THERMOPHYSICAL PROPERTIES OF THIN METAL FILMS

A. T. Pugachev, Yu. A. Volkov,
and N. P. Churakova

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The article discusses methods and results of comprehensive investigations of the thermal conductivity, thermal diffusivity, heat capacity, and structure of films of metals $10-10^2$ nm in thickness.

Despite the substantial progress made in the study of films and their wide use in numerous areas of science and technology, there has been relatively little study of the thermophysical properties of thin films [1,2]. These properties may be determined not only by the nature of the material, but also by its geometric, structural, and substructural features. The most significant differences between the properties of films and bulk solids should be found within the thickness range $10-10^2$ nm [1-3].

Studies have recently been conducted [4-9] on the thermal properties of metal films. These experiments have investigated mainly thermal conductivity, and the results have been interpreted from the point of view of general differences between films and bulk solids. Quantitative description of most of the available empirical data is difficult due either to the lack of necessary studies of film morphology, structure, and substructure or to the fact that the object of the investigations was a film—substrate system, rather than the free film studied in theoretical models.

The objects of study in the present work were $10-10^2$-nm-thick films free of a substrate. The methods used to study bulk solids cannot be directly applied to objects several hundreds of atom layers in thickness. Thus, we first developed methods of comprehensive study which would enable us to determine thermal conductivity, thermal diffusivity, and heat capacity under one set of conditions on one specimen while studying the structure of the object at the same time.

METHODS AND OBJECT OF INVESTIGATION

It is well known that the comprehensive study of thermophysical properties is based on experimental data on the space—time distribution of temperature in a specimen and on the quantity of energy absorbed or released. Temperature fields in metals are conveniently determined from the temperature dependences of given physical parameters. Properties are calculated from thermal conductivity equations for the given experiment. This general approach was used in elaborating the following methods: films were heated by Joule heat inside the chamber of an electron-diffraction instrument, while the temperature fields were computed from electron-diffraction patterns or from electrical measurements.

Electron-Diffraction Methods

A rectangular film separated from its substrate was secured at both ends in a special attachment and placed in the electron-diffraction chamber. The film was heated in a vacuum by passing a direct current through it. We measured the current in the film and its electrical resistance and obtained electron-diffraction patterns of different sections of the heated film by the transmission method. The steady-state and transient temperature fields of the film were recorded on stationary and moving photographic plates, respectively [5,10]. The fields were computed from the diffraction patterns, from data from precision measurements of the lattice parameter by means of the known coefficient of thermal expansion. Temperature measurement accuracy was ±5°C.

In calculating the temperature fields it was assumed that the coefficients of thermal expansion of thin films and bulk solids are the same [11, 12]. Special tests conducted as

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part of the present work showed that the coefficient of thermal expansion of thin films has a tendency to increase with a grain size $D \leqslant 10$ nm. Thus, the application of the electron diffraction method to such a highly dispersed film requires that we have additional data on its coefficient of thermal expansion.

The original equation for determining the thermophysical properties was a one-dimensional equation of thermal conductivity for a thin film heated in a vacuum by a direct current:

$$\frac{\partial T}{\partial \tau} = \frac{K\partial^2 T}{\partial x^2} - \frac{2K\sigma\varepsilon\,[T^4 - T_0^4]}{\lambda t} + \frac{KJ^2\rho}{m^2 t^2 \lambda}\,. \tag{1}$$

For steady-state temperature fields $\partial T/\partial \tau = 0$ Eq. (1) is conveniently written as,

$$I^2 R = 2\lambda m t \left.\frac{dT}{dx}\right|_{x=l} + 2m\sigma \int_{-l}^{l} \varepsilon\,(T^4 - T_0^4)\,dx. \tag{2}$$

If R_i and $T_i(x)$ are determined empirically for certain values of I_i, then with a film of known geometry Eq. (2) can be used to calculate thermal conductivity and emissivity.

The coefficient of thermal diffusivity was determined from the equation

$$\frac{\partial T}{\partial \tau} = K\frac{\partial^2 T}{\partial x^2} - 2K\varepsilon\sigma\,(T^4 - T_0^4)/\lambda t \tag{3}$$

with the following initial and steady-state boundary conditions

$$T(x,\ 0) = T(x),\ T(\pm l,\ \tau) = T_0.$$

This equation describes the transient temperature fields after the current is turned off. To determine thermal diffusivity, Eq. (3) was solved at point $x = 0$ for different values of K. The integration was performed on a computer by the finite-differences method. Here we used the values of $T(x)$, λ, and ε found by solving the steady-state problem for the given specimen. The coefficient of thermal diffusivity was determined by comparing the empirical curves of $T(0,\ \tau)$ with those calculated for different values of K.

Specific heat was computed from experimental data on thermal conductivity and thermal diffusivity.

It must be noted that several terms were omitted in Eq. (1) for the elementary section of the film, these terms having accounted for heating of the film by the electron beam, Thomson heat, the thermal conductivity of the residual gas, and radiation from the lateral surface of the film. An analysis of the temperature fields, special studies of the heating of a thin film by an electron beam, and calculations showed that the above terms were two or more orders less than the Joule energy and could be ignored.

Electrical Methods

As shown by the electron-diffraction studies, the temperature along the heated film is described by a parabola. This allowed us to change over from the local temperature to the mean temperature and use electrical methods normally used to study bulk solids [13,14] to investigate the thermal properties of films. The methods used in the present work are based on measurement of the power given off in the film and the average temperature of the latter.

At low magnitudes of heating $T(x) - T(l) \ll T(l)$ Eq. (1) reduces to a simple relation, from which we determined thermal conductivity

$$I^2 R = 6\,\lambda m t \Delta\overline{T}/l + 8m\sigma\varepsilon T^3(l)\,\Delta\overline{T}, \tag{4}$$

where

$$\Delta\overline{T} = \frac{1}{2l}\int_{-l}^{l} [T(x) - T(l)]\,dx.$$

The value of $\Delta\overline{T}$ was calculated from the temperature coefficient of resistance. At $\Delta\overline{T} < 20°\mathrm{C}$ and a specimen length $\sim 2\cdot 10^{-3}$ m, the radiation term in (4) does not exceed 5% of the Joule energy and may be accounted for in the form of a small correction of the values of ε found in [15].

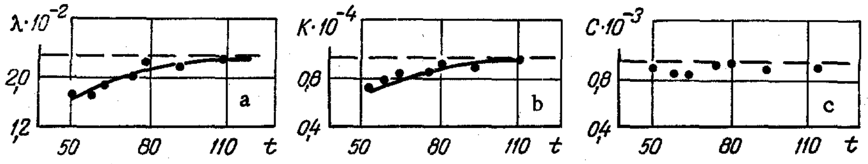

Fig. 1. Dependence of thermal conductivity λ, thermal diffusivity K, and heat capacity C of Al films on thickness t. Points denote empirical values and solid lines — calculated values for the external size effect ($p = 0$, $r = 0$); dashed lines show values of λ, K, and C of massive aluminum. $\lambda \cdot 10^{-2}$, W/m·deg, $K \cdot 10^{-4}$, m^2/sec, $C \cdot 10^{-3}$, J/kg·deg; t, nm.

The ideas of determining thermal conductivity by electrical and electron-diffraction methods are similar. With closing of the current circuit, the temperature field is described by Eq. (1) with boundary and initial conditions $T(\pm l, \tau) = T_0$ and $T(x, 0) = T_0$. This equation was numerically integrated on a computer, after which we plotted the dependence of mean temperature on time for different values of K. For the same boundary conditions, we experimentally evaluated the function $\Delta\bar{T}(\tau)$ and determined the value of K according to the agreement between empirical and calculated (on the computer) values of $\Delta\bar{T}(\tau)$.

The heat capacity of the film was determined from the initial section of the curve $\Delta\bar{T}(\tau)$:

$$C = \frac{I^2 R}{\left.\dfrac{\partial \Delta \bar{T}}{\partial \tau}\right|_{\tau=0}} 2lmdt, \tag{5}$$

We supplied a single rectangular pulse of current of $5 \cdot 10^{-4}$–10^{-3} sec duration to the film. Voltage was recorded on an oscillograph. Here we recorded the dependence of voltage on time on the film and a reference resistor. This made it possible to determine the current flowing through the film and the dependence of the mean temperature on time. The values of λ, K, and C were determined to within ∿10% using the above methods.

The principal advantages of these methods is that they permit comprehensive study of the thermophysical properties of free (of a substrate) films, with diffraction control of the structure and phase composition of the object during the experiment.

The objects of the experiment were thin films of Al and Au condensed in a vacuum of $\sim 10^{-3}$ Pa. The metals were heated by the induction method. The condensation rate was ∿10 nm/sec. Atomic beams of Al and Au were condensed on cermet substrates at room temperature, with preliminary deposition of a sublayer of salt. Film thickness was measured with a piezoelectric vibrator with an accuracy of 5%. The resulting specimens were separated from the substrate, secured to the special attachment, and annealed in the vacuum chamber of the electron-diffraction instrument. The Al films were annealed at 470°K, while the Au films were annealed at 330 and 520°K.

In order to analyze the empirical data and check the agreement between the theoretical models and the conditions of the experiment, we studied the geometry and structure of the study objects by the methods of optical and electron microscopy. The specimens were rectangular in form and had no visible macrodefects. The decrease in thickness along the length was ∿1%.

RESULTS AND DISCUSSION

The results of the experimental determination of the thermal properties of thin films of Al and Au at room temperature are generalized in Figs. 1 and 2. It follows from the figures that the coefficient of thermal conductivity increases with an increase in thickness for both the films with a structure close to the original structure (Au, annealed at 330°K) and those films annealed at higher temperatures. Annealing of Au films leads to a 30-50% increase in the coefficient of thermal conductivity, it being significant here that the measurements were made on the same specimens. This means that the dependence of thermal conductivity on thickness is due both to the thickness and the structure of the objects.

The above-noted change in thermal conductivity with thickness in the temperature range

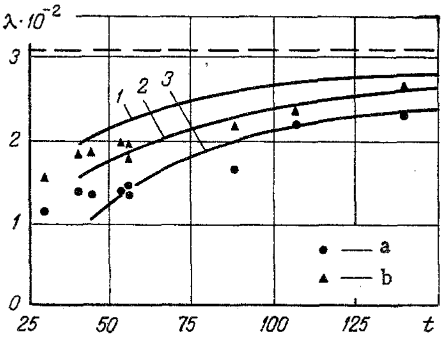

Fig. 2. Dependence of thermal conductivity λ of Au films on thickness t: a, b) annealed at 330 and 520°K; 1) external size effect for p = 0, r = 0; 2 and 3) external and internal size effects for p = 0.17, r = 0.26, D = t, and p = 0.17, r = 0.26, D = 2t, respectively.

where the coefficients of thermal and electrical conductivity are connected is, as shown below with the Wiedermann–Franz equation, predicted by theories of size effects developed for the electrical conductivity of films [16,17]. A quantitative description of data on the thermal conductivity of polycrystalline films is difficult due to the lack of theories that take into account the actual structure of the object. The authors in [17] derived a dependence of the conductivity of polycrystalline films on thickness with certain simplifying (but close to reality) assumptions. In the general case, the theoretical function $\lambda(t)$ does not have an analytical solution. However, for films for which t, $\bar{D} \sim l_0$, it is approximated by the expression

$$\lambda = \lambda_0 [1 - 3(1 - p) l_0/8t - 3l_0 r/2D(1 - r)]. \tag{6}$$

The term $3(1 - p)l_0/8t$ accounts for the contribution of scattering of conduction electrons by film surfaces (external size effect), while $3l_0 r/2D(1 - r)$ accounts for the grain boundaries (internal size effect).

According to data from the electron microscope studies, grain size in the Al films is about three times the thickness. In such polycrystalline films at p = 0, l_0 = 32 nm, and r = 0.15 [17], the contribution of grain boundaries to conductivity is small, and the function $\lambda(t)$ is satisfactorily described by the external size effect theory for the case of diffuse scattering of electrons by the film surfaces (Fig. 1a).

As can be seen in Fig. 2, the empirical values of λ for Au lie below the curve predicted by Eq. (6) for the case p = 0 and r = 0. For a quantitative description of the function $\lambda(t)$ for Au films, it is necessary to have the values of p, r, and D. Since grain size was determined experimentally and thermal conductivity was measured on the same specimens, but with different structures, the values of p and r may be determined from Eq. (6). For gold films annealed at 330 and 520°K, grain size is related to thickness by the relations $\bar{D} \sim t$ and $\bar{D} \sim 2t$, respectively. Assuming that p and r are independent of thickness and grain size, we found that p = 0.17 and r = 0.26. These are averaged values for the films investigated.

As is evident from Fig. 2, curves 2 and 3, calculated from Eq. (6) for the indicated values of $\bar{D}$ and p = 0.17, r = 0.26, and l_0 = 40 nm [1], describe the empirical data on λ significantly better than curve 1. However, the empirical data on the thermal conductivity of Au films are not described as well by the theory as is the data for Al films. This difference is due mainly to the discrepancy between the actual structure of the films and the theoretical model [17]. The theory assumes that the grains are free of lattice defects. The Al films approximate this model more closely. There are stacking faults, stacking-fault tetrahedra, and microvoids about 50 Å in diameter occupying a total volume of several percent in the grains of Au films annealed at 330°K. The stacking-fault tetrahedra have been completely annealed at 520°K, but the stacking faults and microvoids remain.

The empirical results from measurement of thermal diffusivity in relation to thickness are similar to the data on thermal conductivity: the coefficient of thermal diffusivity increases with an increase in thickness and values of K characteristic of the bulk metal (Fig.

Fig. 3. Lorenz number for Au (1, annealing at 330°K; 2, annealing at 520°K) and Al (3) films. Dot–dash line, values of L for bulk metals. $L\cdot 10^8$, $W/\Omega\cdot deg^2$; t, nm.

1b) are reached at $t \sim 10^2$ nm. The values of K for the Au films were lower than for the bulk metal throughout the thickness range. Annealing of the Au films increased thermal conductivity. The increase in K was proportional to the increase in λ. It follows from this that the change observed in the coefficient of thermal diffusivity is due only to a change in thermal conductivity.

Figure 1c shows the specific heat of Al films calculated from empirical values of thermal diffusivity and conductivity. The data on film density needed for the calculations was taken from sources in the literature. According to the latter, the density of films of the investigated thickness agrees within 3-5% with the density of bulk metals [18,19]. As can be seen from Fig. 1c, the value of C is independent of thickness and is in satisfactory accord with the data for massive metal.

While the heat capacity of Al films was computed from data on λ and K found by the electron-diffraction method, the heat capacity of the Au films was determined directly by the pulse method and from the values of λ and K. According to the results obtained by the two methods, the specific heat of the Au films annealed at 330°K was 127 ± 7 J/kg·deg, and was 128 ± 7 J/kg·deg after annealing at 520°K. These values coincide with the specific heat of bulk gold C = 126 J/kg·deg.

It is known that the thermal conductivity of metals may be represented in the form of the sum of the electronic λ_e and lattice λ_l components. The value of λ_e is substantially greater than λ_l for pure bulk metals, as reflected by the Wiedemann–Franz law. In thin films, the electronic component of thermal conductivity may be suppressed due to diffuse reflection of conduction electrons by the surfaces of the film, grain boundaries, vacancies, interstitial atoms, dislocations, etc. This leads to a relative increase in the contribution of λ_l to the thermal conductivity of the film and, thus, to an increase in the Lorentz number. But since $\lambda_l \sim 10^{-2}\lambda_e$ and since the thermal conductivity of the films is only several times lower than that of the bulk metal, there is no basis for expecting a substantial change in the Lorentz number of the films. This conclusion is supported by the empirical data (Fig. 3). The value of L was determined from measurements of thermal and electrical conductivity made on the same specimens under the same conditions. As follows from Fig. 3, the Lorentz numbers of the investigated films found by the electron-diffraction and electrical methods are independent of thickness or structural state and are, within the limits of accuracy imposed by the methods of measurement used, equal to the corresponding values of L of the bulk metals. Observance of the Wiedemann–Franz law in this case is evidence that heat is transferred in thin polycrystalline films of metals principally by the electron mechanism.

NOTATION

$2l$, m, t, film length, width, and thickness, respectively; T(x, τ), film temperature at point x at time instant τ; x = 0, film center; ρ, resistivity; λ, λ_0, thermal conductivity of film and bulk metal, respectively; K, thermal diffusivity; C, specific heat; ε, integral emissivity into hemisphere; σ, Stefan–Boltzmann constant; R, total film resistance; I, electrical current through the film; L, Lorentz number; $\Delta\overline{T}$, film mean heating; l_0, mean free path length of electrons; p, electron reflection coefficient of film surface coefficient; r, electron reflection coefficient of grain boundaries; $\overline{D}$, mean size of grains in the film plane; T_0, ambient temperature; d, film density.

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