Usage of supersonic cold gas-dynamic spraying (CGDS) for obtaining a catalytic coatings for systems of steam reforming of fuel and chemical heat recovery

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The problem of development of new technologies dedicated for creation of materials which are capable to ensure implementation of active thermal protection of a HFV, unique propulsion system, systems of directional power transmission and protection against radiation is one of the major ones among the problems of HFV creation.

The complex of problems related to materials for creation of hypersonic flight vehicles includes development of catalytic materials for the power unit; materials with high heat conductivity for systems of active thermal protection, materials with high thermal stability for the combustion chamber of a new type; materials for magnetoplasmachemical engine (MPCE); magnetic materials for creation of a MPCE duct; materials for protection against electromagnetic radiation.

Now among the priority directions in the field of materials technology the development of materials with non-equilibrium structure – amorphous, nanocrystal and intermetallic compounds of a catalytic class for creation of thermochemical reactors and amorphous materials- solders for constructions creation are being developed most of all.

The feature of the indicated classes of materials is a qualitatively new level of mechanical, physicochemical, magnetic and other properties that provides a considerable expansion of their functional capabilities and usage in many areas of industry. The majority of developers of the indicated materials mention the close relation of the properties with Technologies of their obtaining.

The most complexity according to our opinion is connected with development of technology of catalytic coating obtaining as in this case combination of high strength and high porosity of a catalytic layer should be reached.

For obtaining a catalytic material for systems of steam reforming of fuel the usage of combination of the following methods is the most expedient:

- Cold gas-dynamic spraying;
- Plasma spraying in an oxidizing medium;
- Ionic - plasma or magnetron spraying;
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- Chemical deposition of activators.

The structure of a catalytic element represents a multilayer design consisting of several functional layers including: the metal carrier, porous catalytically active layer, layer of promoter (activator) (fig. 1).

**Structure of the catalyst on the metal carrier**

![Structure of the catalyst on the metal carrier](image)

- Development of a strong high porous catalytic carrier;
- Creation of the layer of activator on a catalytic carrier surface.

The known methods (drossing deposition, pulverization, plasma spraying) have the considerable disadvantages bounded or with low strength, or with impossibility to ensure the required properties and structure of obtained coatings. In this connection from our point of view the most perspective for obtaining the catalytic coatings for systems of steam reforming of fuel and chemical heat recovery is the method of supersonic cold gas-dynamic spraying.

However, the mechanism of interaction of evaporated dusts with a substrate now is studied unsufficiently well. Based on the experience, available for us, which one was accumulated during fulfilment of joint researches with the specialists of Mozhaiskiy’ Academy of Space and Engineering the following mechanism of interaction exists. At rather small velocities of particles flow (as a rule, in subsonic range) the abrasive processing of a plastic substrate by firm particles of evaporated dust takes place. At increasing of speed up to 2 Mach the formation of adherent layer in the beginning of a cluster type and then solid type is observed. At further increasing of speed of a gas flow the abrasive processing of a ductile material is again observed, possibly, because the speed of elastic deformation of a substrate at these speeds of interaction exceeds the
speed of plastic deformation of deposed firm particles. The more simple mechanism, apparently, is observed at study of materials comparable on hardness.

Based on results of the work [12] it is possible to make a conclusion that for each material there is a critical speed of its interaction with a substrate at which one the deposition of coating starts. Increasing the speed of a gas flow it is possible to obtain the coatings practically of any metal if the elastic and plastic characteristics of a deposed material and substrates are comparable.

The CGDS installation of a “Dymet” type (fig. 2) consists of the following main units:

1. Compressed air tanks;
2. Air cleaning system;
3. Ohmic heater of operating gas (air);
4. Laval nozzle;
5. Control panel of the installation;
6. Feeders (metering devices).

Fig. 2 Principal diagram of the installation of the "cold" gasdynamic spraying

The principle of the method is that the compressed air after the cleaning system through the pressure regulator moves in the chamber of ohmic heater in which one it is heated up to the operation temperature and than is passed to a supersonic nozzle. The applied dust from the feeder moves in a nozzle zone and is caught by passing air. On output of a supersonic nozzle the high-velocity jet of a mixture of hot air with dust is formed.

The coating deposition is made with usage of two independently working metering devices in one of which there is an aluminium which is used as a bounding metal and in the second one there is a catalytic material γ-Al2O3. The adhesive layer is applied from the first metering device, then the second metering device is switched on and the catalytically active layers with the fixed porosity are deposed.

For obtaining the coating with required strength of adhesion at usage of heterogeneous materials of dust and substrate the optimum from our point of view is the alteration of speed of a
gas flow and evaporated particles at the simultaneous control and fixation of temperature of a gas flow and evaporated particles. Alongside with the solution on the materials problems we had to decide a lot of problems on metrology support of experimental installation. Researches conducted together with the group of specialists of physical faculty of the St.-Petersburg State University headed by Dr. I. Ch Mashek, Head of Department, have allowed to develop the required diagnostic equipment. In particular, the CGDS installation was equipped with the special systems of measurement of:

- linear speed of a gas flow based on a difference between dynamic and static pressure;
- temperature of a gas flow based on thermoelectric effect;

There are developed and realized the systems of measurement of:

- speed of heterophase flow based on effect of Doppler frequency shift;
- temperature of particles with usage of the infrared (IR) radiometer.

Usage of the developed methods of measurement and diagnostic of a two-phase flow has allowed to study distribution of speed, temperature and concentration of firm particles in a cold supersonic two-phase flow and also to evaluate technical and technological capabilities of the equipment used at working with a gas flow (see fig. 3, 4, 5).

![Graph showing temperature and velocity](image_url)

**Fig. 3.** Static temperatures of a dust of a non-equilibrium material with amorphous structure
From fig. 2, 3 it is visible, that static temperature of the dust of a non-equilibrium material with amorphous structure and catalytic material practically does not depend on its concentration in a flow and it does not exceed 100 °C.

The measurements of speed of a dust particles of a non-equilibrium material with amorphous structure and material of the catalytic class were made on two distances from a nozzle cut - 15 mm and 50 mm at different productivity of metering device and operating pressures of CGDS installation. Their average results are shown in the Table 1 and 2.

### Table 1

<table>
<thead>
<tr>
<th>Distance from nozzle shear, mm</th>
<th>Efficiency, g/sec</th>
<th>Operating pressure, atm</th>
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<tbody>
<tr>
<td>15</td>
<td>2,5</td>
<td>316 5,5 36</td>
</tr>
<tr>
<td></td>
<td>1,7</td>
<td>304 306 300</td>
</tr>
<tr>
<td>50</td>
<td>2,5</td>
<td>177 238 286</td>
</tr>
<tr>
<td></td>
<td>1,7</td>
<td>220 318 318</td>
</tr>
</tbody>
</table>

Fig. 4. Static temperatures of a catalytic material
From the given data it is visible that the optimization of the technological process of spraying of coatings should be conducted on two main parameters:
- Interval from a nozzle shear;
- Variation of speed of a heterophase flow.

On the basis of conducted studies the optimization of technological processes of obtaining the coatings on the basis of catalytic and non-equilibrium materials was conducted.
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The given optimized parameters are the basic, i.e. allow to obtain, at their reproduction a broad range of coatings from different materials for a solution of a problem of creation of hypersonic flight vehicles. As a result of optimization of a technological process of obtaining of coating the following samples were obtained:

- thin-wall heat exchange devices of aluminium for the systems of chilldown of exhaust gases of small-sized gas-turbine plants. Thus the dusts of a Al – Si system were deposed on aluminium which are good solders at consolidation of thin-wall constructions.

- systems of protection against electromagnetic radiation of technical means and biological objects. Thus the alloys on the Co basis with amorphous structure were used;

- durable and corrosion stable coatings which one have shown high physical-mechanical characteristics.