Thermophysical Properties of RDX

by Martin S. Miller

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Thermophysical Properties of RDX

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Abstract

Measurements of the thermal conductivity and thermal diffusivity of RDX (cyclotrimethylenetrinitramine) over the ambient temperature range -20°to +50°C are reported using a recently developed transient technique for small specimens of energetic material. These data are obtained from 95% of TMD, pressed-powder specimens. Both the thermal conductivity and derived values of the specific heat are in good agreement with previous measurements made at somewhat higher temperatures.

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1. INTRODUCTION

Thermal properties of pure nitramines are of considerable interest to the energetic-materials community, yet accurate measurements of these properties are nontrivial and almost nonexistent in the open literature. Propellants and plastic-bonded explosives typically contain more than a two-thirds mass fraction of RDX (cyclotrimethylenetrinitramine) or HMX (cyclotetramethylenetetranitramine). Because the individual crystals in these composites are randomly oriented relative to one another, there is a particular need for thermal properties of these nitramines in polycrystalline form. This note reports simultaneous measurements of the thermal conductivity and thermal diffusivity of pressed-powder specimens of RDX using a technique recently developed for small test specimens of energetic materials[1]. These data were obtained for specimen temperatures ranging approximately between -20°C and +50°C.

2. EXPERIMENTAL

The technique used is fully described by Miller and Kotlar[1], but a brief summary is provided here for convenience. The experimental setup is designed to provide a close approximation to the mathematically ideal case of a step-function heat flux emanating from the planar boundary between two semi-infinite solids. Experimentally, the heat flux is generated by the sudden onset of resistive heating of a 5-μm-thick Constantan foil. Due to the finite heat capacity of the foil, a nonideal step-function heat flux is produced by a step-function current in the foil. The extent to which measurements of the diffusivity are affected by this nonideality has been determined[2]. Under the conditions reported here, the resulting error is less than 2.5%. The test specimen approximates one of the two semi-infinite solids, and a material of known thermal properties (polymethylmethacrylate) approximates the other. Under present conditions, the finite thickness of the specimen contributes less than 1% error to the reported measurements. The test specimen consists of two separate parts, a wafer 0.7 mm thick by 6 mm diameter and a "backup" piece 6.5 mm long by 6 mm diameter. Between these two specimen parts is interposed a 5-μm-

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thick Chromel/Alumel foil-type thermocouple. After the sudden onset of the heat flux, the temperature between the two specimen pieces is measured for a period of about 4 s and compared to the exact solution of the idealization. Values of the diffusivity and conductivity are found by a nonlinear least-squares fit of the solution to the data. The overall accuracy of the method is estimated to be about 5%.

The test fixture described in Miller and Kotlar[1] consists of a cylindrical copper block with voids suitably milled from the interior to provide support for the foil, specimen, and thermocouple. Although the original description of the technique was confined to ambient laboratory temperature, copper was used in anticipation of the need to equilibrate the specimen rapidly to various temperatures and to provide a uniform-temperature surround for the specimen in order to measure thermal properties at different temperatures. Temperature control of the specimen was achieved by soldering copper tubing to the exterior of the fixture and fitting it with a mineral-fiber insulation jacket. A 50% ethylene glycol mixture with water was then circulated through the tubing from a temperature-controlled reservoir. Auxiliary experiments were performed to determine the time needed for the fixture to reach various steady-state temperatures before testing could begin.

The RDX powder used in this study was obtained from Waltham Abbey, England and was of higher purity than the U.S. military grade. High pressure liquid chromatography (HPLC) analysis revealed it to have a 1% HMX impurity. The wafer and backup piece were formed separately by pressing in a steel die to about 95% of theoretical maximum density (TMD). After pressing, the specimen pieces were desiccated for several weeks prior to testing.

3. RESULTS

Tests were performed at four temperatures spanning the approximate range of -20°C to +50°C. The averages and standard deviations of five experiments at each temperature are given

in Table 1. All measurements were performed on a single composite specimen. These data may be compared with prior work over a complementary temperature range. Figure 1 shows our data for thermal conductivity along with that of Shoemaker, Stark, and Taylor[3], who used a laser-flash method on a pressed-powder specimen. The agreement is good. Another comparison is afforded by measurements of the specific heat using differential scanning calorimetry (DSC), also reported by Shoemaker, et al.[3] Utilizing the definition of thermal diffusivity, $\alpha = \lambda/(\rho c_p)$, where α is the diffusivity, λ is the thermal conductivity, ρ is the mass density, and c_p is the specific heat, we computed a value for the specific heat from our measured values of conductivity and diffusivity. We assumed a value for the powder density of 1.716 g/cm³ based on 95% of TMD (1.806 g/cm³)[4] mentioned previously. The resulting comparison is shown in Figure 2 along with the addition of a third set of data given by Dobratz[4]. The agreement among all three data sets is good. Shoemaker, et al.[3] state that military-grade RDX was used in their experiments. This means that up to about 20% of HMX may have existed as an impurity in their test specimens; no chemical analysis was reported by these authors. Also, no information on sample purity was given for the data quoted in Dobratz[4].

Table 1. Measured Thermophysical Properties of Polycrystalline RDX

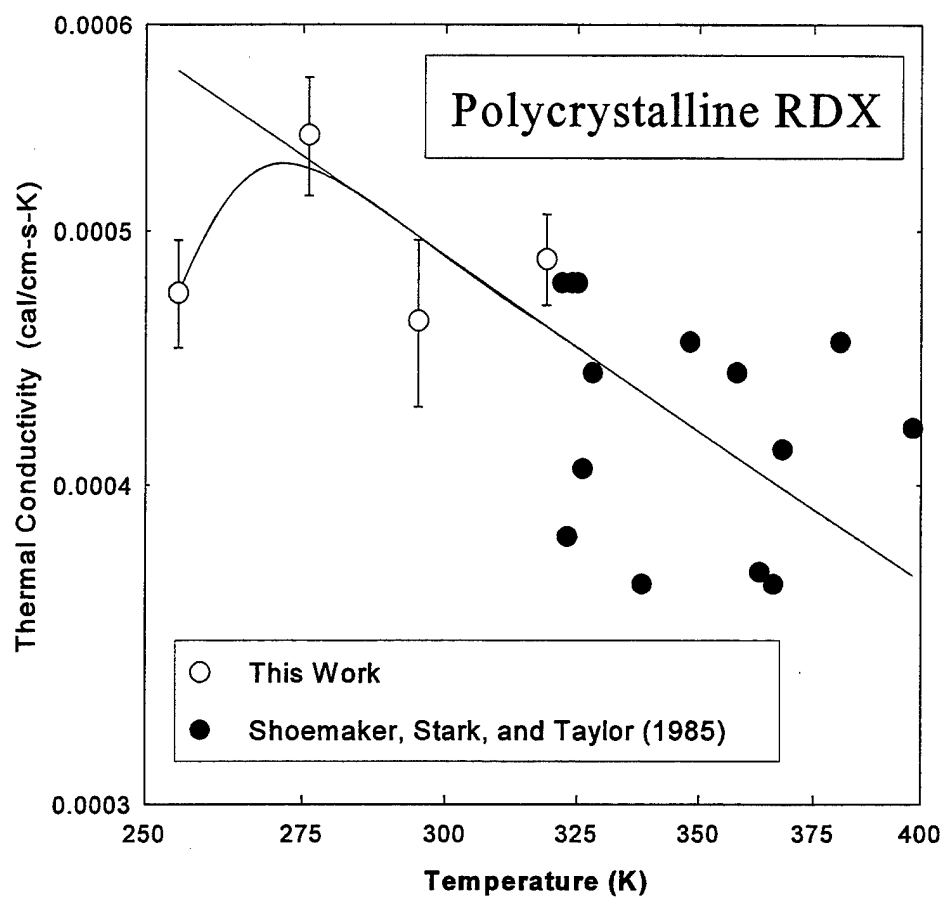| Temperature (K)	$10^4 \times$ Thermal Conductivity (cal/cm-s-°C)	$10^3 \times$ Thermal Diffusivity (cm²/s)
255	4.74 ± 0.22	1.32 ± 0.04
276	5.44 ± 0.28	1.32 ± 0.04
295	4.62 ± 0.34	1.08 ± 0.05
320	4.88 ± 0.19	1.09 ± 0.02

Figure 1. Thermal conductivity of polycrystalline RDX: open circles - present data, filled circles - data of Shoemaker, et al.,[3] thin line - *0.147/T*, heavy line - $\lambda(T)$ functionality suggested by composite data set (See Section 4).
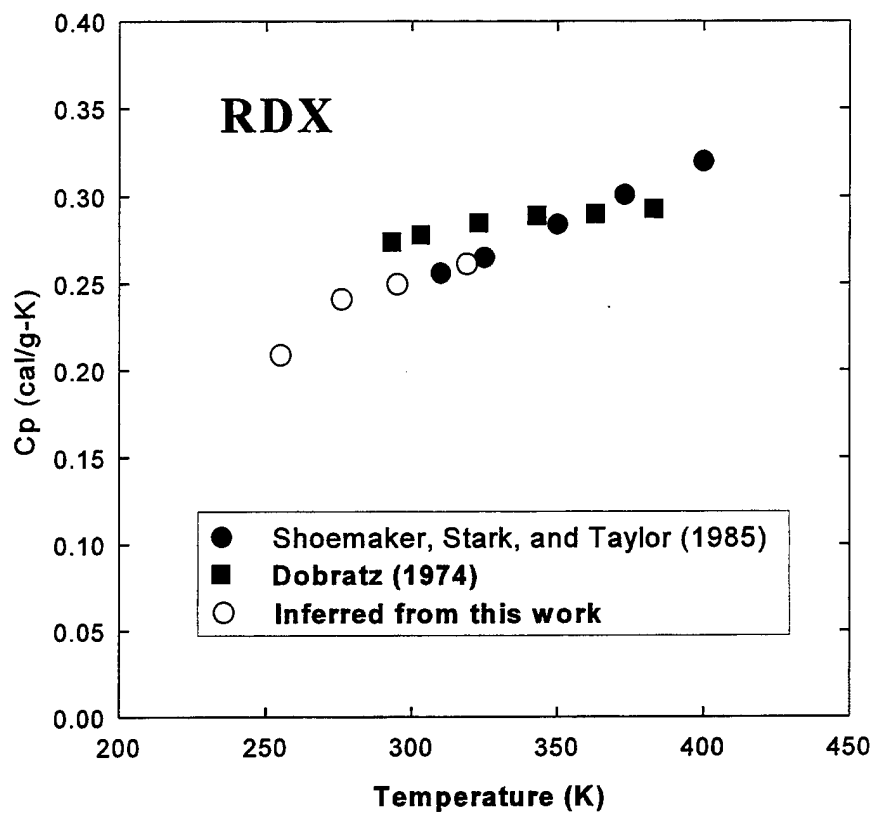
4

Figure 2. Specific heat of RDX: filled circles - DSC data of Shoemaker, et al.[3], filled squares - data from Dobratz[4,] open circles - inferred from present conductivity and diffusivity data.

4. DISCUSSION

According to theory[5] the intrinsic thermal conductivity of a dielectric crystalline material (i. e., the conductivity in the absence of lattice imperfections) has a *1/T* temperature dependence at high temperatures. For this reason the data of Figure 1 are plotted on a log-log scale, and the thin straight line is a least-squares fit of the function *b/T* to the combined data sets excluding the point at lowest temperature. The resulting value of *b* is 0.147 in the units appropriate to the figure. In the low-temperature limit, λ increases with temperature, according to theory[5]. A peak is thus expected on theoretical grounds in the curve $\lambda(T)$. The line *b/T* is consistent with the standard deviations of our three highest temperature measurements and the data of Shoemaker, et al.[3]; however, our lowest temperature measurement is almost five standard deviations below the *b/T* line. We therefore speculate that our data encompass the maximum in $\lambda(T)$ for RDX and draw the heavy curved line in Figure 1 to suggest a functionality consistent with all of the data. Further measurements at still lower temperatures would be desirable to confirm this behavior but were not possible within the constraints of this work. Interestingly, the value of *b* obtained from a least-squares fit to the Shoemaker, et al.[3] data alone differed from the value obtained from a fit to our data alone (excluding the data at 255 K) by only 0.3%, a fact which is not immediately evident from Figure 1, but one which adds confidence to the combined-data fit. Finally, we note that the fit, $\lambda(T) = b/T$, found above should provide a reasonable basis for extrapolation up to the melting point 478 K, provided that the application times considered do not permit appreciable thermal decomposition to occur.

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