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Thermal Diffusivity of Solid and Liquid Yttrium, Gadolinium and Terbium[1]

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ABSTRACT

We present the results of thermal diffusivity investigations for solid and liquid yttrium, gadolinium and terbium at the temperature range 1700-2100 K. Our measurements are carried out with the help of a new mounting based on the original method being a new version of temperature-waves one.

Effective thermal diffusivity frequency dependence (the effect of relaxation) is registrated at the neighbourhood of polymorphic transformation and melting temperatures as well as in liquid state, indicating existence of the additional accounts to heat transfer. These accounts being separated experimentally, we have picked out one, which is caused by electron and phonon heat transfer mechanisms. Claster model is used for interpretation of relaxation effects observed at the phase transitions. The relaxation time of the structure clasters has been estimated.

The relaxation effects in liquid state are due mainly to the influence of the capillar convection, which is caused by the existence of the temperature dependence of the surface tension coefficient. This process contribution falls as the temperature wave frequency increases.

Non-relaxation part of the effective thermal diffusivity depends basically on the properties of rare-earth metals electron sistem. Thermal diffusivity of liquid Y, Gd and Tb exhibit a tendency to growth, that can be explained within the framework of the electron theory based on the two-band model of N.Mott.

KEY WORDS: charge and energy carrier scattering, claster, convection, Mott's model, phase transition, rare-earth metals, temperature-wave experimental method, thermal diffusivity.

1. INTRODUCTION

Thermophysical properties of rare-earth metals (REMs) in liquid state are insufficiently investigated. Thermal diffusivities of yttrium and gadolinium have been measured only in works of Novikov et al.[1,2]. Thermal diffusivity of liquid terbium has not been measured earlier. Nowdays there are no clear ideas about the behavior of liquid rare-earth metals thermal diffusivity at the broad high temperature range, behavior features of thermal diffusivity under melting being not turned out. These circumstances prevent to clear up features of physical processes, which determine the rare-earth metals special properties. In particular, this problem includes: turning out the role of different charge carrier and energy scattering mechanisms in REMs at high temperatures, clearing up if the Mott's model can be used to describe REMs properties in liquid state, exposing REMs polymorph transformation and melting kinetic features, and some other aspects. Present work is one of the first steps to the solution of the problems considered.

2. MEASUREMENTS

2.1. Specimens

Polycrystal metals investigated contained the following quantity of impurities: 0.12 % for Y, 0.08% for Gd and 0.05 % for Tb. The main impurities were: H, C, N, O, F, Si, Ca, Cu, Fe as well as accompaning REMs. The ratio of metals electrical resistances at room temperature to that at 4.2 K (relative resistances) were 4.5, 13 and 15 for Y, Gd and Tb respectively. The samples, located in the tantalum crucibles 17 mm in diameter and 20 mm height, were placed to the high temperature vacuum kiln with tungsten heater. Air had been pumped out to the pressure of 10^{-3}Pa in the kiln. Then the kiln had been filled with helium

under the pressure of 10^5Pa. Titanium absorbers were used to take up active gases remaining unabsorbed.

2.2. Procedure

The samples were heated to the temperature 2000 K, and then little by little cooled with the kiln to the temperature 1000 K. After that a laser was switched on and its radiation, having passed mechanical amplitude modulator, had an influence on the uncovered surface of the sample, erasing temperature wave in the latter. Amplitude modulation frequency for laser radiation (temperature wave frequency) was changed in the range of 2 - 25 Hz, modulating function being meander (periodical right-angled). Temperature oscillations on the central part of the illuminated region were converted to the electrical signal by means of a photo-sensor. Special measurement mounting provided quasi-optimal estimation of the first harmonic parameters of this signal. Illuminated field diameter varied with the help of collimator within the limits of 3 - 5 mm, reception region diameter of the photo-sensor being 2 mm. Sample's mean temperature was changed step by step throuth 5 K. Temperature wave characteristics measurements were carried out in the quasi-stational regime.

During the experiment sample's mean temperature and oscillation phase shift of the photo-sensor signal with the attitude to the oscillations of the thermal flow (laser radiation), influencing on the sample's surface, had been measured. On the basis of these measurements in accordance with the method [3], relative thermal diffusivity of the investigated material was calculated. To receive the absolute values data of works [4-6] were used. Relative root-mean-square measurement error for thermal diffusivity did not exceed 7%.

3. EXPERIMENTAL RESULTS

The investigation results have shown, that thermophysical properties of Y, Gd and Tb at high temperatures are very similar. Let's consider the principal peculiarities of these properties on the example of gadolinium. In Fig.1 line 3 displaces the results of present work, data of works [2,5] being represented by lines 1 and 2 respectively. Thermal diffusivity of gadolinium in solid state at HCP phase is practically independed of temperature. At the neighbourhood of structure HCP-BCC transformation thermal diffusivity polytherm, being calculated from the low frequency temperature waves measurements, displaces anomalies looking like local extrema (for details see [7]). As temperature wave frequency increases, the intensity of these anomalies reduces, disappearing under the frequencies more than 30 Hz [7]. The polytherm break, after which thermal diffusivity growth is observed in BCC phase, corresponds to the structure transition temperature. Our data for this temperature interval, produced in Fig.1 (line 3), correspond to the frequency 3.3 Hz. Analogous anomaly is observed in the thermal-diffusivity polytherm at the neighbourhood of melting temperature. Intensity of the peak reducing with temperature wave frequency growth, the peak's amplitude however exceeds the measurement error essentially at the frequency 25 Hz. Thermal diffusivity of gadolinium does not have frequency dependence at temperatures lower than 1500 K.

Measurements results above the melting temperature also have the frequency dependence (see Fig.1). The frequencies of temperature waves being low, sharp growth of thermal diffusivity under heatihg is observed. Wave frequency rise leads to gradual reduction of the $a^*(T)$ polytherms, and so the experimental results at

the frequencies more than 14 Hz coincide within the limits of measurement error, indicating a moderate growth of the liquid gadolinium thermal diffusivity under heatihg.

Comparison of present work results with published data [2] indicates their satisfactory accordance within the limits of measurement error. However, in contrast to [2], we have got information about the temperature wave characteristics under the phase transitions.

4. DISCUSSION

There are two basic heat conduction mechanisms in solids in paramagnetic phase: electron and phonon ones [8]. These mechanisms are lagless and can't cause the observed frequency dependence of the measurements results. So there are additional mechanisms of heat accumulation and transfer at the neighbourhood of polytherm-transformation and melting temperatures as far as in liquid state. Let's consider these additional mechanisms, which have influence on the results of measurements.

The experiment shows that REMs structure transformations and melting occur in the temperature range 50-80 K, which is some times more than the temperature difference on the central part of the sample and at the sighted region boundary. Therefore phase transitions considered are " spreaded ", occuring naturally in the temperature interval not at the fixed temperature. Two phases of matter co-exist in this temperature range: low-temperature and high-temperature, and so the substance represents a heterophase system, its thermophysical characteristics being effective and therefore depending on thermal influence parameters as far as on matter structure. Temperature oscillations in sample vary the ratio of

phase quotas. This process is accompanied by the configuration energy change, which displays as effective heat capacity increase and leads to reduction of the effective thermal diffusivity $a^*(T)$.

However the anomaly behavior of effective thermal diffusivity is accompanied by growth of $a^*(T)$ as far as its fall (see Fig.1). Thermal diffusivity increase is caused by something additional mechanism of heat transfer, for example, a diffusion of structure clasters [9]. The claster model of structure phase transition is the only one that allows to give an uncontradictionly interpretation of the experimental results. Claster formation processes determine configuration contribution to the system enthalpy and are responsible for the system effective heat capacity growth as far as for the additional temperature wave lag, which is seen in the effective thermal diffusivity reduction. Clasters diffusion (the diffusion of structure, not of a substance or mass) accelerates the process of heat transfer, leading to the increasing of $a^*(T)$, that explains the appearance of local maxima at the neighbourhood of structure transition and melting temperatures.

The experimental results treatment has discovered that relaxation time for structure clasters, appearing under structure transformations, is 15-30 ms. Relaxation time for clasters, appearing under melting, is some times smaller. Temperature wave frequencies being high enough, structure clasters contributions to the $a^*(T)$ become neglectable and effective thermal diffusivity tallies with its real value determined by the electron and phonon mechanisms. For the structure phase transitions the region of temperature waves high frequencies begins from 30 Hz.

Thermal diffusivity of liquid homogeneous REMs also depends on the wave

frequency and so it is effective. This dependence shows, that along with lagless electron and phonon parts, there is a lag mechanism of heat transfer. For liquid state the latter one is a natural convection. There are two reasons of the convection in our case. In the first place, liquid motion in the whole volume appears thanks to the fact that the temperature of the open (top) surface of the investigated sample becomes smaller than at the depth. Secondly, liquid motion at the surface arises due to the surface tension forces (capillary convection). Really on the liquid surface there is a radial temperature gradient. This leads to the appearance of the uncompensated surface forces, moving the liquid.

Convection increases the total heat conduction of the system. Liquid temperature oscillations, caused by the temperature wave, results in the oscillations of the convective currents parameters, effective thermal diffusivity of liquid being affected. Convection contribution is the most important at low frequencies. The frequency of the temperature wave increases, convection part of the $a^*(T)$ reduces. Capillary convection is connected with the displacement of thin liquid surface layers only, their mass being comparatively small. Thus when the wave frequency increases, at first the influence of the liquid volume convection reduces, and after that only - of the capillary convection. At the limit of high frequencies effective thermal diffusivity of liquid coincides with the real one, caused by the electron and phonon mechanisms. Using $a^*(T)$ frequency dependence data, one can estimate parameters of viscosity and (or) surface tension coefficient temperature dependence.

Periodical heating methods, and in particular the temperature waves one, permits anybody to separate different contributions to the thermophysical prop-

erties of matter comparatively easy. It is one of the many important advantages of such methods.

Let's analyse the investigation results for true thermal diffusivity, the latter data being obtained at the limit of high frequencies of temperature waves. High temperature solid REMs properties studies have shown, that phonon mechanism part of heat transfer in the REMs is neglectable at high temperatures [4,6]. The main heat transfer mechanism is the electron one. It is important to clear up, what electron scattering mechanisms are essential in the REMs at high temperatures. In [4] there is a conclusion, that impurity and magnetic scattering mechanisms are not effective in solid REMs at high temperatures, whereas in magnetic metals (such as Gd and Tb) at middle temperatures the role of magnetic scattering mechanism is great. In Fig.2 thermal diffusivities of liquid Y, Gd and Tb are represented. One can see, that they don't differ essentially and so the basic electron scattering mechanisms are the same. In Y there is no magnetic scattering mechanism, therefore, the basic scattering factor for electrons in liquid REMs is the phonon one.

As it is shown in [4,6], satisfactory description of solid REMs properties is given by the Mott's 2-band model of electron energy spectrum. One of the application conditions of this model is that the density of states N_d of the heavy d–electrons must exceed essentially the density of states N_s of the light s–electrons at chemical potential level. Just in this case 2-band mechanism will determine kinetic parameters of metal [8]. At low temperatures, as the calculations show, N_d/N_s is about 50-100 [10]. The density of states N_d reduces with heating (and so one can see thermal diffusivity growth, which is inexplicable in

the one-band model). In particular, as it is shown in present paper, thermal diffusivity of REMs increases in the liquid phase, therefore N_d reduce continues. Our evaluations, carried out with the help of results of [4], improve, that in the whole REMs heating up to 2000 K leads to the no more than 4 times reduce of N_d. It means, that Mott's model can be perfectly used to describe the liquid REMs properties.

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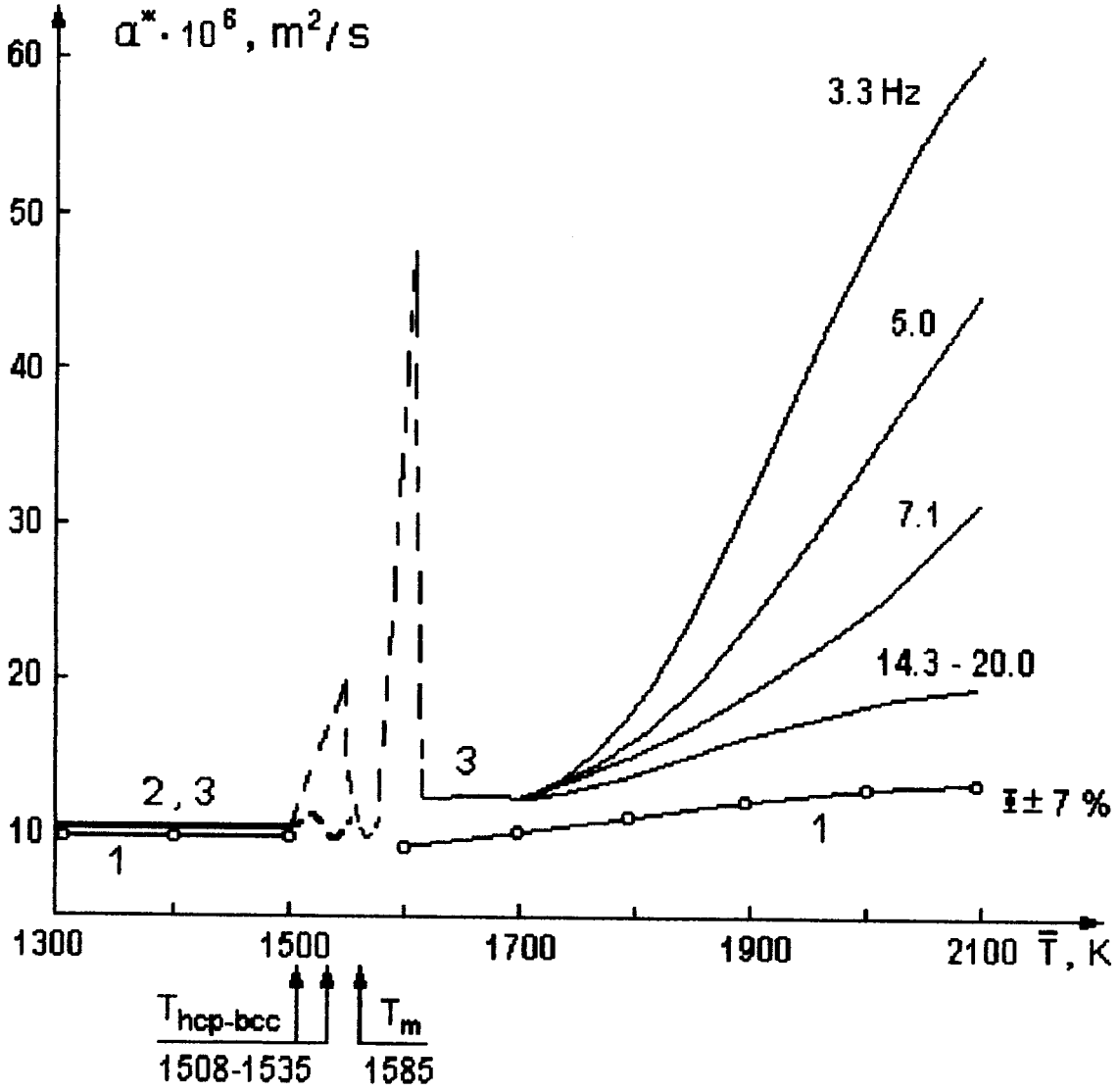
FIGURE CAPTIONS

Fig.1 Thermal diffusivity of solid and liquid Gd.

Fig.2 Thermal diffusivity of liquid Y,Gd,Tb.


a*·10^6, m^2/s
60
50
40
30
20
10
3.3 Hz
5.0
7.1
14.3 - 20.0
3
2, 3
1
1
I ± 7 %
1300
1500
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T_m
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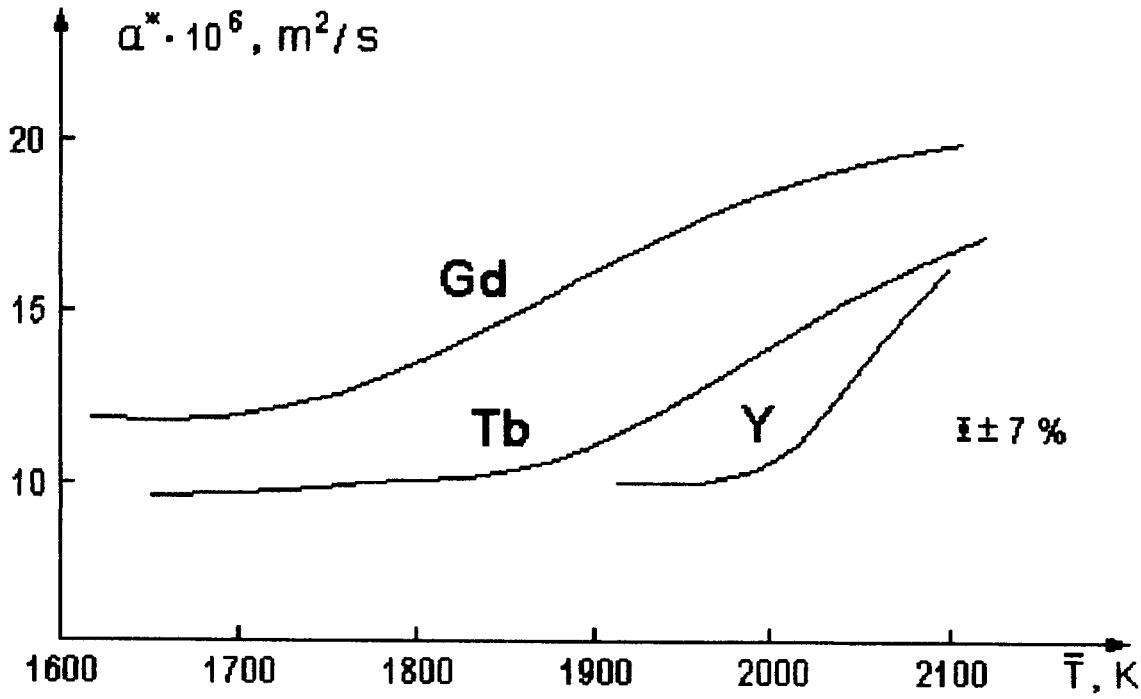
α*·10⁶, m²/s
20
15
10
Gd
Tb
Y
±7 %
1600
1700
1800
1900
2000
2100
T̄, K