THERMOPHYSICAL PROPERTIES OF LANTHANIDES AT HIGH TEMPERATURES

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Results of measurements of heat capacity, thermal diffusivity, and thermal conductivity of yttrium, gadolinium, holmium, and lutecium in the temperature range 1100-2100°K are presented. The behavior of the thermophysical properties with phase transitions is discussed.

At the present time, Soviet and foreign researchers are directing increasing attention toward studying the thermophysical properties of rare-earth metals (REM) in the solid and liquid phases. This interest stems from both the wide prospective applications of REM in modern technology, as well as from the important scientific meaning of such work.

Many of the unique properties of lanthanides and their compounds are related to the specific electronic structure (gradual filling of the 4f shell). This structure is reflected in the anomalously high values of the heat capacity, small changes in thermal and electrical conductivity on melting, and the presence of polymorphic transformations in the solid phase.

Unfortunately, the thermophysical properties are primarily studied for the elements representing the light, cerium subgroup, and with the greater part in the solid state. Therefore, we carried out an investigation of heavy lanthanides: gadolinium, holmium, and lutecium in the solid and liquid states. We studied the states of yttrium in order to clarify the laws governing the change in the thermal parameters of the entire IIIA group of elements in the periodic system.

In choosing a method for carrying out the investigation, we took into account such modern requirements of the experimental technique as the comprehensiveness and precision of the quantities being studied, and fast response and automation of the measurement process. Only some of the various nonstationary methods satisfy all the indicated requirements. These methods include those based on the regular thermal regime of the II and III kind. In the present article, we develop a new, comprehensive version of the pulsed method, which permits measurement of the heat capacity and thermal diffusivity of the specimens being studied in a single run [1]. The essence of the method consists of the following: the inner surface of a hollow cylinder made of the metal being studied is subjected to a U-shaped short heating (or cooling) pulse. The nature of the temperature change is recorded on the opposite side. Analysis of the temperature curves, as well as information concerning the intensity of the heating and geometry of the sample, permit determining the heat capacity and the thermal diffusivity, and therefore, the thermal conductivity as well. Thus, the entire complex of thermophysical properties turns out to be measureable in a single experiment run.

In this work, we used specimens with the following purity: Gd — 99.93%; Ho — 99.90%; Lu — 99.90%; and, Y — 99.89%. Analysis of the systematic errors in the results shows that they consist primarily of the errors in determining the heating intensity (current and voltage measurement), measurement of the geometry of the specimen, and the introduction of corrections for the role of the crucible wall. Estimates of these components give a total systematic error of 3-4% for measurements of heat capacity, 2-3% for measurements of thermal diffusivity, and 5-7% for measurements of thermal conductivity.

Figure 1a shows the results of the investigations of the thermophysical properties of yttrium and lutecium, and Fig. 1b shows the results for gadolinium and holmium. Within the limits of the experimental error, our data on heat capacity agree with the results of

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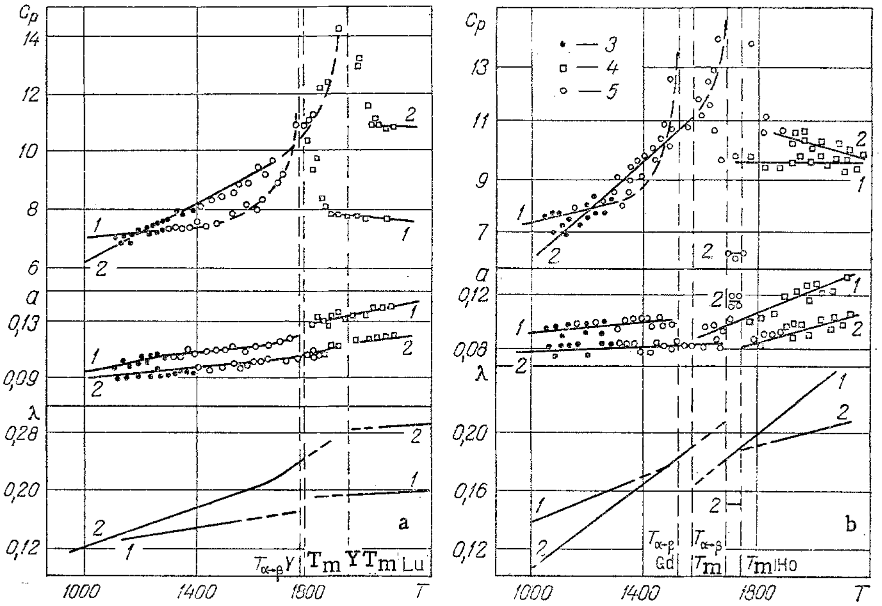

Fig. 1. Thermophysical properties: a) yttrium (1) and lutecium (2); b) gadolinium (1) and holmium (2); 3) heating pulse; 4) cooling; 5) periodic heating. T, °K. T_m is temperature of melting.

[2, 4, 6] and [3]. In order to explain the steep increase in heat capacity near the melting temperature, we can use the suggestion of I. I. Novikov, which explains this effect as the result of the formation of vacancies. Graphing these results in semilogarithmic coordinates $\ln(\Delta c_p \cdot T^2)-1/T$ yields a linear function.

The difference of the heat capacities in the liquid state and the values in the solid state near the temperature for a polymorphic transformation does not exceed 7%. The noticeable jump in the heat capacity of holmium in the β phase is interesting. Thus jump confirms the sharp change in the heat capacity with phase transitions of the second kind.

The results of measurements of the heat capacity of holmium and gadolinium in the liquid state agree with the data in [3] to within 3% near the melting temperature. There is no information in the literature concerning higher temperatures.

The absolute values of the heat capacity of holmium, gadolinium, and lutecium in the solid and liquid states exceed the corresponding results for most of the low-melting metals. This is a characteristic property of all lanthanides. The heat capacity of yttrium on the average is 20% lower than that measured for REM.

The absolute values of the thermal diffusivity and thermal conductivity for all metals studied in the solid phase coincide with the corresponding data in [2, 4, 6] and partially with the results in [5]. Some of the deviations of our data on the thermal conductivity of holmium and gadolinium (up to 15-20% at $T \approx 1300$ K) from the data in [5] can be explained by the effect of anisotropic factors as well as by errors in the calculation of the thermal conductivity in [5], where only the thermal diffusivity was measured, while the values of the heat capacity were taken from [3], wherein these values in their turn were calculated from the enthalpy.

Data on the thermal diffusivity and thermal conductivity of the metals studied in the liquid state are obtained for the first time.

The nature of the temperature dependence of the thermal diffusivity and thermal conductivity is similar for all the lanthanides studied. A jump in the β phase was only observed in holmium. No noticeable change was found in the temperature diffusivity and thermal conductivity on melting.

The results of the studies of thermophysical properties of solid and liquid Gd, Ho, and Lu show that the characteristic features of REM, viz., the relatively high value of the heat capacity and small jumps in the thermal diffusivity and thermal conductivity on melting, are typical of the metals studied.

Data on the heat capacity of liquid gadolinium, holmium, and lutecium confirm and refine the parallel behavior of the heat capacity of liquid REM and the specific Gibbs free energy found in [7]. The results for yttrium lead to the conclusion that the smallness of the jumps in the thermal diffusivity and thermal conductivity on melting are general properties of all group IIIA elements in the periodic system.

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EXPERIMENTAL INVESTIGATION OF VACANCY EFFECTS IN PURE METALS

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The energy for the formation of vacancies in copper ($2.1 \cdot 10^{-19}$ J (1.3 eV)), platinum ($2.56 \cdot 10^{-19}$ J (1.6 eV)), and titanium ($1.9 \cdot 10^{-19}$ J (1.2 eV)) are determined from the results of measurements of the enthalpy and heat capacity of the latter in deformed and annealed states.

The study of the thermodynamic properties of nonequilibrium states of metals permits determining the energy characteristics of defects in the crystalline structure. In what follows, we describe experiments for determining the energy of vacancy formation, based on the measurement of enthalpy and heat capacity of metals in equilibrium and nonequilibrium states.

Measurements of the enthalpy and the heat capacity of a deformed metal in the recrystallization region yield the values of the enthalpy and heat capacity of the given metal in the nonequilibrium state; measurements of the undeformed, carefully annealed metal yield values of the enthalpy and heat capacity in the equilibrium state. Comparison of the values of the enthalpy and heat capacity obtained for the same range of temperatures establishes reliably the magnitude of the energy of vacancy formation. Indeed, the equilibrium concentration of vacancies is given by

$$c = A \exp\left\{-\frac{E}{kT}\right\}. \tag{1}$$

In the nonequilibrium state, the vacancy concentration c' is not equal to the vacancy concentration in the equilibrium state and can be found from the following considerations. Assume that the formation of excess vacancies has occurred as a result of deforming the metal, which is characterized by the stress appearing in the metal on deformation. Its

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