The study of high-temperature stability of the heat-resisting intermetallide coating

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Abstract The article presents the results of a study of the processes occurring in a heat-resistant intermetallic coating under ultrafast thermal heating by a laser beam. Workers, guide vanes and other parts of the hot tract of gas turbine engines are operated at elevated temperatures, pressures and speeds. Significantly increase the life of such parts by applying heat-resistant coatings that protect the surface from high-temperature oxidation, erosion, and softening of the base material. The plasma coating consists of an intermetallic (β-phase) compound. A pulsed-periodic laser with pulse energy \( E = 5, 10, 15, \) and 30 J was used for thermal heating. Upon heating, surface melting of the fusible phases occurred and the integrity of the surface layer of the coating was violated. By changing the parameters of laser radiation, it is possible to carry out express diagnostics and comparative tests of coatings, as well as to predict their behavior in extreme conditions.

1. Introduction
Reliability service of machines is limited by the operating life of working, stator blades and other parts of the hot path of gas turbine engines operating under extreme conditions (at high temperatures, pressures and speeds). It is possible to increase significantly the operating life of such parts by applying heat-resistant coatings protecting the surface from high-temperature oxidation, erosion, softening of the base material. Heat resistance and thermal stability are important indicators of protective properties of coatings. It is necessary to carry out long-term tests to measure the coating life and to study the mechanism of high-temperature changes in the coating [1]. As an alternative method, it is proposed to use the method of ultrafast thermal heating based on the application of laser irradiation [2].

2. Methods of research
The studies were carried out on model samples of intermetallide coating (200 \( 10^{-6} \) m thick) obtained by the high-energy plasma spraying method at the unit Thermoplasma-50. To form a heat-resistant intermetallide coating, a powder mixture of PIHX20K20IO13 grade with a dispersion of the basic particle fraction of about 80 \( 10^{-6} \)m was selected.

For thermal heating, a repetitively-pulsed laser LRS-150A with laser radiation parameters was used: wavelength \( \lambda = 1.06 \ 10^{-6}\text{m}, \) pulse duration \( \tau = 14 \ 10^{-3}\text{s}, \) pulse energy \( E = 5, 10, 15 \) and 30 J, laser
irradiation spot diameter ~ 4 mm. The phase constitution of the thermal barrier coating was investigated by the method of X-ray diffraction analysis with a diffractometer "Drone-3M" (Cu-Kα radiation). The microstructure of the coating was examined by the TESKAN-VEGA II scanning electron microscope, and the elemental analysis in the scanning line was performed by the INCA Energy-250 energy dispersive spectrometer. A quantitative calculation of porosity was performed on the electronic micrographs of the surface and cross-section micrographs of the coating using the Good-Grains program. The microhardness of the coating material before and after the laser altering was measured on the microhardness tester «IMT-3» at the indenter load of 1 N. The surface roughness of the coating was determined on the tester TR200 by the parameter Rₐ (arithmetic average roughness).

3. Results of the research

The phase composition of the starting powder mixture of ПНХ20П20Ю13 grade is an intermetallide compound (Ni,Me)Al (β-phase). After plasma spraying, the coating contains two intermetallide compounds: (Ni,Me)Al (β-phase) and (Ni₃Me)Al (γ'-phase), wherein the main phase in the coating is β-phase. The formation of γ'-phase in the coating is the result of the phase transformation β→γ' due to the high-temperature effect of the plasma stream.

Studies have shown that there is a layered grain microstructure in the cross-section of the coating (figure 1). Heating of particles in plasma jet during the spraying process causes melting of sprayed material particles and rapid recrystallization (time of indurating of particles 10⁻⁵ – 10⁻⁷ s) promotes fixation of metastable structural conditions [3,4]. Similar dendritic structures are formed by laser treatment of intermetallide powders as a result of ultra-fast crystallization [5]. The grains are elongated because of the plastification of particles of powdered material with high kinetic energy deposited on the supporting plate during high-energy plasma exposure. Between the plasticized particles, mainly elongated micropores are visible. In the cross-section of the coating, there are inclusions of the drop phase of about 2.5 10⁻⁶ m) formed before precipitation on the supporting plate. They have a regular spherical shape due to the complete melt-through of the fine powder particles. The boundaries of the elongated coating grains are bordered by oxide phase inclusions. Analysis of the elemental composition distribution in the area of grain interlayers showed that at the grain boundaries there is a synchronous surge of the intensity of aluminum and oxygen reflections, which indicates the oxidative processes accompanying the intermetallide coating formation with the formation, mainly, of aluminum oxides. Intermetallide grains in addition to the main elements Ni and Al in solid solution contain Co and Cr, and such elements as C and Cr participate in the formation of the carbide phase.

![Figure 1](image_url)

(a), x1000  (b), x4000

**Figure 1.** The microstructure of intermetallide coating obtained by the high-energy plasma spraying

The surface texture has roughness with the parameter Rₐ = 7 mcm. Parameters of physical and mechanical properties of the intermetallide coating are given in Table 1, of compounds NiAl Ni₃Al are given in Table 2.
Table 1. Physical and mechanical properties of the intermetallide coating

| Characteristics        | Values |
|------------------------|--------|
| Total porosity, %      | 5,4    |
| Closed porosity, %     | 4,4    |
| Open porosity, %       | 1,0    |
| Density, g/sm³         | 8,3    |
| Microhardness, GPa     | 4,20   |
| Roughness Ra, 10⁻³ m   | 7,0    |

Table 2. Physical and chemical properties of compoundings NiAl и Ni₃Al [9-14]

| Physical property               | NiAl | Ni₃Al |
|---------------------------------|------|-------|
| Electrical resistance, 10⁻⁸ Ω/m| 8-16 | 37,4  |
| Conductivity for heat, W/mK    | 76   | 28    |
| Linear factor of thermal expansion, 10⁻⁶/K⁻¹ | 14-15 | 8,5; 16 |
| Young’s modulus, GPa           | 190:290 | 173-200 |
| Specific heat capacity, J/g K  | 0,54 | 0,64  |
| Melting point, K(°C)           | 195(1638) | 1668 (1385) |
| Connection type                | metal/ion-covalent | covalent/ metal |

Laser heating causes the following groups of processes on the solid surface: emissive processes (gas desorption; thermoionic emission; thermal electron emission; emission of neutral atoms; heat emission); structural processes (recrystallization; amorphisation of glass-ceramics of thin metal films; Mutual diffusion of heated layers; Surface chemical reactions (local oxidation; restoration); Thermomechanical effects (thermal expansion; an occurrence of thermoelectromotive force; Generation of shock waves in the solid body); physical transitions (melting; evaporation) [6].

The main parameter of the laser altering is the temperature of material surface heating $T_n$. For its evaluation, the formula which links the value $T_n$ with the power of current of heat $P$, which propagates deep into material, and time of laser pulse action $\tau$ [7-9], is used:

$$T_n = \frac{2P\lambda}{(\alpha + \lambda)\nu}$$ (1)

$\lambda$=28 WmK – conductivity for heat; $\alpha$ - thermal diffusivity coefficient, it determines the rate of thermal balance in the coating at instantaneous switching of the thermal source, $\alpha$=5,3 x 10⁶ m²/s, computed using the following formula:

$$\alpha = \frac{\lambda}{\rho C_p}$$ (2)

$\rho$ - density (table 1); $C_p$ - thermal capacity (table 2).

It may be noted that formula (1) is valid also for metals and a rectangular pulse. The laser pulse used in this experiment is trapezoidal. For its approximation, it is necessary to remove with a squared impulse from the general time of influence its edge sites (their total duration $\Delta \tau \sim 2 \times 10^{-3}$). Therefore during the calculations instead of $\tau$ the value $\tau_{eff} = \tau_{o} - \Delta \tau = 12 \times 10^{-3}$s was used in the formula (1).

The distance to be covered by the heatwave in the material over time $\tau$ can be estimated by formula (3). The size of the heated-up area increases due to the thermal conductivity in proportion to this parameter [6].

$$l \sim \sqrt{\alpha \tau}$$ (3)

The formula [7] was used to estimate the thermal stream power of the laser irradiation on the surface of the coating:

$$P = E \frac{2A}{\pi \sigma \tau_{eff}}$$ (4)
E - the energy of laser pulse (5, 10, 15 J), $n = 2.2$ - coefficient of the laser irradiation beam compression by focusing lens, $S_1$ - the area of focused pulse spot on the coating surface ($S = 1.3 \times 10^{-5}$ m$^2$), $A$ - coefficient of laser radiation absorption by coating surface.

It should be noted that reflected and absorbed electromagnetic waves are not formed at the interface but in the substance matter. For non-transparent solids, the proportion of incident monochromatic radiation absorbed by the body is determined by its absorption capacity (in case of normal incidence):

$$A = 1 - R = \frac{4n}{(n+1)^2 + k^2}$$

That is, «A» can also be calculated from measurement data of optical constants or complex index of refraction ($A = 0.383$). Table 3 shows values of $n$, $k$ and $R$ at room temperature for some metals in the visible and infrared regions [16].

Substituting the values of the above parameters in the Eq. (4), the heat current power $P = 31 \times 10^6$ W/m$^2$ ($E = 5$ J), $P = 62 \times 10^6$ W/m$^2$ ($E = 10$ J), $P = 74.5 \times 10^6$ W/m$^2$ ($E = 12$ J), $P = 93 \times 10^6$ W/m$^2$ ($E = 15$ J), $P = 185 \times 10^6$ W/m$^2$ ($E = 30$ J). At these power levels, estimation of the surface temperature of the coating according to formula (1) gives values of 793 K (520 °C), 1313 K (1040 °C), 1518 K (1245 °C), 1823 (1550 °C) and 3358 K (3085 °C), respectively.

Under the laser irradiation, in accordance with the amount of absorbed stream, the material is heated, melted and evaporated, and cooled at the end of the altering. After any of the steps listed above (heating, melting, evaporation), a crystallization process (a structural change) is possible.

Surface oxidation occurred on all coating samples after laser irradiation, regardless of the laser pulse energy. It is indicated by the increased intensity of oxygen apexes. The synchronicity of the aluminium and oxygen apexes indicates the presence of aluminium oxide (figure 2). The oxidation process involves several stages: oxygen adsorption on the surface, free metal electron banding or a growing oxide, diffusion and electromigration of metal and oxygen ions to interfacial boundaries and chemical reaction to form a new oxide layer [15].

No visible changes have been revealed on the surface of the sample during the laser beam exposure with $E = 5$ J, but the analysis of the elemental composition made it possible to determine small areas with a diameter of up to 50 $10^4$ m (dark spots), in which the intensity of Ni, Cr and Co is minimal, and synchronous reflections of Al and O are the highest possible (figure 2b). No large cracks were found in the exposure area. The microhardness of the coating in this zone is 730 GPa.

A dark spot with a diameter of about 3 mm with light inclusions and a blurred outline is visible on the surface of the samples with $E = 10$ J and $E = 12$ J. White irregular-shaped areas are from 0.28 mm x 0.28 mm to 0.85 mm x 0.28 mm. The distribution of the elemental composition showed in these zones an increase of the intensity of Ni, Cr and Co and a decrease of Al and O in comparison with the main dark spot zone, in which the intensities of Ni, Cr and Co are at a minimum level. However, it should be noted that the intensities of Ni, Cr and Co in the light zones correspond to the intensities of these elements in the coating in the initial state. The material in these areas has a dendritic structure. The dark grey area over the entire surface is covered in cracks (figure 2c, d, 3a, d, c). It can be assumed that during the laser beam exposure, melting occurred (melting points are given in Table 3), and therefore, the disintegration of the intermetallic phase into components and the boiling of the least low-melting aluminium. During the superfast cooling, a sinterskin (dark grey zone) that covers the surface of the coating was formed. As the laser energy increases, the temperature on the surface increases too, and therefore, the amount of evaporated low-melting phase becomes larger, so large light zones of the microconstituent are visible on the surface of the samples. The microhardness of the coating in this zone is 735 -935 GPa.
Figure 2. Morphology of the coating surface: a - in initial state, x100; after laser altering with the pulse energy b - 5 J; c - 10 J, d - 12 J, e - 15 J; f - 30 J, x50

(Table 3. Melting temperature)

| Principle (Phase) | Ni  | Co  | Cr   | Al  | Ni$_3$Al | NiAl  | Ni$_2$Al |
|------------------|-----|-----|------|-----|-----------|-------|----------|
| Melting temperature, °C | 1455 | 1495 | 1856 | 660 | 1380      | 1638  | 1132     |
| Boiling temperature, °C | 2900 | 2960 | 2671 | 1450 |           |       |          |

When solid bodies are heated, various changes in structure, the so-called structural-phase transitions, can occur. Since exposure to high-powered light flux is accompanied by the temperature rise of the material, it is obvious that the laser heating of the substance under certain conditions can also lead to the phase changes. With the rapid cooling, which is characteristic of laser altering, the reverse transition, as a rule, does not have time to be completed, so "freezing" of high-temperature states occurs [15]. In addition to the resizing, change of shape and internal structure, the cooling rate has a noticeable effect on the homogeneity of the chemical composition of the crystallizing volume. At first, when the cooling rate is high, the different areas have the same composition corresponding to the initial composition, since the diffusion redistribution of elements manages to occur during the crystallization process both in the liquid and solid phases. With the cooling rate increase, diffusion redistribution of elements in the solid phase does not manage to occur. As a result, areas of grains that were solidified at the beginning of crystallization (central axes of dendrites) are enriched with high-
melting elements, and areas solidified at the end of crystallization are enriched with low-melting elements. Dendritic segregation occurs [16].

When the laser pulse energy increased to 15 J and 30 J, the contour of the exposure zone became clearer, the quantity of light (enriched with Ni, Cr and Co) regions increased. The microhardness of the coating is 555 - 850 GPa.

![Figure 3. Coating surface after laser exposure with the pulse energy: a, b, c - 10 J; d, e, f - 15 J](image)

4. Conclusion
Testing of the laser altering method with different pulse energy showed the possibility of rapid evaluation of high-temperature stability of the intermetallic coatings. Surface melting of low-melting phases and violation of the crippling of the surface layer of heat-resistant coating to the depth of 1-2 intermediate layers occurred during the heating process. The inner layers retained their integrity and phase composition. By changing the parameters of laser irradiation, it is possible to perform rapid diagnostics and comparative tests of coatings, as well as to predict their behavior under extreme conditions.

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