F. V. Bunkin, N. A. Kirichenko, and B. S. Luk'yanchuk. *Structures associated with laser oxidation of metals.* The dynamic features of thermochemical processes occurring in a laser radiation field are dictated by the combined effect of the chemical state of the medium and the space-time distribution of the thermal energy introduced into the medium on absorption of the laser radiation.[1,2] New (compared with classical macrokinetics) feedback channels are formed in the laser radition field between the chemical, thermal, etc., degrees of freedom of the system. By varying the parameters of the laser radiation (intensity, wavelength, etc.) it is possible to control the type of feedback and to form in a directed manner trigger, free-oscillatory, etc., active properties in a chemical medium which in the absence of laser radiation does not have such properties. Many self-organization phenomena can be modeled and studied experimentally more easily in such nonequilibrium chemical media than in other types of media.

In traditional macrokinetics the active properties of the chemical medium are formed by choosing the materials themselves, for example, the components of the Belousov-Zhabotinskiĭ reaction. In laser macrokinetics this is done by selecting the characteristics of the radiation to which the medium is exposed.

The nonlinear dynamics of thermochemical processes in laser macrokinetics depends not only on the characteristic features of the chemical interaction of the reagents, but also on their optical properties. This situation can be illustrated using the example of the dynamics of the reversible reaction $A \rightleftarrows B$ in a laser radiation field. The cross sections for the absorption of radiation by the substances A and B depend on the wavelength of the laser radiation and the temperature and pressure of the medium. For the visible or UV regions, where $\hbar\omega \gg kT$, the temperature dependence of the cross sections is insignificant. In the IR region, where $\hbar\omega \sim kT$, strong temperature dependence of the cross sections is characteristic for most molecules. This difference in the optical characteristics of media in the visible and IR regions makes the dynamic properties of the system under study qualitatively different. For example, when exposed to visible and IR radiation the medium does not exhibit free-oscillations.[3,4] In the case of IR radiation, however, soft and hard regimes of free oscillations are possible.[5]

In distributed systems active point-like elements interact with one another via the transport of matter, energy, charge, etc. The development of instabilities in such systems can be accompanied by the spontaneous appearance of dissipative structures. Problems of this type have usually been studied in macrokinetics and other disciplines for homogeneous media, consisting of identical active elements. Such structures have also been observed in laser macrokinetics.[2] An even wider class of self-organization phenomena can, however, be observed in inhomogeneous media, where the active elements are no longer identical. The development of this new direction in the theory of self-organization began only recently.

In laser macrokinetics attention is devoted primarily to self-organization in systems where the inhomogeneity is dictated by the spatial distribution of the intensity of the incident laser radiation. As a concrete chemical system we shall examine metals, which oxidize when heated by laser radiation in air. We shall point out some types of effects and structures observed in such systems.

a) Peaking and localization in problems of laser heating of metals

As a metal oxidizes its absorptivity A changes as the thickness of the oxide layer z increases. If $A'_z > 0$, positive feedback is established in the system between the chemical and thermal degrees of freedom, which leads to the development of thermochemical instability.[1] Calculations show (see Ref. 6) that when heat conduction and the inhomogeneous (Gaussian) distribution of the laser radiation intensity are taken into account thermochemical instability develops in the regime with compression of the thermal field (LS regime). Localized dissipative structures of this type were predicted earlier in the physics of combustion, plasma physics, etc. However we do not know of direct experiments on the observation of LS structures in physical systems, let alone quantitative comparison of theory and experiment. In laser macrokinetics, however, this problem is solved relatively simply.

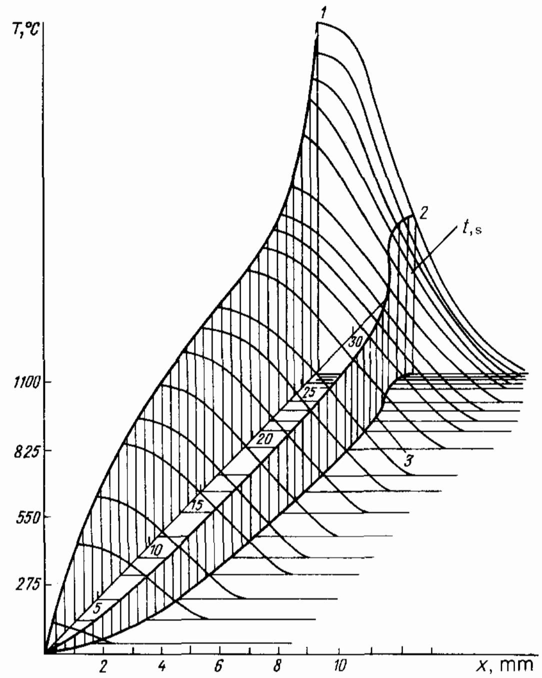

FIG. 1. The spatial profile of the temperature field in a titanium plate as a function of time as the plate is heated by a continuous 40 W CO_2 laser. The dimensions of the surface of the plate are 30×3 mm^2, and the plate is 0.5 mm thick. The radiation spot on the surface of the plate was an ellipse with the dimensions 6×0.5 mm. 1) The temperature $T(0,t)$ at the center of the radiation spot; 2) the temperature at the level $0.5T(0,t)$; 3) effective radius of localization of the temperature field at the level $0.5T(0,t)$.

Figure 1 shows an experimental graph of the structure of the thermal field under conditions of oxidation of a thermally thin strip of titanium exposed to continuous CO_2 laser radiation. The law of compression of the thermal field agrees well with the logarithmic dependence predicted for this one-dimensional case: $r_T(t) = r_0[\alpha + \beta \ln(1 - t/t_0)]^{-1}$, where r_0 is the radius of the Gaussian beam, t_a is the activation time of the instability at the center of the beam, and α and β are constants expressed in terms of the known parameters of the problem.[6]

b) Autostructures on the surface of sublimating oxides

The formation of oxides on the surfaces of some metals is accompanied by simultaneous sublimation of the oxide layer (for WO_3, for example, at temperatures $T > 800$ °C). Theoretical analysis and experiments show that by varying the laser radiation intensity the combination of oxidation and sublimation enables the formation of an active point-like element in such a medium, exhibiting slave, trigger, or free-oscillatory properties.[7] When the intensity distribution is nonuniform a system consisting of different types of active elements forms: for example, for some values of the intensity of a Gaussian beam the central region is passive, this is fol-

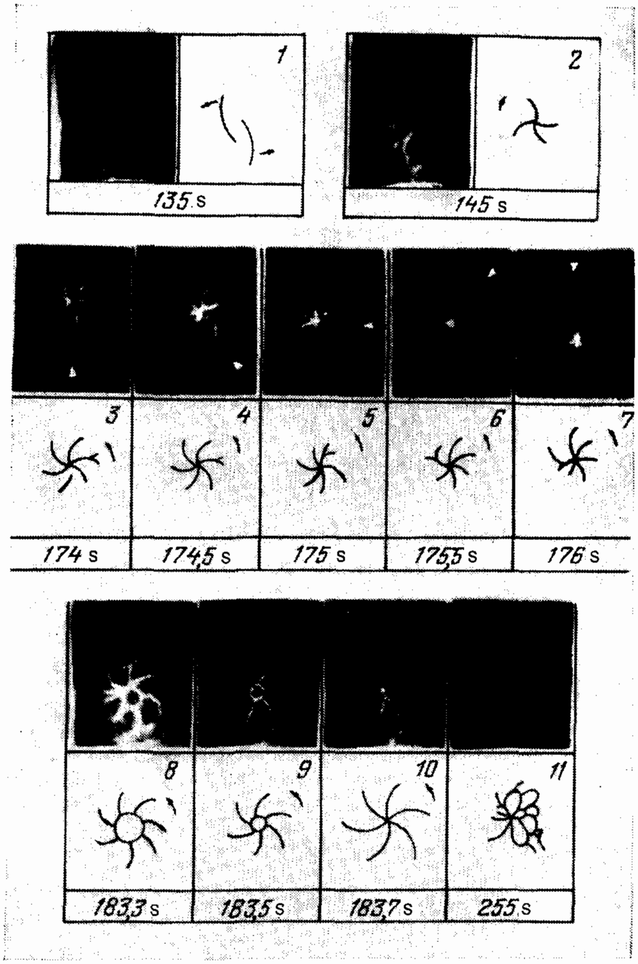

FIG. 2. Series of photographs of the surface of a vanadium target heated by a continuous 152 W YAG laser. The radiation beam is 24 mm in diameter, and the plate is 0.9 mm thick. The rotational frequency of the structure ≈ 0.25 Hz.

lowed by a ring of slave elements, which is followed by free-oscillatory elements, etc. The interaction of these elements via heat conduction leads to new types of self-organization of the system as a whole. The following phenomena were discovered in the numerical solution of some variants of this problem[8]: spatially localized free-oscillatory structures, noisy limit cycles, nontrivial laws governing the development of chaos (not described on the basis of Feigenbaum's ideas about the characteristics of one-dimensional images), spatial division of the frequency of free oscillations, etc. These calculations show that diverse dynamic regimes of the behavior of the system and diverse types of structures can be realized by forming with the help of laser radiation diverse spatial configurations of free-oscillatory, trigger, and other active zones.

c) Hydrodynamic structures on the surface of liquid oxides

Some oxides (for example, V_2O_5) melt at a lower temperature than the metal itself. Under laser heating hydrodynamic flows arise in the liquid oxide: volume (owing to convection in a nonuniformly heated liquid) and surface (owing to a change in the surface tension of the oxide). The competition between these flows in regions where they flow in different directions gives rise to the appearance of new types of structures (steady-state and non-steady-state), which differ from structures of the Benard or Marangoni cell type. Such structures were observed with laser heating of solutions of electrolytes[9] and liquid oxides.[10]

Figure 2 shows the structures observed in the case of oxidation of vanadium.[1)]

As the thickness of the oxide layer increases with time a cascade of bifurcations of the change in the number of arms of the spiral wave rotating around the axis of the laser beam is observed. The process terminates with the completion of a stationary cellular structure, formed with the "closing" of the arms of the spiral wave.

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