Investigation of structure formation in thin films by means of optical pyrometry

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Abstract. The paper presents an approach to the identification of structural and phase changes in high-speed processes of spraying coatings and high-temperature synthesis of three-dimensional products from metal and ceramics. A method for evaluating the spectral degree of blackness of materials by means of optical pyrometry is described. An experimental complex was developed to study the degree of blackness of the surface of molybdenum, tantalum and tungsten foils in the process of stationary heating by electric current. The results of complex experimental studies are presented, showing that a jump in emissivity makes it possible to detect a change in the aggregate state of matter (liquid - solid), phase transitions, exo- and endothermic reactions in thin films, and also to determine characteristic temperatures with an error of 0.1–1.5%.

1. Introduction

Thermal spraying of coatings, direct laser construction of three-dimensional parts and surfacing use high temperatures to activate various mechanisms for the transformation of dispersed substances into a new material with unique characteristics. Localization of structure formation processes in thin films on the product surface allows the coating to give functional-gradient properties, and the study of temperature and phase dynamics directly during coating synthesis makes it possible to effectively improve such sputtering technologies.

Dynamic electron microscopy and dynamic diffractography of X-ray diffraction and synchrotron radiation are recognized methods for studying structural and phase changes in a substance [1, 2]. However, the practical application of appropriate equipment for the observation of structure formation in "in situ" mode is hampered by the specifics of the deposition. The present work, the authors sought to show that the spectral degree of blackness of a material can act as an intermediary in studying the dynamics of phase states in thin films, and the proposed method of measuring this property by means of optical pyrometry is sufficiently sensitive to identify phase transformations and determine their characteristic temperatures.

2. Principles of measurement and experimental equipment

The approach is based on the fundamental dependence of the optical properties of materials on the micro- and macrostructures of the surface of a solid or the interaction of molecules and atoms in melts. The combination of methods of luminance and spectral pyrometry allowed the authors to estimate the monochrome emissivity of the material by its thermal radiation [3, 4]:

\[
\varepsilon_s = \exp \left( \frac{C}{\lambda_b} \left( \frac{1}{T_s} - \frac{1}{T_b} \right) \right),
\]

(1)
where $\varepsilon_s$ is the estimate of the spectral degree of blackness of the material at the wavelength $\lambda_b$; 
$C = 14388 \ mkm \cdot K$; $T_s$ and $T_b$ – spectral and brightness temperature at the wavelength $\lambda_b$.

It is theoretically shown that in the part of the spectrum where the emissivity does not change with the wavelength, the estimate value coincides with the real value [5]:

$$\frac{\varepsilon_s}{\varepsilon} = \exp \left[ \frac{\lambda_b}{C} \frac{d(\ln \varepsilon)}{d\lambda} \right], \quad (2)$$

where $\varepsilon$ is the actual value of the spectral degree of blackness at the wavelength $\lambda_b$. In addition, to identify the phase transition in the process of heating or cooling the material, it is important to control the jump or a sharp change in the absolute value of the function of the spectral degree of blackness.

In the course of the research, stationary heating of film metallic materials with a constant electric current was used. Samples were placed on argon at a constant pressure. The reactor had a cylindrical wall of optical quartz to control the thermal radiation of the sample. In addition to the reactor, the experimental complex included four automated systems: a system for measuring the brightness temperature field, a spectral pyrometer, a programmable current source, and a sample positioning system (figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Experimental complex (1 – optical system of the spectral channel of the complex (Computar MLH-10x); 2 – bandpass filters in thermal imaging channels (SL-525-40, SL-725-40); 3 – PhotonFocus digital camera (MV1-D1024E-CL); 4 – stereo microscope Altami CM0655; 5 – spectrometer Aseq LR1-T; 6 – metal foil sample; 7 – reactor for high-temperature heating of samples (RTH) with electric current; 8 – programmable current source PSH-2035; 9 – vacuum pump; 10 – 3D sample positioning system).}
\end{figure}

The thermal imaging and spectral channels of the complex had a common sight area in the form of a circle with a diameter of 200 μm, where the measurements of thermal radiation were performed at a wavelength of 525 and 725 nm [6].

3. Experimental results and discussion

The object of study was a foil of tungsten, tantalum and molybdenum with a thickness of 50 and 100 microns. The main idea of the experiment was to make impurity O, C, N atoms diffuse onto the sample surface to form solid solutions and chemical compounds, heat the resulting compounds to phase transformation temperatures and investigate the behavior of the spectral degree of blackness on the surface. During the experiment, a stationary temperature field was formed on the sample surface. The temperature of the cooled electrodes did not exceed 300-400 degrees, and its maximum was in the middle part of the sample. The end of the transients in the sample was controlled by the established value of current and voltage. The pyrometry of the sample was carried out at several points on the
An increase in the electric current in the sample caused a change in the temperature field and a redistribution of the phase composition on the sample surface. The experiment was completed by interrupting the electric current, which attracted the freezing of the last phase distribution (figure 2).

Figure 2. Tungsten sample, hardened at the time of the destruction of the whiskers (1 – pure tungsten; 2 – whiskers; 3 – tungsten oxides; 4 – tungsten and tungsten oxides; 5 – tungsten at the point of attachment to cooled electrodes).

The stationarity of the temperature field in the experiment allowed us to compare the data of local pyrometric studies at different power of heat release with the structure and microelement composition of the phases of frozen samples (figure 3).

Figure 3. The results of comprehensive studies of tantalum samples.

By abrupt changes in the function of the spectral degree of blackness, phase transformation points were identified, and the corresponding temperatures were determined according to the graph of the spectral temperature (figure 4). In the experiment with tantalum samples, 5 characteristic temperatures were found. $T_0$ is the saturation temperature of the surface layer of the sample with O and C impurity atoms. Based on the analysis of the Ta-O phase diagram, it was concluded that $T_1$ – corresponds to the melting temperature of the $\alpha$-Ta (O) + $\alpha$-Ta$_2$O$_5$ eutectic. This makes possible the dissolution of impurity atoms in it and the occurrence of isothermal combustion with the formation of gaseous carbon oxides, which leave the sample. Reducing the concentration of O and C leads to the formation of a solid solution $\alpha$-Ta (O) and again starts the process of accumulation of impurity atoms on the surface of the sample. A sharp decrease in the spectral emissivity of a tantalum sample at temperature
T_2 corresponds to the non-equilibrium transition $\alpha$-Ta (O) $\rightarrow$ $\alpha$-Ta (O) + L_2. T_3 corresponds to the phase transition $\alpha$-Ta (O) + L_2 (65 at.%) $\rightarrow$ $\alpha$-Ta (O) + L_1 (43 at.%). When heated to T_4, phase oscillations were initiated on the sample. A further increase in the power of heat release in the sample led to an increase in the oscillation frequency “liquid-solid”, but did not contribute to the excess of the temperature threshold T_4. The cause of the destruction of the sample, according to the authors, was its strong erosion and embrittlement.

**Figure 4.** Determination of characteristic temperatures of structural-phase changes and construction of probable concentration curves of impurity atoms on the surface of tantalum samples.

The experiment revealed that a jump in the radiation coefficient in remote regions of the sample occurs at different source powers, but at the same spectral temperature (figure 5).

**Figure 5.** Dependence of the spectral emissivity of molybdenum on the temperature near the phase transition point.
Micro thermal imaging survey allowed to register the process of crystal formation on the surface of tungsten and molybdenum samples (figure 6), as well as to investigate the dynamics of oscillations of the aggregate state (solid-liquid) in tantalum samples at a constant source power with a spatial and temporal resolution of 2.9 μm and 500 μs, respectively.

![Micro thermal imaging survey](image)

**Figure 6.** Interrelation of thermal images of a tungsten sample with spectral emissivity and temperature in the general field of view of a thermal imager and spectrometer (image size 2x2.9 mm).

### 4. Conclusion

Experimental studies have shown that the evaluation of the spectral degree of blackness by means of optical pyrometry makes it possible to identify structural changes in the surface layer of materials and to determine characteristic temperatures with an error of 0.1–1.5%. The proposed approach is complementary to the methods of electron microscopy and X-ray and synchrotron diffractography. The latter contribute to the establishment of the interrelation of the type "spectral emission coefficient – the structural-phase state of a substance", and the means of optical pyrometry guarantee a high spatial and temporal resolution in the study of fast processes of structure formation.

### Acknowledgments

The work was carried out within the framework of the RFBR projects No. 18-08-01475 and 18-08-01152, and also supported by grant No. 13-01-20 / 28 "Leading Scientific School of the Ugra State University".

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