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INVESTIGATION OF HEAT RESISTANCE OF PLASMA COATINGS FROM TiAl INTERMETALLIC WITH APPLICATION OF PARAMETRIC OXIDATION DIAGRAM

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ABSTRACT

Heat resistance of plasma coatings from TiAl intermetallic was studied by heating in air environment at temperatures of 700–1000 °C with determination of the change of sample weight and plotting of the parametric diagram of heat resistance, as well as phase composition of coatings before and after testing. It was determined that titanium oxide (TiO_2) is the main product of TiAl coating oxidation, and at higher temperatures it is a mixture of TiO_2 and Al_2O_3 oxides. Titanium nitride (TiN), TiO, Ti_2O, Ti_2O_3 oxides and Ti_3Al intermetallic were found in the scale composition. Kinetic dependencies of oxidation process were used to perform calculations of heat resistance parameters for temperatures of 700–1000 °C that allows assessment of durability of TiAl intermetallic coating for any temperatures up to 1000 °C. Calculations of average oxidation rate showed that heat resistance diagrams can be used to determine the main heat resistance characteristics: specific weight loss and uniform corrosion depth.

KEYWORDS: plasma spraying, intermetallics, Ti–Al system, heat resistance, oxidation, parametric diagram

INTRODUCTION

Intermetallics are a unique class of materials with a wide range of useful properties. Due to that they are used as structural alloys and coatings that ensure corrosion resistance.

As regards titanium intermetallics (TiAl, Ti_3Al), owing to such characteristics as high melting temperature, low density (two times lower than that of nickel-based superalloys (3.9–4.2 g/cm^3)), high strength in a broad temperature range, higher creep resistance and fatigue strength, high modulus of elasticity and good oxidation resistance, they can complete with nickel-based superalloys in such industries as aviation and rocket technology.

So, application of titanium aluminide leads to lowering of part weight by 20–30 %, fuel consumption up to 20 %, noise by 50 % and NO_x emissions by 80 % [1]. TiAl intermetallics can be used as a protective material for titanium alloys, as it has higher oxidation resistance than the regular titanium alloys, and presence of an intermediate diffusion layer between the coating and base ensures good adhesion on the interface without brittle phase formation.

Titanium aluminides are promising for application in such industries as medicine, chemical and nuclear engineering, where such characteristics as corrosion and high-temperature resistance are of special importance, alongside other properties.

Analysis of published data [2–7] on heat resistance of TiAl intermetallic and alloys on its base indicate that the temperature range of their application is equal to approximately 600–850 °C (at higher temperatures their mechanical properties and oxidation resistance are relatively low). It is known that limit operating temperatures of aluminium alloys are equal to 450 °C, and those of titanium alloys are 600–700 °C. At the same time, aluminium oxide Al_2O_3 has oxidation protection properties at up to 1425 °C.

Practically in all the works, devoted to investigation of oxidation processes of Ti–Al system intermetallics, there is a statement that TiO_2 titanium and Al_2O_3 aluminium oxides are the main oxidation products. Here, only Al_2O_3 is capable of forming a continuous film that slows down the oxidation process.

Predominant formation of Al_2O_3, compared with TiO_2 depends on Al content in the intermetallic, partial pressure of oxygen and temperature.

So, work [2] devoted to study of Al_3Ti and TiAl oxidation process shows that Al_3Ti oxidation stability at 1000 °C for 48 h is 30 times better than that of TiAl. At this moment TiAl loses Al, transforms into Ti_3Al on the interface of TiAl and scale, and Ti diffusion through an Al_2O_3 layer and TiO_2 formation only enhance TiAl oxidation.

As shown by the results of work [8] devoted to study of the influence of partial pressure of oxygen on oxidation of Ti–Al system intermetallics, at temperatures from room to 1000 °C predominantly Al_2O_3 forms already at very low pressure (5 mBar), and at increase of oxygen pressure TiO_2 formation becomes the predominant process. At 1000 °C new oxide phase forms namely Al_2TiO_5.

The main factor that limits TiAl application area is the fact that this alloy has poor oxidation resistance at temperature above 800 °C, as the outer layer of oxide scale consists of TiO_2, or a mixture of TiO_2 and Al_2O_3 oxides, but not of Al_2O_3 protective layer. Owing to close affinity of Ti and Al to oxygen, TiO_2 and Al_2O_3 oxides grow competitively at the same rate on TiAl surface during oxidation that is confirmed by Ti–Al–O constitutional diagram [7, 8]. Mixed scale cannot prevent further oxidation of TiAl, that is why TiAl has a lower oxidation resistance at high temperatures.

More over, at oxidation in air titanium simultaneously reacts with oxygen and nitrogen. Nitrogen dissolution in rutile lattice leads to formation of a defective lattice, acceleration of oxygen diffusion and increase of oxidation rate. Formation of titanium nitrides in air prevents appearance of Al_2O_3 protective layer [9].

As regards the work in the field of technology and application of protective coatings based on Ti-Al intermetallic system, they are not very numerous. Known are only studies of producing coatings by magnetron sputtering. So, authors of work [4], produced good quality coatings from $TiAl_2$, which demonstrated a high resistance at temperatures of 800–900 °C at oxidation in air. Work [3] presents the results of producing gradient and multilayer coatings, using magnetron sputtering. Here, in gradient coatings Al content increased in the direction from the base to the surface, and in multilayer coatings the layers formed in the same direction from Ti_3Al towards TiAl and $TiAl_3$. Coatings showed good oxidation resistance at the temperature of 750 °C.

While the mechanism of interaction of TiAl system intermetallics with oxygen is quite well studied, the information on heat resistance of these materials in the form of protective coatings is scarce, and especially the works on assessment of their life prediction are not available now.

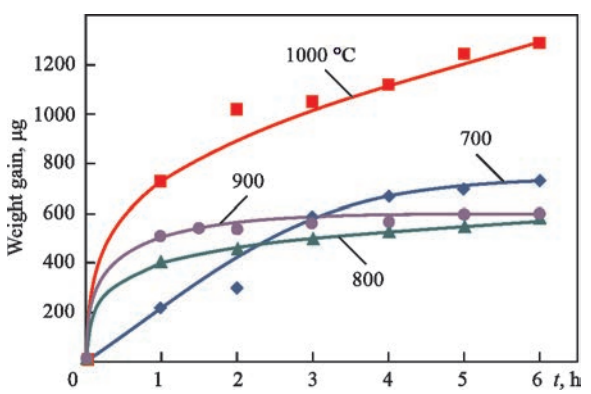

Figure 1. Kinetic dependencies of oxidation of TiAl powder

At the same time, the task of studying the coating heat resistance consists not only in evaluation of the coating role in base metal protection, but also in prediction of the service life of metal-protective coating system under the real service conditions.

The objective of this work was investigation of heat resistance of plasma coatings from TiAl intermetallics and plotting parametric diagrams of oxidation to assess the coating life at up to 1000 °C temperatures.

INVESTIGATION PROCEDURE

TiAl powder (PVT65Yu35 alloy) with particle size of ≤ 80 μm was used to produce coated samples.

Plasma spraying (PS) of coatings was performed in UPU-8M unit at the following parameters: I = 500 A; U = 40 V, plasma gas (Al + N_2) flow rate — 25 l/min, L = 120 mm.

In order to study the coating heat resistance, samples were made from St45 grade steel in the form of "acorns" of 15 mm diameter and 20 mm length (coating thickness was 700–800 μm).

Investigations of heat resistance of both the powders and coatings were conducted by continuous welding of samples at temperatures of 700–1000 °C and isothermal soaking of up to 6 h.

Weight method (sample weight gain) was selected in connection with the fact that only solid products can form at oxidation of Ti–Al system samples.

The high-temperature testing unit allowed weighing the tested samples directly in the furnace, as it is fitted with analytical scales, from one arm of which the sample is suspended on a thin platinum wire. The unit had automatic regulation of temperature with the accuracy of ± 5 °C, analytical scales ensured the accuracy of up to ± 0.1 mg.

Coating structure and phase composition were studied by the methods of metallography (Neophot-32 microscope fitted with digital camera attachment). X-ray diffraction phase analysis (XRPD) was performed in DRON-3 diffractometer in CuK_α-radiation with a graphite monochromator with 0.1° stepping and 4 s exposure time in each point with further computer processing of digital data. Phase identification was performed using ASTM data base.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Analysis of kinetic dependencies of the process of TiAl powder oxidation revealed that in the entire temperature range of 700–1000 °C the process obeys the time parabolic law with parabola exponent close to 2, that is indicative of the fact that the diffusion stage is the limiting link of the process (Figure 1). Here,

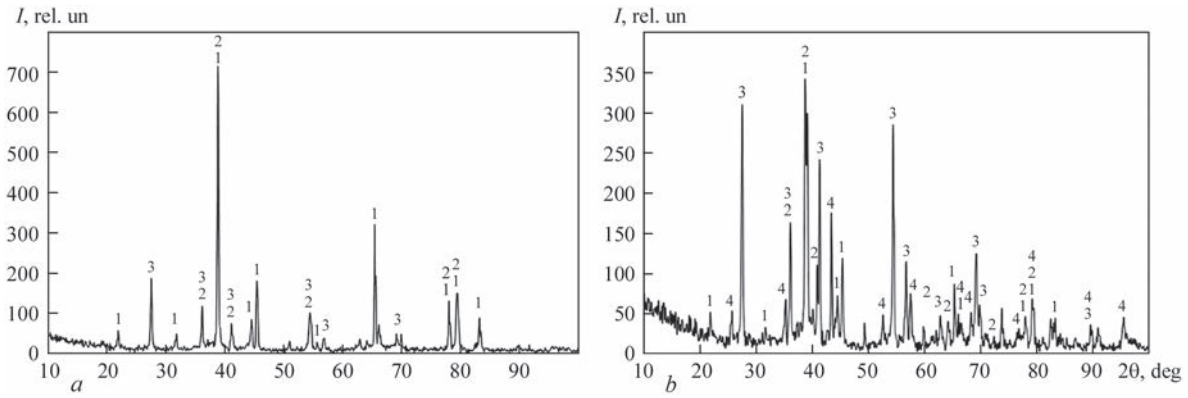

Figure 2. Roentgenograms of TiAl powder after oxidation at the following temperatures, °C: *a* — 700; *b* — 800; 1 — TiAl; 2 — Ti_3Al; 3 — TiO_2; 4 — Al_2O_3

TiO_2 titanium oxide is the main product of oxidation of TiAl powder at the temperature of 700 °C, and at 800 °C and higher temperatures Al_2O_3 forms in addition to TiO_2 (Figure 2).

The processes of oxidation of plasma coatings and powders are described by parabolic dependence (Figure 3). However, the speed of process development is considerably higher in the first case (see Figure 1), which is attributable to the size of the surface in contact with oxygen.

Comparison of phase composition of coatings after heat resistance testing with as-deposited coatings (Figure 4) showed that oxidation at all the temperatures leads to increase of the content of TiO_2 and TiN phases, which formed in the coating during spraying as a result of interaction of powder particles with air, present in the plasma jet. More over, TiO, Ti_2O, Ti_2O_3 titanium oxides were detected in oxidation products in small quantities, in addition to TiO_2, similar to Al_2O_3 formation in the case of TiAl powder oxidation at temperatures above 800 °C. Quantity of TiO_2 oxide grows with temperature increase.

At metallographic analysis of coatings after heat resistance testing (Figure 5) it was found that coatings remain dense, without delamination from the base, and oxide film forms on their surface.

Note that the oxide film thickness becomes greater at temperature rise, and at 900 °C it has a clear two-layered structure.

As was earlier noted, investigation results showed that the rate of oxide layer growth on the powders and coatings from TiAl intermetallics is a diffusion-controlled process (parabolic oxidation, Figures 1, 5). Here, either metal cation diffusion through the oxide to the surface and their interaction with oxygen on oxide/gas, or oxygen anion diffusion inside through the oxide and their interaction with metal on metal/oxide. Judging from the two-layer structure of the scale, a combination of both the processes is in place here.

One of the important characteristics of the protective heat-resistant coatings is prediction of their service life. Such a prediction can be made by plotting the parametric diagrams of heat resistance [10, 11].

Parametric diagram of heat resistance is the dependence of coating material weight loss (gain) at oxidation on heat resistance. Heat resistance parameter is a physical quantity, which changes in time with the rate proportional (with an opposite sign) to the true rate of oxidation of coating material, calculated by the values of relative losses (gain) of its weight.

The procedure for plotting the parametric diagrams consists in determination of n and Q values, where n is the exponent of parabolic dependence of oxidation process, Q is the activation energy.

Exponent n is determined from the experimental kinetic dependence of specific weight gain (loss) q on time t:

$$q^n = K \cdot t,$$

where K is the constant of oxidation rate, which transforms into the following linear dependence when plotted in "lg$q$–lg$t$" logarithmic coordinates:

$$n \lg q = \lg K + \lg t \text{ or } \lg q = 1/n \lg K + 1/n \lg t.$$

Hence, n = ctg α in time–$\Delta m/s$, mg/cm^2 coordinates, where α is the angle of inclination of a straight line to abscissa axis or it can be calculated by the following formula:

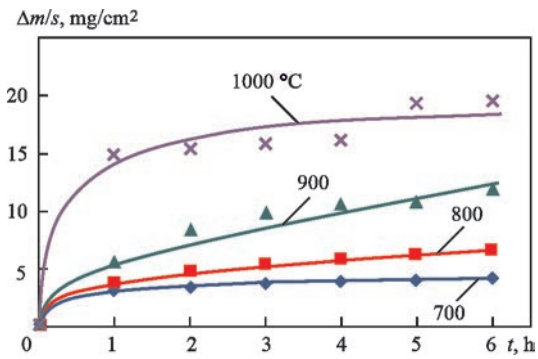

Figure 3. Kinetic dependencies of plasma coating oxidation

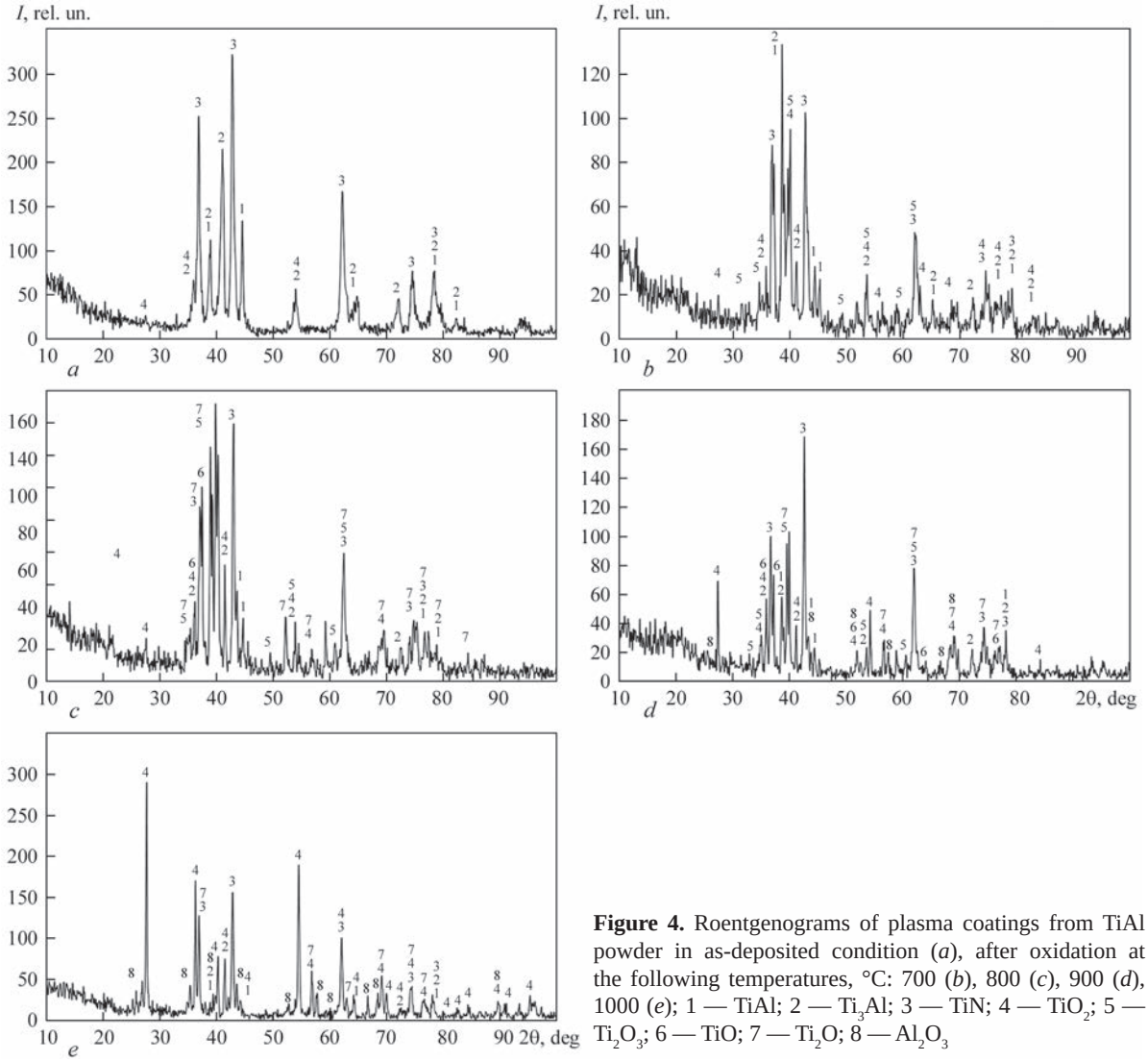

Figure 4. Roentgenograms of plasma coatings from TiAl powder in as-deposited condition (*a*), after oxidation at the following temperatures, °C: 700 (*b*), 800 (*c*), 900 (*d*), 1000 (*e*); 1 — TiAl; 2 — Ti_3Al; 3 — TiN; 4 — TiO_2; 5 — Ti_2O_3; 6 — TiO; 7 — Ti_2O; 8 — Al_2O_3

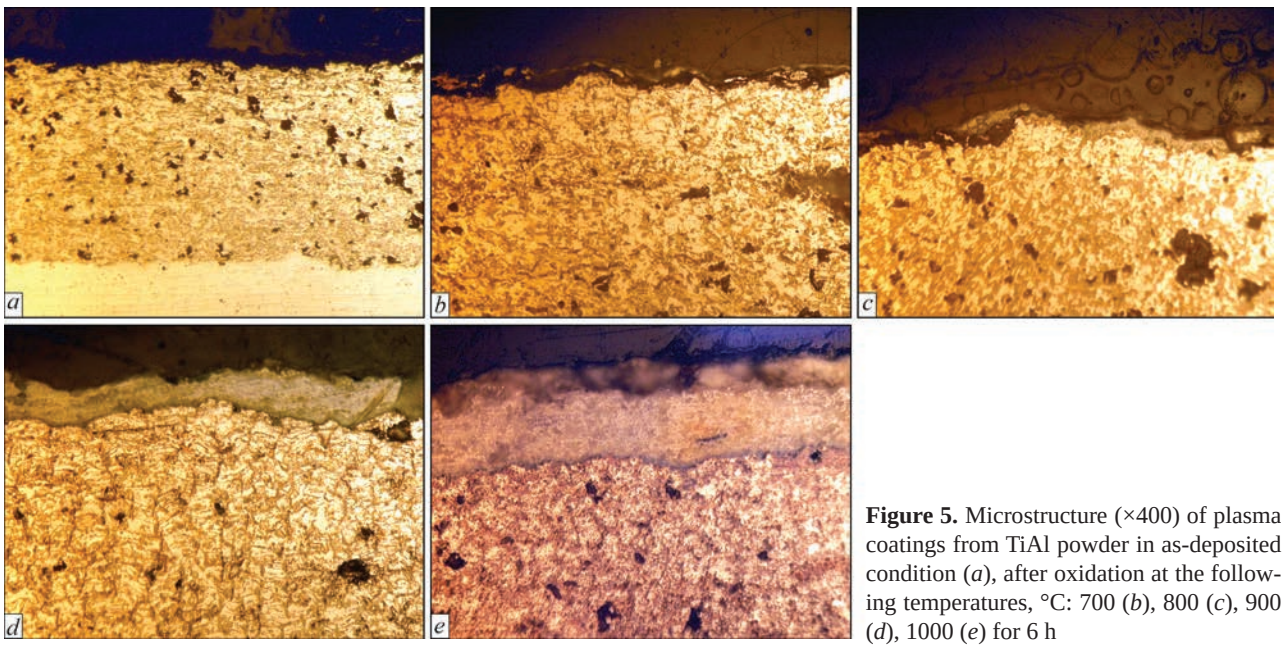

Figure 5. Microstructure (×400) of plasma coatings from TiAl powder in as-deposited condition (*a*), after oxidation at the following temperatures, °C: 700 (*b*), 800 (*c*), 900 (*d*), 1000 (*e*) for 6 h

Table 1. Results of calculation of the parameters of plasma coating heat resistance

Temperature, *K*	$10^3/T$, 1/K	Oxidation time, h	lg *t*	Specific weight gain, mg/cm^2	lg *q*	(*Q*lg*e*)/*RT*	Heat resistance parameter, (*P*)
973	1.027	1	0	3.185	0.503	11.986	11.986
		2	0.301	3.450	0.538		11.685
		3	0.477	3.715	0.570		11.509
		4	0.602	3.842	0.584		11.384
		5	0.699	4.057	0.608		11.287
		6	0.778	4.234	0.627		11.208
1073	0.932	1	0	3.740	0.572	10.869	10.869
		2	0.301	4.805	0.682		10.568
		3	0.477	5.446	0.736		10.392
		4	0.602	5.940	0.770		10.267
		5	0.699	6.320	0.800		10.170
		6	0.778	6.680	0.825		10.091
1173	0.852	1	0	5.674	0.754	9.925	9.925
		2	0.301	8.468	0.928		9.624
		3	0.477	10.00	1.000		9.448
		4	0.602	10.58	1.025		9.323
		5	0.699	10.858	1.036		9.226
		6	0.778	11.862	1.074		9.147
1273	0.785	1	0	14.887	1.173	9.16	9.160
		2	0.301	15.42	1.188		8.860
		3	0.477	15.84	1.200		8.684
		4	0.602	16.18	1.209		8.560
		5	0.699	19.40	1.288		8.462
		6	0.778	19.63	1.293		8.383

$$n = \lg\frac{t_2}{t_1} \Big/ \lg\frac{q_2}{q_1}, \qquad (1)$$

where t_1, t_2 are the two values of time (h) on the kinetic dependence which are quite far apart; q_1 and q_2 are specific gains (losses) of the coating weight (g/cm^2) during the oxidation time, which correspond to t_1 and t_2 values.

Accuracy of calculation of exponent *n* by formula (1) is the higher, the greater the distance between t_1 and t_2 values.

Activation energy of the oxidation process (*Q*) is determined using temperature dependence $K = K_0 \cdot \exp(-Q/RT)$ through the tangent of φ angle formed by a straight line on lg *q* – 1/*T* graph after taking the logarithm: $\lg K = \lg K\,(-Q/RT)\lg e$.

Activation energy can be calculated also by the following formula:

$$Q = \frac{n \lg q_2/q_1 \cdot R}{\lg e\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}, \qquad (2)$$

where *e* is the base of natural logarithms; *R* is the universal gas constant; T_1 and T_2 are temperature values, *K*, rather far apart in lg *q* – 1/*T* plot; q_1, q_2 are the specific weight gains (losses) which correspond to temperature values T_1 and T_2.

Similar to calculation of *n* value in this case it is recommended to select T_1 and T_2 values that are quite far apart.

Value of heat resistance parameter (*P*) is determined, proceeding from the value of activation energy of the coating oxidation process, calculated by formula (1) and (2), as well as using the results of tests conducted to derive lg*q* – lg*t* and lg*q* – 1/*T* dependencies:

$$P = \frac{Q \lg e}{RT} - \lg t. \qquad (3)$$

Results of calculation of heat resistance parameter based on investigation of kinetic dependencies of plasma coating oxidation process at 700–1000 °C temperatures are shown in Table 1.

Conducted studies allowed assessing the life of protective coatings for any temperatures up to 1000 °C by plotting the parametric heat resistance diagrams (Figure 6).

Parametric method allows calculation of the average rate of metal corrosion (oxidation) [12]. Specific weight loss (gain) and metal corrosion depth (film thickness) at the specified temperature and time of exposure in oxidizing environment can be determined by two methods. One of them is analytical which consists in the following: a parameter is calculated by formula (3), then an ordinate is drawn from the respective point on *P* axis of parametric diagram (Figure 6) up

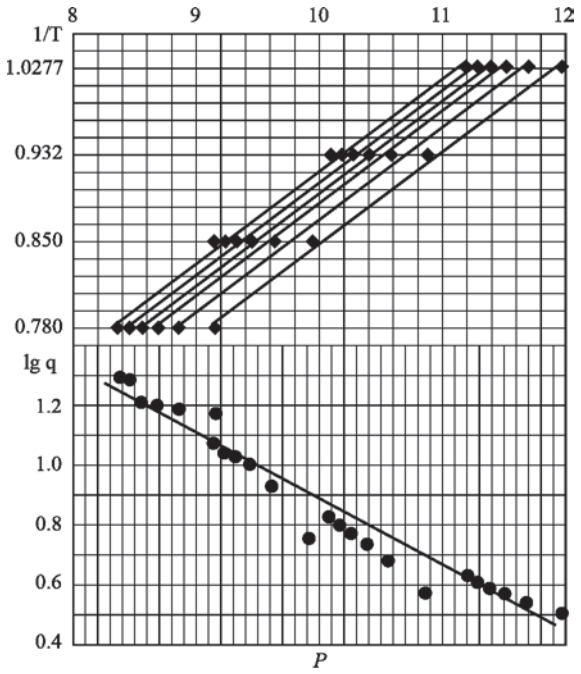

Figure 6. Combined parametric constitutional diagram of the plasma coating with nomogram

to crossing with the parametric line and an abscissa is drawn from their crossing point to lg q axis, where the sought value of weight gain (loss) or metal corrosion depth (film thickness) can be read. The specified values of metal oxidation time and temperature are used to determine by the parameteric diagram the value of weight loss (gain) or corrosion depth (film thickness). Then, $v = q/t$ ratio is used to determine the average rate of metal corrosion during the specified time. Here, it is assumed that oxidation starts when the metal has a clean surface, i.e. the metal does not oxidize up to the moment, when $t = 0$. If it is necessary to determine the average corrosion rate for time period $t_1 - t_2$, then first q_1 and q_2 values, corresponding to the beginning and end of this period, are found from the parametric diagram, and then the average rate is calculated by the following formula:

$$V_q = \frac{q_2 - q_1}{t_2 - t_1}. \quad (4)$$

The second method to determine the heat resistance characteristics is graphic. It is simpler so that it does not require any calculations. In this case, for convenience of using the parametric diagram, so as not to calculate the parameter values, the diagram is combined with $P - 1/T$ nomogram (Figure 6), and axes P of the nomogram and the diagram are parallel, have the same scale and the origins of coordinates on both the axes are located opposite each other. At simultaneous application of the diagram and the nomogram the heat resistance characteristics are determined by the calculated data of heat resistance parameter, finding

Table 2. Calculations of average corrosion (oxidation) rate of TiAl plasma coating using parametric diagram of heat resistance

Temperature, K	q_2	q_1	V_q
1023	5.52	4.52	0.25
1113	6.57	5.58	0.2475

first the specified temperature values on nomogram axis $1/T$, and then the specified time line on the nomogram, and only after them – the parameter (on diagram upper axis) and so on, as in the first case. All these operations are reduced to displacements on the nomogram and the diagram. As an example, Table 2 gives the calculation results for t_1 = 1.5 h, t_2 = 5.5 h.

CONCLUSIONS

1. Heat resistance of TiAl powders from PVT65Yu35 alloy and plasma coatings from it was studied by heating in an air environment up to 700–1000 °C with determination of sample weight change and plotting the parametric diagram of heat resistance.

2. As a result of analysis of kinetic dependencies of TiAl powder oxidation process it was found that the process obeys the parabolic law in the entire temperature range of 700–1000 °C, i.e. the limiting stage is diffusion. The main oxidation product at the temperature of 700 °C is TiO_2 titanium oxide, and at 800 °C and higher temperatures also Al_2O_3 aluminium oxide forms.

3. At coating oxidation in the studied temperature range, TiO_2 and Ti_2O_3 titanium oxides are found as additional phases. Quantity of TiO_2 oxide becomes greater with temperature increase.

4. Oxide film thickness at testing temperature rise is increased, and at 900 °C it has a clear two-layer structure that is indicative of the fact that during the diffusion process the oxide film forms both on metal-oxide and oxide-gas interfaces.

5. It is found that specific weight gain (mg/cm^2·h) was 0.18–0.62 and it increased up to 3.28 at 1000 °C.

6. Use of the plotted parametric diagram allows assessment of the life of TiAl-based coatings for any temperatures up to 1000 °C.

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CONFLICT OF INTEREST
The Authors declare no conflict of interest

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