The study of high-temperature stability of the thermoprotective coating made of zirconium dioxide

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Abstract. Laser heating method is proposed for the evaluation of high-temperature stability of thermal protective coatings of zirconium dioxide. Structural-phase state of plasma thermal protective coating of zirconium dioxide has been investigated after laser pulse altering with a different energy. Processes of phase transformation, melting and recrystallization are registered. It has been found that the degradation of the coating affects the surface layers with a thickness of several layers. By changing the parameters of laser radiation it is possible to carry out rapid diagnostics and comparative tests of heat resistance of ceramic protective coatings obtained by different methods from different initial materials.

1. Introduction

Nowadays thermoprotective coatings made of zirconium dioxide are widely used in power engineering to protect parts of the hot section of gas-turbine engines (rotor and guide blades, nozzles, burners, flame tunnels). With the development of high-temperature gas turbines, coatings that are used under extreme conditions (at temperatures above 1000 °C in the environment of burning gases and high temperature gradients at starting loads) have met higher standard requirements. Ceramic coatings are also more often used in the aerospace industry to protect the surface of rocket engine nozzles and aircraft fuselage elements [1, 2].

Heat resistance and thermal stability are important indicators of protective properties of the coatings. Long-term tests with using high-temperature furnaces or test-bench equipment are required to evaluate the durability of the thermal protection coating and to study the mechanism of high-temperature degradation [1]. As an alternative method, it is proposed to use the method of ultrafast thermal heating based on the application of laser irradiation [3]. The ongoing processes in plasma coating made of zirconium dioxide during the ultrafast thermal heating achieved with laser beam have been investigated.

2. Methods of research

The Research has been conducted on model samples made of titanic VT-20 alloy (thickness of 2 mm) with the thermoprotective coating made of zirconium dioxide (~ 1.5 mm thick) applied on an intermetallic underlayer of the «Ni-Co-Cr-Al-Y» system with the method of high-energy plasma spraying using the "Termoplazma-50" unit) (figure 1a). Powder mix (with the following structure: 7 %
Y$_2$O$_3$; 0.05 % SiO$_2$; 0.05 % Al$_2$O$_3$; 0.05 % Fe$_2$O$_3$; 0.02 % TiO; ZrO$_2$ - the rest) with spherical shape of particles and the phase constitution on the basis of tetragonal phase T-ZrO$_2$ was used for the ceramic covering formation.

A repetitively pulsed LRS-150A laser with the following laser emission parameters was used for the heating: wave length $\lambda = 1.06$ мкм, impulse duration $\tau = 14$ мс, pulse energy $E = 5, 10, 15$ joule (J), diameter of laser irradiation spot is 4 mm.

Figure 1. The appearance of samples with the coating made of zirconium dioxide in the original state (a) and after the laser altering with different pulse energy (b).

The phase constitution of the thermoprotective coating was identified by X-ray analysis on (an X-ray diffraction meter "Drone-3M" Cu-K$_{\alpha}$-radiation). The microstructure of the coating was examined by the TESKAN-VEGA II (scanning electron microscope), and the elemental analysis down the scanning line was performed by the INCA Energy-250 (energy dispersive spectrometer) and on Niton XL2 Analyzer. A quantitative calculation of porosity was performed with the electronic microphotographs of the surface and the cross-section area of the coating using the Good-Grains program.

The microhardness of the coating material before and after the laser altering was measured by the microhardness tester PMT-3 at an indenter load of 2 Н. The surface roughness of the coating was identified with the tester TR200 out of the arithmetical mean deviation of the profile.

3. Research results

Structural-phase state of the coating made of zirconium dioxide was analyzed in the original condition. It was found out by the method of X-ray analysis of crystal structure that the main phase of the coating is zirconium oxide with the tetragonal type of the crystal latitude (T-ZrO$_2$). During the process of dusting, high-temperature cubic phase K-ZrO$_2$ (~ 10 %) is formed in the coating under the influence of high-temperature plasma flow, which is higher than 2370 °C [4] (according to the phase diagram "ZrO$_2$-Y$_2$O$_3$")..

The microstructures of the surface and inner layers of the zirconium dioxide coating were examined by the method of optical and electron microscopy. Zirconium dioxide coating is white and has a homogeneous structure of the surface without foreign inclusions and defects (chips and microcracks) (figure 1a). On the coating surface, there are local micropores from 5 to 20 µm in diameter (figure 2a). The apparent porosity is assumed to be approximately 4 %. The microstructure of the coating cross-sectionally consists of layers with thickness of 5 – 10 µm and the columnar structure of ZrO$_2$ grains (figure 2b). The size of the cross-section area of the columns is about 100 - 200 nm (figure 2b). Spherical microinclusions (1 - 2 µm in diameter) that were hardened during the settling-down of fused particles on the substrate, as well as micropores, are visible in the microstructure (figure 2b). The sealed porosity is about 4 %.

Elemental analysis of the coating’s cross-section area showed that the stoichiometric composition of the main component (ZrO$_2$) of the powder mixture is preserved in the coating. This is evident from the synchronous arrangement of zirconium and oxygen lines (figure 3). In the original state, the average value of the hardness of the covering is about $H_{\mu}=12$ GPa, and the average value of the surface roughness parameter $R_a$ is about 2.54 microns (6a class).
Figure 2. Electronic microphotographs of the surface (a) and the cross-section (b) of zirconium dioxide coating in the original state.

Figure 3. Distribution of elements in zirconium dioxide coating in the original state.

The main parameter of the laser altering is the heating temperature of the $T_M$ material surface. For its evaluation, the formula that links the value $T_M$ with the power of the current of heat $P$, which extends deeper into the material, and the time $\tau$ of the laser pulse altering is used [5]:

$$T_M = \left( \frac{2P}{\lambda} \right) \left\{ \left( \frac{a \cdot \tau}{\pi} \right) \right\}^{1/2},$$  \hspace{1cm} (1),

where $\lambda=21.5$ W/mK – conductivity for heat and $a=9.35 \cdot 10^{-6}$ m$^2$/c – temperature conductivity of the coating made of zirconium dioxide [6, 7]. It is worth mentioning that this formula is valid also for metals and rectangular pulse. The laser pulse used in this experiment is trapezium-shaped. For its approximation, it is necessary to remove its border regions from the general time of laser impulse altering with a squared impulse (their total duration $\Delta \tau$ is about $2 \cdot 10^{-3}$ s). Therefore in the formula (1) instead of $\tau$, $\tau_{\text{eff}} - \tau_{\text{off}} - \Delta \tau = 1.2 \cdot 10^{-3}$c was used in making the calculations. To estimate the power of the current of heat of laser radiation on the surface of the coating, the following formula was used [5]:

$$Zr$$

$$O$$
\[ P = E \cdot n \cdot A/ S \cdot \tau_{\text{eff}} \]  \hspace{1cm} (2),

where \( E \) – laser pulse energy (5, 10, 15 J), \( n = 2.2 \) – laser beam compression factor by the focusing lens, \( S_1 \) - area of focused pulse spot on the coating surface (\( S = 1.3 \times 10^{-5} \text{ m}^2 \)), \( A \)– absorption index of laser radiation by the coating surface (\( A = 0.8 \)) [8]. By substituting the values of the indicated parameters in the formula (2), the power of the current of heat is \( P = 5.6 \times 10^7 \text{ W/m}^2 \) at \( E = 5 \text{ J} \), \( P = 11.2 \times 10^7 \text{ W/m}^2 \) at \( E = 10 \text{ J} \), \( P = 16.8 \times 10^7 \text{ W/m}^2 \) at \( E = 15 \text{ J} \). At these power levels, the evaluation of the temperature of the coating's surface according to the formula (1) gives the following values of 984 °C, 1969 °C and 2953 °C, respectively.

The experiment showed that after the unit impulse (with energy \( E = 5 \text{ J} \)) impacts the coating, the appearance of the coating surface hardly changes, but isolated micropores appear (figure 4b). With greater magnification, the affected area does not have a clearly defined boundary (figure 5a), and a melted spot about 100 \( \mu \text{m} \) in diameter (figure 5b) is visible in its center. The X-ray phase analysis showed that laser heating stimulates phase transformation of \( \text{T-ZrO}_2 \rightarrow \text{K-ZrO}_2 \) resulting in the cubic phase \( \text{K-ZrO}_2 \) becoming the main in the affected zone. This transition from a phase to another in the system "\text{ZrO}_2+7 \% \text{ Y}_2\text{O}_3" should take place at a temperature of above 2000 °C [4]. In fact, the temperature on the surface of the coating exceeds the design temperature. On the other hand, exposure to the shock wave accompanying the laser irradiation may shift the phase transformation temperatures towards smaller values. Since the transition is followed by the loss of microscopic volume of the material, it provokes the appearance of micropores (3-6 \( \mu \text{m} \) in size) and a grid of microcracks (figure 5c). Analysis of the elemental composition showed synchronous arrangement of reflexes of metals (zirconium and yttrium) and oxygen, which indicates stoichiometric composition of oxides in this coating zone (figure 7). Microhardness of the coating material in a spot \( H_{\mu} = 12.5 \text{ GPa} \).

![Figure 4](image-url)

**Figure 4.** Optical micrograph of zirconium dioxide coating surface in the original state (a) and after the laser altering with different pulse energy: b - \( E = 5 \text{ J} \), c - \( E = 10 \text{ J} \), d - \( E = 15 \text{ J} \).
Figure 5. Electron microscopic images of the laser altering zone with the pulse energy of $E = 5$ J.

Laser pulse heating with the energy $E = 10$ J is accompanied by coating melting process, which should start at a temperature 2680 °C [4]. A melted, roundish dark gray color spot appears in the zone of laser altering (figure 4c). Electronic microphotographs show a clear boundary with the original material, the spot over the entire area is covered with micropores and a grid of microcracks (figure 7a). The material of fragments located between cracks has a finely crystalline structure (with grain size of 1-3 µm) due to ultrafast recrystallization (figure 7c). There is a similar pattern but even more pronounced with the energy $E = 15$ J (figure 4d and 8). Elemental analysis showed that in the thin surface layer, the main elements of the coating (Zr, Y, O) predominate in different areas of the spot (figure 9, table 1). Hardness of material in a zone of laser influence is $H = 13.5$ GPA (with a depth of indenting of 2.4 microns).

With laser heating with a pulse of 10 and 15 J, surface melting and ultrafast recrystallization occurred, accompanied by cracking of a thin surface layer with a thickness of several interlayers. The inner layers of the heat protective coating retained their integrity and phase composition.
Figure 7. Electron microscopic images of the laser altering zone with the pulse energy of $E = 10$ J.

Figure 8. Electron microscopic images of the laser altering zone with the pulse energy of $E = 15$ J.

Figure 9. Areas of spectra in the zone of laser impact with pulse energy of $E = 15$. 
Table 1. Elemental composition at different sites in the zone of laser impact with pulse energy of $E = 15$ J.

| Range / element | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| O               | 28.86 | 36.91 | 39.58 | 33.22 | 23.42 | 24.44 | 41.84 | 32.25 | 44.40 |
| Al              | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Si              | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Ti              | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| V               | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Fe              | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Y               | 3.24  | 2.72  | 3.46  | 3.88  | 3.99  | 3.29  | 2.52  | 3.11  | 2.90  |
| Zr              | 67.89 | 60.37 | 56.95 | 62.91 | 72.59 | 72.27 | 55.64 | 64.64 | 52.69 |
| Sum             | 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00|

In order to initiate the coating destruction process, the laser pulse energy was increased to $E = 20$ J. In extreme heating conditions, fragments of the upper surface layer were peeled off with thickness in the 2 interlayer (figure 10 a, b). Preserved columnar zirconium dioxide grains are visible in the cross-section of the chips (figure 10 c).

4. Conclusion

Testing of the laser altering method with different pulse energy showed the possibility of rapid evaluation of high-temperature stability of thermal barrier coatings of zirconium dioxide. It is possible to carry out rapid diagnostics and comparative tests of the heat-resisting quality of ceramic protective coatings obtained by different methods from different ingoing materials by changing the parameters of laser radiation.

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