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THE FORMATION OF THERMAL BARRIER COATINGS BY THE METHOD OF PYROLYSIS SALTS ZR-Y IN AR-HE-H2 PLASMA

ABSTRACT. The technology for the formation of nanostructured ceramic thermal barrier coating by injection of precursor $ZrO_2–Y_2O_3$ in the plasma is worked out. An experimental setup for the deposition prekurosora $ZrO_2–Y_2O_3$ is designed and constructed. Prototypes of a thermal barrier coating are received on this equipment, spraying regime is worked out. The results of temperature cycling test (under the regime of the cycle—100°C–1150°C (15 min)–100°C) showed that the advantage of the obtained coating over conventional ceramic plasma is 40%. This result is explained by the fact that vertical cracks serving compensators stresses are formed in the coating. The number of cracks can be controlled by adjusting the deposition conditions (flow precursor spray angle, plasma power, etc.) Authors suggest that the precursor alloying $ZrO_2–Y_2O_3$ by oxide of rare earth metal (Gd, Yb, Nd, Er) will increase the operating temperature of the coating due to phase stability at temperatures above 1200°C.

KEY WORDS. The formation of thermal barrier coatings by the method of injection precursor in plasma, pyrolysis salts, precursor, aqueous solution of salt, modes of spraying, experimental equipment, cyclic testing, the basic reactions in plasma, the structure of the coating.

Introduction

In modern gas turbine, a heat protection layer on duct surfaces of cooled blades provides a reduction in the temperature of a heat-resistant superalloy for more than 100°C at a thickness of the ceramic layer of 150 microns [1]. As a result, it is possible to improve the efficiency of the engine by increasing the operating temperature of gases or enhance the resource. In practice, the following methods of the formation of a heat-resistant ceramic coating are widely distributed: the method of plasma spraying (PS) [2] and the method of electron-beam evaporation with vapor deposition (EB) [3]. The ceramic plasma coating $ZrO_2–7Y_2O_3$ on the nozzle blades has been used since the 1980s. Pretty simple and inexpensive technology allows having the coating of heat conduction coefficient of λ less than 1 W/mK [4]. However, the layer microstructure is characterized by numerous defects—incomplete fusion, porosity and horizontal cracks, which determine low resistance to thermal-cycling loads in operation and rapid destruction [4].

Due to its columnar structure, electron-beam coating resists thermal fatigue much better, but it has higher values of λ and oxidation rate at the joint with the sublayer [5]. An extremely high cost of an EB unit should be considered as well.

The results of [6, 7, 8] show that pyrolysis of salt solutions Zr-Y in the plasma of low temperature Ar-He-H_2 allows to form heat-resistant coatings (HRC) with a high resistance to thermal-cycling loads (twice higher than the HRC formed by PS method). The method of plasma spraying of precursor (PSP) ZrO_2–Y_2O_3 has been proposed relatively recently (significant works appear not earlier than 1999) and has not yet found practical use in the industry. Among the major impediments there are lacks of independent experimental results on thermal-cycling and erosion resistance of coatings; there is no data on the testing of PSP method in a gas turbine or a burner. However, low cost of the process combined with a high potential for some properties (for example, low heat conduction coefficient and better resistance to thermal shocks compared to EB and plasma coatings [9]), determines the relevance of experimental work.

Injection of the aqueous solution of salts Zr-Y in plasma can be carried out using either a spray nozzle or an air-blast atomizer [10, 11]. For the first case it is required an injector with a diameter of 80 ... 150 μm (usually, it is manufactured using high precision laser technology). The result is characterized by the possibility of obtaining layers with low porosity, a small number of peripheral particles, high materials utilization ratio (MUR). There are main disadvantages of a spray nozzle: low productivity, strict requirements for clean standards of the premises, filtration rating and liquid pressure (otherwise, the injector is clogged and loses efficiency, and cleaning of fine channels is possible only with the help of ultrasonic technique). There are no fine channels in the structure of an air-blast atomizer, it is resistant to contamination but an atomizer is tapered and as a consequence there are a large number of peripheral particles, substantial porosity, and low cohesive strength of the layer. In general, when droplets of the precursor contact with the plasma jet at a sufficient concentration, one can observe decomposition, evaporation of solvent (water), pyrolysis of ceramic particles, sintering and burning of nanoparticles (Fig. 1).

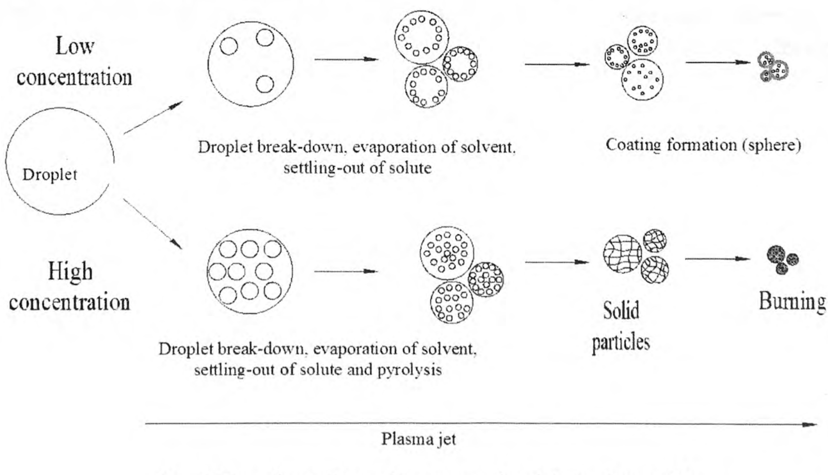

Fig. 1. Transformations of precursor droplets in plasma [7]

After droplets of the solution have reached the hottest part of plasma (Fig. 2., area III), they are transforming (Fig. 1) and form a more dense coating than the particles trapped in the area of lower temperature (Fig. 2., area II) [5]. In area II (Fig. 2) the particles do not have time to undergo the total synthesis and they come to the surface in the initial state. There, under the influence of temperature of plasma they form a sphere. Spheres, in their turn, develop vertical cracks, which have a positive impact on the thermal-cycling loads and function as compensators at thermal expansion of the base. The porosity of the coating obtained is not more than 18–20% and it can be adjusted with the concentration of the solution [8]. As a result, a heat-resistant coating from nanostructured ceramics ZrO_2–Y_2O_3 is formed on the surface.

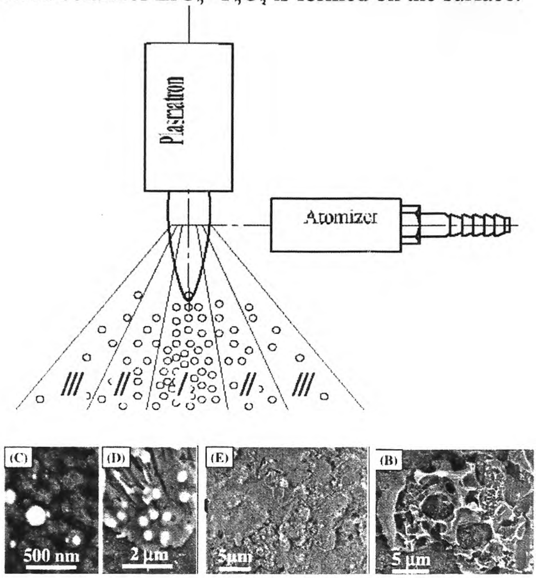

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Fig. 2. The formation of the coating [7]

Experimental procedure

To evaluate PSP method, a PSP pilot unit was designed and constructed. The basic parts of the unit are a plasma torch (60 kW) with an automatic arc length; an upgraded power box APR-404 with open-circuit volts at 160 V; a cooling system of plasma torch based on water-to-water heat exchanger; a supply module of plasma-supporting gases with a mass flow controller Ar, He, and H_2; a coating chamber equipped with the mechanisms of the sample rotation and displacement of the plasma torch.

The injection of precursor ZrO_2–7% Y_2O_3 in plasma was carried out using an air-blast atomizer (the dimensions of the flow are shown in Fig. 3). With the atomizer working, the precursor is drawn into stub pipe 1, and spraying gas (argon)—into stub pipe 2. In the atomizer channel, gas emulsifies, crushes and scatters the solution.

Thereby, due to a close contact, it is provided the solution crushing efficiency and momentum exchange between the liquid and air in a long and narrow channel. A two-phase jet with an opening angle of about 15 degrees is formed at the output of the atomizer. The atomizer is mounted on the plasma torch in compliance with axial dimensions (Fig. 3).

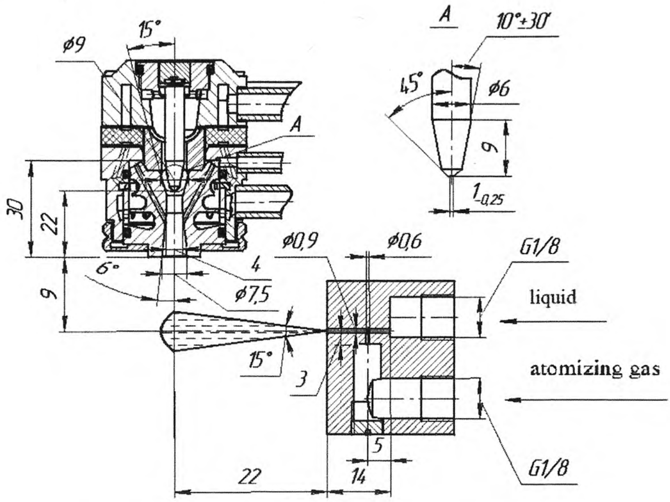

Fig. 3. The sketch of the flow of the plasma torch and nozzle.

Before forming ceramic heat-resistant coating, the samples were covered with metal heat-resistant layer PKH-27YU7S3I of 170 μm using conventional plasma method and thermal diffusion annealing was carried out in vacuum at 1050°C during 4 hours. Spraying mode is shown in Table 2. To form the ceramic layer, acetate aqueous solution ZrO_2–7% Y_2O_3 (precursor) with the concentration of 150 g/liter was chosen. The experimental work with the aqueous solution of salts and $ZrOCl_2$ and $Y(NO_3)_3$ showed no significant difference in the structure and thermal-cycling tests; pollutant emissions and contamination of the coating chamber are much higher. The mode of precursor deposition: I-410A, U-90B, Ar_{lp}—60 l/min, H_{2lp}—16 l/min , He_{lp}—32 l/min, h-65 mm, precursor flow—35 ml/min (at the pressure of precursor—2 atm and the pressure of the atomizing gas—3.2 atm).

Pyrolysis of the precursor with hydrogen chloride takes place in plasma under the influence of temperature:

$$ZrOCl_2 + 2H_2O \rightarrow ZrO(OH)_2 + 2HCl;$$
$$ZrO(OH)_2 \rightarrow ZrO_2 + H_2O;$$
$$Y(NO_3)_3 \rightarrow YONO_3 + 2NO_2 \uparrow + 0.5O_2 \uparrow;$$
$$YONO_3 \rightarrow 0.5Y_2O_3 + NO_2 \uparrow + 0.25O_2 \uparrow.$$

The effect of addition of erbium, ytterbium, neodymium and gadolinium oxides into coating under traditional plasma and EB formation of heat-resistant coating is studied in [12]. The efficiency reduction due to heat conduction of these additives may be up to 52%. The thermal conductivity of the ceramic layers with a thickness of 250 μm with 4% (molar) of additives of neodymium and ytterbium oxides is 0.86 and 0.89 W/mK correspondently at room temperature [5]. When forming a heat-resistant coating with PSP method, it is possible to alloy additionally the ceramic precursor with the salts of the rare earth materials, which will lead to phase stability at the temperatures above 1200°C:

$$\left[\frac{Yb}{Gd}\right](NO_3)_3\cdot\left[\frac{5}{6}\right]H_2O \rightarrow \left[\frac{Yb}{Gd}\right]ONO_3 + 2NO_2\uparrow + 0.5O_2\uparrow;$$

$$\left[\frac{Yb}{Gd}\right]ONO_3 \rightarrow 0.5\left[\frac{Yb_2O_3}{Gd_2O_3}\right] + NO_2\uparrow + 0.25O_2\uparrow.$$

As a result, a nanostructured heat-resistant coating ZrO_2 + 7% Y_2O_3 with additives of oxides of rare earth materials is formed on the surface.

When working with the acetate precursor ZrO_2–Y_2O_3 there is no particularly harmful emission, which makes it less dangerous to human health:

$$ZrO(CH_3COO)_2 + 5H_2O \rightarrow ZrO_2 + 4CO_2\uparrow + 8H_2;\uparrow$$

$$2YO(CH_3COO) + 5H_2O \rightarrow Y_2O_3 + 4CO_2\uparrow + 8H_2\uparrow.$$

During spraying, the temperature on the surface of the sample did not exceed 700–750°C. A typical structure of the surface of the heat-resistant coating is shown in Figure 4. The analysis of the microstructure of the coating by means of electronic microscope JEOL JSM6510LV showed the presence of spherical particles of ZrO_2 + 7%Y_2O_3, the particles with complete and partial penetration, alloying and transverse microcracks. Crosscut microcracks function as voltage compensators in the ceramic layer occurring during the cycle (heating–cooling) due to a different thermal expansion coefficient with the base metal. The number of cracks can be controlled by adjusting the operating mode of the nozzle.

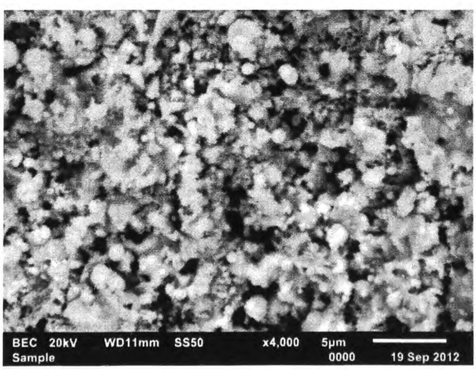

Fig. 4. The structure of the coating formed by PSP method

To carry out a comparative analysis, the samples with a traditional heat-resistant coating formed by plasma method were prepared. Powder PKH27YU7S3I of fraction 80 μm was used as the heat-resistant metal undercoat; powder ZrO_2 + 7% Y_2O_3 of fraction 40–80 μm was used as a ceramic layer. The spraying modes are job-proved and presented in the table below.

Table

Powder	Flow rate of plasma-forming gas, l/min				Spraying distance, mm	Coating thickness, μm	I, A	U, B
	Arlp	H2lp	He	Ardp				
PKH27YU7S3I	43,7	11,7	35	8	110	170	350	75
ZrO2+7%Y2O3	55	22	35	8	80	120	450	90

Determination of thermal stability of a heat-resistant coating

One way to determine the thermal resistance of the coating is to carry out a thermal cyclic test. The principle of method is to determine the number of cycles (heating-cooling that approximately simulates the start and stop of a gas turbine engine) up to the destruction of heat-resistant coating [6].

Heating to 1150°C was carried out in the electric-tube furnace PTK-1.4–40. By test it was found, that heating the sample up to the operating temperature makes 15 minutes, and cooling the sample in air without forced cooling to 150°C—20 minutes. The samples are placed on the mounting (Fig. 5) made of a high-temperature material HN60W without a contact with the heat-resistant coating. Loading and unloading of the samples was carried out manually to meet the heating time, endurance (20 minutes) and cooling.

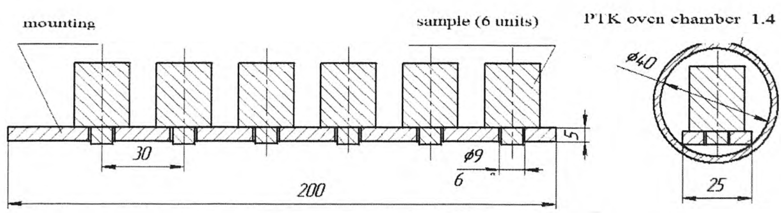

Fig. 5. The mounting with the samples for thermal cyclic tests.

During each cycle, the samples are visually monitored to find out spalling spots, chipping, cracking and destruction of the heat-resistant coating. These defects are visible to unaided eye at the sample temperature of 750°C and above.

Thermal cyclic tests showed that the samples with a traditional heat-resistant coating formed by plasma method withstood 60–80 cycles to complete destruction. Ceramic coating flaked in large solid parts. The surface of the metal underlayer is oxidized.

The samples with the heat-resistant coating formed by PSP method ZrO_2 + 7%Y_2O_3 until destruction withstood 100–130 cycles, which is by 40% more compared to previous samples. There are underlayer oxides with uniform concentration on the surface of the ceramic layer. Destruction occurs in the form of particles chipping, a typical size of which is 10 mm^2.

PSP method ZrO_2–Y_2O_3 is of great interest in the field of turbo-machinery and theoretically allows forming coatings for advanced gas turbine engine nozzle apparatus of the 5th generation. Scientific research and experimental work in this area is needed to confirm the preliminary results. In case of a successful outcome of experimental studies, this technology can be recommended for mass forming heat-resistant coating on the rotor and nozzle blades of gas turbine engines.

Conclusions

PSP pilot unit has been designed and constructed to form a ceramic heat-resistant coating by plasma spraying precursor ZrO_2–Y_2O_3 method.

The technology to form a heat-resistant coating using aqueous salt solution Zr-Y and acetate precursor ZrO_2–Y_2O_3 is completed.

It has been established that the injection of the precursor with an air-blast atomizer provides a stable process in comparison with a jet injection.

In terms of thermal cyclic tests at the cycle temperature of 100°C–1150°C, (20 minutes)—100°C it is specified that the heat-resistant coating formed by plasma spraying precursor ZrO_2–Y_2O_3 method is 40% more stable in comparison with the coating formed by a traditional plasma method, which ensures the necessary overhaul period of a gas turbine engine.

It has been proposed to alloy additionally precursor ZrO_2–Y_2O_3 with the oxides of rare earth metals Gd and Yb in order to fix phase stability at temperatures above 1200°C and to improve heat resistance of the heat-resistant coating.

The research allows us to recommend (after the test of blades in the gas turbine engine) the developed technology for forming a heat-resistant coating on the nozzles and rotor blades of a turbine of a gas turbine engine operating at the temperatures up to 1200°C.

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