THE FORMS OF THE TRANSFER OF THERMAL ENERGY IN METALLIC PLASMA DEPOSITED COATINGS AND A QUALITATIVE ASSESSMENT OF THEIR THERMAL CONDUCTIVITY

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The forms of thermal energy transfer in plasma deposited metallic films in an atmospheric medium are examined and a qualitative assessment of the effective thermal conductivity of these films is put forward.

In modern technology films deposited using a plasma flux (plasma deposition) are widely used together with other forms of coatings.

The advantages of producing coatings by plasma deposition are as follows:

a) the high temperatures of the plasma flux make it possible to melt substances with practically any melting point [1];

b) on deposition in a controlled atmosphere (inert or other), the oxidation of the separate particles of the deposited substances may be avoided;

c) multilayer deposits, for example, structures with an intermediate insulating layer, are deposited using a plasma flux;

d) layers with a high density may be obtained because of the high velocity of the gas forming the plasma, the high temperature of the substrate, and the correctly chosen controlling medium;

e) nearly all metals, ceramics, and graphites may be used as substrates;

f) the temperature of the substrate and the energy characteristics of the plasma flux may be varied depending on the technical requirements of the deposits.

It is well known [2, 3] that metals deposited on a substrate by plasma deposition in atmospheric conditions by a wire have a coarsely textured structure which consists of extended grains with nonuniform porosity containing separate coarse extended pores with a large content of oxide or metallic protoxide consisting not only of higher oxides, but also of various transition phases, and this was observed, for example, in tungsten consisting of WO_3, W_4O_{11}, and other phase states.

Thus, for a given technology of plasma deposition, the metal consists of pure metal (grains), metal oxide, and in some cases of protoxide (copper), covering the separate grains and groups of grains, and also pores which are oriented mainly parallel to the substrate and filled with air or gas.

The effective thermal conductivity of plasma deposited nickel and tungsten is shown in Fig. 1, where we see that the value of λ_{eff} of plasma deposited metal is considerably smaller (1.5 to 2 orders) than that of pure metals, and $\lambda_{eff} = f(T)$ represents a parabolic curve.

The process of heat transfer in such mechanically bound granular materials is fairly complicated and takes place in the following modes of transfer:

a) electrons (conduction in pure metals, i. e., in the grains themselves);

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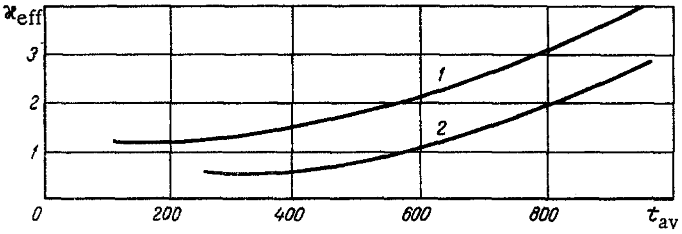

Fig. 1. Experimental results on effective thermal conductivity (W/m • deg) of plasma-dusted metals (t, °C): 1) tungsten, authors' data; 2) nickel.

b) the phonons of the elastic vibration of the crystal lattice (in oxides and impurities);

c) photons of the radiated energy (in the pores);

d) molecular thermal conductivity (in gas filled pores);

It is usual to reduce all the mechanisms of energy transfer in porous materials to one standard process of "thermal conduction" [4]. In this case the coefficient of this standard effective conduction will be

$$\varkappa_{\text{eff}} = \Sigma\varkappa_e,\ \varkappa_{\text{ph}}, \varkappa_{\text{fm}}, \varkappa_{\text{м}}. \tag{1}$$

There is no doubt that this expression for the effective thermal conductivity has no physical significance, but it makes it possible to assess the total effect of energy transfer.

Let us examine the separate mechanisms of thermal energy transfer in metallic plasma deposited coatings.

1. The Thermal Energy Transfer by the Elastic Vibrations of the Crystal Lattice (Phonons). The transfer of thermal energy by phonons is characteristic of dielectrics; it also occurs in disordered metal alloys, in contaminated metals like the plasma deposited metals, since they contain oxides. In pure metals this transfer is 1 to 2% of the electron thermal conductivity [5].

In analogy with the kinetic theory of gases, the thermal conductivity of the phonon gas will be

$$\varkappa_{\text{ph}} = \frac{1}{3}\, c_{\text{ph}} u l_{\text{ph}}. \tag{2}$$

The theoretical analysis of thermal conduction in dielectrics is mainly concerned with determining the phonon-free path which is determined by two processes, namely, the geometrical phonon scattering by impurities, boundaries, etc., and phonon–phonon scattering. The presence of anharmonic interactions in the lattice is connected with the phonon interactions which restrict the magnitude of the free path. It is well known that the effect of anharmonic interactions in the lattice is very complex, and some approximate calculations [6] show that the phonon-free path length is proportional to $1/T$ (at high temperatures) and to $\exp(\theta/2T)$ at low temperatures.

The geometry of the oxide film covering the metal particle has a considerable effect in limiting the phonon-free path length. Thus, when l_{ph} becomes comparable with the thickness of the oxide film, the limiting value of l_{ph} is determined by this thickness, and the thermal conductivity begins to depend on the dimensions of the oxide film, i. e.,

$$\varkappa_{\text{ph}} \cong \frac{1}{3}\, c_{\text{ph}} u \delta_{\text{fm}}. \tag{3}$$

From the analyses we see that the dimensions of the oxide films covering the metal particles are very small; from fractions of a micron to several microns.

Therefore it is a very complex process to take into account the effect of the phonon component. It is impossible in practice to determine the thermal conductivity of the oxide film experimentally.

Apart from that, the existing data on oxides in the literature [7, 8] are given mainly only for the higher oxides after a corresponding thermal treatment and in certain conditions. Therefore the use of these data for a qualitative estimate of the effective thermal conductivity of the deposited metals leads to substantial errors.

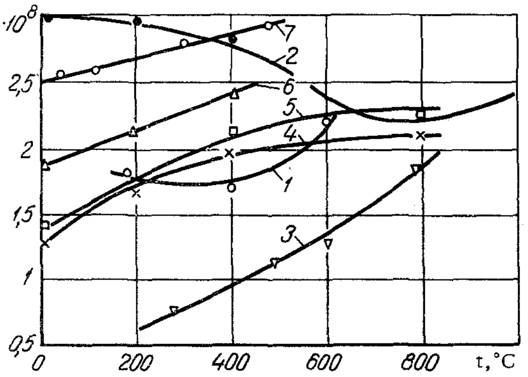

Fig. 2. Lorenz number as function of temperature (L, W • ohm/(°C)^2: 1) plasma-dusted tungsten; 2) tungsten [7]; 3) plasma-dusted nickel; 4) 99.97% [12]; 5) 99.2% [12]; 6) 99.98% [12]; 7) 99.99% [7].

2. Thermal Energy Transfer by Electrons. In metallic particles and grains, the thermal energy is mainly transferred by electrons, and it is known that in pure metals the phonon thermal conductivity is only 1 to 2% of the electron conductivity, since the free electrons in metals are an additional source for phonon scattering reducing the role of phonon scattering by thermal nonuniformities in the structure [6].

Taking into account the fact that electrons obey the Fermi–Dirac statistics, the thermal conductivity can be written in the following form:

$$\varkappa_e = \frac{\pi^2}{3}\,\frac{Nk^2T\tau}{m}, \tag{4}$$

the electrical conductivity

$$\frac{1}{\rho} = \frac{Ne^2\tau}{m}. \tag{5}$$

Since the conduction electrons are the energy carriers both in electrical conduction and thermal conduction, there is a relation between the thermal and electrical conductivity expressed in the form of the Wiedemann–Franz law, i.e.,

$$\varkappa_e\rho = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 T, \tag{6}$$

and the Lorenz number connecting this dependence with temperature,

$$\frac{\varkappa_e\rho}{T} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 = L. \tag{7}$$

The Lorenz number for metals is known [7] and consists of $\Sigma L = L_e + L_{latt}$; L_e gives the main contribution (98-99%). The dependence of the Lorenz number on temperature with different contents of chemically pure nickel is shown in Fig. 2; the curve for plasma deposited nickel in atmospheric conditions is also shown there. The content of pure nickel in it was ~ 81-82% (by volume). It should be noted that L increases at temperatures above 800°C approaching the value of L for monolithic nickel. Apparently, the contribution of the electron energy transfer increases at the expense of the beginning of agglomeration of the separate metal particles and partial removal of oxide films and gas from the pores.

3. Molecular Thermal Energy Transfer in the Pores of the Coatings. According to the molecular kinetic theory, the thermal energy transfer in the gas-filled pores takes place at the expense of molecular motion.

At temperatures far from the critical temperature, and at low pressures, most gases may be considered as ideal; then

$$\varkappa_{M,0} = \frac{c_V l_M \gamma}{3}\sqrt{\frac{3RT}{\mu}}. \tag{8}$$

For systems with fine pores [9] in which the dimensions of the pores are comparable or smaller than the length of the molecular free path, the thermal conductivity of the gas at atmospheric pressure is lower than its molecular thermal conductivity and is determined by a relation which is valid for the transition region ($l_M = \delta$, $\mathrm{Kn} = l_M/\delta$). The thermal conductivity of the gas in the intermediate vacuum

$$\varkappa_{M,v} = \frac{\varkappa_{M,0}}{1 + \dfrac{2k}{k+1}\left(\dfrac{2-a_1}{a_1} - \dfrac{2-a_2}{a_2}\right)\dfrac{\mathrm{Kn}}{\mathrm{Pr}}}. \tag{9}$$

From the given equation it follows that $\mathrm{Kn} \ll 1$ and $l_M \ll \delta$ (the continuum region, i.e., the region of low pressures and low vacuum). For $l_M \gg \delta$, $\mathrm{Kn} \gg 1$ (high vacuum region), the equation (9) takes the form

$$\varkappa_{M,v} = \frac{c_V\gamma\delta(k+1)\,\mathrm{Pr}}{6k\left(\dfrac{2-a_1}{a_1} - \dfrac{2-a_2}{a_2}\right)}\sqrt{\frac{3RT}{\mu}}. \tag{10}$$

The coatings obtained by plasma deposition have pores of dimensions of several microns to tens of microns (sometimes hundreds) depending on the method, for example, for plasma deposited nickel [2]. In this case the Knudsen number $\mathrm{Kn} = 1\text{-}10^{-2}$, and therefore the heat transfer in the pores of the coating (nickel, tungsten) is determined by the laws characteristic for the intermediate vacuum for which the thermal conductivity of the gas in the pores is lower than its molecular thermal conductivity and is $(1 \cdot 10^{-3}\text{-}1 \cdot 10^{-2})$W/m · deg.

4. Transfer of Radiant Thermal Energy in Pores of Deposited Metals. Since the plasma deposited metals have a considerable porosity with pore dimensions from several to tens of microns, a drop in radiant thermal energy in the pores, naturally, occurs. If we consider the photon gas [10] as ideal, $\varkappa_r = c_{phot} l_{phot} u/3$, its thermal capacity will be

$$c = \frac{16\, n^3 T^3 \sigma}{a}, \quad u = \frac{a}{n} \text{ and } l_{phot} = \frac{1}{\alpha}.$$

From this the radiant thermal conductivity

$$\varkappa_r = \frac{16}{3}\, n^2 \sigma\, \frac{T^3}{\alpha}. \tag{11}$$

Since the applicability of the given equation is determined by a number of factors, namely, 1) a small drop in the thickness of the layer, 2) the small value of $1/\alpha$ compared with the linear dimensions of the specimen, 3) isotropic properties of the crystal, we considered the radiant heat transfer in the pores using a different form of expression, i.e., for a known temperature distribution over the surface of some arbitrary pore, the quantity of heat passing through it by radiation may be found, and for a sufficiently small temperature difference may be expressed as [11]

$$q = 4\, \varepsilon \sigma T^3 \Delta t, \tag{12}$$

and the radiant thermal conductivity as

$$\varkappa_r = 4\, b d \varepsilon \sigma T^3. \tag{13}$$

The results obtained for $\varkappa_r$ for pores in plasma deposited metals have very small values $(0.14\text{-}12.0) \cdot 10^{-3}$ W/m · deg (the calculations were made for plasma deposited nickel).

The qualitative estimates made for the effective thermal conductivity of deposited granular pores of metals showed that the following factors have an effect on the decrease in the thermal conductivity:

1) the granular composition of the specimen;
2) the decrease in the electron energy transfer at the expense of the small metal particles comparable with the length of the free path of the electrons in oxide films and gaps;
3) the decrease in the phonon energy transfer at the expense of the small dimensions of the oxide film which in a number of cases are comparable with the crystal lattice dimensions;
4) the porosity of the specimen and the transfer of energy in the pores by radiation, and thermal conduction of the gas during intermediate vacuum which is considerably smaller than the transfer in the pores due to molecular thermal conduction.

NOTATION

$\varkappa_{eff}$, $\varkappa_e$, $\varkappa_{ph}$, $\varkappa_r$, and $\varkappa_M$	are the effective, electronic, phonon, radiant, and molecular thermal conductivities, respectively;
c_{ph}	is the heat capacity of the grid;
u	is the mean velocity of the phonon;
l_{ph}	is the free path length of the phonon;
T	is the absolute temperature;
δ_{fm}	is the thickness of the oxide film;
θ	is the Debye characteristic temperature;
ρ	is the specific electric resistance;
N	is the number of electrons per unit volume;
e	is the value of the electron charge;
τ	is the time of the field action on the freely moving charge (relaxation time);
m	is the particle mass;

l_M	is the free molecular path length;
R	is the gas constant;
γ	is the gas density;
μ	is the molecular mass of gas equal to m/g;
a_i	is the accommodation coefficient;
Kn	is the Knudsen number;
Pr	is the Prandtl number;
P	is the gas pressure;
n	is the refraction factor;
M	is the molecular weight of gas;
a	is the light velocity in vacuum;
l_{phot}	is the free path length of the photon;
α	is the absorption coefficient;
2r	is the diameter of the capillary equal to the characteristic dimension δ;
c_V	is the volume heat capacity of gas;
c_{phot}	is the heat capacity of the "photon" gas;
ε	is the radiative capacity of the pore;
d	is the largest gap in the direction of heat flux;
σ	is the Boltzmann constant;
q	is the specific heat flux;
b	is the geometric factor;
$b = 1$	for pores in the form of plane-parallel layers and cylindrical pores with axes parallel to the heat flux direction;
$b = 2/3$	for spherical pores;
$b = \pi/4$	for cylindrical pores with axes perpendicular to the heat flux direction.

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