MODEL OF VAPOR-PHASE OXIDATION
OF METAL PARTICLES

V. I. Shevtsov

The problem of oxidation of metal vapor, which is usually accompanied by heterogeneous oxidation of the metal at high temperatures, is solved analytically. Expressions are proposed for the contribution of vapor-phase processes in the limiting cases: for the initial moment of oxidation at which oxide films are either very thin or still absent; and for transition of the oxidation process to a steady-state regime in which the oxide layer is so thick that gas-phase processes occur almost completely within the oxide layer. The obtained results can be used for a more precise determination of the mechanism of high-temperature oxidation of various metals and for an adequate interpretation of measurement results.

Use of various metals at high temperatures and over a wide range of pressures (for example, as a combustible in rocket propellants and in ramjets or as a reagent in high-temperature synthesis of new materials) requires information on the processes occurring during their high-temperature corrosion. This problem is most acute in calculation of the conditions of metal ignition using the available data on oxidation kinetics.

Naturally, the oxidation kinetics of metals in the high-temperature region has been studied at temperatures somewhat below the self-ignition points of the metals. It was quite reasonable to use thus obtained kinetic constants to calculate ignition with a certain extrapolation of these constants with respect to the ignition temperature. Nevertheless, even a small extrapolation of kinetic oxidation constants (for example, for magnesium even by a few tens of degrees) did not allow one to predict with reasonable accuracy self-ignition conditions. In this connection, rather probable but poorly founded concepts of a specific "preignition oxidation kinetics," of differences in the kinetics of "solid-phase and fluid-phase oxidation," of "the effect of first- and second-order phase transitions on oxidation" [3], etc. have appeared. All of these and some other processes affect in one or another way oxidation kinetics, but there is still no acceptable proof of their governing or, at least, correcting role in high-temperature corrosion.

To clarify these questions, experimenters determined the "kinetics of preignition oxidation" by an indirect method, i.e., kinetic data were determined by solution of the inverse problem using the results of investigation of metal ignition under various conditions assuming the applicability of the theory of thermal breakdown at the ignition moment [4, 5]. The instantaneous transition of metals from the heterogeneous oxidation regime upon ignition into the vapor-phase combustion regime could hardly fit into the available concept. This gave rise to a number of works on the possibility of such a transition and its stability from an energetic viewpoint [6–8].

In addition, even for relatively low temperatures (far below the ignition point) experimental facts were found that contradict the existing hypothesis that the classical heterogeneous oxidation mechanism is in one or another way determined by diffusion of reagents through the oxide film. Thus, beginning with a certain temperature, which is typical of each metal, through pores and cracks that did not disappear in subsequent
oxidation were found in oxide films. It is obvious that, from the viewpoint of heterogeneous diffusive oxidation, a jump in the oxidation velocity should occur at this moment. This, however, is not observed in practice, and the presence of through pores and cracks in the oxide film is simply ignored by the theory. It is not clear, for example, why for magnesium and beryllium the rates of metal evaporation of through pores and cracks coincide quantitatively with the oxidation rate (naturally, in conversion to the metal). Another fact to be explained is that a decrease in the oxidizing-medium pressure or a decrease in the oxidizer content of the medium produce a significant increase in the oxidation rate. Finally, it is doubtful that the coincidence of the activation energy of the oxidation process and the evaporation heat for some metals is accidental.

All of these and some features of the high-temperature oxidation of metals suggested that it is necessary to take into account the evaporation of the metal in the oxidizing atmosphere.

Zelenskii et al. [9] developed a rather convincing phenomenological model of vapor-phase oxidation as applied to magnesium. This allowed them to explain some previously incomprehensible phenomena, at least, at a qualitative level. The contribution of vapor-phase processes to the mechanism of magnesium oxidation and ignition for the limiting case (when the entire oxide resulting from metal-vapor oxidation remains on the particle surface) was qualitatively estimated in [3, 10]. It was found that in many cases of interest the rate of magnesium oxidation can be described only by vapor-phase processes, without involvement of heterogeneous oxidation. In this connection, the necessity of developing a quantitative theory of vapor-phase oxidation became even more acute. Actually this raises the question of the applicability of the classical model of high-temperature corrosion for the entire group of metals.

This work is intended to construct a quantitative mathematical model of vapor-phase processes in high-temperature oxidation of metals. It is obvious that in some cases the contribution of vapor-phase processes to the oxidation mechanism can be rather insignificant. Nevertheless, allowance for this contribution will lead to a clearer understanding of the role of these processes in each particular case and will help in interpreting experimental facts.

As a working hypothesis we chose the vapor-phase oxidation model proposed in [9]. Its essence is as follows. Beginning with a certain temperature, because of the difference in linear-expansion coefficients between the oxide film and the metal, through pores and cracks that do not disappear in subsequent oxidation appear in the film. The metal vapors diffuse inside the pores and react with an oxidizer which is supplied from the environment. The oxide formed inside the pores precipitates mainly on their walls. A portion of metal vapor that did not react inside the pores diffuses outward to the oxidizing atmosphere and reacts there. The oxide formed near the specimen surface is partly entrained, and the remaining part of the oxide precipitates on the surface and increases the thickness of the oxide layer. In a mathematical form this can be represented as

\[
\frac{dm}{dt} = \gamma \mu_k J_m - \mu_s J_s, \tag{1}
\]

where \( \frac{dm}{dt} \) is the rate of increase in mass, \( \gamma \) is the stoichiometric coefficient, \( \mu_k \) and \( \mu_s \) are the molecular masses of oxygen and the metal, \( J_m \) and \( J_s \) are the oxygen flux to the particles and the metal-vapor flux from the particle to space, respectively.

Hence, it is obvious that in measurements of only the increase in mass (namely this quantity is the main parameter in experimental determination of the oxidation kinetics of metals) one has no guarantee that the measurement results are adequate to the concepts of a heterogeneous diffusive oxidation mechanism. In any case, the assertions that a protective diffusive mechanism of oxidation exists require a more serious substantiation to eliminate other factors (e.g., vapor-phase processes) that can affect the measured parameters.

Thus, the stated problem is reduced to determination of the metal-vapor flux to the pores and the oxide-vapor flux to the environment. The solution of this problem for a finite-size specimen, for example, a metal particle in an oxidizing atmosphere, is of most interest for practice. Mathematical description of this model is a conjugate problem composed of two parts. The first (internal) part describes mass transfer and oxidation of metal vapor inside the pores. The oxide formed inside the pores precipitates on the walls. The second (external) problem describes mass transfer of metal and oxide vapors in the medium near the specimen surface. The statement of the problem is quasi-stationary.