

KINETICS OF OXIDE FILM GROWTH DURING LASER HEATING

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The kinetics of oxidation of the surface of a copper target in air by CO₂-laser radiation are examined with consideration of the thermodiffusion and thermo-emf mechanisms.

The interest of a number of researchers in questions of laser oxidation of metals has made it necessary to consider the various mechanisms underlying processes which accompany growth of an oxide film on a surface during laser heating [1-9]. In [1, 2] and a number of other studies it was postulated that oxidation kinetics follow Wagner's law [10], written for thick oxides and high temperature oxidation in parabolic form:

$$\frac{\partial \xi_B}{\partial t} = \frac{d}{\xi} \exp \left[-\frac{T_d}{T(0, t)} \right], \quad \xi(0) = \xi_0. \quad (1)$$

A number of studies have touched upon nonisothermal mechanisms for the oxidation process. Among these are: a diffusion mechanism for change in absorptivity upon oxidation [4], consideration of the contribution of thermodiffusion for transport of cation vacancies through the oxide layer [5, 11], hydrodynamics of oxygen supply from the air due to temperature change upon rapid oxidation [6], thermo-emf, mechanisms of oxidation kinetics [7], the effect of non-stoichiometry of oxide composition on laser oxidation processes [8], etc.

The present study will analyze the interaction of laser heating rate, with consideration of absorptivity of the oxide-metal system $A(\xi)$, and the kinetics of oxide film growth in the process of radiation absorption. We will consider oxidation of a massive copper target by continuous CO₂-laser radiation with consideration of the dependence of $A(\xi)$ on oxide layer thickness on the metal surface. The mathematical formulation of the problem includes the one-dimensional thermal conductivity equation with temperature-independent thermophysical constants, with radiation absorption being a surface process with $A(\xi)$ taken from [3]:

$$\begin{aligned} \frac{\partial \xi}{\partial t} = \frac{\partial \xi_B}{\partial t} \exp \left[\frac{\gamma T_d}{T(0, t)} \left\langle 1 - \frac{T(0, t)}{T(\xi, t)} \right\rangle \right] \times \\ \times \left\{ \int_0^{\xi} \exp \left[-\frac{(1-\gamma) T_d}{T(0, t)} \left\langle 1 - \frac{T(0, t)}{T(x, t)} \right\rangle \right] dx \right\}^{-1} \end{aligned} \quad (2)$$

for the following process parameter values: $T_d = 10,000$ K, $\gamma \sim 0.2$ (for Cu₂O).

The technique of solving the problem was discussed in sufficient detail in [3] and will not be presented here. Figure 1 shows time dependences of oxide layer thickness (curves 1a, 2a) and oxide free surface temperature $T(\xi, t)$ (curves 1b, 2b), calculated for two forms of the oxide growth rate law. The initial period of the process up to temperatures ≤ 800 K (low temperature oxidation) is characterized by coincidence of the temperature regime and the functions $\xi_B(t)$ and $\xi(t)$, which can be explained by the low temperature gradient in the oxide layer. Further heating and thermochemical reaction lead to significant acceleration of the diffusion rate due to motion of cation vacancies [10]. This produces a shift in the temperature maximum due to existence of inverse feedback: heating-growth in temperature and oxide thickness-oscillations in $A(\xi)$ -heating, together with earlier melting of oxide on the boundary.

Figure 2 shows the ratio of the rates ν of thermodiffusion and isothermal oxidation as a function of radiation action time ($\nu = (\partial \xi / \partial t) / (\partial \xi_B / \partial t)$). The complex oscillating character of this dependence can apparently be explained as follows. The first maximum ($\nu \sim 3$) occurs at a surface temperature of ~ 450 K, with oxide-metal boundary temperature of ~ 400 K. There is practically no change in oxide thickness and the temperature increases significantly ($\sim \sqrt{t}$), as does, consequently, the temperature gradient. Then the temperature growth rate decreases, while the oxide layer thickness continues to increase, as a result of which dt/dz decreases, which leads to a reduction in the value of ν . At

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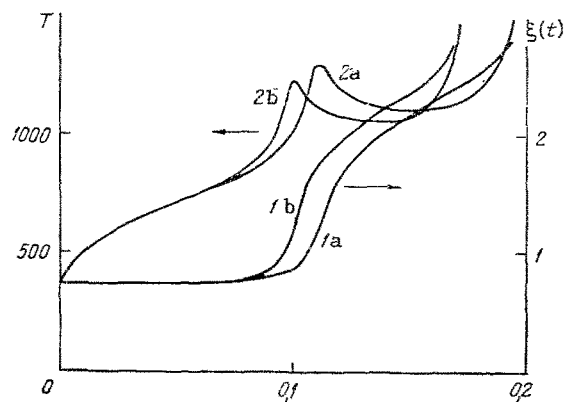


Fig. 1. Time dependences of temperature T of free surface and oxide film thickness ξ for isothermal (a) and thermodiffusion (b) oxidation. T , K; $\xi(t)$, μm .

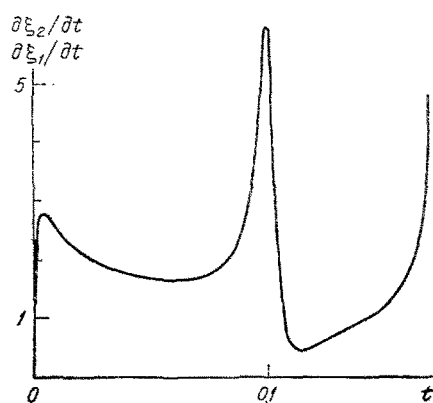


Fig. 2

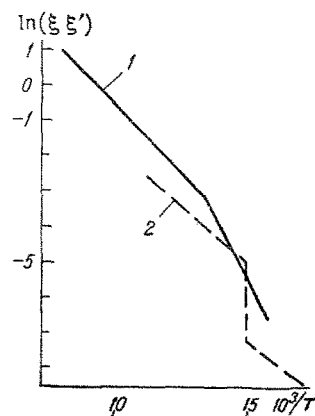


Fig. 3

Fig. 2. Ratio of oxidation rates ν for thermodiffusion and isothermal mechanisms. t , sec.

Fig. 3. Oxide film growth rates vs temperature: 1) laser heating of thermally thin target; 2) isothermal oxidation. $\ln(\xi\xi')$, $\mu\text{m}^2/\text{sec}$. T , K^{-1} .

the second maximum of the absorptivity $A(\xi)$ a significant increase in temperature begins [3] and ν increases to 6. Decrease in temperature leads to decrease in the thermodiffusion component of the vacancy flux and brings about retardation of the reaction rate ($\nu < 1$).

These features of oxide film growth kinetics during laser heating are shown in Arrhenius coordinates in Fig. 3. The oxide film thickness was measured during isothermal laser oxidation by an optical technique involving monitoring the reflection coefficients of diagnostic radiation at 0.63 and 10.6 μm wavelengths. It was established that for temperatures $T > 440^\circ\text{C}$ the laser oxidation rate was above isothermal. The experimental points of Fig. 3 lie on two straight lines, which correspond to different thermodiffusion constants which differ from the isothermal ones. The increase in the laser oxidation rate can be explained within the framework of the thermo-emf mechanism [7]. As x-ray structural analysis established, for $T > 440^\circ\text{C}$ the oxide consists primarily of cuprous oxide Cu_2O , which agrees with the data of [12]. For n-type Cu_2O the oxidation process is controlled by transport of the Cu^+ copper ion. In this case the thermo-emf field will accelerate motion of metal ions to the reaction boundary, which encourages increase in the oxidation rate as compared to isothermal. For $380^\circ\text{C} < T < 440^\circ\text{C}$ the rates of laser and isothermal oxidation are approximately the same. This is related to the presence in the oxide film composition of a layer of cupric oxide CuO , the thickness of which becomes dominating at $T < 380^\circ\text{C}$. For the n-type oxide CuO the thermo-emf field will hinder supply of reagents to the reaction zone, which then causes the reduction in reaction rate, as was demonstrated in [9].

In [5, 9, 13], also dedicated to thermodiffusion oxidation, the process was examined without consideration of the time dependence of the temperature field, i.e., in the quasistationary approximation. This leads to neglect of oscillations

in absorptivity and temperature and the unjustified conclusion that for p-type semiconductors (for example, Cu_2O) the reaction rate is always higher than isothermal, which, in particular, contradicts the dependence of Fig. 2.

Further development of these approaches will involve a more correct treatment of the absorption mechanism than that of [3], i.e., of the dependence $A(\xi)$, possibly in the form presented in [13], and consideration of spatial effects of the problem.

NOTATION

t , pulse action time; ξ , oxide layer thickness; $A(\xi)$, oxide-metal system absorptivity; d , constant of parabolic oxidation law; T_d , activation temperature of thermochemical oxidation of copper; γ , thermodiffusion constant in oxide layer; $T(x, t)$, temperature field in oxide; x , spatial coordinate; ξ_0 , initial oxide thickness; $\partial\xi_B/\partial t$, isothermal oxidation rate; $\partial\xi/\partial t$, oxidation rate with consideration of thermodiffusion; ν , ratio of thermodiffusion and isothermal oxidation rates.

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