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NITRIDE AND CARBIDE COATINGS SYNTHESIS ON THE SURFACE OF REFRACTORY METALS BY LASER ACTION

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Abstract - Experimental results on the laser-plasma synthesis of compounds of refractory metals on the surface of solids (nitrides, carbides, oxy carbides, etc.) are presented. Physico-chemical processes taking place during the effect of laser radiation on the materials in the gas atmosphere in a wide range of pressures are discussed.

1 - INTRODUCTION

The use of highly concentrated energy fluxes (HCEF) for the production of coatings with special properties (high microhardness, corrosion resistance, etc.) on components is a highly promising method. The HCEF usually include the fluxes in which the density of the energy flux \( q \) exceeds \( 10^4 \) W/cm\(^2\) (electron and ion beams, laser radiation focused on the small-diameter area, fluxes and bunches of low-temperature plasma, etc.).

The high density of the flux makes it possible to obtain within a short period of time (several ms) high temperatures on the surface of solids; these temperatures are higher than the melting point and cannot be produced by less concentrated energy fluxes. A plasma cloud starts to form in the vicinity of the solid with increasing flux density. As a result of recent extensive research into the plasma and laser-plasma processes, the HCEF, especially laser radiation (LR), can now be used to produce areas on the surface of solids and, in many cases, coatings with special physico-chemical properties /1,2/.

The physico-chemical processes taking place during the effect of LR on the materials in the gas atmosphere in a wide range of pressures are usually associated with the development, in the vicinity of the surface of the solid, of a low-threshold optical breakdown leading to the formation of a plasma bunch whose evolution determines the development of phenomena on the surface of solids.

The A.A. Baikov Institute of Metallurgy of the USSR Academy of Sciences is carrying out intensive research into the physical and physico-chemical processes taking place during the combined effect of plasma generated by the effect of LR which has passed through the plasma bunch. The combination of
the processes occurring in the conditions of LR is referred to as laser-plasma treatment /2/.

2 - MAIN RESEARCH DIRECTIONS AND EXPERIMENTAL CONDITIONS

The investigations into the physical and physico-chemical processes taking place in the course of the laser-plasma effect on metals may be divided into three main directions.

1. Experimental and theoretical examination of the optical breakdown in dense gases under the effect of LR in the vicinity of materials with various properties; examination of the evolution and physical properties of the plasma cloud.

2. Examination of the changes in the physico-chemical properties of the surface layers of materials after the laser-plasma effect, including the main geometrical, phase, and structural characteristics of the zones formed after the effect of LR and plasma.

3. Formulation of theoretical considerations on the mechanism of surface synthesis of various inorganic compounds and the processes of oxidation and reduction of metals.

The first direction associated with the examination of the optical breakdown of dense gases in LR has been actively followed in our research. An important role in these investigations is played both by experimental investigations and mathematical modelling (simulation) of the process /3/.

In recent years, the second and third directions have been followed in the A.A. Balkov Institute of Metallurgy /4,5/ and a number of other organisations /6-8/. The interest expressed in these investigations is associated with the fact that the detected phenomena can be utilised in the development of metallurgical and processing processes. A number of processes may be used for hardening the surface layers of materials and several other processes appear suitable for the formation of surface layers and coatings with new properties.

The experiments described in this article were carried out in a number of laser systems with various energy and space-time characteristics of radiation (GOS-30M, GOS-300, GOS-1001, Kvant-16, KTN-102, etc.). The experimental setups were similar and differed only in small details. Metallic specimens were placed in a high-pressure chamber which was filled with a gas with controlled composition and pressure; LR was introduced into the chamber through a special window. The LR parameters (pulse time, energy flux density, etc.) were inspected during the experiments, and the development of the processes in the zone of interaction of LR with metals was recorded by high-speed filming. The duration of the radiation pulses equaled units of ms, and continuous LR was used in a number of experiments. The plasma-forming gases were CO₂ (pressure 1-55 atm), H₂, Ar, He, N₂, CH₄ (pressure 1-140 atm) and, in some cases, mixtures of these gases. In addition to the effect of LR on materials in a dense gas atmosphere, attention was also given to the effect of pulsed and continuous LR on the materials immersed in transparent carbon-bearing liquids.

3 - LASER-PLASMA SYNTHESIS OF NITRIDES OF REFRACTORY METALS

The formation of nitride zones and coatings on the surface of metals is of great importance for a number of components since the nitrides are characterized by high wear resistance, high chemical stability in various corrosive media, high resistance to fire, and number of other properties which are important for application in practice.

The promising nature of laser-plasma production of nitrides is determined by the following advantages in comparison with the traditional methods:
the possibility of strict localization of nitrided zones (this is great importance for a number of applications);
- high rates of synthesis of the nitride zones;
- the possibility of producing nitride coatings with the properties differing from those of the identical coatings produced by other methods.

We shall examine the special features of the synthesis of surface layers of the nitrides of refractory metals using a Nd laser with pulse time 1 ms. The laser-plasma synthesis of titanium nitride at high nitrogen pressures was described for the first time in /9/ where the important role played by the surface laser plasma in the formation of the nitride layer was reported.

Subsequent investigations were carried out to determine the relationship between the dynamics of laser plasma, the conditions of action of LR and the formation of a specific structure of nitride layers for a wide range of refractory metals, such as Ti, Zr, Hf, Ta, Nb, Mo, etc. X-ray diffraction analysis showed that in irradiation of the metallic sheets in nitrogen at a pressure of $p = 40$ atm and higher, nitrides whose composition is similar to stoichiometric form on the surface in the case of Ti, Zr, Hf, whereas in the case of Nb, Ta, Mo these nitrides are similar to lower nitrides of the Me$_x$N type. Metallographic examination revealed differences in the structures of the zones of action caused by the parameters of the process.

We shall examine these differences using Ti as an example /10/. At nitrogen pressures near the atmospheric pressure, the nitrided zone consists of a thin layer of titanium nitride ('monolayer') with a columnar-dendritic structure and of a narrow band of the $\varepsilon$-phase or a mixture of the $\alpha + \varepsilon$ and $\varepsilon + \text{TiN}$ phases whose total thickness varies in the range 1-5 mcm. These layers are followed by a softer layer of the solid solution of nitrogen in alpha metal and by transition layer whose microhardness is lower than that of the parent metal.

The increase of nitrogen pressure causes changes in the structure of the zone of synthesized nitride. The thickness of the nitrided layer and of the layer of the $\varepsilon$-phase increases to 150-200 mcm, whereas the thickness of the layer of the solid solution in alpha titanium decreases until this layer completely disappears at a nitrogen pressure of around 40-60 atm (Fig. 1).

![Graph](image_url)

**Fig. 1** - Dependence of the thickness of titanium nitride layer on nitrogen pressure. 1 - $q = 6.5 \cdot 10^6$ W/cm$^2$, 2 - $4 \cdot 10^6$, 3 - $1.5 \cdot 10^6$. 
Fig. 2 - Dependence of the optical density of nitrogen plasma on time. 
\[ \tau = 1 \text{ ms}, \ q = 3 \times 10^6 \ W/cm^2, \ p = 74 \text{ atm}. \]

At nitrogen pressures of \( p > 40 \text{ atm} \), the microstructure of the zone of action contains several 'monolayers' of nitride which are placed on top of each other and separated by bands of the \( \varepsilon \)-phase. It is evident that these changes in the structure of the synthesized layers of the nitride should be associated with the self-oscillatory processes taking place in the 'laser beam-plasma-target surface' system at pressures exceeding approximately 10 atm /\text{11/}. These changes may be explained as follows. The variations of the optical density of plasma \( \rho \) with time are shown in Fig. 2 which gives the time dependence of the coefficient of relative transmittance of \( \text{IR} \) from the target in the experiments with the nitrogen plasma at various densities of the \( \text{IR} /\text{12/}. \)

The effect of HCEF on metals is accompanied by the formation of micro- and macroscale structures in the melt and gas phase. The beam radius of HCEF \( r_0 \) is the natural scale for this division. The inequality \( 1 \ll r_0 \) applies to the characteristic dimension of the microstructure 1, whereas for the large-scale structure it is its characteristic dimension \( h \) of the order of beam radius \( h \sim r_0 \). The dimension of the structure reflects the scale of the most effective interaction of the specific structure of the melt and the gas medium with HCEF. The large-scale structures are determined by the pulsations of the temperature of the melt and the density of the gas medium formed as a result of excessive self-oscillations or owing to the use of HCEF periodic in respect of time, or due to the combined effect of both factors.

In certain conditions typical of the given specimen and process parameters, there are disruptions in the distribution of nitride layers caused by the development of turbulence and movement of the melt in the pool (Fig. 3). The appearance of turbulence may be caused by the build-up of the self-oscillations in the system.

The microhardness of the layers also changes in accordance with the variation of the structure of the zone of action of \( \text{IR} \) in the depth; the most
marked changes are detected in the transition from the nitride layer to the layer of the of the solid solution and from the latter to the parent metal. The typical values of microhardness are equal to, kgf/mm²: for the nitride layer 4000 - 2000, for the solid solution layer 300 - 900, for the transition to the parent metal 200. The microhardness within the limits of each layer depends on the process parameters.

4 - EFFECT OF CONTINUOUS LASER RADIATION ON METALS IN NITROGEN ATMOSPHERE

We shall discuss briefly the processes of synthesis of nitride compounds during the effect of continuous laser radiation with the wavelength of \( \lambda = 1.06 \) mcm in the nitrogen atmosphere on metals in the pressure range 1 - 80 atm. In laser-plasma treatment of Ti and Zr sheets, the thickness of the nitride layer was equal to 150 mcm at the atmospheric pressure and dropped to 20 mcm with the pressure increasing to 80 atm. The cross sections of titanium nitride for the pressures 1, 30 and 80 atm are shown in Fig. 4.
5 - LASER-PLASMA SYNTHESIS OF SURFACE LAYERS OF CARBIDES OF REFRACTORY METALS

The experimental set-up used in synthesis of carbides on the surface of components of refractory metals is identical with that used also in the synthesis of nitrides, only carbon-bearing gases CO$_2$ and CH$_4$ are used as the plasma-forming gases.

We shall discuss the main special features of laser-plasma synthesis of the carbides /13/. The thermochemical effect of the plasma cloud formed in the vicinity of the surface of metals in the atmosphere of chemically active carbon-bearing gases makes it possible to synthesize on their surface the carbide, oxycarbide or carbohydride coatings, depending on the process parameters and the gas used.

In CO$_2$, the carbide synthesis processes were examined at the pressure varying from 5 to 60 atm. The density of the radiation flux of a pulsed Nd laser ($\tau \sim 1$ ms) was $10^6 - 10^7$ W/cm$^2$. The initial materials were the metals of the groups IV-VI with an impurity content not higher than 0.2%.

The dependence of the thickness of synthesized compound on the gas pressure contains an extremum and at a pressure of $p = 30$ atm reaches its maximum value of approximately 90-100 mcm. With a further increase of the CO$_2$ pressure the thickness of the carbide layer decreases. For CO$_2$ pressure of $p = 58$ atm, the thickness of the carbide layer in the centre of the zone of action of LR does not exceed 5 mcm, whereas at the edges its thickness increases to tens of micrometers. At a gas pressure of 25-35 atm the examined zone has a complicated structure consisting of alternating usually three light and three dark layers. The microhardness in the transition from the layer to layer smoothly varies from 1600-1600 to 1100-1200 kgf/mm$^2$. The formation of a multilayer structure of the carbides is evidently linked with fluctuations of the optical density of the plasma and, consequently, with the oscillations of the surface temperature; this was also detected in carbide synthesis, i.e., in the development of self-oscillatory processes in the LR-body surface system.

X-ray phase analysis of the zones shows that oxycarbides of the metal form on the surface of the metal in the CO$_2$ atmosphere. For example, at a flux density of $q = 5 \cdot 10^6$ W/cm$^2$ (the target was made of Ti) and a CO$_2$ pressure of $p = 30$ atm the titanium oxycarbide Ti$_{0.4}$O$_{0.52}$, and oxycarbide ZrO$_{0.8}$O$_{0.17}$ forms on Zr in the same conditions. With an increase of the gas pressure, the composition of the oxycarbides is displaced to higher carbon content and lower oxygen content. Specifically, at a CO$_2$ pressure of $p = 50$ atm a pure carbide without oxygen forms.

Fig. 5 - Diameter (a) and depth (b) of the zone of carbidizing in the effect of LR on Zr in relation to methane pressure.
In the methane atmosphere, the synthesis of metal carbides under the effect of LR is characterized by the following. The diameter of the zone in which zirconium carbohydride is synthesized assumes the minimum value at a methane pressure of \( p = 50 \) atm (Fig. 5), and the thickness of the carbide layer rapidly drops. This is caused by the effect of competing processes affecting the formation of the plasma bunch, ion composition, and its interaction with the metal surface.

We shall discuss briefly the laser-plasma synthesis of carbides in liquids. The investigations carried out in the accordance with the above experimental set-up were conducted in various carbon-bearing liquids, such as pentane, hexane, heptane, toluol. As in methane, carbohydrides of the group IV metals form on the surface of these metals, whereas carbohydrides or carbides can form on the surfaces of the metals of the groups V and VI, depending on the treatment conditions. For example, in laser treatment of metallic targets in toluol, the tungsten carbide forms on the surface of tungsten (the composition is similar to stoichiometric), whereas a carbide with composition Mo\( _2 \)C forms on the surface of a Mo sheet. Diffraction patterns of the zones of synthesis on the surface of Ta sheet show simultaneously lines of the tantalum carbohydride and Ta\( _2 \)C carbide. The relative hydrogen content of the carbohydride in the resultant coatings depends on several factors, such as the density of the LR flux, the chemical composition of carbon-bearing liquid, the thickness of the layer of this liquid on the surface of the metal sheet, etc.

6 - CONCLUSIONS

The experimental data described in this article represent part of the investigations embracing a wide range of gas pressures and compositions, parameters of the specimens, and also the space-time and energy parameters of LR. The results illustrate certain possibilities of laser-plasma treatment.

REFERENCES