MEASUREMENT OF Nb_3Ge HEAT CAPACITY

M. P. Orlova, Ya. A. Korolev,
M. I. Bychkova, T. O. Ponomareva,
and I. D. Giller

UDC 537.316.62:536.7.764

The heat capacity of massive Nb_3Ge specimens (cast, annealed, and rapidly quenched) is measured by the adiabatic calorimetry method with periodic heat supply over the temperature range 5-30°K. Measurements and data collection were completely automated.

The heat capacity of single-phase Nb_3Ge obtained as a film by chemical precipitation has been measured from 4 to 29°K [1]. The specimens had a $T_c = 21.8$°K. The temperature dependence followed Debye's law to 29°K ($\Theta_D = 302$°K from the measurements). The specimen composition, determined by x-ray diffractometry, proved to be 99.5% of the phase A-15 of Nb_3Ge and 0.5% of the tetragonal phase Nb_5Ge_3. The lattice dimension $a = 5.139$ Å. A correction of ~20% was introduced in the C_p measurements, and the measurement accuracy was estimated by the authors at ±4% up to 8°K and ±2% above 8°K.

In [2] $C_p(T)$ was measured from 4 to 80°K for Nb_3Ge, obtained as a film by chemical evaporation, with a film thickness 10 times larger than in [1]. The quantity a varied from 5.199 to 5.140 Å in various specimens. The authors indicated the presence of a second phase Nb_5Ge_3. The temperature dependence of $C_p = \gamma T + \beta T^3$ and $\Theta_D = 280$°K, which was significantly less than in [1], and the authors of [1] maintain that the composition of these specimens was 70% A-15 Nb_3Ge and 30% tetragonal Nb_5Ge_3.

High-temperature superconductivity was determined in [3] in massive specimens prepared by fusing pressed specimens. Specimen weight varied from ~10 to 12 g, and T_c of the various specimens was from 17.3 to 20.5°K, with some ingots prepared by this method showing $T_c \sim 7$°K. No phase analysis results were presented.

In [4] $C_p(T)$ and $\chi(T)$ were measured for Nb_3Ge specimens prepared by melting Nb and Ge in Alundum crucibles. X-ray studies showed the presence, together with the phase A-15 ($a = 5.170$ Å), of 5 vol. % of another structure, apparently the eutectic $Nb_3Ge + Nb_5Ge_3$. T_c proved equal to 6.9°K. $C_p(T) = \gamma T + \beta T^3$, just as in previous studies. The function $\chi(T)$ from 26 to 270°K decreased monotonically by ~5%.

In the present study $C_p(T)$ was measured for massive specimens of Nb_3Ge which were cast and not annealed, annealed after measurement, and produced by accelerated cooling from the melt. The materials used in producing the Nb_3Ge were monocrystalline semiconductor grade germanium and niobium with an impurity content of 0.19%. Specimens were obtained by fusing in the suspended state (levitation method). The fused drop was poured into a copper mold maintained at room temperature. The original charge weighed ~15 g. In the heat-capacity measurements ~40 g of cast specimen were used, obtained in this manner. After measurements,

TABLE 1. Phase Relationships in Specimens Studied, %

Specimen characteristic	Nb_3Ge	Nb_5Ge_3
Rapidly quenched	87,5	12,5
Cast, annealed	79,7	20,3
Specimen from [4]	86	14

High-Temperature Institute, Academy of Sciences of the USSR. Baikov Metallurgy Institute, Academy of Sciences of the USSR, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 41, No. 6, pp. 1073-1077, December, 1981. Original article submitted April, 11, 1981.

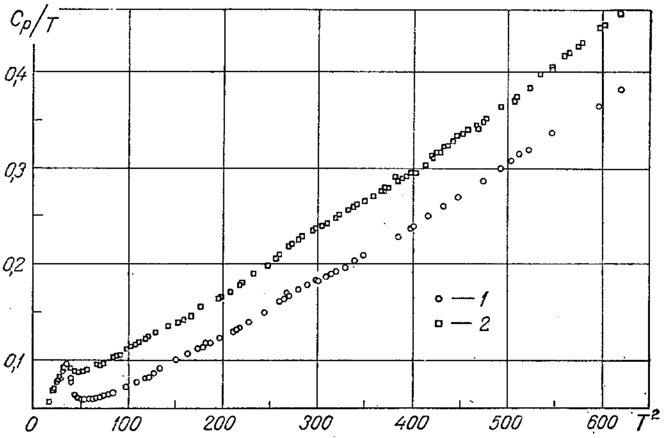

Fig. 1. Function $C_p/T(T^2)$ for annealed (1) and rapidly quenched (2) specimens. C_p/T, J/(kg·deg); T^2, °K^2.

the specimen was annealed for 100 h at a temperature of ∿750°C and cooled in water. The heat capacity of the annealed specimen was then measured. The rapidly quenched specimens were obtained by pouring the melt onto a massive rotating disk. Cooling rate for a 10-g charge comprised 10^6-10^7 deg K/sec. The microstructure of the cast and annealed specimens differed. X-ray analysis confirmed the presence of the two phases Nb_3Ge and Nb_5Ge_3. For Nb_3Ge the lattice constant $a = 5.178$-5.180 Å, while for Nb_5Ge_3 $a = 10.148$ Å and $c = 5.152$ Å. The diffractogram lines were intensely broadened, probably because of inhomogeneities in the A-15 phase and the presence of defects. T_c ∿5.9°K for the cast specimens, ∿6.7-6.8°K for the rapidly quenched, and ∿6.1-6.3°K for the annealed ones (measurements performed by the induction method), which indicates an increased Nb content in the compounds, as confirmed by x-ray analysis. According to chemical analysis the Ge content was ∿20.38 mass % for the annealed specimen.

Heat capacity was measured by the usual adiabatic calorimeter method with periodic heat introduction. Germanium and platinum thermometers (constructed and calibrated at VNIIFTRI) were used for temperature measurement. Measurements and data collection were completely automated [5]. The equipment was first use to measure $C_p(T)$ for corundum, which is recommended as a calorimetric reference material [6], and the accuracy of C_p determination was found to be ∿0.6% at 6°K and ∿0.01% at 90°K. Each specimen was measured over a lengthy time period. Individual series of measurements overlapped in temperature. At 15-25°K a series of experimental points was taken with both platinum and germanium thermometers. The heat capacity of the rapidly quenched specimen was measured at 142 temperature points, that of the cast specimen, at 189 points; after measurements this specimen was annealed and measured at 92 points.

Figure 1 shows the function $C_p/T(T^2)$ from ∿7 to ∿23°K for two specimens studied. The low-temperature superconductive transition occurs at ∿6-6.1°K. These values are somewhat below T_c as determined by the inductive method. In the rapidly quenched specimen this transition is smeared and weakly expressed. The heat capacities of cast and annealed specimens differed somewhat. For the latter the heat capacity is ∿2.4% higher at 7°K, with the difference decreasing with increase in temperature, and at ∿18°K the values coincide within the limits of measurement accuracy. The heat capacity of the rapidly quenched specimen is significantly greater than that of the annealed one (by ∿47-44% at 7-12°K), while with increase in temperature to 20°K the difference decreases to 15%.

In the $C_p/T(T^2)$ curve, aside from the low-temperature superconductive transition with T_c ∿6°K there is an irregularity and "excess" heat capacity at ∿11-12°K for the rapidly quenched and annealed specimens, and at ∿17-18°K (by 2-3%) for all specimens. These irregularities can be seen clearly in Fig. 2, where the data are presented in the coordinates C_p/T^2 (T). Their appearance is caused by the presence of a small quantity of the Nb_3Ge phase A-15 with high T_c. It should be noted that such an increase in heat capacity at 17-18°K was not observed in previous studies, and to test the validity of the results, we additionally measured $C_p(T)$ for a copper specimen analyzed at VNIIFTRI and suggested as a reference material. The function C_p/T^2(T) for the copper was smooth.

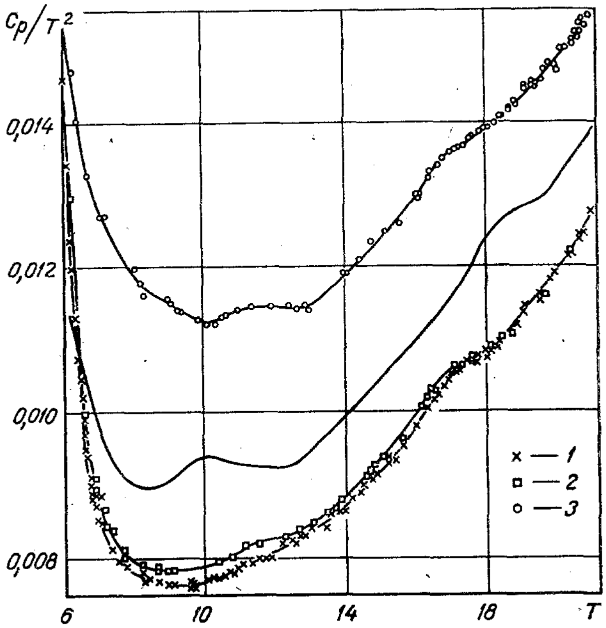

Fig. 2. Function $C_p/T^2(T)$ for unannealed (1), annealed (2), and rapidly quenched (3) specimens. For comparison, function $C_p/T^2(T)$ for Nb_3Ge + 8 at. % Si (smooth curve) is also shown. C_p/T^2, J/(kg·deg K^2); T, °K.

Using the data of [1], in which the authors maintained that the specimens were 99.5 wt. % A-15 Nb_3Ge and 0.5 wt. % Nb_5Ge_3, we calculated the phase content of the present specimens. Table 1 shows the phase content of the specimens studied at 24°K (in mass %). The rapidly quenched specimen contains more Nb_3Ge and possibly more of the high-temperature A-15 phase. Annealing at 750°K produced practically no change in phase composition.

In contrast to the results of a preceding study, we did not succeed in the usual processing of the experimental data in the Debye approximation $C_p = \gamma T + \beta T^3$, since γ, as determined from $C_p/T(T^2)$, proved to be negative. (Nonfulfillment of the Debye approximation has been noted previously, e.g., in [7]). It is possible that this behavior is caused by some other contributions to heat capacity or by peculiarities of the phonon spectrum of the high temperature heat capacity component, and will require further study.

NOTATION

Θ_D, Debye temperature; a and c, lattice parameters; C_p, specific heat at constant pressure; γT, electron heat capacity in normal state; βT^3, lattice heat capacity; χ, magnetic susceptibility; T, temperature; T_c, superconductive transition temperature.

LITERATURE CITED

1. G. R. Stewart, L. R. Newkirk, and F. A. Valencia, "Specific heat of single phase Nb_3Ge," Solid-State Commun., 28, No. 7, 417-420 (1978).
2. I. M. E. Harper, T. H. Geballe, L. R. Newkirk, and F. A. Valencia, "Low-temperature thermal and electrical properties of chemical vapor-deposited Nb_3Ge," J. Less Common Met., 43, No. 5, 5-11 (1975).
3. N. N. Mikhailov, I. V. Voronov, and O. A. Lavrova, "Superconductivity of massive Nb_3Ge above 20°K," Pis'ma Zh. Eksp. Teor. Fiz., 19, No. 8, 510-512 (1974).
4. V. I. Surikov, A. K. Shtol'ts, P. V. Gel'd, and L. A. Ugodnikova, "Low-temperature heat capacity and magnetic susceptibility of $Nb_{3.3}Ge_{0.7}$," Izv. Vyssh. Uchebn. Zaved., Fiz., 17, No. 5, 121-124 (1974).
5. M. P. Orlova, Ya. A. Korolev, and L. M. Kheifets, "Automation of heat-capacity measurements in the range 4.2-273°K," Zh. Fiz. Khim., 54, No. 1, 246-248 (1980).
6. M. P. Orlova and Ya. A. Korolev, "Corundum reference material for low-temperature calorimetery," Zh. Fiz. Khim., 52, No. 11, 2756-2759 (1978).

7. C. H. Cheng, K. A. Cupta, E. C. van Reuth, and P. A. Beck, "Low-temperature specific heat of bcc Ti—V alloys," Phys. Rev., 126, No. 6, 2030-2033 (1962).

DETERMINATION OF THE CHARACTERISTICS OF POLYMER DECOMPOSITION USING THE SEMIINFINITE BODY METHOD

P. V. Nikitin and A. E. Pirogov

UDC 536.21:541.12.127

The problem of determining the kinetics of the decomposition and thermophysical properties of polymers from a one-dimensional temperature field is investigated. An analytic solution is obtained under the condition that the rate of decomposition depends strongly on temperature.

Thermal decomposition of polymers is customarily described by some single chemical kinetic equation. The characteristics entering into this equation are, generally speaking, effective (overall) characteristics, and for this reason can depend on the conditions under which the polymer is heated. Usually, decomposition kinetics are determined by thermal analysis methods with their characteristic special heating conditions. The purpose of this paper is to develop a method for determining the decomposition characteristics under conditions when the material being studied is a semiinfinite body, heated on one side. The use of this method is interesting, for example, for obtaining the characteristics of heat-resistant coatings [1]. The conditions for functioning of the coating are similar to those described above, but differ considerably from the conditions realized in thermal analysis.

The starting data for determining the characteristics is the temperature field. For this reason, in order to solve the problem, it is necessary to use the complete system of equations of heat and mass transfer and chemical kinetics, written for the decomposition zone. Then, the thermophysical properties of the material (thermal conductivity and others) are described together with the kinetics as well.

1. We are concerned with one-dimensional heating of a semiinfinite body. The mathematical model of the decomposition of polymer materials is well known [1]. However, it should be noted that Arrhenius' law has, apparently, limited applicability. This is indicated by the existing differences in the kinetic characteristics, obtained under different experimental conditions, their dependence on the heating rate, and other characteristics. For this reason, we will write the kinetic equation in generalized form, taking into account the variability of the decomposition characteristics

$$\partial\varepsilon/\partial\tau = w(\varepsilon, T), \tag{1}$$

where $0 < \varepsilon < 1$ is the degree of transformation. The following condition is imposed on the temperature dependence of the decomposition rate $w(\varepsilon, T)$

$$\Delta T = \left| w(\varepsilon, T)/\left(\frac{\partial w}{\partial T}\right)_{\varepsilon} \right| \ll T. \tag{2}$$

The quantity ΔT is essentially the characteristic temperature interval in which the decomposition occurs. If $w \sim \exp(-E/RT)$, then (2) gives $E/RT \gg 1$, which is satisfied for most polymers, even taking into account the spread in the data for E.

We will not write out the general equations of heat and mass transfer in the decomposition zone [1], rather we will limit ourselves immediately to approximate equations taking into account the following considerations. Since ΔT, according to (2), is small, the characteristic width of the decomposition zone and the decomposition time τ_d will also be small. It is then natural to assume that the processes in the decomposition zone are quasistationary and will be described by transfer equations, in which the time derivative $\partial/\partial\tau$ is replaced by $-v(\partial/\partial y)$. The quasistationary equations admit a number of transformations [2-5], lowering their order and reducing the problem to the solution of the heat balance equation

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 41, No. 6, pp. 1078-1082, December, 1981. Original article submitted November 10, 1980.