phonon scattering by U processes. Then thermal diffusivity increases through structural relaxation because of the increase in the mean free path of the phonons (Fig. 5) [3].

The exception from the mentioned rule is shown by the last mean value of specific heat (Fig. 4) and thermal diffusivity (Fig. 5), where the measured values change apparently in the opposite way (sequences S_{12}, S_{13}). This is indicated probably by the last isotherm at 400°C (sequence S_{12}) in which the measured thermophysical parameters gradually changed, e.g., specific heat decreased and thermal diffusivity increased (Fig. 8). The structure of the investigated material approaches the nearly equilibrium state corresponding to 400°C after annealing at this temperature. This tendency for equilibrium caused small adjustment of the atoms. An abrupt change of the temperature to room temperature creates the nonequilibrium state, because the material needs some time to establish the structure which corresponds to the nearly equilibrium state at room temperature. It means that the thermodynamic state of the specimen at room temperatures before (sequence S_{11}) and after (sequence S_{13}) annealing at 400°C is different.
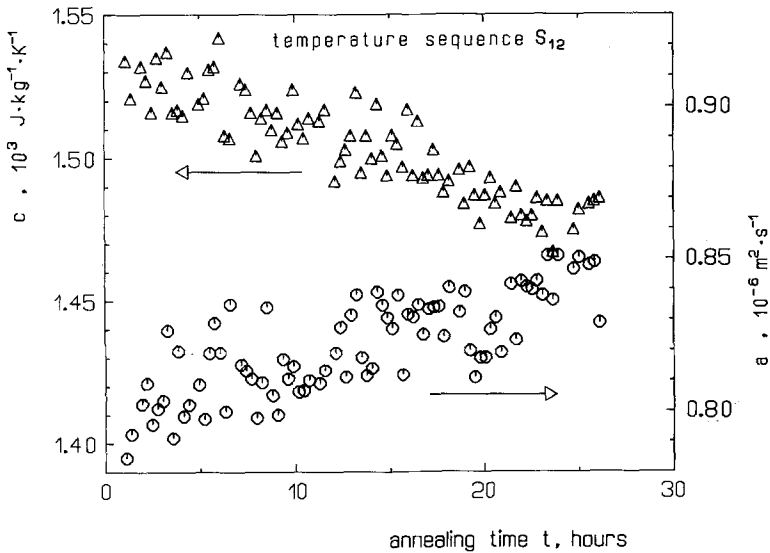

Fig. 8. Specific heat ($\triangle$) and thermal diffusivity ($\bigcirc$) of the composite annealed at 400°C.

These different thermodynamic states are responsible for the different values of the thermophysical parameters. Similar behavior of thermal diffusivity was noted for sintered metals [9].

5. CONCLUSIONS

A model of the composite was suggested in which regions in nearly equilibrium states and regions in nonequilibrium states exist. Physical properties, in our case specific heat, thermal diffusivity, and thermal conductivity, depend on the thermodynamic state of the studied material. The thermodynamic state of the studied materials depends on the composition and the technological treatment procedure, which usually involves deviation from the equilibrium state. The nonequilibrium regions can undergo structural changes through

(i)   chemical reactions, which cause scatter in specific heat and in thermal diffusivity; and

(ii) structural relaxations, which influence specific heat and thermal diffusivity through the anharmonicity of the interatomic potential. The contribution from anharmonicity vanishes and specific heat decreases, while the thermal diffusivity increases through structural relaxation.

The above-mentioned conclusions are applicable for glasses, polymers, ceramics, sintered materials, and highly doped monocrystals.

REFERENCES

1. S. M. Rekhson, *J. Non-Cryst. Solids* **84**:68 (1968).
2. O. V. Mazurin, *J. Non-Cryst. Solids* **87**:392 (1968).
3. Ľ. Kubičár, in *Proc. Second Int. Conf. Metal. Mater.*, Smolenice, May 22–26, 1989, P. Duhaj, P. Mrafko, and P. Švec, eds. (Trans Tech, Switzerland–Germany–UK–USA, 1990), p. 165.
4. J. Krempaský, *Cs. cas. fyz.* **B12**:353 (1962).
5. Ľ. Kubičár, *Pulse Method of Measuring Basic Thermophysical Parameters* (Elsevier, Amsterdam; Veda, Bratislava, 1990).
6. Ľ. Kubičár and J. Spišiak, *High Temp. High Press.* **20**:619 (1988).
7. W. A. Phillips, *Amorphous Solids at Low Temperatures* (Springer, New York, 1981), p. 160.
8. G. Grimvall, *Thermophysical Properties of Materials* (Noth-Holland, Amsterdam, 1986).
9. W. Neumann and A. Hallen, in *Thermal Conductivity 20*, D. P. H. Hasselman and J. R. Thomas, Jr., eds. (Plenum Press, New York, 1989), p. 71.