

PROPERTIES OF METALS DEPOSITED ON A SUBSTRATE BY THE PLASMA METHOD

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Methods of investigating the thermal and electrical conductivity, emissivity, and linear expansion of metal coatings are proposed. Certain experimental data are presented.

Metals deposited on a substrate by the plasma method are being used for preventing corrosion [1], increasing emissivity, reducing and increasing electrical and thermal contact resistances, etc.

We have investigated the following coefficients: 1) thermal conductivity, 2) electrical conductivity, 3) emissivity, 4) linear expansion.

The electrical and thermal conductivity and emissivity were investigated in water-cooled electrovacuum apparatus (vacuum  $10^{-4}$  mm Hg).

The measuring instruments included an R-56 ac potentiometer and a class 0.1 or 0.2 ac ammeter inserted in the secondary circuit of a stepdown transformer across a class 0.2 current transformer.

For the temperature measurements we made exclusive use of chromel-alumel thermocouples with individual calibration.

The thermocouple emf was measured with an R-330 or R-307 dc potentiometer.

The coefficient of linear expansion was determined in an air atmosphere.

The methods of investigation and the experimental results for certain metals are described below.

To determine the thermal conductivity we employed the stationary (absolute) method:  $\lambda$  was found from the known temperatures of the inner and outer surfaces of the coating and the heat flux  $q$ .

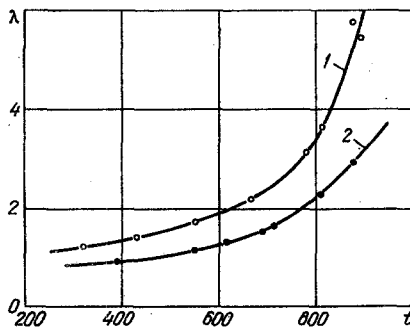


Fig. 1. Thermal conductivity  $\lambda$  (W/m·deg) as a function of temperature (°C): 1) copper; 2) nickel.

The specimens on which the metal was deposited were niobium tubes coated with aluminum oxide by the plasma method. Before deposition of the metal the surface was polished to obtain a tenth class finish. The thermocouples were imbedded in the aluminum oxide coating, the thermocouple buttons first being rolled

into a thin strip and led out onto the polished surface of the aluminum oxide. The outside temperature of the metal coating was measured with thermocouples contact-welded to the surface.

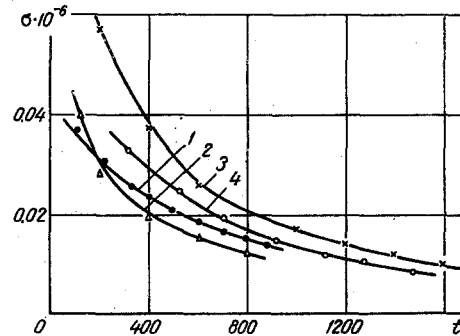


Fig. 2. Electrical conductivity  $\sigma$  (ohm<sup>-1</sup>·cm<sup>-1</sup>) as a function of temperature (°C): 1) copper; 2) nickel; 3) tungsten; 4) molybdenum.

The heater was made of niobium tubing. In the regions opposite the ends of the specimens the heater section was reduced, which made it possible to obtain a one-dimensional heat flow on the working section.

The heat flux was determined from the electrical power.

The niobium specimens received the following coating thicknesses: nickel-1.6-1.7 mm; copper-1.13-1.14 mm.

The temperature dependence of the thermal conductivity is shown for nickel and copper in Fig. 1. As may be seen from the graph, these coatings have a low thermal conductivity (0.5-6.0 W/m·deg).

The sharply reduced  $\lambda$  as compared with bulk metals is attributable not only to the porosity of the coatings but also to the oxide films formed on the individual metal particles in the process of plasma deposition.

The method of determining electrical conductivity was based on the direct determination of the electrical resistance from the measured electric current and voltage drop on the working section of the specimen.

The substrate specimens were tubes coated with aluminum oxide by plasma deposition. A film of the investigated metal was deposited (again by plasma deposition) on the polished surface (tenth class finish) and then polished to obtain a tenth class finish. Electric current was supplied to the coating through copper bars.

The working section was selected where the temperature field was nearly uniform. The distance between the potentiometer taps (working section) was measured correct to 0.02 mm, and the cross section

of the metal coating was measured correct to 0.01 mm with a micrometer. Having determined the electrical resistance and measured the geometric dimensions of the specimen, one can easily obtain the electrical conductivity of the metal.

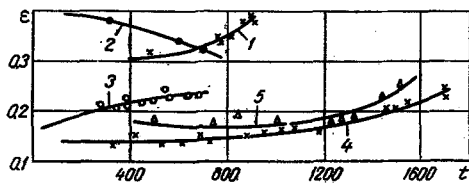


Fig. 3. Integral emissivity  $\epsilon$  as a function of temperature ( $^{\circ}\text{C}$ ): 1 and 2) copper and nickel, untreated; 3, 4, 5) nickel, tungsten, and molybdenum (10-th class surface finish).

The specimen was heated from a single-phase power supply across an OSU-20 stepdown transformer, and the current was regulated with an RNO-250-10 variable-ratio oil transformer. A voltage stabilizer was included in the primary circuit of the transformer.

Temperature measurements up to  $1200^{\circ}\text{C}$  were made with surface-mounted thermocouples, above  $1200^{\circ}\text{C}$  with an optical pyrometer.

Specimens coated with copper, nickel, tungsten, and molybdenum were investigated.

The density of the specimens was 20–22% less than that of the cast metal.

The data presented in Fig. 2 represent the temperature dependence of the electrical conductivity after 5 hr at the following temperatures:  $1700^{\circ}\text{C}$  for tungsten,  $1500^{\circ}\text{C}$  for molybdenum,  $1000^{\circ}\text{C}$  for nickel, and  $850$ – $900^{\circ}\text{C}$  for copper.

It is typical that the original and final (after heat treatment) measurements should not coincide. This is primarily associated with stripping of the oxide films formed between the metal particles and impurities included during deposition.

The error in measuring the electrical conductivity was 3%.

The method used to investigate the integral emissivity of the coatings was based on the determination of  $\epsilon$  from heat flux measurements (electrical power) and the surface temperatures of the specimen and the chamber  $T_c$ :

$$\epsilon_{\text{red}} = \frac{Q}{\sigma \left[ \left( \frac{T_1}{100} \right)^4 - \left( \frac{T_c}{100} \right)^4 \right] F}, \quad (1)$$

where

$$\epsilon_{\text{red}} = \frac{Q = I \Delta U}{\epsilon_1^{-1} + \frac{d_1}{d_c} [(\epsilon_2^*)^{-1} - 1]}. \quad (2)$$

Here,  $\epsilon_1$  is the unknown emissivity of the specimen;  $\epsilon_2^* = \epsilon_2(T_m)$ ;  $T_m = (T_1 T_2)^{1/2}$ ;  $F = \pi d_1 l (1 + \alpha t_1)^2$ .

We investigated specimens coated with copper and nickel without a mechanical finish and nickel, molybdenum and tungsten specimens with a tenth-class surface finish.

The heater was made of niobium tubing. In the regions corresponding to the ends of the specimen the heater cross section was reduced (to obtain a one-dimensional heat flow).

The error of the emissivity measurements was 5% at  $800^{\circ}\text{C}$ , 7% at  $200^{\circ}\text{C}$ , and 11% at  $1500^{\circ}\text{C}$ , since measurements above  $1000^{\circ}\text{C}$  were made using an OPPIR-017 type optical pyrometer with a simulated black body (opening in specimen). The results are presented in Fig. 3.

The measurements were made after a preliminary heating under vacuum (there was no oxide film on the surface of the deposited metal).

One of the factors determining the compatibility of metal coating and substrate is the coefficient of linear expansion. We investigated this characteristic for nickel and copper, using a simple and reliable mechanical method.

The elongation was determined with an IKV-1 optimeter. The specimen was mounted on a flat quartz base welded to the bottom of a quartz test tube. The expansion of the specimen was transmitted to the optimeter pin by a quartz feeler located inside the quartz test tube to which a sleeve connected with the optimeter was attached. The quartz test tube was placed in a thermostated furnace. The length of the furnace was such as to ensure an isothermal section measuring 30–35 mm. The specimen temperature was determined with a thermocouple which passed through the quartz feeler and made contact with the top of the specimen.

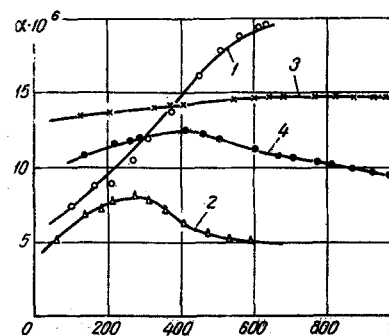


Fig. 4. Coefficient of linear expansion  $\alpha$  ( $\text{deg}^{-1}$ ) as a function of temperature ( $^{\circ}\text{C}$ ): 1 and 2) copper with the layers oriented parallel and perpendicular to the instrument axis, respectively; 3 and 4) nickel with the layers similarly oriented

The measurements were made at a monotonic heating rate of 2 deg/min.

The mean coefficient of linear expansion was calculated as follows:

$$\bar{\alpha}_l = \frac{\Delta l + \epsilon \Delta l_{\text{qu}}}{l_0 t} + \bar{\alpha}_{\text{qu}}. \quad (3)$$

The uncompensated expansion of the quartz system did not exceed 3 microns at the maximum experimental temperature.

The displacement of the reference point was found after the apparatus had cooled to the initial temperature.

In preliminary experiments we used specimens of Cr18Ni9Ti steel in the form of solid cylinders 7 mm in diameter and from 10 to 20 mm long. These specimens were first annealed. The measurements were made on the interval 20–100° C. Comparison of the results with the data of [3], which were similarly obtained, showed that the greatest deviation (5%) occurs at low temperatures (to 150° C), while at high temperatures the discrepancy is less than 1%. The reproducibility of the data was 0.5%. These discrepancies are fully consistent with the calculation error, which is 4% at 100° C, decreasing to 1% at 1000° C.

The specimens were made as follows: a layer of the test material 5–7 mm thick was deposited on a brass disk 15 mm in diameter and 1 mm thick and then removed and worked to the required dimensions.

The effect of plasma deposition (for thicknesses of 1.5–4 mm) is that of one layer deposited on another with oxide films and pores running parallel to the substrate in the gaps between. At the interface the metal is more intensely oxidized than at the grain boundaries. The stratification causes a certain "anisotropy" of the deposited metal; accordingly the coefficient of linear expansion was determined twice—on specimens with a parallel and perpendicular orientation of the layers relative to the specimen axis.

The values for nickel and copper measured on two specimens with different orientation of the layers are presented in Fig. 4. In the case of a perpendicular orientation the coefficient is less for the coating than for the bulk metal. The maximum deviation is 30%. Specimens with parallel layers and the bulk metal have almost the same  $\bar{\alpha}_+$ .

Since the properties of the plasma-deposited coatings differ sharply from those of the bulk metal, the structure of the coatings deserves attention.

The coatings are porous and consist chiefly of the lower or higher oxide of the metal. The pores are non-uniform and vary in shape and size. The deposited metal is brittle, easily split off, and does not possess the ductility characteristic of the bulk metal (e. g., copper).

Moreover, at large thicknesses (1.5–4 mm) separation of the layers is observed.

The sinterability of the metal particles is very poor, but heating in a vacuum or an inert medium to a temperature close to the melting point of the metal and holding for 15–20 hr causes the metal at the surface to fuse together to a depth of 20–30 microns.

Obviously, the properties of metals deposited in an inert medium approach those of the bulk metal, since there is no oxidation.

The density and oxidation of the metal particles depend on the plasma torch operating conditions, the size of wire employed, the distance between the electrode and the specimen, etc.

#### NOTATION

$\Delta U$  is the voltage drop at the selected section;  $I$  is the electric current;  $\epsilon_{red}$  is the reduced emissivity of chamber-specimen system;  $\epsilon_2$  is the emissivity of the inside surface of a chamber made of Cr18Ni9Ti steel;  $T_C$  is the temperature of inside chamber surface;  $T_1$  is the surface temperature of the specimen;  $F$  is the surface area of the specimen, determined with allowance for thermal expansion;  $d_1$  and  $d_C$  are the diameters of the specimen and the chamber, respectively;  $l$  is the length of the working section of the specimen;  $\Delta l$  is the elongation of the specimen as measured with an optimeter on heating from initial temperature  $t_0$  to  $t$ ;  $\epsilon \Delta l_{qu}$  is the correction composed of corrections for uncompensated expansion of the quartz system and the displacement of reference point, owing to disturbance of mechanical contact between the specimen and the quartz parts;  $\bar{\alpha}_{qu}$  is the mean coefficient of linear expansion for quartz in the temperature interval from  $t_0$  to  $t$  [2];  $l_0$  is the length of the specimen at the temperature  $t_0$ .

#### REFERENCES

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