Laser annealing of porous defects in metals

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Abstract. In present paper a self-consistent model of laser annealing of porous defects in metals is presented. In the proposed model, the defects represent empty isolated pores whose dimensions are much less than thickness of the metal coating. Reduction of porosity occurs due to pore collapse in the molten pool under surface tension forces. In this case the research showed that pore collapse dynamics depends considerably on the pressure in the molten material. From the equality of the negative pressure in the melt and the capillary pressure the applicability bound of the model is determined. It is the critical melting rate of porous material at which pore collapse is still possible.

1. Introduction
The porosity is one of the common defects of metal coatings produced by plasma or magnetron deposition. The use of laser annealing makes it possible to remove these defects, to change the surface relief, microstructure, and roughness [1]. Depending on the coating deposition method, pores can be both empty and gas-filled. The nature of the change in the porosity of the material under laser annealing depends significantly on the gas content in individual pores. For example, in the case of gas-filled pores, the reduction of porosity may occur due to thermocapillary drift of bubble in an inhomogeneously heated melt [2]. For empty pores, a probable mechanism for reducing porosity will be their collapse in the molten material under the action of surface tension forces. In this study, we developed a self-consistent model of pore collapse dynamics during laser annealing of porous defects in metals. For the case of constant velocity of the melting front motion, the thickness of the melt layer in which complete pore closure occurs is determined. The critical melting rate of porous material is found, which is the criterion for the applicability of the proposed model.

2. Theoretical model
Consider a porous metal material exposed to the action of a pulsed laser radiation. Laser pulse irradiation of the coating surface results in material heating and melting. The porosity of the material is small, and isolated spherical pores with dimensions equal in order of magnitude to the size of the original defects are formed on the melting front moving to the depth of the solid phase.

2.1. Thermocapillary drift
In the case of gas-filled pores, the main mechanism for the movement of bubbles in the molten pool may be of thermocapillary drift (the effect of Marangoni-Benard). This mechanism is due to the
surface tension temperature dependence and the inhomogeneity of heating of the bubble surface during the melting of metallic materials by laser radiation. Due to the presence of high values of temperature gradients in the melt, the surface of the bubble turns out to be heated non-uniformly, which results in the appearance of tangential thermocapillary force on it, causing the liquid to move in the direction of decreasing temperature, and the bubble relative to the fluid in the opposite direction. Thus thermocapillary drift can lead to a significant reduction of porosity in the near-surface layers of the material.

We estimate the velocity of the bubble motion in a vertical temperature gradient. To calculate, we use formula [3]:

$$ V = -\frac{R_0}{3\mu} \left( \frac{\partial \sigma}{\partial T} \right) \frac{\partial T}{\partial z} $$  \hspace{1cm} (1)

where $R_0$ is the bubble radius, $\mu$ is the dynamic viscosity coefficient, $\sigma$ is the surface tension coefficient, and $\frac{\partial T}{\partial z}$ is the temperature gradient.

Then for the case of indium with initial porosity $\Phi_0 = 0.01$, pore radius $R_0 = 10^{-4}$ cm, $\mu = 1.9 \cdot 10^{-2}$ g/cm/s, the surface tension gradient $\left( \frac{\partial \sigma}{\partial T} \right) = -0.09$ erg/cm$^2$$^\circ$C, and the temperature gradient $\frac{\partial T}{\partial z} = 6.5 \cdot 10^4$°C/cm, corresponding to laser action of nanosecond duration with the flux density $q = 0.1$ J/cm$^2$, the bubble velocity is $V = 100$ cm/s. It should be noted that this estimate is valid only for a small porosity of the material, when the pores can be considered single.

2.2. Pore collapse under surface tension forces

If the pores are considered empty, then fluid motion in the melt can be characterized by two spatial scales: the local motion on the pore size scale and the averaged homogeneous melt motion. Moreover, these movements can be separated. The local fluid motion causes the molten material to flow into pores and their collapse. The velocity of such flow depends on the relation between the capillary and the near-pore pressures. It is obvious that flowing of material into the pores should be accompanied by melt motion from the irradiated surface to the collapse region and hence the appearance of the corresponding averaged macroscopic motion, which is defined by the pressure difference on the free surface and at a given melt depth. Thus, the dynamics of the melt flow into pores and its translational averaged motion from the surface to the collapse region appear self-consistently related by the pressure at a given depth.

The equation of motion and the continuity equation which describe the macroscopic averaged melt motion, neglecting the viscosity, are given by

$$ \frac{\partial \rho \dot{V}}{\partial t} + \nabla \cdot \rho \dot{V} = 0, \hspace{1cm} \frac{\partial \rho \dot{V}}{\partial t} + \frac{\partial}{\partial x} \rho \dot{V} = 0. \hspace{1cm} (3) $$

The spherical cavity boundary motion in the moving liquid element under the action of surface tension and external pressure is described by the Rayleigh equation [4]

$$ R(t') \frac{d^2 R}{dt'^2} + \frac{3}{2} \frac{dR^2}{dt'^2} + \frac{2\sigma}{\rho R(t')} + \frac{4\mu}{\rho R(t')} \frac{dR}{dt'} = -\frac{p}{\rho} \hspace{1cm} (4) $$

with initial conditions

$$ R(0) = R_0, \hspace{0.5cm} \dot{R}(0) = 0. \hspace{1cm} (5) $$
where $R$ is the pore radius, $t'$ is the time after the passage of the melting front through the pore, $\sigma$ is the surface tension coefficient, $\mu$ is the dynamic viscosity coefficient, $\rho$ is the material density, and $P$ is the external pressure.

3. Results and discussion

We consider the case of constant melting front velocity, and hence, the melt motion velocity. Then the equations (2) and (3) take on form:

$$\frac{p}{\rho} + \frac{\nu^2}{2} = \text{const}, \quad (6)$$
$$\rho V = \text{const}. \quad (7)$$

From the solution of the system of equations (6) - (7), taking into account the relation between the average density of the material and the porosity:

$$\phi = 1 - \frac{\rho}{\rho_0}, \quad (8)$$

where $\rho_0$ is the material density in the absence of pores, in the first-order smallness approximation, we obtain the pressure in the melt near the melting front:

$$P = P_0 - \rho_0 \cdot V_m^2 \cdot \phi, \quad (9)$$

where $P_0$ is the pressure on the free surface, $V_m$ is the melting front velocity.

We can see that this pressure is lower than that on the free surface by $P_0 \rho_0 V_m^2 \phi$, which provides molten material flow from the surface to the melting front. The pressure (9) is external for the moving boundary of the spherical cavity described by equation (4).

To solve equation (4) it is convenient to pass to the coordinate system associated with the melting front motion, that is, we pass from the dependence $R(t')$ to the dependence on the melting front coordinate $z$.

We introduce the following dimensionless variables: the radius $y = \frac{R}{R_0}$ and coordinate $u = \frac{z}{L_0}$, where

$$L_0 = \left(\frac{\rho_0 V_m^2 \rho_0}{3 \sigma}\right)^{1/2}$$

determines the spatial scale of the region in which the pore radius decreases.

In the new variables, equation (4) can be reduced to the form

$$y \frac{d^2y}{du^2} + \frac{3}{2} \left(\frac{dy}{du}\right)^2 + \frac{1}{y} \left(1 + \alpha \frac{dy}{du}\right) + \beta (1 - \delta y^3) = 0 \quad (10)$$

with the initial conditions

$$y(0) = 1, \quad \frac{dy}{du}\bigg|_{u=0} = 0, \quad (11)$$

where

$$\alpha = \frac{8 \mu^2}{\sigma \rho_0 R_0}, \quad \beta = \frac{P_0 R_0}{2 \sigma}, \quad \delta = \frac{\rho_0 V_m^2 \phi}{P_0}. \quad (12)$$

The coefficient $\alpha$ is defined by the liquid viscosity, $\beta$ is the ratio of external and capillary pressures, $\delta$ defines the pressure difference between the free surface and at the melting front.

If viscosity is neglected in equation (10), that is, set $\alpha = 0$, then the solution can be represented in the implicit form:
In the case of the external pressure smallness in comparison with the capillary pressure, when $\beta \ll 1$, integral (13) is

$$u = \int_{y}^{1} \frac{y^{3/2}dy}{\sqrt{1-y^2+\frac{2\epsilon}{\pi}(1-y^2)(1-\frac{\delta}{2}(1+y^2))}}. \quad (13)$$

Then the region in which complete pore collapse occurs, that is radius $y = 0$, is $u_0 = \frac{1}{\sqrt{2}} K\left( \frac{1}{\sqrt{2}} \right) \approx 1.31$.

In the case of nonzero parameters (12) equation (10) can be solved only numerically. In the figure 1 the pore radius variation with the distance to the melting front, normalized to the full width of the pore collapse region is presented. This solution is obtained for the case of indium with initial porosity $\phi_0 = 0.01$, the pore radius $R_0 = 10^{-4}$ cm, the melting rate $V_m = 7 \cdot 10^{-4}$ cm/s, and the pressure at infinity $P_0 = 1$ atm. The calculation used the following material parameters: the compact material density is $\rho_0 = 7.31$ g/cm$^3$, the dynamic viscosity coefficient is $\mu = 1.9 \cdot 10^{-2}$ g/cm-c, and the surface tension coefficient is $\sigma = 556$ erg/cm$^2$. The parameter $L_0$ turned out to be equal to $L_0 = 5.7 \cdot 10^{-4}$ cm.

For the given problem parameters, the width of the region in which the pores collapses was calculated. It was $L = u_0 L_0 = 7.5 \cdot 10^{-4}$ cm. In addition, in figure 1, an analytical approximation of the numerical solution (10) and solution (13) is given by a function of the form

$$\bar{y} = (1 - u^2)^{7/18}. \quad (15)$$

Also on the inset of figure 1 the dependence of the pressure variation in the pore collapse region on the distance to the melting front is represented. According to (9), the pressure difference in the collapse region is proportional to $V_m^2 \phi_0$. At the considered melting rate and initial porosity, the negative values of the pressure are implemented in the collapse region. In order to molten material
flow into empty pores during melting and pore collapse occur under surface tension forces, the condition

$$\frac{2\sigma}{R_0} > |P_0 - \rho_0 \cdot V_m^2 \cdot \Phi_0|$$

should be satisfied.

When the pressure in the melt and capillary pressure are equal, the process of pore collapse stops, which imposes constraints on the applicability of the proposed model. In order that pore collapse would occur during porous material melting by laser radiation in the quasisteady mode, the melting rate should be lower than a certain critical melting rate $V_{cr}$. The critical melting rate is determined from the equality of the right- and left-hand sides of inequality (16). At the pressure on the free surface $P_0 \ll \rho_0 \cdot V_m^2 \cdot \Phi_0$ critical melting rate is

$$V_{cr} = \sqrt{\frac{2\sigma}{\Phi_0 \rho_0 R_0}}$$

In our case the critical melting rate is $V_{cr} = 1.2 \cdot 10^4$ cm/s. An analysis of the numerical solution of equation (10) at variations of $\Phi_0, R_0, V_m$ shows that the width of the region in which pore collapse occurs is a universal function depending on the ratio $V_m/V_{cr}$; as the melting rate $V_m$ approaches critical value $V_{cr}$, the collapse region size increases. The asymptotics of the increase in the region in which collapse occurs, can be obtained at $V_m/V_{cr} \to 1$; in this case $L \sim L_0 \cdot \left(1 - \frac{V_m^2}{V_{cr}^2}\right)^{-1/2}$.

The estimate of the pore collapse time showed that for indium with a pore radius $R_0 = 10^{-4}$ cm, it is about 10 ns. While for the same parameters of the problem, the time of defect removal to the surface due to the thermocapillary drift does not exceed 10 µs.

4. Conclusions

The present paper considers pore removing mechanisms during laser annealing of porous defects such as the thermocapillary drift of a bubble caused by the surface tension temperature dependence and the pore collapse under surface tension forces. The analysis of the pore collapse dynamics shows that the principal role is played by the pressure in the molten material. On the one hand, it defines the velocity of melt homogeneous motion from the surface to the collapse region; on the other hand, the velocity of the melt flow into empty pores. In addition, the equality of pressure in the melt and capillary one leads to stop the pore collapse, which imposes a limitation on the applicability of the proposed model. The criterion of model applicability is the critical melting rate of the porous material, in which the pore collapse is still possible.

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