

THERMOPHYSICAL PARAMETERS FOR THE COMBUSTION PRODUCTS FROM
TETRAZOLE-SODIUM TETRAZOLATE MIXTURES

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Measurements have been made on the thermal conductivity and specific heat of the powder product from quenching in nitrogen applied to the gas-liquid flame formed by the combustion of a tetrazole-sodium tetrazolate mixture in weight proportion 3:1. The thermal conductivity on the whole is a nonmonotone function of temperature in the range 100-450 K and has some local turning points associated with the multicomponent structure and the phase transitions associated with chemical and structural transformations.

Processes in a macroscopic system can be divided into slightly and highly nonequilibrium ones. In a nonconservative system near equilibrium, stability arises in any process under conditions of minimum entropy production, while far from equilibrium, in the nonlinear region, the ordering and stability are due to extensive energy dissipation [1]. There are many examples of such organization for hydrodynamic systems such as Benard cells and Taylor cylinders, and also in chemical reactions, in particular in the combustion of a mixture of tetrazole with sodium tetrazolate [2, 3]. That combustion produces a flame consisting not only of gaseous products but also liquid ones, which leads to a spheroidal form for the flame. Research on this unusual organization is designed to elucidate applications and requires the determination of thermophysical characteristics before and after combustion.

We have measured the thermal conductivity and specific heat and examined the morphology of the product from quenching in nitrogen applied to the gas-liquid flame formed by the combustion of a 3:1 weight proportion tetrazole-sodium tetrazolate mixture. The product was made by pouring the flame from the burning specimen into nitrogen. This gave a hollow spheroidal casting, which had been found to consist of sodium salts such as the cyanide and cyanamide, together with a nitrogen-carbon polymer. The specific heat was measured with a Mettler TA 3000 thermal analyzer, with the temperature dependence of the thermal conductivity determined by means of a suite based on an IT- λ -400 instrument, which operates as a dynamic calorimeter. The specific-heat specimens were provided by the finely ground product, which was pressed at 1.7×10^8 N/m² into disks 15 mm in diameter and 1-2 mm thick. The surface morphology was determined with a Nanolab-7 scanning electron microscope.

Results. Figure 1 shows the thermal conductivity λ as a function of temperature T at 120-450 K for four specimens with differing bulk densities. The behavior of $\lambda(T)$ is fairly typical of the entire range, although the values differ somewhat in magnitude from specimen to specimen. In all cases, the conductivity is comparable as regards order of magnitude with those for other poor conductors such as granular materials in air. The characteristic particle size was 10-100 μ m, which provided porosities from 0.25 to 0.47 in accordance with the packing density. High internal microporosity was present in the original quenched product and meant that the factors governing the heat transfer included the important one of contact thermal conduction, where the contact between particles represents an additional resistance to the heat flux, which contracts down on passage from one particle to another and results in local changes in the temperature gradient and more extensive phonon scattering [4]. Nevertheless, it is doubtful whether the observed $\lambda(T)$ can be ascribed to contact effects.

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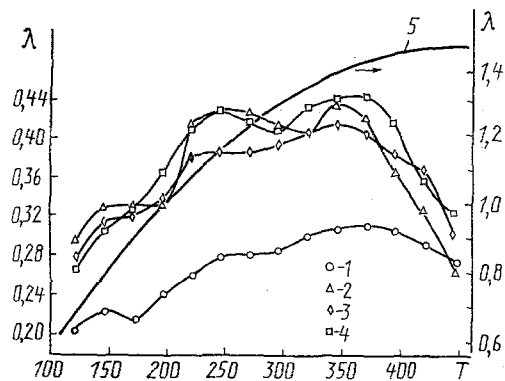


Fig. 1. Temperature dependence of the thermal conductivity for specimens pressed from the previously ground quenching product to various densities: 1) 1671.3 kg/m³; 2) 1707.7; 3) 1775.9; 4) 1887.1; 5) fused silica; λ in W/m·K) and T in K.

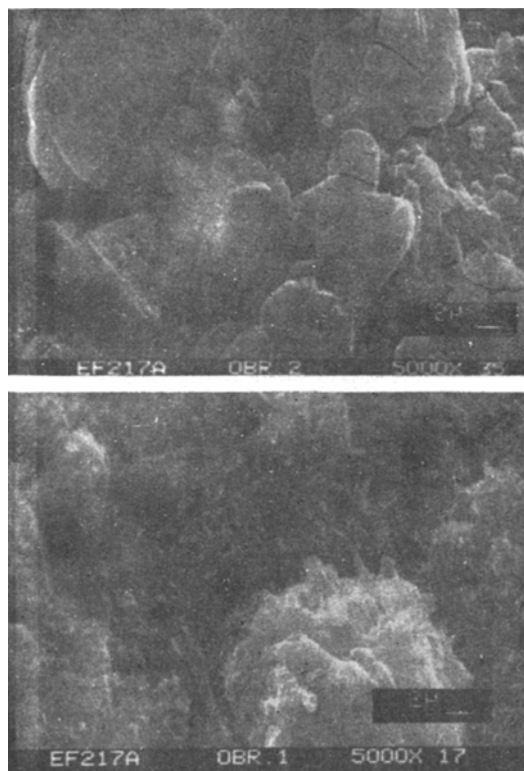


Fig. 2. Photomicrographs of two particularly characteristic parts of the porous solidified mass from a gas-liquid flame, ×5000.

Leaving aside the composition, we consider how the physical state and structure affect the heat transfer. X-ray diffraction indicates that the initial powder has a crystalline component, and there is probably also a vitreous phase, since the formation of it predominates over crystallization at sufficiently high quenching rates. Figure 2 shows two very characteristic porous parts of the surface before the specimen was ground. A similar surface appearance applies for the inner parts of the quenched product. The initial porosity suggests that the powder particles have submicroporosity. The differences in surface appearance may be due to differences in structure, but there may also be phases differing in composition. Figure 1 shows for comparison the temperature dependence of the conductivity for fused quartz, which indicates that one can assume a vitreous state to interpret the results only with certain reservations, namely that there are certain transformations in the material, since curve 3 in Fig. 1 has local turning points and inflections, in contrast to the monotone behavior of curve 5.

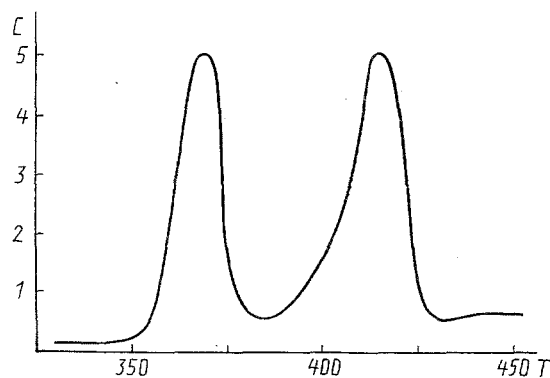


Fig. 3. Specific heat of the powdered quenched product as a function of temperature T , with C in $J/(g \cdot K)$.

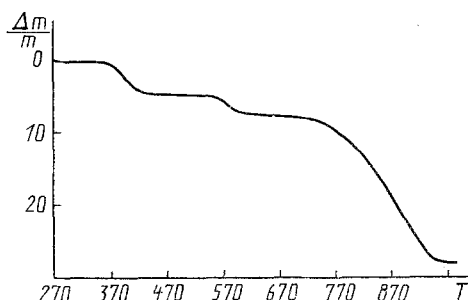


Fig. 4. Thermogravimetric data from quenched product in the powder state, $\Delta m/m$ in %.

The magnitude and the temperature dependence of the conductivity for the crystalline phase are in general defined by the usual formula, which contains the specific heat C , the acoustic-wave speed v , and the phonon mean free path l . In a polycrystalline medium similar to ours, the actual pattern fits this only to a very limited extent, which is governed by the relation between the characteristic single-crystal grain size L and the range l . For $T \gg \Theta$ and $T \ll \Theta$, that formula applies, while for $T \approx \Theta$, when v is only slightly dependent on T because of changes in the elastic moduli and density, the conductivity is inversely proportional to temperature, while at low temperatures, where the number of effective phonons producing scattering with reversal is exponentially small and l is much greater than L , the conductivity is determined by the temperature dependence of the specific heat. A polycrystalline component will determine the behavior of $\lambda(T)$ at the boundaries of our temperature range, particularly the low-temperature part, because the sizes of the polycrystalline blocks do not exceed those of the particles, while the liquid-nitrogen quenching does not allow the crystallites to grow to a substantial size ($L \ll 10 \mu m$).

Figure 3 shows the temperature dependence of C , which indicates that these mechanisms are accompanied by additional factors, particularly in the high-temperature range. The Dulong and Petit law traditional for insulators does not apply, and $C(T)$ shows two sharp turning points, which indicate transformations involving heat absorption. The wide temperature ranges for the turning points indicate that the structure alters in one or more components.

We consider in more detail the heat transfer by the components as regards their chemical type. For example, sodium cyanide and cyanamide in the usual state cannot provide the undulating $\lambda(T)$. $NaCl$ ($\rho = 2.02 \text{ g/cm}^3$) has a monotone behavior, with λ decreasing for $T > 273 \text{ K}$, while porous sylvinite containing rocksalt inclusions with density $\rho \approx 1.69 \text{ g/cm}^3$ also shows monotone $\lambda(T)$, but in this case increasing slightly to saturation, the values for $\lambda(t)$ in $W/(m \cdot K)$ at T , in K , being:

T	273	298	323
λ (NaCl)	1,789	1,756	1,705
λ (sylvinite)	0,841	0,867	0,867

This smooth behavior can hardly result in these local turning points in narrow ranges. The physical state of the matrix is important to the transfer, i.e., the high porosity in the powder, which allows the material to take up water from the air either chemically or by ordinary adsorption, when the water fills the small pores and freezes at 200-273 K. At higher temperatures, the ice begins to melt and leave the material, as is evident from the thermogravimetric results, with the weight falling above 370 K (Fig. 4).

To a certain extent, the transfer may be affected by the nitrogen-carbon polymer, in the ordinary or filled states. A polymer composite on the whole is a very complicated system and can cause substantial changes in the heat transfer because of structural transformations and relaxation effects. Polymer relaxation occurs over a wide temperature range and is governed by the molecular type: The smaller the critical unit or the dipole moment in it, the lower the temperature of activation for a particular relaxation process that affects the macroscopic characteristics. The physical properties are governed by the structures in the macromolecular chains, which may be flexible or rigid and which may have linear, branched, or grid structures [5]. The complicated product from the combustion here may also show structural transformations in the filled polymer at $T \approx 150$ K, where there is a local turning point in $\lambda(T)$. If the specimen is heated above 370 K, the polymer softens and the proportion of amorphous component increases, which reduces the thermal conductivity.

These studies on this product involve uncertainties over the interpretation, but do indicate some features of the structure and enable one to judge the properties of the components and the solid-state changes. The wide temperature range enables one to examine various mechanisms in the nonequilibrium and equilibrium thermal processes, since such a powder is a combination of crystalline and amorphous phases, and this enables one to identify the phase transitions associated with chemical and structural changes and thus to determine the viability ranges and applications when the thermophysical properties are important.

NOTATION

L is characteristic single-crystal grain size; l is phonon mean free path; v is speed of sound; T is temperature; θ is Debye temperature; λ is thermal conductivity; C is specific heat; $\Delta m/m$ is mass loss.

LITERATURE CITED

1. P. Glensdorf and I. Prigogine, *The Thermodynamic Theory of Structure, Stability, and Fluctuations* [Russian translation], Moscow (1973).
2. A. I. Lesnikovich, V. V. Sviridov, G. V. Printsev, and O. A. Ivashkevich, *Nature*, **323**, No. 1090, 706-707 (1986).
3. A. I. Lesnikovich and G. V. Printsev, *Zh. Khim. Fiz.*, **9**, No. 12, 1648-1652 (1990).
4. G. N. Dul'nev and Yu. P. Zarichnyak, *Thermal Conductivities of Mixtures and Composites* [in Russian], Leningrad (1974).
5. L. L. Vasil'ev, G. I. Bobrova, and S. A. Tanaeva, *Porous Materials in Cryogenic Engineering* [in Russian], Minsk (1979).