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MASS TRANSFER IN THE PROCESS OF PULSED LASER ALLOYING OF TITANIUM IN NITROGEN VAPORS

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UDC 536.25:535.21

Thermocapillary mass transfer accompanying pulsed laser alloying of titanium in vapors of liquid nitrogen is studied. The impurity concentration fields are determined by the methods of numerical modeling. The numerical and experimental results are compared.

Mass transfer accompanying laser alloying of materials is the subject of intense scientific studies [1]. It has been shown in a number of experiments, for example, in [2-4], that the redistribution of impurities occurs practically over the entire depth of the melt pool. This in its turn results in the formation of different structures of the zones of alloying. Since in technological applications the characteristic pulsed laser exposure times do not exceed $\tau = 1-6$ msec the impurity can spread by the diffusion mechanism to a characteristic depth of several microns, while the melt pool is several hundreds of microns deep. Then forced convection in the melt pool is one of the main physical mechanisms for mass transfer over the entire depth of the pool and its determines the concentration field of the alloying component in the zone of laser action. In many cases, for relatively low energy flux densities, when evaporation is insignificant, thermocapillary convection is the dominant hydrodynamic process occurring in the melt. It is determined by the significant nonuniformity of the density of the incident energy flux over the radius of the heating spot and by the temperature dependence of the surface tension of the liquid metal. As a rule, the thermocapillary force is directed toward decreasing temperature, which gives rise to motion of the melt at the free surface from the center of the heating spot to the edges of the pool formed. In this paper we present the results of modeling of nonstationary thermocapillary mass transfer in a melt pool under pulsed action of laser radiation on titanium in a gaseous medium and we present experimental data on the alloying of titanium iodide in an atmosphere formed by the vapors of liquid nitrogen.

Model of Thermocapillary Mass Transfer. We shall study the nonstationary melting of a bulk sample of titanium by laser radiation. We assumed that the free surface of the melt pool is flat; the thermal conductivity and the thermal diffusivity of the liquid and solid phases as well as the density and dynamic viscosity of the melt are constant; the energy

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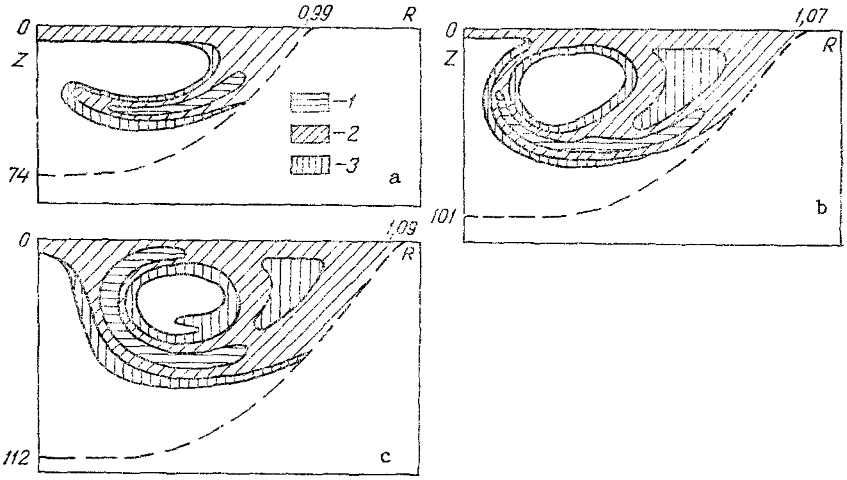

Fig. 1. Impurity concentration field for the times τ = 2.4 msec (a), 3.3 msec (b), and 3.7 msec (c); $q = 5 \cdot 10^4$ W/cm^2, $k = 100$ cm^{-2} (alloying in nitrogen vapors). R, mm; z, μm.

flux density q(r) absorbed by the surface of the melt pool is given by Gauss's law $q(r) = q_0 \exp(-kr^2)$; the parameters of the interaction — the power density and the interaction time — are such that the boiling point is not reached on the surface of the liquid phase; $\mathrm{Re}^* \ll 1$, $\mathrm{PrRe}^* \ll 1$ ($\mathrm{Re}^* = (uR/\nu)(S/R)^2$ is the reduced Reynolds number and Pr is the Prandtl number, for liquid metals $\mathrm{Pr} \ll 1$), which is achieved when the flow velocities of the melt are low and the pool is shallow, i.e., its diameter is much greater than its depth. This problem was studied on the basis of the indicated assumptions in [5-8], where the two-dimensional nonstationary velocity field of the melt in the pool with a moving phase interface was determined in a cylindrical coordinate system. The motion of the liquid phase has a vortex structure, and in the region near the center of the heating spot the melt moves toward the surface of the pool while on the surface it moves from the center to the edges of the pool. The vortex is strongly flattened in the axial direction: with the exception of narrow regions near the center of the heating spot and the turning points of the flow the liquid moves practically parallel to the free surface.

Convective mass transfer of impurity in the melt pool was modeled numerically by the method of particles [9, 10]. At each moment in time the alloying elements were redistributed in two stages. At the first stage the flow of impurities from the gas phase to the free surface of the melt was given in the form of a constant flux of particles. The radial coordinates of these particles were played out by the method of inverse functions [11]. At the second stage (convective mass transfer) the coordinates of the moving particles were calculated using predictor-corrector schemes [9] and the velocity field from [5]. It was assumed that the particles do not interact with the melt or with each other.

Experiment. Bulk samples of titanium iodide were exposed to pulsed laser radiation with $\lambda = 1.06$ μm and pulse width τ = 1-6 msec on LTU-2M and GOS-301 setups with the beam incident vertically. The samples were placed in a chamber filled with liquid nitrogen so that their irradiated surface was not wetted, i.e., the samples were in a semisubmerged state, which made possible laser treatment of titanium in the atmosphere formed by nitrogen vapors with the temperature of the sample equal to 77 K [12, 13]. Under such experimental conditions the processes occurring as the melt solidifies are more rapid and do not affect as strongly the change in the concentration field owing to thermocapillary mass transfer only. The energy flux density of the incident radiation was varied in the range $q = 10^4$-$6 \cdot 10^7$ W/cm^2; the concentration factors were equal to k = 50-200 cm^{-2}.

X-ray structural analysis was performed on a DRON-2.0 x-ray diffractometer in CoK_α radiation. Metallographic analysis of the zones of laser action was performed with the help of a NEOPHOT-21 microscope.

Discussion. We shall study the computed (Fig. 1) and real (Fig. 2) structures of the concentration fields of the impurity (nitrogen) in the zone of interaction of the laser radiation and titanium in an atmosphere of liquid-nitrogen vapors. The different energy flux densities in Fig. 2 correspond to the different times in Fig. 1. Increasing the energy flux density results in an increase of the temperature gradient on the surface of the melt and therefore in intensification of the thermocapillary convection; on the other hand, the melt velocities are a rapidly increasing function of time [5]. Thus both factors - the increase in the flux density of the laser radiation and the increase in the interaction time — intensify the mixing of the melt, which is manifested in analogous laws of mass transfer of the alloying element. In a real experiment it is simpler to vary the energy per pulse while in the calculations it is easier to vary the interaction time.

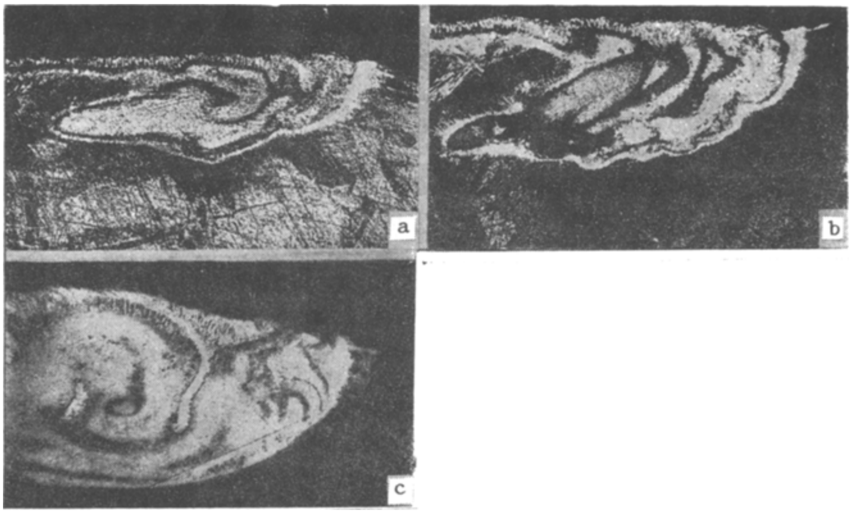

Fig. 2. Structure of the transverse cross section of the zone of laser interaction with titanium iodide alloyed in nitrogen vapors: a) $q = 5 \cdot 10^4$ W/cm^2; b) $9 \cdot 10^4$ W/cm^2; c) $3 \cdot 10^5$ W/cm^2; $\tau = 4.5$ msec; $k = 100$ cm^{-2}. × 200.

To make it more convenient to display the computed behavior of the mass transfer, in Fig. 1 the region of alloying is divided into three subregions (denoted in the figure by the cross hatchings 1-3). The first subregion corresponds to concentration of the alloying element from 0.5 to 1 (maximum concentration). The second subregion corresponds to the range of concentrations 0.1-0.5 and the third subregion corresponds to concentrations up to 0.1. The maximum concentration at a given moment in time is taken to be 1, while the true value of the impurity concentration (in atomic percent or percent by weight) changes with time and is determined by the parameters of the alloying process. The dashed line is the interface between the phases.

At the initial stages of mass transfer the impurity is concentrated on the surface of the melt, and the region of the local maximum of the concentrations of the order of 10 μm in depth and of the order of 0.1 of the diameter of the heating spot is located in the peripheral region at the edge of the pool. At this stage the impurity hardly penetrates into the pool. This structure of the impurity concentration field is characterized by a distribution of the alloying component practically in the plane of the free surface with a ring-shaped region of maximum concentration at the edge of the melt zone.

With time and as the increase of the radius of the pools slows down (the melting now proceeds primarily into the volume of the material) the impurity moves along the front of melting, which results in a transfer of the region of maximum concentrations of the alloying element from the surface zone into the volume of the material and stretching of this region along the interface of the phases (Figs. 1a and 2a). Since at the starting stages of mass transfer the velocity of the front of melting is higher than the velocity of axial motion of the melt the region of propagation of the impurity detaches from the surface of the interface, thereby falling into the zone with lower axial velocities, which results in separation of the alloyed region from the melting front. This results in the formation of a zone of alloying in the form of a strip, which extends into the volume and toward the center of the melt pool, which results in deep penetration of the impurity.

Because of the vortex structure of the melt flow the impurity then moves toward the free surface of the melt. By this time the maximum depth of penetration of the alloying component is equal to about 2/3 of the instantaneous depth of the pool. The formation of a ring-shaped structure of the alloying zone with weak penetration of the impurity into the central region is a direct consequence of the vortex motion of the melt. For the laser radiation parameters studied in the calculations in the range of absorbed energy flux densities $q = 10^4$-$5 \cdot 10^4$ W/cm^2 and concentration factor $k = 50$-200 cm^{-2} the formation times of the ring-shaped alloyed structures range from 3 to 5 msec.

The ring-shaped form of the region of alloying could become the reason for the appearance of layered structures, previously observed in the experiments of [2, 3, 12], in the zone of remelting. Figure 1 shows the zone of remelting in which the alloying component formed a layered system after mixing. Thus in Fig. 1b as the depth of the pool increases the following appear in sequence: a subregion enriched with impurity flowing from the gas phase; a subregion with low impurity content near the moving center of the vortex; a subregion enriched with the alloying component owing to convective mass transfer from the surface; and, finally, a subregion depleted of impurity owing to separation of the alloyed zone from the front of melting. Figure 2b shows an analogous structure. Here the impurity is

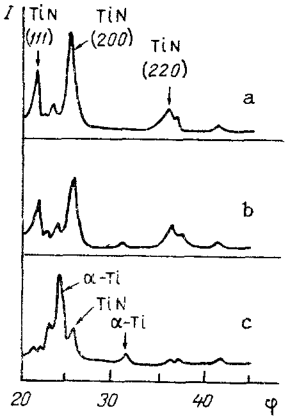

Fig. 3

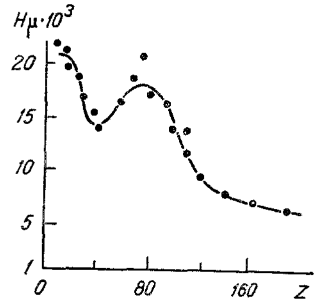

Fig. 4

Fig. 3. Change in the intensity of x-ray lines I over the depth of the zone of the titanium iodide melt after laser action in nitrogen vapors: a) Z = 0 (surface); b) Z = 10 μm; c) Z = 150 μm. I, pulses/sec; φ, deg.

Fig. 4. Distribution of the microhardness H_μ over the depth of the zone of laser action Z; $q = 3 \cdot 10^5$ W/cm^{-2}, τ = 4.5 msec, k = 100 cm^{-2}. H_μ, MPa.

redistributed over the melt pool as follows: the dark regions consist of nitrogen-hardened titanium and the light-colored sections represent dendrites of titanium nitride, oriented in the direction of heat outflow. Traces of the vortex motion which the impurity undergoes can be seen along the boundary of the melt pool. Figure 3 shows the change in the intensity of the diffraction of Ti and TiN, obtained by layerwise analysis, over the depth of the sample. Diffraction lines were recorded from the (111), (200), (311), and (222) planes, belonging to TiN with an fcc lattice. One can see from the figure that as the depth increases the intensity of the α-titanium line at first decreases (the depth Z = 10 μm) and then increases (the depth Z = 150 μm). The intensity of the TiN line is maximum at Z = 0 and Z = 10 μm. Figure 4 shows the distribution of microhardness over the depth of the zone of laser action. The maximum values (10,000-20,000 MPa) correspond to surface layers of the zone of remelting with a high content of titanium nitride. As the depth increases the microhardness decreases to 3500-8000 MPa. Because of the layered nature of the zone of remelting the change in the microhardness is nonmonotonic. With the transition to the starting structure of titanium a jump to minimum values of the microhardness occurs.

Increasing the laser action time, the temperature gradient on the surface, as well as other factors that intensify the mixing result in a more uniform redistribution of the impurity in the melt pool with a noticeable minimum of the concentration in the region near the center of the vortex. The number of revolutions completed by the impurity in the pool increases in the process.

In Fig. 1c such structures of the remelting zone are shown for the time τ = 3.7 msec and Fig. 2c shows such structures for the energy flux density $q = 3 \cdot 10^5$ W/cm^2.

Conclusion. The good qualitative agreement between the experimental results on pulsed laser alloying of titanium in liquid-nitrogen vapor and the calculations of the concentration fields based on the model of thermocapillary convection in the melt pool shows that in the range of interaction parameters studied the main mechanism of mass transfer is surface-tension-driven motion of the melt, owing to the nonuniformity of the temperature distribution over the surface of the melt pool. The discrepancies between the experimental results and the computed dependences are connected with a number of factors, among which the nongaussian real spatial distribution of the laser radiation intensity should be singled out.

NOTATION

τ, pulsed interaction time of the laser radiation; q, energy flux density of the laser radiation; k, concentration factor; r, radius; Re^*, reduced Reynolds number; u, velocity of the melt; R, radius of the heating spot; Pr, Prandtl's number; ν, kinematic viscosity of the melt; S, depth of the melt pool; λ, wavelength of the laser radiation.

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INVESTIGATION OF MASS AND HEAT TRANSFER PROCESSES IN LASER ALLOYING OF IRON FROM PREDEPOSITED COATINGS OF REFRACTORY METALS

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UDC 621.793.7

The laws of mass and heat transfer in laser alloying of Armco iron from predeposited coatings of molybdenum and chromium were determined experimentally.

Introduction. The processes occurring during laser working of metals are characterized by strong nonuniformity, complicated hydrodynamics, high rates of cooling, and a number of other features, determining the formation of alloys with a large range of physical and chemical properties on metal surfaces. Laser surface alloying and, in particular, alloying from predeposited coatings occupies a special place in the large flow of publications on the problems of laser modification of surface [1, 2]. However most works reflect peculiar cases of the alloying of surfaces of specific brands of alloys performed in order to increase the working characteristics of the alloys. The use of different types of laser setups, treatment regimes, and materials of the base and alloying components for these purposes makes it much more difficult to systematize the experimental data. No publication gives experimental data on the development of alloying processes; the structure, the phase composition, and the distribution of the alloying component over the pool of the crystallized melt after irradiation are primarily studied. Theoretical studies of the mass and heat transfer processes primarily reduce to the construction of a model of the distribution of the alloying component by the thermocapillary mechanism [3]. Without a detailed study of the mass and heat transfer processes, determining the formation of the modified layers, it is impossible to optimize the parameters of the laser radiation and the conditions of laser treatment in the process of laser alloying from predeposited coatings. In this work, with the help of fast optical pyrometry and photoelectronic recording and metallographic and electron-microscopic studies some characteristics of the mass and heat transfer accompanying laser alloying of iron from predeposited coatings of molybdenum and chromium were determined.

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