

A STUDY CONCERNING THE EFFECTIVE THERMAL
 CONDUCTIVITY OF PLASMA-DEPOSITED ALUMINUM
 OXIDE COATINGS SUBJECTED TO RADIATIVE HEATING
 OVER THE 100-900°C TEMPERATURE RANGE

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UDC 546.623:536.2

It is shown that microstructural changes in aluminum oxide coatings deposited together with modifying additives result in a much higher thermal conductivity without an impairment of electrical insulation characteristics.

Many technical applications require coatings which combine good electrical insulation characteristics with a sufficiently high thermal conductivity. One material which can satisfy these requirements is plasma-deposited aluminum oxide. The highly unbalanced conditions of a film deposition process produce very specific structural properties, as a result of which the effective thermal conductivity of plasma-deposited oxides with a 5-15% porosity is by one order of magnitude lower than that of their sintered equivalents [1, 2]. The aim of this study here was to establish the feasibility of increasing the thermal conductivity of plasma-deposited aluminum oxide coatings.

The scarcity and certain inconsistency of published data make it necessary to determine the thermal conductivity of sprayed aluminum oxide coatings experimentally. Accordingly, we have measured the effective thermal conductivity of plasma-deposited coatings which contain aluminum oxide as the basic ingredient.

For measuring the thermal conductivity of deposited films we selected an appropriate variant of the steady-state method (Fig. 1). The standard specimen was made of fused quartz, with an outstanding stability of optical properties and suitable for a wide temperature range. In accordance with the VNIIM procedure, taking into consideration the semitranslucency of fused quartz at temperatures above 500°K, we corrected the results of measurements for the radiative component of heat transfer with a proper accounting for the optical properties of the boundary and for the selective absorption characteristics of that material [3].

Considering that the various deposition techniques produce films of finite thickness, we had flat specimens fabricated into disks 3-4 mm thick and 23-25 mm in diameter. The coating, separated from the substrate, was then ground on all sides down to a class 6 surface finish (8-10 μ roughness). The

TABLE 1. Calculated Relation between the Effective Thermal Conductivity of the Ceramic Material and Microstructural Parameters

Effective thermal conductivity, W /m ² deg	Contact area	Size of micro-cracks, μ	Grain size, μ
5,3	0,1	10 ⁻²	5
10,2	0,3	10 ⁻²	100
10,1	0,3	10 ⁻²	5
9,1	0,3	10 ⁻¹	5

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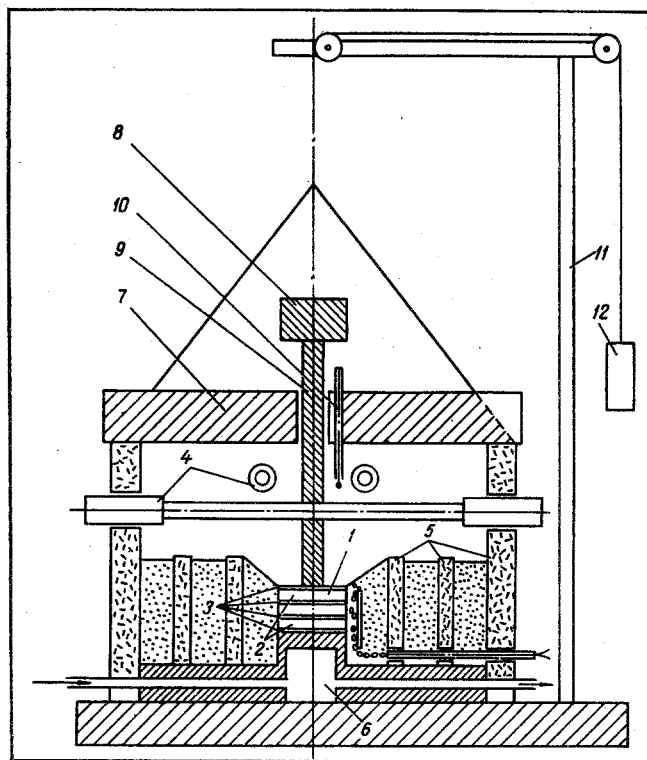


Fig. 1. Test apparatus for measuring the thermal conductivity: 1) test specimen; 2) standard specimens; 3) spot-check thermocouples; 4) Sillite rods; 5) protective rings; 6) refrigerator; 7) fireclay lid; 8) load; 9) alundum tube; 10) thermocouple; 11) support rig; 12) counterweight.

thermal conductivity was measured under conditions of purely radiative heating from Sillite rods. In order to reduce any heat leakage by radiation, we surrounded the array of specimens with three concentric protective rings of asbestos cement with quartz sand as filler. According to the results of control measurements, the thermal insulation here ensured a difference of not more than 4% between thermal fluxes through the first and the second standard specimen. The steady-state temperature drops across test specimens were measured with four spot-check differential Pt/PtRh thermocouples. The readings were recorded on a model PP-63 potentiometer (accuracy class 0.5). The system of specimens and thermocouples was placed on top of a refrigerator, pressed tightly against it by a 3 kg/cm² pressure producing load. This pressure reduced the thermal contact resistance between specimens and thermocouples. The temperature-dependence of this thermal resistance was calculated according to the formula by Shlykov [4], with the surface characteristics taken into account, and was systematically accounted for in the measurements.

The thermal conductivity of the test specimens was determined over the 200–900°C temperature range. The temperature curve was plotted on the basis of at least three simultaneous readings taken on three specimens of the same composition. The correction for the contact resistance R_c amounted to approximately 25% of the intrinsic thermal resistance of the specimen R_s . The correction for the radiative component of heat transmission through a quartz specimen increased with rising temperature, reaching 100% at 800°C. The maximum random error of measurements, with the precision of instruments and with the corrections for radiative thermal fluxes as well as the thermal contact resistance taken into account,

$$\frac{\delta(\lambda)}{\lambda} = \sqrt{2 \left[\frac{\delta(H)}{H} \right]^2 + 2 \left[\frac{\delta(\Delta T)}{\Delta T} \right]^2 + \left[\frac{\delta(Q)}{Q} \right]^2 + \left[\frac{\delta(R_c)}{R_c} \right]^2},$$

was estimated at 14–16%. Within a 95% confidence level, the standard derivation from the mean

$$2\sigma = \sqrt{\frac{\sum \Delta \lambda_i^2}{n(n-1)}}$$

was equal to 0.12 W/m·deg and this was well within the limits of the calculated systematic error.

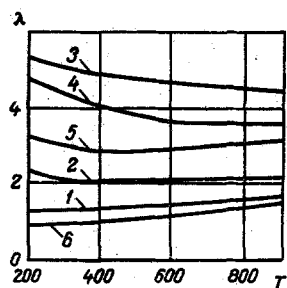


Fig. 2. Thermal conductivity λ (W/m · deg) as a function of the temperature T (°C) for plasma-deposited coatings with aluminum oxide as the matrix and various additives: 1) extra pure Al_2O_3 ; 2) analytical grade Al_2O_3 ; 3) $\text{Al}_2\text{O}_3 + 0.3\%$ MgO; 4) $\text{Al}_2\text{O}_3 + 1\%$ MgO + 1.5% Co_2O_3 ; 5) $\text{Al}_2\text{O}_3 + 1\%$ MgO + 1.5% Cr_2O_3 ; 6) $\text{Al}_2\text{O}_3 + 2\%$ Y_2O_3 .

The effective thermal conductivity of ceramic materials is a function of many variables: composition, porosity, pore shape and dimensions, temperature, thermal conductivity and pressure of the gaseous medium, etc. The choice of a structural model to describe deposited oxide was made on the basis of an analysis of a real structure in the given test material [5]. The Dul'nev-Zarichnyak-Litovskii model [6] applicable to systems with mutually penetrating components, accounting for the effects of microcracks and intergranular contact areas as well as of the grain dimensions on the effective thermal conductivity, was found suitable and, in fact, the most rational one for characterizing the effective conductivity of deposited films.

An experimental analysis of how the many factors affect the thermal conductivity presents a quite complex task. This is so, because a great number of laborious tests would be required and, above all, because of the difficulty in preparing specimens with a rigorously fixed microstructure. In view of this, theoretical methods of calculating the thermal conductivity appear very attractive. On the basis of the adopted thermal model [6] and with the aid of a model BÉSM-4 computer, we have analyzed the effect of structural parameters on the thermal conductivity of the material. Typical results for 100°C are shown in Table 1, indicating a substantial role played by the interlinkage between individual grains. Thus, a threefold increase in the size of the contact area brings about an almost twofold increase in the thermal

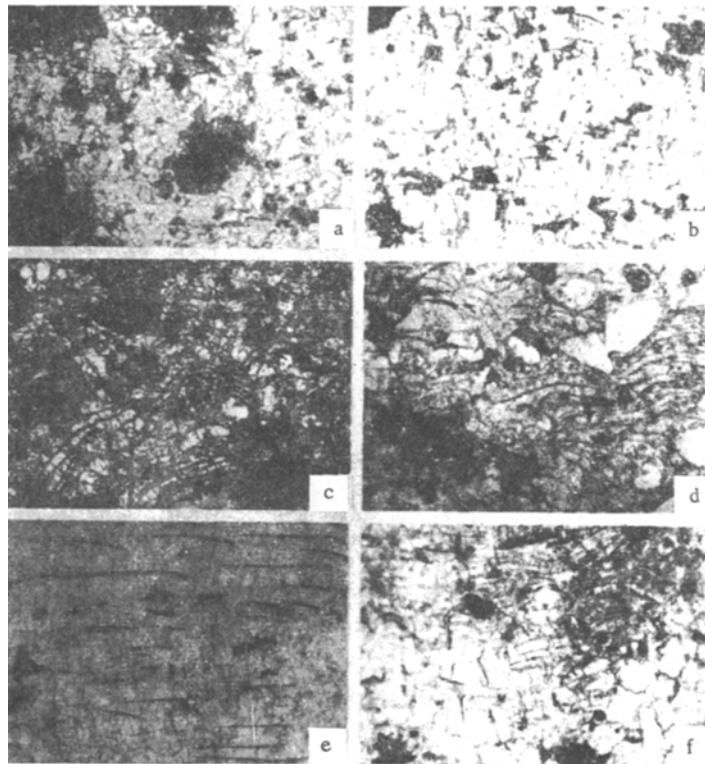


Fig. 3. Microphotographs of coating section, with $\times 340$ magnification: a) extra pure Al_2O_3 ; b) analytical grade Al_2O_3 ; c) $\text{Al}_2\text{O}_3 + 0.3\%$ MgO; d) $\text{Al}_2\text{O}_3 + 1\%$ MgO + 1.5% Co_2O_3 ; e) $\text{Al}_2\text{O}_3 + 1\%$ MgO + 1.5% Cr_2O_3 ; f) $\text{Al}_2\text{O}_3 + 2\%$ Y_2O_3 .

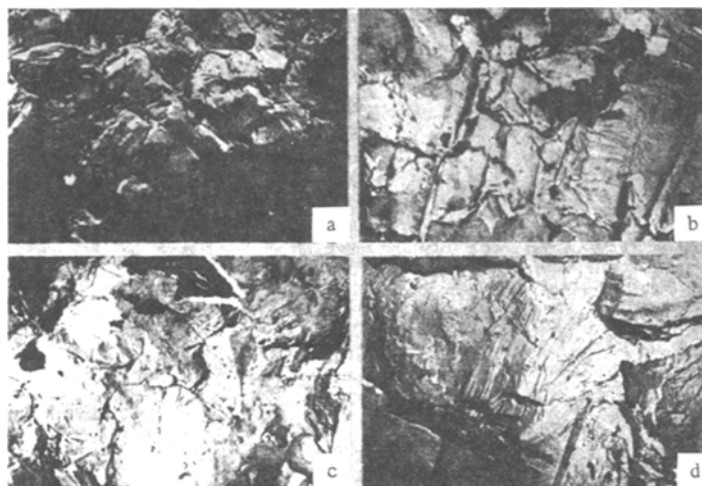


Fig. 4. Photographs of coating fractures, taken under an electron microscope: a) analytical grade Al_2O_3 ($\times 1800$); b) $\text{Al}_2\text{O}_3 + 0.3\% \text{MgO}$, ($\times 2400$); c) $\text{Al}_2\text{O}_3 + 1\% \text{MgO} + 1.5\% \text{Co}_2\text{O}_3$, ($\times 1800$); d) $\text{Al}_2\text{O}_3 + 2\% \text{Y}_2\text{O}_3$, ($\times 1800$).

conductivity, while a change in the width of microcracks by one order of magnitude affects the thermal conductivity by only 10% and a change in the grain size by a factor of 20 affects the thermal conductivity by only 1%. The results of this analysis point out the ways for a controllable improvement of the thermal conductivity.

In order to increase the intergranular contact area in deposited aluminum oxide, we added doses of metallic oxides forming with it either solid solutions or chemical compounds [7]. Modifiers added in small amounts (2 to 3%) concentrate along the grain boundaries in the form of solid solutions or chemical compounds with the matrix material, without reducing the electrical insulation characteristics of the coating and almost without altering the bulk properties of the deposited material. At the same time, they are capable of substantially altering the surface properties of fused droplets, which leads to a more solid bond. In our experiment we used the following additives (Table 2): magnesium oxide, cobalt oxide, chromium oxide, and yttrium oxide.

The results of measurements pertaining to the effective thermal conductivity of plasma-deposited specimens are shown graphically in Fig. 2. It can be seen here that the thermal conductivity varies only slightly with temperature, which can apparently be explained by the effect of microcracks.

We compared the effective thermal conductivity of the test materials with the thermal conductivity of extra pure aluminum oxide containing not more than 10^{-4} - $10^{-3}\%$ additives. The thermal conductivity of analytical grade aluminum oxide was found to be approximately 1.5 times higher than that of extra pure aluminum oxide, according to the graph, the former containing up to 1% of technological impurities. The most significant effect here has an addition of magnesium oxide (0.2 to 0.4%), which raises the thermal conductivity of the ceramic material by a factor of 3 to 4 above that of extra pure aluminum oxide. An addition of cobalt oxide or chromium oxide is less effective: the thermal conductivity is increased only by a factor of 2 to 3 (Table 2).

TABLE 2. Effect of Modifying Additives on the Thermal Conductivity of Plasma-Deposited Aluminum Oxide Coatings

Al_2O_3 matrix	Mineral analysis of additive, %				Overall porosity, %	X-ray structural analysis	Thermal conductivity, W/m·deg
	MgO	Co_2O_3	Cr_2O_3	Y_2O_3			
Extra pure	—	—	—	—	13,3	γ -phase	1,3—1,6
A. g.	—	—	—	—	9,7	γ -phase	2,3—2,1
A. g.	0,3	—	—	—	9,8	γ -phase	5,3—4,5
A. g.	1,0	1,5	—	—	6,8	$\alpha + \gamma$ -phase	4,8—3,6
A. g.	1,0	—	1,5	—	9,9	γ -phase	2,9—3,3
A. g.	—	—	—	2,0	6,8	γ -phase	0,9—1,5

Note. A. g.) analytical grade.

The increase in thermal conductivity remains a predominant trend as long as the entire amount of added oxides contributes to the formation of contact bridges between grains; as soon as the added amount exceeds the amount necessary for increasing the contact area attainable under given conditions, new phases (defective structures) begin to form inside the crystals, and the thermal conductivity begins to decrease [8]. This phenomenon could be what causes an addition of 0.3% MgO to be more effective in raising the thermal conductivity than is an addition of 1% MgO with other ingredients. Large amounts of magnesium oxide in the interstices can exist as a separate phase and, in this case, the spinel layer which has formed splits away on the MgO side [9] and thus the contact between grains weakens.

Microscopic examination (Figs. 3 and 4) has confirmed that specimens with the highest thermal conductivity have also the closest packed structure. An exception are specimens with an admixture of yttrium oxide: these are close packed but have the lowest thermal conductivity, because of microcracks appearing as specimens with a low concentration of pores and cracks are cooled. Nevertheless, material with an admixture of yttrium oxide seems to us promising in terms of higher thermal conductivities, inasmuch as the effect of microcracks can be overcome by a proper design of the deposition process.

Our study has shown that, by altering the microstructure of ceramic materials, it is possible to effect a controllable change in their thermal conductivity.

NOTATION

λ	is the thermal conductivity, W/m · deg;
T	is the temperature;
ΔT	is the temperature drop;
R_c	is the thermal contact resistance, $m^2 \cdot \text{deg}/W$;
R_s	is the thermal resistance of a specimen;
Q	is the thermal flux density, W/m^2 ;
H	is the specimen thickness, mm.

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