THERMAL CONDUCTIVITY OF PLASMA-SPRAYED ALUMINUM OXIDE

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Results are shown of a study concerning the thermal conductivity of plasma-sprayed aluminum oxide, depending on the spray technology and the heat treatment.

As a consequence of developments in plasma metallurgy, industry has been provided with simple, convenient, and inexpensive methods of depositing coatings, profiling parts, and fabricating multilayer systems as well as composite materials.

Plasma-sprayed aluminum oxide is rather often found in use as thermal insulation in both surface coatings and in interlayers. Naturally, quite many studies have been made concerning its thermal conductivity [1-4]. The results are diverse, inasmuch as the thermal conductivity of this material is closely tied to its phase constitution, to the grain-size distribution in the raw powder, and to other technological aspects of the plasma-spray process, i.e., the kind of plasma generating gas and its flow rate, the type of spray nozzle, the shape and the temperature of the substrate, etc.

For example, during plasma spraying on an air-cooled cylindrical substrate (diameter 12-15 mm, thickness 1.0-1.5 mm), with the cylinder rotating (1.0 to 1.5 rpm on a turntable) and the nozzle moving forward under the following process conditions:

a) arc parameters: current 420 A, voltage 65 V;

b) plasma generating gas: argon – hydrogen mixture;

c) flow rate of the gases: argon 70 liters/min, hydrogen 4.5 liters/min;

d) rate of argon flow to the feeder 7.5 liters/min;

e) distance to the coated surface 200 mm, with a powder grade ch.d.a., grain size 20-100 μ, and a model GN-5r spray nozzle, one obtains a material structure consisting of discrete elongated Al_2O_3 particles oriented parallel to the substrate and separated by pores. In a section normal to the substrate axis the grain size varies from 3 to 15 μ and the pore size up to 25 μ. In a section parallel to the substrate axis the grain size is somewhat larger (tens of microns, some larger than 100 μ). Moreover, the particles here alternate in layers of finer and coarser ones.

In this way, the structure of a plasma-sprayed Al_2O_3 coating under such process conditions resembles the grain structure of compact powders.

The spray process can be analyzed on the basis of the material structure forming on given substrates (large size) (Fig. 1). The flame into which particles enter will be tentatively divided into three zones: central, intermediate, and peripheral in terms of the temperature profile across a plasma arc section [5-7]. Thus, the particles moving within the central zone of the flame will melt down completely in the last stage of travel, colliding against the solid surface and deforming with a possible breakup and fragmentation into smaller particles. Coarse particles which move through the intermediate zone soften along the surface and, therefore, do not completely deform during collision. Finally, particles which move along the edge of the flame retain their shape during collision. Inasmuch as the substrate is moved relatively to the plasma jet, there occurs a superposition of particles from the central, the intermediate, and the peripheral zone of

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 24, No. 1, pp. 106-111, January, 1973. Original article submitted February 10, 1972.

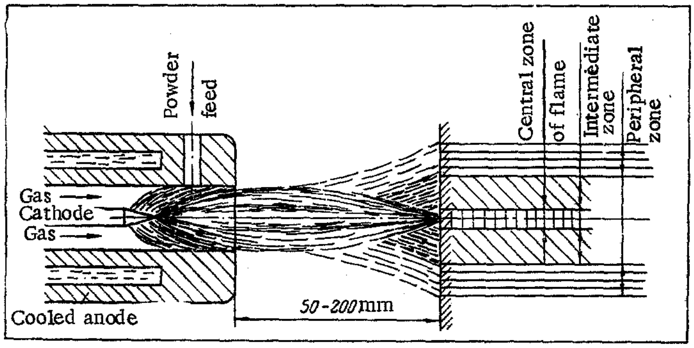

Fig. 1. Schematic diagram of the spray process.

the flame. The result is a material of rather complex structure, as just described, consisting of the δ-phase because, as is well known, during melting in a plasma arc and fast cooling on a substrate, even particles of the α-modification transform into the δ-phase similar to the well-known γ-modification of alumina [8, 13].

Under the same spray conditions, however, it is possible to produce also other structures by only changing the shape and the dimensions of the substrate. As an example, let us consider spraying on a flat substrate in the shape of a disk and without cooling. Let the disk have a diameter smaller than 20 mm and a thickness of 2 mm, let a negligible amount of heat be removed from it by natural cooling, while the disk substrate is placed on a thermally insulated base and the spray nozzle is stationary during the spray process so that the central zone of the flame falls (sectionwise) on the center of the disk. Since the flame temperature is much higher along the axis than at the periphery [5-7], the substrate is struck by completely molten particles which deposit on the surface as a liquid, but the first layer (several tens of microns) deposited on the "cold" surface solidifies without having time to take on the next layer and then, as the substrate is heated up by the plasma jet, the liquid particles deposit on the just solidifying surface so that the material structure becomes a mixture of alumina and corundum, the latter slightly modified, and the δ-phase deposits directly on the substrate.

Inasmuch as plasma-sprayed aluminum oxide resembles a random mixture, i.e., a powder of diverse grain shapes and sizes (this applies to a material deposited on a cooled cylindrical surface), an experimental verification can evidently be based on the thermal conductivity of Al_2O_3 powders with different packing densities. The characteristics of such powders are given in Table 1 together with some characteristics of plasma-sprayed aluminum oxide.

Results of thermal conductivity measurements on powders and on Al_2O_3 plasma-sprayed on various metallic substrates, cylindrical and flat ones, are shown in Fig. 2.

We will discuss some of the results. The trend of the test curves for the powders is the same regardless of the packing density, while the test curve for plasma-sprayed material is a cubic parabola, but the test points before and after partial heat treatment lie within the range of curves for the powders. It may be assumed, therefore, that the same mechanisms operate during the heat transfer but, when powders are tested in air (as in our case), the thermal conductivity is made up of three components: phonon, radiant, and molecular – the last one being rather insignificant according to Knudsen's theory [10]. All these mechanisms operate also in plasma-sprayed Al_2O_3, but the molecular thermal conductivity includes now that of air as well as that of the plasma generating gas and it is not practically possible to separate the two, since part of the pores fills up with air and part with gas. Inasmuch as the tests were in this case performed under vacuum (10^{-4}-10^{-5} torr) and through-porosity varied from 35 to 12% (it decrease d as the layer thickness was increased from 0.2 to 1.5 mm), only two mechanisms of heat transfer were assumed to operate in a coating, namely phonon and radiant transfer, while the gas was evacuating from the pores. Furthermore, in the case of thin Al_2O_3 layers [11], heat radiated not only through the pores but also through the coating. The geometry of the powders was not varied by packing or was varied slightly, unlike in the case of plasma spraying with an appreciable spread in the size and shape distribution of particles.

Thus, for these reasons, the trends of the respective $\lambda = f(t)$ curves are not the same.

Plasma-sprayed aluminum oxide was studied on various kinds of metallic substrates: grade Kh18-N10T steel, grades VN1 and VN2 niobium, grade TO-4 alloy, titanium, copper, tungsten, molybdenum,

TABLE 1. Characteristics of Specimens Made of Powders and of Plasma-Sprayed Al_2O_3

Item number	Powder grade	Density of powder grains, g/cm^3	Density of tested layer, g/cm^3	Pressure (on unit surface), g/m^2	Volume fraction of solid particles, %	Weight fraction of solid particles, %	Size of powder grains (particles), μ	Phase constitution	Application
1	E-98 (USA)	3,98	—	23,2	0,46—0,63	—	—	—	[9]
2	B-45 (USA)	3,95	—	29,4	0,43—0,53	—	—	—	[9]
3	Ch. d.a. (USSR)	3,86	—	0	0,3—0,4	—	20÷100	γ-phase	—
4	Plasma-sprayed Al_2O_3, raw powder grade ch.d.a., γ-phase	—	3,2—3,3	—	—	0,7—0,8	—	10% α-phase, 90% δ-phase	Sprayed on cooled cylindrical substrate, diameter 15 mm, from a distance 200 mm
5	Plasma-sprayed Al_2O_3, raw powder grade ch.d.a., γ-phase	—	3,4—3,5	—	—	0,85 0,9	—	Up to 50-60% α-phase remainder δ-phase	Sprayed on disc substrate, commensurate in size with the central zone of the flame

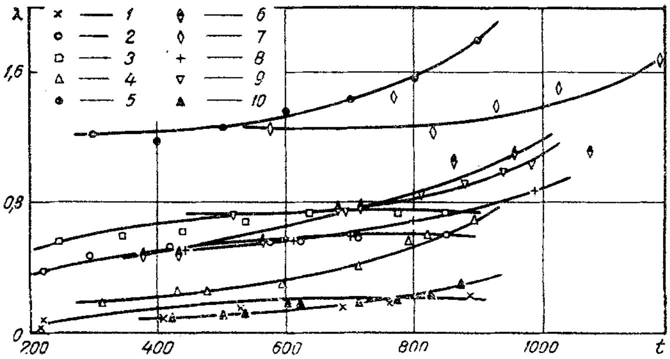

Fig. 2. Thermal conductivity λ (W/m·deg) as a function of the temperature t (°C), for powders and plasma-sprayed coatings: 1) powder grade ch.d.a. (item 3 in Table 1); 2) powder grade B 45 (item 2 in Table 1); 3) powder grade E-98 (item 1 in Table 1); 4) plasma-sprayed Al_2O_3 (item 4 in Table 1) before heat treatment; 5) plasma-sprayed Al_2O_3 (item 5 in Table 1) without heat treatment; 6) plasma-sprayed Al_2O_3 with heat treatment at t = 1000-1050°C under vacuum (10^{-5} torr) on Nb substrate and argon–hydrogen mixture as the plasma generating gas; 7) the same, except heat treatment at t = 1350°C; 8) plasma-sprayed Al_2O_3 before heat treatment on TO-4 alloy substrate with nitrogen as the plasma generating gas; 9) the same, except with heat treatment at t = 1030°C; 10) peeling after three heat cycles (maximum temperature 1000°C).

grade 20 steel, etc. A few features affecting the thermal conductivity of plasma-sprayed aluminum oxide have been revealed in this study.

First of all, on cooled cylindrical grade Kh18N10T or Kh18N9T steel and niobium substrates, i.e., on substrate materials having different thermal conductivities, the thermal conductivities of Al_2O_3 were close (Fig. 2) before heat treatment but different after 8 h of heat treatment at t = 1000-1050°C: on

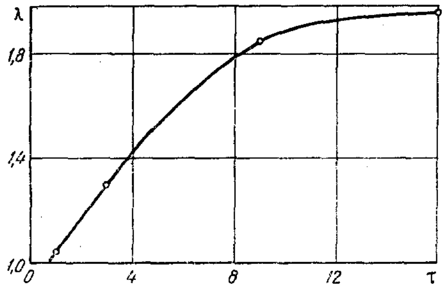

Fig. 3. Thermal conductivity of plasma-sprayed aluminum oxide λ (W/m · deg) as a function of time τ(h) at a 1300°C temperature.

the niobium substrate the thermal conductivity increased even through 6-7 heat cycles. On grade Kh18N10T and grade Kh18N9T steel substrates the trend was opposite, the coating peeled and cracked parallel to the cylinder axis, with the thermal conductivity decreasing sharply through 2-3 heat cycles (specimen layer thickness 0.5-1.0 mm).

Secondly, a high thermal conductivity can be attained by spraying on an uncooled substrate at a temperature comparable to that of the central zone in the flame and without movement of the spray nozzle, resulting in a thermal conductivity close to that of plasma-sprayed Al_2O_3 after full heat treatment (Fig. 2). We note that the coating may not have been completely heat treated on all substrates, inasmuch as the heat-treatment temperature was rather high and above 800°C.

Thirdly, as the technological process conditions, namely the plasma generating gas and other parameters were changed as, for example, by using nitrogen at a flow rate of 50 liters/min and a plasma arc 350 A strong at 80 V with a similar spray nozzle, the thermal conductivity was found higher than in the first mode, even with the material not heat treated (Fig. 2). The thermal conductivity of Al_2O_3 on the grade VN2 niobia substrate as a function of time at a constant temperature of 1300°C, is shown in Fig. 3.

Furthermore, the first tests have indicated a variation in thermal conductivity with thickness, essentially in the case of 0.2-0.5 mm layers and at temperatures 500°C. Up to those temperatures the thermal conductivity varied insignificantly and depended very slightly on the layer thickness. Evidently, the variation in thermal conductivity was here related to:

1) the different heat treatment of the material by the empirical method of shifting the power density levels;

2) the changes in the spray process made by manual adjustments, depending on the experience and skill of the operator;

3) the effect of the emissive power of the substrate (in the case of thin layers [11]), inasmuch as that emissive power was high [12].

The thermal conductivity of Al_2O_3 was studied experimentally by steady-state methods, inasmuch as at high temperatures (above 800-900°C there occur structural changes in a layer) certain metallic substrates (steel, copper, etc.), applicable only up to their reduction temperatures and up to certain thicknesses (on a cylindrical substrate of grade Kh18N10T steel, for example, the coating thickness should not exceed 0.5 mm) would not withstand sudden temperature changes, unless high thermal stresses appeared and caused the coating to break down.

The following test methods were used in this study:

a) the steady-state absolute method of heating a cylindrical specimen by radiation from an insulated heater: the specimen here was a substrate with deposited coating;

b) the steady-state absolute method with a cylindrical substrate used as the heater;

c) the steady-state method of shifting the power density levels, with the heater insulated from the specimen, the temperature field made uniform by tapering the section toward the ends;

d) the steady-state method of shifting the power density levels, with a specimen produced by spraying on a cylindrical substrate-heater made up of two or several layers of different thicknesses;

e) the steady-state relative method [8], with the thermal flux established according to a reference specimen and with the test specimens produced in the form of Al_2O_3 pellets first sprayed and the substrate then removed.

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