THERMAL DIFFUSIVITY OF REINFORCED PLASTICS
AT ELEVATED TEMPERATURES

V. I. Tyukaev, A. T. Nikitin,
V. A. Vinoslavskii, and A. G. Shashkov

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Results of measurements of the thermal diffusivity of precoked asbestos, glass, and carbon Textolite composites in the temperature range from 900° to 2800°K are reported. The nature of the temperature dependence of the thermal diffusivity and of the dependence of the thermal diffusivity on the composition of the materials is explained.

Plastics used as structural, electrical insulating, heat lagging, and sound insulating materials, and other materials, consist of synthetic polymers, organic or inorganic reinforcements, and several other components in small amounts. Several materials based on reinforced plastics were investigated under conditions of contact with a high-temperature environment, and it was found that a low rate of destruction at temperatures to 3500°K typified asbestos-reinforced, glass-reinforced, and carbon-reinforced plastics [1, 2]. Plastics including coking resins in their composition form [2], when heated: 1) a zone of completely coked material; 2) a zone of pyrolysis, or a zone of thermal decomposition of the constituent composite plastics; 3) a zone filled with the initial material.

Each of these zones corresponds to a certain range of temperatures dictated by the thermal stability of the polymer used. In the case of phenolic resins which have gained their greatest popularity as binders of composite materials, the maximum rate of thermally induced degradation is observed in the 570-870°K temperature range, which corresponds to the conditions typifying the second zone. In the case of coking materials, as shown by calculations, the effectiveness of thermal lagging is affected most seriously by the thermal conductivity of the coked layer and by the rate of decomposition of the binder [3, 4].

There are reports on investigations of the heat-transfer properties of some reinforced polymers in the temperature range 300-600°K, and also on determinations of the effective values of heat-transfer coefficients for glass fiber reinforced plastics up to 900°K [5, 6]. But under conditions where a high-temperature

TABLE 1. Variation of Physicomechanical Properties of Textolites in Coking Process

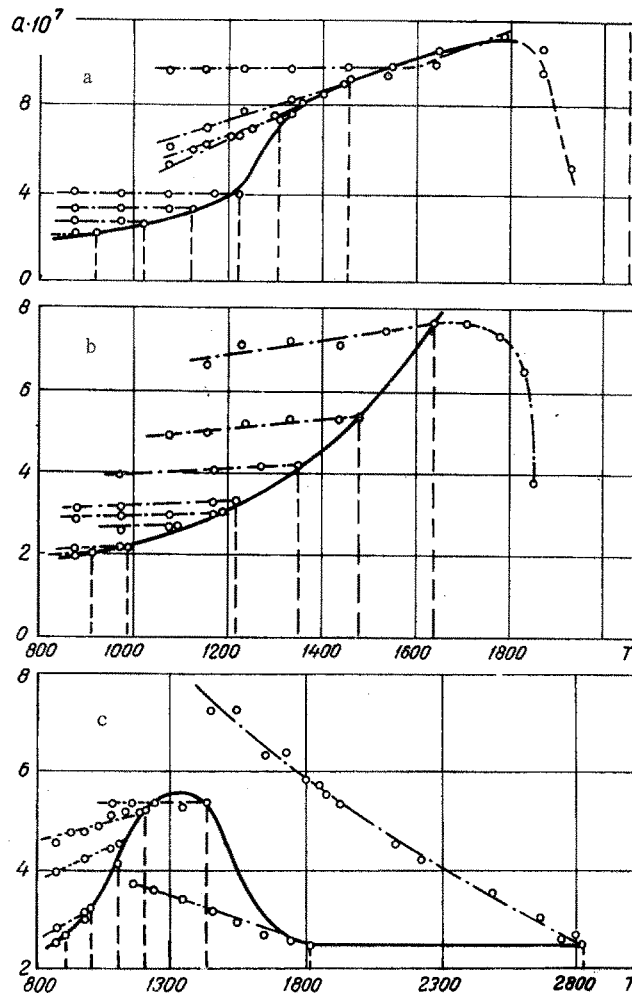| Designation of material	Content of binder in original material, wt. %	Mass per volume prior to coking, kg/m³	Mass per volume after coking at 823°K, kg/m³	Mass loss after coking at 823°K, wt. %	Compressive strength, MN/m²		Shrinkage after coking at 823°K, %		Further shrinkage of specimens after annealing at 1200°K, %	
					before coking	after coking	along layers	across layers	along layers	across layers
Asbestos textolite	32	1740	1460	25.8	105.52	34.32	2.3	8.2	2	4.7
Glass textolite	40	1540	1450	16.1	117.87	19.22	3.4	3.6	1.6	3.2
Carbon textolite*	40	1360	1200	20.6	101.98	21.28	1.42	2.2	1.6	3.5

*Specimens coked at 873°K.

Fig. 1. Dependence of thermal diffusivity (m²/sec)
on temperature (°K): a) asbestos Textolite composite;
b) glass Textolite composite; c) carbon Textolite com-
posite; - - -) indicate stabilization (annealing) tem-
perature; - • - • -) curves indicate temperature depen-
dence of thermal diffusivity before and after anneal;
○) denotes experimental data point.

medium affects reinforced plastics, the temperature on the surface of the plastics may run as high as 2000°K
or even higher. However, the information on heat-transfer properties of reinforced plastics at elevated tem-
peratures now available in the literature is scanty [7, 8]. Numerical values of the heat-transfer charac-
teristics of materials in the range from room temperature to the working temperature on the surface are
needed for the design and calculation of optimum thicknesses of thermal lagging.

Investigations of the thermal diffusivity coefficient of precoked glass, asbestos, and carbon Textolite
composites were carried out on a high-temperature facility, following a procedure described in another
article [9]. The thermal diffusivity was determined in accordance with the method of Kraev [10, 11] on
cylindrical specimens 25.5 mm in diameter and 76.5 mm long, in a high-temperature furnace assembled
on the basis of a TVV-4 crucible vacuum tungsten furnace. Before the experiment was carried out, the
facility was roughed down to a residual pressure of 1.333 N/m², and then filled with pure argon of grade A
to a pressure of 1.03·10⁵N/m². The electrical components of this test facility consist of a ROT-25 /0.5
autotransformer, and a OSU-40 /0.5 stepdown transformer. Up to 1300°K, the processes were carried out
by the retardation method with the aid of Chromel—Alumel thermocouples, and at higher temperatures by
means of a photoelectric pyrometer using special luminous readout connections [9].
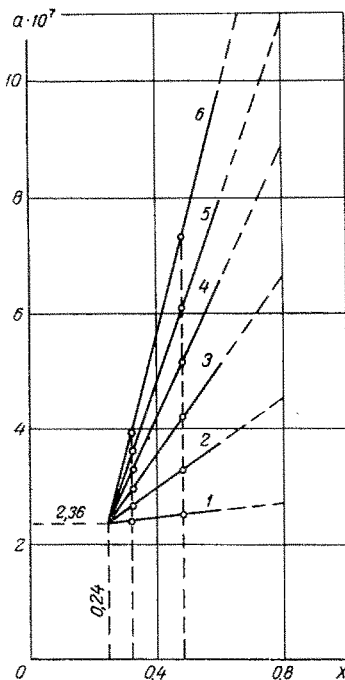
Fig. 2. Dependence of thermal diffusivity (m^2/sec) of coked asbestos Textolite composite on content of polymeric binder, at temperatures: 1) 973°K; 2) 1023; 3) 1073; 4) 1123; 5) 1173; 6) 1223.

The specimens investigated were based on a phenolic resin with a coke number of 54%, and several reinforcing fabrics: AT-1 asbestos fabric, KT-11 high-silica fabric, UUT-1 carbon-impregnated fabric. The Textolite composites were sintered at 433° ± 5°K under 10^6 N/m^2 pressure. Cylindrical specimens with axes parallel to the plane of the fabrics were machined from the sintered plates. The specimens were coked in a tubular graphite furnace at 820°K in a nitrogen atmosphere under 1.03 · 10^5 N/m^2 pressure until volatile products were no longer given off. The specimens to be coked were lined up along the axis of the graphite tubular furnace within which the temperature drop did not exceed 10°K.

As a result of pyrolysis of the binder and dehydration of the reinforcing fillers, physical and chemical changes took place in the material. Ultimate chemical analysis showed the composition of the coking resin to vary in the direction of increasing carbon content and decreasing hydrogen and oxygen contents with increasing temperature. The mass per volume decreased at the same time, and the mechanical properties of the plastics deteriorated severely while porosity and thermal conductivity increased. The change in some of the properties in response to elevated temperatures affecting the plastics under investigation is reflected in the data in Table 1.

Since the cylinder method was used in this work, the values of the thermal diffusivity were averaged if the materials were anisotropic. Of course, the difference in the thermal diffusivity along the layers and across the layers may amount to roughly 40% in the case of asbestos Textolite composite at temperatures to 900°K. On the other hand, however, the formation of a secondary carbon backbone in the bulk of the material comprising the specimen, and a further increase in porosity at temperatures above 900°K, will equalize conductivity in the various directions. Potentiometric measurements of the temperature field during the heating process showed, for all the materials studied in this work, that temperatures at a 9 mm radius practically coincide in the directions along the layers and across the layers. In the thermal sense the materials studied are thus found to be isotropic.

The temperature dependence of the thermal diffusivity in the case of asbestos Textolite composite, glass Textolite composite, and carbon Textolite composite is plotted in Fig. 1. Annealing at the corresponding temperature, indicated by the vertical broken lines, lasts one hour, after which the furnace is allowed to cool down, held at a certain level for some time, and following that a slow rise in temperature is brought about to the previously attained temperature at which the properties of the material become stabilized. The heating rate of the specimens is 0.45 deg/sec. The dot-dash curves indicate the change in the thermal diffusivity as a function of the temperature after the regular stabilization. Extrapolation of this temperature dependence of the annealing temperature makes it possible to attain the corresponding value of the thermal diffusivity. The experiment was staged in such a way that the temperature on the surface of the specimen would not be above the stabilization temperature.

In all the coked Textolites investigated, we observe, as seen in Fig. 1, an initial rise in the thermal diffusivity with increasing temperature. The transfer of heat takes place, of course, through the solid backbone and through the gas in the pores. It is evident in the diagram that the composition and structure of the materials affect the thermal diffusivity.

In the case of coked carbon Textolite composite consisting entirely of carbon, the thermal diffusivity in the 870°-1170°K range is slightly higher than in coked glass Textolite composite. At 1170°K, the coked glass Textolite composite contains about 71% silicon dioxide and 29% carbon by weight.

The heightened content of binder in the materials greatly increases the thermal diffusivity in the range up to 1300°K, but the specific contribution of radiative transfer of heat in the pores becomes greatly enhanced, on the other hand, with further rise in the temperature, as confirmed by the steeper rise in
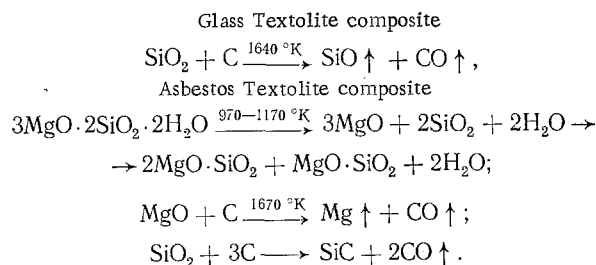
the curve in the 1300-1650°K range in the case of asbestos Textolite composites and glass Textolite composites. In the case of carbon Textolite composites, the rise in temperature is accompanied by a monotonic decline in the thermal diffusivity in the 1370°-1770°K range of temperatures, as is typical of graphitized materials.

Thermal decomposition in the 873°-1173°K temperature range, accompanied by release of volatiles and by structuration of the coke residue, contributes to a further increase in the porosity of the materials investigated. The total porosity of the coked materials increases with increased binder content, and amounts to 30-40% of which 10-15% is accounted for by closed porosity. The dimensions and shape of the closed pores, the composition of the gas in the pores, and the emissivity of their walls, appear to also exert a marked effect on radiative heat transfer.

As the binder content in the material is increased, the temperature dependence of the thermal diffusivity in the 873°-1223°K temperature range also declines. On the curves of constant composition $X_1 = 0.32$ and $X_2 = 0.48$ (see Fig. 2), values of the thermal diffusivity are marked off at temperatures in the 973°-1223°K range. If the isotherms are now approximated by straight lines, these will intersect at a point having the coordinates $a = 2.36 \cdot 10^{-7}$ and $X = 0.24$. A point with these coordinates corresponds to a material whose thermal diffusivity is independent of the annealing temperature. Using the relationship illustrated in Fig. 2, we can immediately indicate a series of values of the thermal diffusivity without staging an experiment by specifying nothing more than the binder content. The equation of the family of isotherms plotted for asbestos Textolite composite in the 870°-1220°K temperature range can be represented in the following form:

$$a_i = 2.36 \cdot 10^{-7} + \left(\frac{\partial a}{\partial X} \right)_{t_i} (X - 0.24).$$

It is clear in Fig. 1 that a change is observed in the nature of the temperature dependence of the thermal diffusivity in asbestos Textolite composites and glass Textolite composites beyond the temperature 1670°K. The falloff in the thermal diffusivity of the materials investigated in the 1670°-1900°K temperature range can be explained by the fact that, at those temperatures, heterogeneous chemical reactions take place with appreciable rates, according to the following schemas [12-14]:

<div align="center">Glass Textolite composite</div>

$$SiO_2 + C \xrightarrow{1640\,°K} SiO \uparrow + CO \uparrow,$$

<div align="center">Asbestos Textolite composite</div>

$$3MgO \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{970-1170\,°K} 3MgO + 2SiO_2 + 2H_2O \rightarrow$$

$$\rightarrow 2MgO \cdot SiO_2 + MgO \cdot SiO_2 + 2H_2O;$$

$$MgO + C \xrightarrow{1670\,°K} Mg \uparrow + CO \uparrow;$$

$$SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow.$$

In view of the fact that the procedure followed in [10, 11] to calculate the thermal diffusivity was based on the solution of the heat conduction equation with no heat sources and no heat sinks, its values beyond the inflection points in Fig. 1a, 1b must be viewed as effective values. The kinetics and thermal effects of the heterogeneous reactions taking place inside the coke residue must be known in order to find the true values of the thermal diffusivity at temperatures upwards of 1400°C.

LITERATURE CITED

1. H. J. Thompson, Missiles and Rockets, 9, No. 6, 26 (1961).
2. N. Beecher and R. E. Rosensweig, ARS Journ., 31, No. 4 (1961).
3. S. J. Tick, J. K. Huson, and R. Greise, J. Spacecraft and Rockets, 2, No. 3 (1965).
4. Yu. V. Polezhaev, Izv. Akad. Nauk SSSR, Mekhan. i Mashinostroenie, No. 5, 157 (1964).
5. O. F. Shlenskii, Yu. P. Barskii, and N. P. Pichugin, Plastmassy, No. 1, 62 (1964).
6. V. S. Bil', and N. D. Avtokratova, Plastmassy, No. 2, 35 (1968).
7. F. T. Dodge T. R. Jackson, and E. J. Barker, Trans. ASME, Series C, 88, No. 3, 87 (1966).
8. Referat. Zh. Mekhanika, No. 2, REF. 2B857 (1967); C. M. Pyron Jr. and C. D. Pears, ASME NHT-46 (1965).
9. V. I. Tyukaev and A. G. Shashkov, in: Heat and Mass Transfer, and the Thermal Properties of Materials [in Russian], Nauka i Tekhnika, Minsk (1969).
10. O. A. Kraev, Teploénergetika, No. 4 (1956).

11. O. A. Kraev, Teploénergetika, No. 4 (1958).

12. B. S. Gulyanitskii and D. M. Chizhikov, Izv. Akad. Nauk SSSR, Otdel. Tekhn. Nauk, No. 11, 13 (1955).

13. R. E. Rosensweig and N. Beecher, AIAA J., 1, No. 8 (1963).

14. J. L. Blumenthal, M. J. Santy, and E. A. Burns, AIAA J., 4, No. 6 (1966).