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Modeling vanadium oxide film growth in the spot of a cw CO_2 laser♣

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In this paper a nonisothermal model which describes the oxide layer thickness evolution and the sample temperature variation in the case of a small vanadium plate in a cwCO_2 laser beam is considered. In the framework of the model the equilibrium temperature T*(P) of the sample; the equilibrium oxide layer thickness x*(P); the moment of time t_0(P) when 1nm oxide layer thickness is achieved; the sample temperature T(t_0(P)) at the moment t_0(P); the moment of time t_1(P) when the equilibrium temperature is achieved; the oxide layer thickness x(t_1(P)) at the moment when the equilibrium temperature is achieved; the growth speed $v(t_0(P))$ at the moment $t_0(P)$ and the growth speed $v(t_1(P))$ at the moment $t_1(P)$ are computed in function of the laser power P, which varies in the range $4 \div 25\,[\mathrm{W}]$. It is shown that starting from the room temperature (T' = 300[k]) if P increases, then $T^*(P)$ increases and $x^*(P)$ decreases at the beginning but after that increases $t_0(P)$ is of order $10^{-9}\,[\mathrm{s}]$ and it is constant; $T(t_0(P))$ is practically equal to the starting room temperature; $t_1(P)$ is of order $10^0 \div 10^1\,[\mathrm{s}]$ and decreases when P increases; $x(t_1(P))$ is of order $10^{-5}\,[\mathrm{m}]$ and decreases when P increases; $v(t_0(P))$ is of order $10^{-1}\,[\mathrm{m/s}]$ and it is constant; due to the evaporation $v(t_1(P))$ is negative it is of order $10^{-8} \div 10^{-9}\,[\mathrm{m/s}]$ and decreases when P increases. In particular it is shown that the experimental results, presented in [7], concerning the oscillogram of the sample temperature, the evolution of the oxide layer thickness can be obtained with high accuracy in the framework of the model. It is found that the oxide layer thickness evolutions for $P = 4\,[\mathrm{W}]$ and $P = 17\,[\mathrm{W}]$ correspond to the two oxide types VO and V_2O_5, as is reported in [7]. How well the computed results are in agreement with other experimental results depends on the smallness of the effect of the processes which were not incorporated in the model. The advantage of this theoretical analysis is the possibility to obtain explicit results from which the limits of the model can be specified and special results can be gleaned. With this aim this study was undertaken.

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1. Introduction

Oxygen incorporation in metals and formation of oxide films on metal surfaces are of fundamental interest and of technological importance. The thermooxidation of metal surfaces by controlled heating was intensively studied by many authors. In [1] the oxidation of polished vanadium (V), which was heated in an oxidizing atmosphere (O_2) to the temperature range 673-873 [K], was studied. By electron diffraction, the induced oxide was identified as V_2O_5 and weight determination prior to and after oxidation indicated a parabolic law for the oxide film thickness evolution. The oxidation of cooper (Cu), aluminium (Al), titanium (Ti), chromium (Cr) and tungsten (W) in an oxidizing atmosphere (i.e. air) and in the thermal field of a $cwCO_2$ laser light was studied in the papers [2-6] with particular attention in every case to the initial stage of the evolution of the oxidation process. In [7], vanadium oxidation in atmospheric air and in the thermal field of a $cwCO_2$ laser light was studied. Particular emphasis is paid to the initial stage and the development of the oxidation process. Quantitative theoretical interpretation of the experimentally recorded data are discussed. Attempts have been made to analyze theoretically the oxidation of metals in [8-15].

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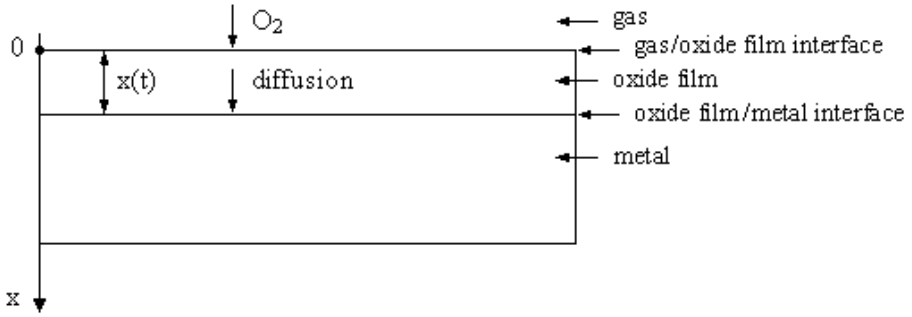


Fig. 1. The oxidation process.

It was established that even in planar case, Fig.1, oxidation process has multistage nature, i.e. for oxidation one has: transport of O_2 from gaseous volume to the gas/oxide film interface, adsorbing O_2 on oxide surface, transport of O_2 through oxide film, chemical reaction at oxide film/metal interface and coupling of the oxygen with the metal. The reaction rate is limited by the slowest stage of the process. The kinetic law, describing the thickness change x at the temperature T of the system, has the form: $\frac{dx}{dt} = f(x,T)$. There are few theoretical models, adequate to experiment, for constructing $f(x,T)$ on a microscopic level using empirical constants and fitted parameters [8, 9]. However, those theories exist only for a few metals and they are valid only for isothermal conditions. One of the most important features of phenomenological theories is that charged particles take part in transport processes, i.e. metal and oxide ions, electrons, charged lattice defects etc. and as a consequence, influence the oxidation kinetics. An electric field always arises from O_2 chemosorption on the oxide film surface. This aspect was first formulated and analyzed by Cabrera and Mott [8, 9].

Two characteristic thicknesses were introduced: $x_1 \approx 10nm$ and $x_2 \approx 100nm$. At oxide layer thickness $x << x_1$ the value of the electric field is very high. In this case Ohm's law should be not used (because the strong current-field nonlinearities). For $x >> x_2$ the electric field does not influence the transport. This is determined by the diffusion flux depending on concentration gradient. The growth theory for $x >> x_2$ (thick oxide layers) was established by Wagner [8, 9, 10]. The concrete kinetic law depends on the type of the conductivity and on the oxide film thickness. There are many forms of kinetic law for very thin $x << x_1$, and for $x_1 < x < x_2$ compact oxide layers (linear, cubic, parabolic, reciprocal parabolic law etc [8], [9]). For thick $x > x_2$ compact oxide films the most important is the parabolic law (Wagner law) $f(x,T) = \frac{d}{x} \cdot e^{-\frac{T_a}{T}}$, where d and T_d are the so-called oxidation constants.

Laser-induced oxide film growth involves new problems. The kinetics differ considerably from isothermal oxidation kinetics. High heating speeds due to the absorption of laser light result in temperature changes which occur faster than the relaxation processes [11, 12]. The nonequilibrium behavior is determined by the stoichiometry of the system [14, 15], optical properties [16, 17], perturbations of the stationarity diffusion conditions [18], generations of defects [19, 20] and the influence of non-steady-state defects on diffusion processes [19, 21].

Kinetic studies of lasers-induced heterogeneous processes on metal surfaces under the influence of external electric fields were made in [22, 23, 24] under the conditions that the electric field influences the processes occuring in the gas phase. In [24] it is shown theoretically and experimentally that in the case of V and Cu oxidation in $cwCO_2$ laser light the external field influences the oxidation rate and the surface morphology.

In [25] a review of laser/assisted metal oxidation experiments is given and results for V targets are presented concerning the manner in which temperature affects the Wagner oxidation constants, and how affects an external electric field the oxidation rate. Morphological peculiarities of grown oxide layers are presented too.

According to [25], the experimentally obtained parabolic rule describing the oxide film thickness evolution at constant temperature in vanadium (V) case can be obtained using the Wagner law:

$$\begin{cases} \frac{dx}{dt} = \frac{d}{x} \cdot \exp\left(-\frac{E_{ox}}{k \cdot T}\right) \\ x(0) = x_0 \end{cases} \quad (1)$$

where:

- x is the thickness of the oxide layer
- t is the time
- d is the oxidation rate constant
- E_{ox} is the activation energy of oxidation

- T is the temperature of the sample
- k is the Boltzmann constant
- $t = 0$ is the initial moment when the prescribed constant temperature T of the sample is achieved.
- x_0 is the thickness of the existing oxide film at $t = 0$.

According to [25], in the case of V the following dependencies hold:

$$d = d_0 \cdot e^{a \cdot T} \tag{2}$$

$$E_{ox} = k \cdot (\alpha \cdot T - \beta) \tag{3}$$

where: $d_0 = 1.62 \cdot 10^{-14} \left[m^2 / s \right]$, $a = 1.9 \cdot 10^{-2}$, $\alpha = 28.03$, $\beta = 9736$.

At the constant temperature T, according to (1), the oxide film thickness $x(t)$ is given by the parabolic law:

$$x(t) = \sqrt{x_0^2 + 2 \cdot d_0 \cdot e^{-\alpha} \cdot e^{\left(a \cdot T + \frac{\beta}{T} \right)} \cdot t} \tag{4}$$

This rule is in agreement with experimental data reported in [7] if the initial oxide film thickness x_0 is bigger than $10^{-6}(m)$, and the sample temperature is $T = 1250[K]$.

In [27] the fabrication of V_2O_5 microtubes, (without any support structure) by continuous wave infrared laser assisted oxidation of V in air is reported. In [28] oxide layer growth due to a $cwIR$ laser, to a pulsed UV laser and to their simultaneous use is presented. The variation of temperature and absorptivity vs. time is demonstrated.

In [26] Wagner oxidation in nonisothermal regime is discussed. The question asked is to what extent the traditional Wagner oxidation law applies to laser-induced oxidation when the heating is rapid? The proposed model for the oxidation process retains the basic Wagner premise, i.e. that the process is diffusion limited and computation made for V shows that Wagner rate law holds for thicker oxide layers, but not at the beginning of the processes.

On the other hand the molecular dynamics (MD) simulation of laser ablation started in [29] was developed for metals in [30] and the shock phenomena for metals reported in [31, 32] suggest to consider for the laser induced metal oxide growth a nonisothermal model.

In [6], in order to describe W (tungsten) oxide layer growth induced by $cwCO_2$ lasers, the nonisothermal model defined by the following system of ordinary differential equations is considered:

$$\begin{cases} \frac{dx}{dt} = \frac{d}{x} \cdot \exp\left(-\frac{E_{ox}}{k \cdot T} \right) - v \cdot \exp\left(-\frac{E_{vap}}{k \cdot T} \right) \\ m \cdot c \cdot \frac{dT}{dt} = P \cdot A + \rho \cdot S \cdot L \cdot \frac{d}{x} \cdot \exp\left(-\frac{E_{ox}}{k \cdot T} \right) - \rho \cdot S \cdot W \cdot v \cdot \exp\left(-\frac{E_{vap}}{k \cdot T} \right) - P_{loss} \end{cases} \tag{5}$$

for x> 0 and T> 0.

In this system: x is the thickness of the oxide layer, d is the oxidation rate constant, E_{ox} and E_{vap} are the activation energies of oxidation and evaporation, respectively, v is the rate of evaporation of the oxide, m is the mass of the sample, c is the specific heat of the sample, P is the incident laser power, A is the absorptivity, ρ is the density of the oxide, S is the surface of the sample, L and W are the specific energies of oxidation and evaporation, respectively, P_{loss} represents the radiative and convective heat loss, k is the Boltzmann constant.

In the present paper, in the framework of the model defined by (5), we show that, it is possible to find: the equilibrium temperature $T^*(P)$ of the sample, the equilibrium oxide layer thickness $x^*(P)$, the moment of time $t_0(P)$ when the 1nm oxide layer thickness is achieved; the sample temperature $T(t_0(P))$ at the moment $t_0(P)$; the moment $t_1(P)$, when the equilibrium temperature is achieved; $x(t_1(P))$ the oxide layer thickness at the moment $t_1(P)$; the speed of the oxide layer growth $v(t_0(P))$ at $t_0(P)$ and $v(t_1(P))$ at $t_1(P)$ and to describe with accuracy the experimentally obtained results reported in [7] for vanadium oxide film growth. The effect of the evaporation is evaluated also. How well all the computed results are in agreement with the experimental results depend on the smallness of the effects of the processes which were not incorporated in the model. The advantage of this theoretical analysis is to obtain explicit results from which the limits of the considered model can be deduced and special results can be gleaned. With this aim this study was undertaken.

2. The existence of the equilibrium

A state x*, T* is an equilibrium of the system (5) if $x(t) \equiv x^*$ and $T(t) \equiv T^*$ is a solution of the system (5). The state x^*, T^* is an equilibrium of the system (5), if and only if x^*, T^* satisfy

$$\begin{cases} \frac{d}{x^*} \cdot \exp\left(-\frac{E_{ox}}{k \cdot T^*} \right) - v \cdot \exp\left(-\frac{E_{vap}}{k \cdot T^*} \right) = 0 \\ \frac{\rho \cdot S \cdot L}{m \cdot c} \cdot \frac{d}{x^*} \cdot \exp\left(-\frac{E_{ox}}{k \cdot T^*} \right) - \frac{\rho \cdot S \cdot W}{m \cdot c} \cdot v \cdot \exp\left(-\frac{E_{vap}}{k \cdot T^*} \right) + \frac{P \cdot A - P_{loss}}{m \cdot c} = 0 \end{cases} \tag{6}$$

System (6) is equivalent to the system:

$$\begin{cases} \frac{d}{x}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-v\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right)=0 \\ L\cdot\frac{d}{x}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-W\cdot v\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right)=\frac{P_{loss}-P\cdot A}{\rho\cdot S} \end{cases} \quad (7)$$

and if $L\neq W$, then system (6) is equivalent to the system:

$$\begin{cases} \exp\left(-\frac{E_{vap}}{k\cdot T}\right)=\frac{P_{loss}-P\cdot A}{(L-W)\cdot v\cdot\rho\cdot S} \\ \frac{d}{x}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-v\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right)=0 \end{cases} \quad (8)$$

Eq. (8.1) has a unique positive solution T^*, and introducing T^* into eq. (8.2) we obtain

$$x^*=\frac{d}{v}\cdot\exp\left(\frac{E_{vap}-E_{ox}}{k\cdot T^*}\right)>0 \quad (9)$$

The couple x^*, T^* obtained in this way is the equilibrium when $L\neq W$.

If $L=W$, then:

$$\frac{P_{loss}-P\cdot A}{\rho\cdot S}=0 \quad (10)$$

and therefore

$$P_{loss}=P\cdot A \quad (11)$$

In general $P_{loss}=\varepsilon\cdot\sigma\cdot T^4$ and it follows that

$$\varepsilon\cdot\sigma\cdot T^4=P\cdot A \quad (12)$$

where ε - the emissivity of the material and σ - the Stefan-Boltzmann constant.

The solution of eq. (12) is $T^*=\sqrt[4]{\frac{P\cdot A}{\varepsilon\cdot\sigma}}$. Substituting this T^* in (9) an x^* is obtained. This couple x^*, T^* is the equilibrium when $L=W$.

Conclusion: The system (5) has a unique equilibrium x^*, T^*. For $L\neq W$, T^* is given by the eq. (8.1) and for $L=W$ by the eq. (12) respectively. x^* is given by eq. (9) in both cases. The equilibrum x^*, T^* depends on P and S so:

$$x^*=x^*(P,S)\quad and\quad T^*=T^*(P,S) \quad (13)$$

The other parameters appearing in the system (*d*, E_{ox}, *v*, E_{vap}, ρ, *L*, *W*, *A*, *c*) are material constants.

3. The stability of the equilibrium

The equilibrium is asymptotically stable when the system evolves to the equilibrium and after a transition period achieves it, even if it was not in equilibrium at the beginning. In order to see if the equilibrium determined in the sequence 2 is asymptotically stable the right hand members of system (5) have to be analyzed. For this purpose denote:

$$f(x,T)=\frac{d}{x}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-v\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right) \quad (14)$$

$$g(x,T)=\frac{\rho\cdot S\cdot L}{m\cdot c}\cdot\frac{d}{x}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-\frac{\rho\cdot S\cdot W}{m\cdot c}\cdot v\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right)+\frac{P\cdot A-P_{loss}}{m\cdot c} \quad (15)$$

and

$$a_{11}=\frac{\partial f}{\partial x}=-\frac{d}{x^2}\cdot\left(-\frac{E_{ox}}{k\cdot T}\right)<0 \quad (16)$$

$$a_{12}=\frac{\partial f}{\partial T}=\frac{d}{x}\cdot\frac{E_{ox}}{k\cdot T^2}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-v\cdot\frac{E_{vap}}{k\cdot T^2}\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right) \quad (17)$$

$$a_{21}=\frac{\partial g}{\partial x}=-\frac{\rho\cdot S\cdot L}{m\cdot c}\cdot\frac{d}{x^2}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)<0 \quad (18)$$

$$a_{22}=\frac{\partial g}{\partial T}=\frac{\rho\cdot S\cdot L}{m\cdot c}\cdot\frac{d}{x}\cdot\frac{E_{ox}}{k\cdot T^2}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T}\right)-\frac{\rho\cdot S\cdot W}{m\cdot c}\cdot v\cdot\frac{E_{vap}}{k\cdot T^2}\cdot\exp\left(-\frac{E_{vap}}{k\cdot T}\right)-$$
$$-\frac{1}{mc}\cdot\frac{dP_{loss}}{dT} \quad (19)$$

According to Hurwitz criterion [33], if at the equilibrium x^*, T^* the following inequalities hold

$$\begin{cases} a_{11}+a_{22}<0 \\ a_{11}\cdot a_{22}-a_{12}\cdot a_{21}>0 \end{cases} \quad (20)$$

then the equilibrium is asymptotically stable.

By calculus:

$$a_{12}=\frac{d}{x^*}\cdot\frac{E_{ox}}{k\cdot T^{*2}}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T^*}\right)-v\cdot\frac{E_{vap}}{k\cdot T^{*2}}\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)=$$
$$=\frac{v}{k\cdot T^{*2}}\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)\cdot\left[E_{ox}-E_{vap}\right]$$

$$a_{22}=\frac{\rho\cdot S\cdot L}{m\cdot c}\cdot\frac{d}{x^*}\cdot\frac{E_{ox}}{k\cdot T^{*2}}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T^*}\right)-\frac{\rho\cdot S\cdot W}{m\cdot c}\cdot v\cdot\frac{E_{vap}}{k\cdot T^{*2}}\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)-\frac{1}{m\cdot c}\cdot\frac{dP_{loss}}{dT}=$$

$$=\frac{\rho\cdot S}{m\cdot c}\cdot\frac{1}{k\cdot T^{*2}}\cdot v\cdot\left[L\cdot E_{ox}-W\cdot E_{vap}\right]\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)-\frac{1}{m\cdot c}\cdot 4\cdot\varepsilon\cdot\sigma\cdot T^{*3}$$

and the condition (20) becomes:

$$\begin{cases} -\frac{d}{x^*}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T^*}\right)-\frac{\rho\cdot S}{m\cdot c}\cdot\frac{1}{k\cdot T^{*2}}\cdot v\cdot\left[L\cdot E_{ox}-W\cdot E_{vap}\right]\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)-\frac{1}{m\cdot c}\cdot 4\cdot\varepsilon\cdot\sigma\cdot T^{*3}<0 \\ -\frac{d}{x^{*2}}\cdot\exp\left(-\frac{E_{ox}}{k\cdot T^*}\right)\cdot\left[\frac{\rho\cdot S}{m\cdot c}\cdot\frac{1}{k\cdot T^{*2}}\cdot v\cdot\left[L\cdot E_{ox}-W\cdot E_{vap}\right]\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)-\frac{1}{m\cdot c}\cdot 4\cdot\varepsilon\cdot\sigma\cdot T^{*3}\right]+ \\ +\frac{v}{k\cdot T^{*2}}\cdot\exp\left(-\frac{E_{vap}}{k\cdot T^*}\right)\cdot\left[E_{ox}-E_{vap}\right]\cdot\frac{\rho\cdot S\cdot L}{m\cdot c}\cdot\frac{d}{x^{*2}}\cdot\left(-\frac{E_{ox}}{k\cdot T^*}\right)>0 \end{cases} \quad (21)$$

Conclusion: If inequalities (20) or (21) hold, then the equilibrium (x*,T*) is asymptotically stable.

The asymptotic stability of the equilibrium assures that it is physically realizable and even if at the beginning the system was not in the equilibrium it evolves in time to the equilibrium.

4. Numerical results

The material parameters for vanadium are presented in Table 1.

Table 1. The material parameters for Vanadium (according Ref. [3, 4, 5]).

Description [units]	Symbol	Vanadium
Thickness of the oxide layer	x	
Oxidation rate constant as a function of temperature [m^2/s]	$d = d_0 \cdot e^{a_1 \cdot T}$	
Oxidation rate constant at constant temperature [m^2/s]	d_0	$1.62\cdot10^{-14}$
Activation energy of oxidation [J]	$E_{ox} = k\cdot(\alpha\cdot T-\beta)$	
Activation energy of evaporation [J]	E_{vap}	$3.84\cdot10^{-20}$
Mass of the sample [kg]	m	$1.566\cdot10^{-5}$
Specific heat of the sample [J / kg·K]	c	490
Incident laser power [W]	P	4 ÷ 25
Absorptivity	A	35
Density of the oxide [kg / m^3]	ρ	3357
Surface of the sample [m^2]	S	$9\cdot10^{-6}$
Specific energy of oxidation	L	11
Specific energy of evaporation	W	35
Radiative and convective heat loss	$P_{loss} = \varepsilon\cdot\sigma\cdot T^4$	
Rate of evaporation of the oxide	$v = a\cdot T+b$	
Boltzmann constant [$m^2\cdot kg/s^2\cdot K$]	k	$1.38065\cdot10^{-23}$
Emissivity	ε	$1.5\cdot10^{-4}$
Stefan-Boltzmann constant [$W/(m^2\cdot K^4)$]	σ	$5.67\cdot10^{-8}$
Other material constants	α	28.03
	β	9736
	a_1	$1.9\cdot10^{-2}$
	a	$8.333\cdot10^{-10}$
	b	$-2.499\cdot10^{-7}$

Using a program MathCAD v.13 the solutions of system (2) were computed for 24 different $cwCO_2$ laser powers (4 ÷ 25 W).

The following equilibriums were found:

Table 2. The equilibriums for different powers P.

P [W]	4	4.5	5	5.5	6	7	8	9	10	11	12	13
$T^*(P)$	636.9	655.9	673.5	689.7	704.9	732.6	757.4	780.1	800.9	820.2	838.2	855.2
$x^*(P)$	2.38E-6	1.83E-6	1.48E-6	1.25E-6	1.08E-6	8.80E-7	7.62E-7	6.91E-7	6.48E-7	6.23E-7	6.11E-7	6.08E-7
	14	15	16	17	18	19	20	21	22	23	24	25
	871.2	886.3	900.8	914.5	927.7	940.3	952.4	964.1	975.4	986.3	996.8	1007.1
	6.12E-7	6.22E-7	6.37E-7	6.56E-7	6.79E-7	7.06E-7	7.37E-7	7.71E-7	8.08E-7	8.49E-7	8.93E-7	9.41E-7

In order to verify the stability of these equilibriums the Hurwitz criterion has been applied.

The computed coefficients a_{ij} in the case P = 4W are:

$$a_{11} = -1.493\cdot10^{-3} < 0;\ a_{12} = 4.691\cdot10^{-11};\ a_{21} = -0.117 < 0;$$
$$a_{22} = -11.457$$

and satisfy (20).

$$a_{11} + a_{22} = -11.459 < 0;\ a_{11}\cdot a_{22} - a_{12}\cdot a_{21} = 0.017 > 0$$

In the case P=17W, the coefficients a_{ij} are:

$$a_{11} = -0.037 < 0;\ a_{12} = 3.838 \cdot 10^{-10};\ a_{21} = -2.913 < 0;$$
$$a_{22} = -33.914$$

and satisfy (20).

$$a_{11} + a_{22} = -33.951 < 0;\ a_{11} \cdot a_{22} - a_{12} \cdot a_{21} = 1.264 > 0$$

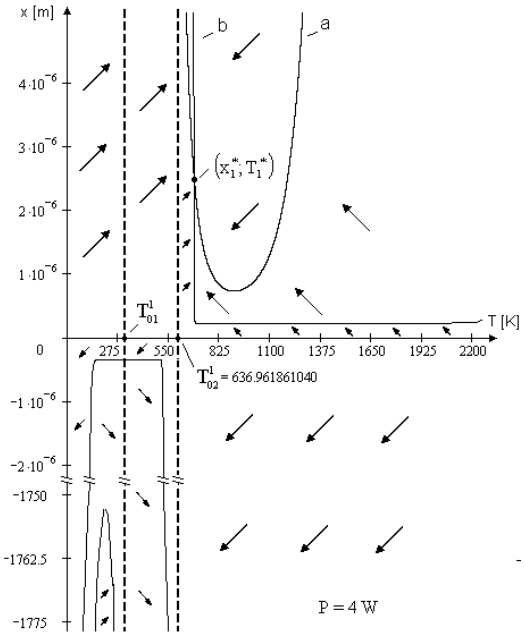
It follows that the steady states are asymptotically stable.

The computed time moments $t_0(P)$, $t_1(P)$; the sample temperature $T(t_0(P))$ at $t_0(P)$; the oxide layer thickness $x(t_1(P))$ at $t_1(P)$ and the growth speeds $v(t_0(P))$, $v(t_1(P))$ are given in Table 3.

Table 3. The dependences of $t_0(P)$, $t_1(P)$, $T(t_0(P))$, $x(t_1(P))$, $v(t_0(P))$ and $v(t_1(P))$ on the laser power P.

P [W]	4	4.5	5	5.5	6	7	8	9	10	11	12	13
$t_0(P)$	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9
$t_1(P)$	10.44	9.68	9.04	8.50	8.03	7.28	6.68	6.20	5.80	5.46	5.18	4.93
$T(t_0(P))$	300	300	300	300	300	300	300	300	300	300	300	300
$x(t_1(P))$	1.47E-5	1.45E-5	1.43E-5	1.41E-5	1.40E-5	1.38E-5	1.36E-5	1.35E-5	1.34E-5	1.33E-5	1.33E-5	1.32E-5
$v(t_0(P))$	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1
$v(t_1(P))$	-2.98E-9	-3.73E-9	-4.48E-9	-5.25E-9	-6.02E-9	-7.57E-9	-9.15E-9	-1.07E-8	-1.23E-8	-1.39E-8	-1.55E-8	-1.70E-8
	14	15	16	17	18	19	20	21	22	23	24	25
	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9	1.2E-9
	4.71	4.52	4.35	4.20	4.07	3.95	3.84	3.74	3.65	3.58	3.51	3.45
	300	300	300	300	300	300	300	300	300	300	300	300
	1.32E-5	1.31E-5	1.31E-5	1.30E-5	1.30E-5	1.30E-5	1.30E-5	1.29E-5	1.29E-5	1.29E-5	1.29E-5	1.29E-5
	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1	4.03E-1
	-1.86E-8	-2.01E-8	-2.17E-8	-2.32E-8	-2.47E-8	-2.62E-8	-2.76E-8	-2.90E-8	-3.04E-8	-3.18E-8	-3.32E-8	-3.45E-8

The phase portraits of the system (5), computed according to [33], are presented on Fig. 2 for P=4W and P=17W, respectively. Physically, of course, only x> 0 has to be considered.



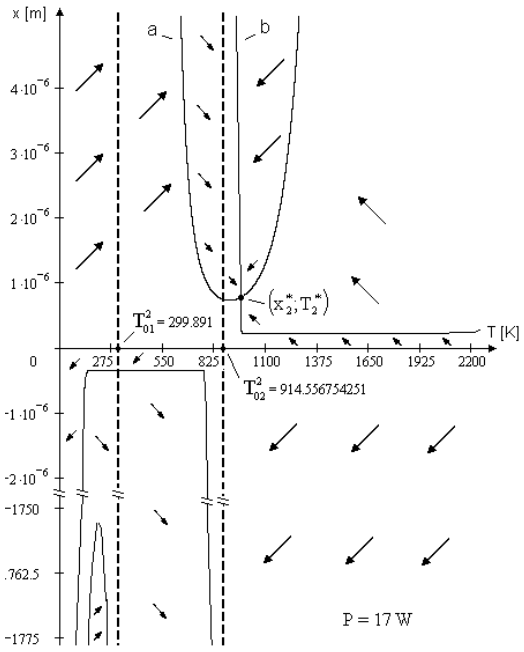


Fig. 2. The phase portraits.

Integrating numerically the system (5), for the initial data given in the experimental paper [7], the following

oscillograms of the sample temperature T were obtained (Fig. 3).

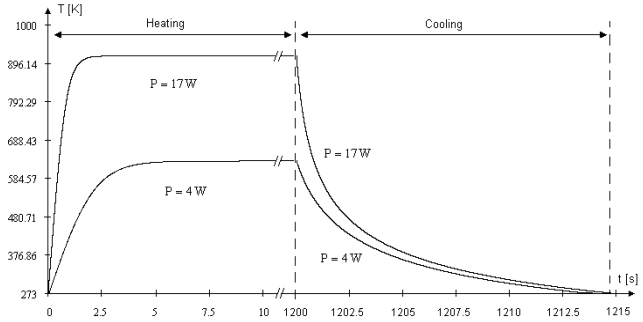


Fig. 3. The computed oscillograms of the sample temperature T for P=4W and P=17W.

This result is in a good agreement with the oscillogram reported in [7].

The computed evolutions of the oxide film thickness for $P = 4W$ and $P = 17W$, respectively, are presented in Fig.4.

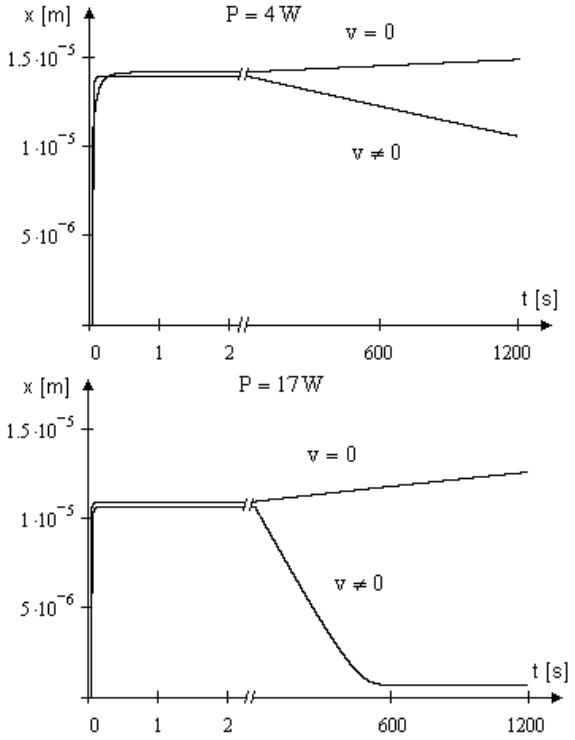


Fig. 4. Evolution of the vanadium oxide layer thickness for $v = 0$ *and* $v \neq 0$ *(P=4W and P=17W).*

In Fig.5 the computed $(x(t), T(t))$ solutions of (5) are represented with $(v \neq 0)$ and without $(v = 0)$ evaporation for P=4W and P=17W, respectively. The curves a, b from the corresponding phase portraits (Fig.2) are drawn as well.

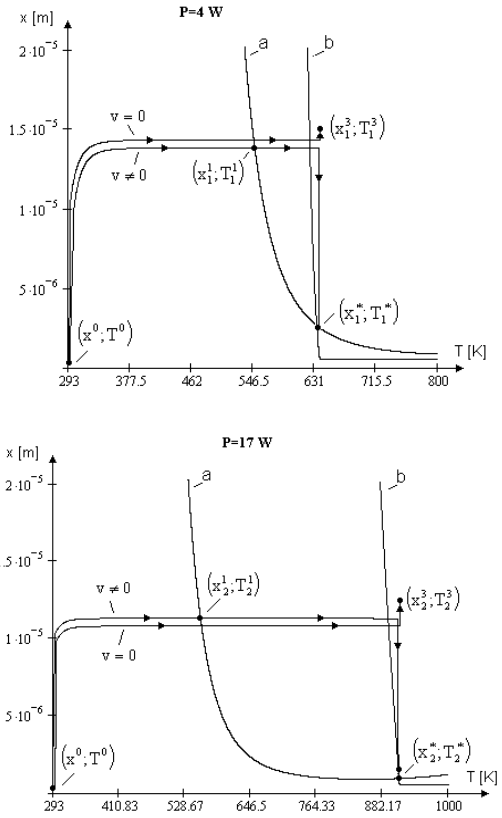


Fig. 5. The computed $(x(t), T(t))$ *pairs with* $(v \neq 0)$ *and without* $(v = 0)$ *evaporation for P=4W and P=17W, respectively (*a, b *are from Fig.2).*

It can be seen, that for P=4W and $v \neq 0$, $(x(t), T(t))$ tends to the corresponding equilibrium (x_1^*, T_1^*), but if $v = 0$, then after the temperature reaches 636.961 [K], $(x(t), T(t))$ has an other evolution and tends to (x_1^3, T_1^3). The effect of the evaporation can be observed only after the temperature reaches 636.961 [K]. For P=17W the phenomenon is similar and the effect of the evaporation can be observed only for T bigger than 914.556 [K].

5. Conclusion

In the considered nonisothermal model which describes the oxide layer thickness evolution and the sample temperature variation in the case of the vanadium oxide film growth in a cwCO_2 laser beam for a small sample it is possible compute and to establish the followings:

1. If the laser power P increases, then the equilibrium temperature $T^*(P)$ increases and $x^*(P)$ decreases at the beginning but after that increases.

2. The moment of time $t_0(P)$ when the 1nm oxide layer thickness is achieved is of order 10^{-9} [s], and is independent on the lasers power P.

3. The sample temperature $T(t_0(P))$ at the moment $t_0(P)$ is practically equal to the starting room temperature ($T' = 300$ [K]).

4. The moment of time $t_1(P)$ when the equilibrium temperature is achieved depends on P and decreases when P increases.

5. The oxide layer thickness $x(t_1(P))$ at the moment $t_1(P)$ depends on P and decreases when P increases.

6. The growth speed $v(t_0(P))$ at $t_0(P)$ is of order 10^{-1} [m/s] and the growth speed $v(t_1(P))$ at $t_1(P)$ due to evaporation is negative and it is of order $10^{-8} \div 10^{-9}$ [m/s].

7. The computed temperature variation and oxide layer thickness evolutions for P=4 [W] and P=17 [W] respectively are in a good agreement with the typical oscilogram of the sample temperature observed experimentally and with the two oxide types (VO and V_2O_5 respectively) reported in [7].

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