ON CONDENSATION GROWTH OF OXIDE PARTICLES DURING GAS-PHASE COMBUSTION OF METALS

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Abstract

The work predicts that the rate of the oxide particle growth during the gas-phase combustion of metals decreases abruptly when the growing particle reaches the certain size. The character value of this size calculated in the work is in a satisfactory agreement with the experimentally observed sizes of oxides formed during the combustion.

Introduction

It is well known that the metal particle combustion can occur in two essentially different regimes. The first one (the so-called heterogeneous combustion) is realized by means of the metal oxidation on the metal particle surface. It is obvious that the size of the oxide particle formed during the heterogeneous combustion is close to the initial size of the burning-out metal particle. The second regime (the so-called gas-phase combustion) proceeds by three sequential steps: 1)metal vaporization; 2)oxidation of the metal vapor with the formation of the intermediate gaseous products of combustion; 3)condensation of the gaseous oxide with the formation of the ultrafine oxide particles. Unlike the first regime, the size of the oxide particles formed during the gas-phase combustion does not practically depend on the initial metal particle size and weakly depends on the burning metal. For example, for all metals (Mg, Al, Ti, Fe, Zr) investigated in [1] the average oxide particle size is about $0.03\text{-}0.1\ \mu m$. The independence of the oxide particles size on the ambient conditions allows to suppose that this size is the "character feature" of the condensation processes. The present work is devoted to the elucidation of the peculiarities of the condensation processes, which leads to the absence of the large oxide particles in the products of the gas-phase combustion of metals.

Without the loss of generality in the work it is considered the combustion of magnesium. The choice of magnesium is caused by the uniformity of the chemical formulas of the gaseous oxide and the condensed one. Also we take into account that magnesium oxide condensation occurs from the gas into the solid phase. However we believe that our conception can be used for the condensation description during combustion of some other metals.

By the condensation description we consider the processes accompanying the growth of the oxide particles. Such processes are following: 1)conductive heat transfer between the particle and the gas 2)particle radiation; 3)adsorption and desorption of the gaseous oxide molecules.

Conductive heat transfer between the ultrafine particles and the gas at high temperatures

Due to the small particle size the conductive heat transfer between the ultrafine particles and the gas occurs in the free-molecular regime. In this case the heat transfer can be described with the help of the so-called energy accommodation coefficient (EAC) α_E [2]. The heat flux from the particle in the gas can be written as

$$q = \frac{\alpha_E}{4} \cdot n_g v \cdot \left(\frac{C_v}{R} + \frac{1}{2} \right) \cdot k_B \cdot \left(T_p - T_g \right), \qquad (1)$$

here C_V is the molar gas heat capacity, R is the gas constant; k_B is the Boltzmann constant; T_p, T_g are the temperatures of the particle and the gas correspondingly; v is the gas molecule mean velocity and the gas molecule concentration

$$n_g = \frac{P}{k_B T_g} \ , \tag{2}$$

where P is the gas pressure. The exact calculation of the EAC value is an unsolvable problem. But the upper estimation of EAC can be obtained only on the base of the detailed balancing principle. This estimation [3] shows that the value of EAC is less than $\frac{1}{i+1} \cdot \frac{\Theta^2}{T_g T_p}$, where i is the number of degree of freedom of a gas molecule; Θ is the Debye temperature of the particle substance. For the typical combustion temperatures EAC is less than *1/600*. As we can see below such small value of EAC leads to the practical thermally isolation of the ultrafine oxide particles from the gas during the particle condensation growth.

Particle radiation

In accordance with the Stefan-Boltzmann law the radiation flux from the particle can be calculated as

$$I = \varepsilon \cdot \sigma T_p^4 \ . \tag{3}$$

For the small particles the particle emissivity ε depends on the particle size r [4]:

$$\varepsilon = A \cdot r \ . \tag{4}$$

The proportionality factor A can be calculated on the base of the Mie-Rayleigh scattering theory [4]. However, as it is shown in [5], the value of A calculated in this way is by an order of magnitude at least smaller than the one, which is necessary to explain the values of the radiation losses during combustion. In our opinion, this fact means that the radiation from the growing oxide particles is essentially nonequilibrium. But in the present work we do not discuss the radiation nonequilibrium. We use only the value of A, which corresponds to the experimentally observed [6] radiation fluxes. This value is about $A \approx 10^6 \ m^{-1}$.

Adsorption and desorption of the gaseous oxide molecules

The flow of the gaseous oxide molecules colliding with the surface of the growing oxide particle can be calculated as

$$j_{col} = \frac{1}{4} \cdot n_{ox} v_{ox} \ , \tag{5}$$

where n_{ox} is the gaseous oxide molecule concentration; v_{ox} is their mean velocity. The collision between the gaseous oxide molecule with particle surface does not mean that the molecule will be adsorbed. The adsorption process is the activated one and it contains of the physical adsorption and the chemical adsorption [7]. In this case, as it is shown in the present work, there are two necessary conditions for the gaseous oxide molecule adsorption: 1)the energy of the oxide molecule is less than the Debye energy of the oxide particle substance; 2)the sum of the energies of the gaseous molecule and of the molecule with which the gaseous molecule forms the bond is more than the activation energy of the adsorption. The calculation made in the present work gives following value to the probability of the adsorption:

$$\alpha_C \approx \frac{T_p}{T_p - T_g} \cdot \exp\left(-\frac{T_A}{T_P}\right) \cdot \left(1 - \exp\left(-\theta \cdot \left(\frac{1}{T_g} - \frac{1}{T_p}\right)\right)\right) , \tag{6}$$

where T_A is the temperature corresponding to the activation energy.

Therefore the flow of the adsorbed gaseous oxide molecules can be written as $j_{ads} = \alpha_C \cdot n_{ox} \cdot v_{ox}/4$. On the base of the detailed balancing principle we can write for the flow of the desorbed (vaporizing) molecules:

$$j_{vap} = \frac{\alpha_C}{4} \cdot n_{sat}\left(T_p\right) \cdot v_{ox} \ , \tag{7}$$

where $n_{sat}(T_p)$ is the concentration of the saturated oxide vapor at the particle temperature.

Heat balance on the growing particle surface

The density of the energy evolved on the surface of the growing particle can be written as

$$E = \left(j_{ads} - j_{vap}\right) \cdot \varepsilon_0 - q - I \ , \qquad (8)$$

where ε_0 is the energy of the gaseous oxide molecule adsorption (for MgO $\varepsilon_0 \approx 6eV$ [8]). The dependence of E upon the oxide particle temperature could be calculated numerically. This dependence is shown in Fig.1 for the different particle sizes at the typical temperature $T_g = 2600\ K$. As the rate of the condensation growth is less than the rate of the heat transfer in the particle we can assume that particle grows at the equilibrium temperature corresponding to $E=0$. As it can be seen from Fig.1 when the particle reaches the certain size its temperature changes abruptly. The dependence of the growing particle equilibrium temperature upon the particle size is shown in Fig.2. This dependence allows us to calculate the dependence of the rate of the particle growth ($w=dr/dt$) upon its size (see Fig.3).

Results and discussions

The calculation made in the present work shows that the temperature of the oxide particle growing during the gas-phase combustion decreases abruptly. It leads to the jump-in change of the rate of the particle growth. The latter one becomes the negligible when the particle reaches the certain size. As it seen from Fig.3 this size is about $0.1\ \mu m$.

The result obtained for MgO particles seems to be general. It apparently explains the absence of the large oxide particles in the products of the gas-phase combustion of metals.

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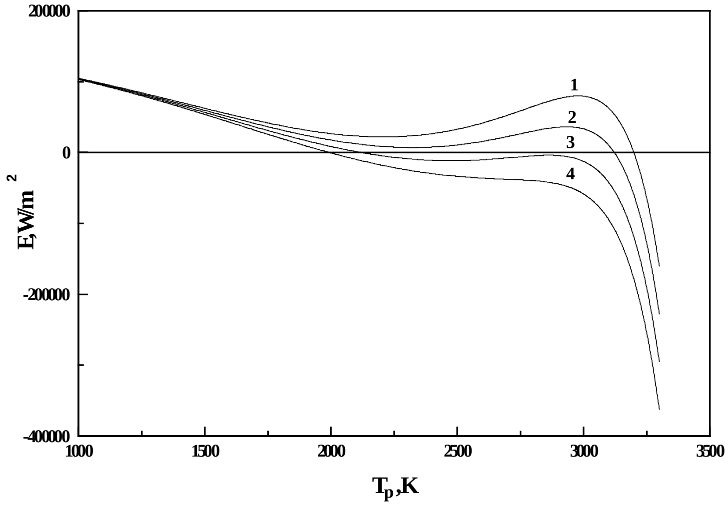

Fig.1. The dependence of the density of the energy *E* evolved on the surface of the growing particle upon the particle temperature T_p for the different particle sizes *r*: 1 - 0.05μm; 2 - 0.06 μm; 3 - 0.07 μm; 4 - 0.08μm.

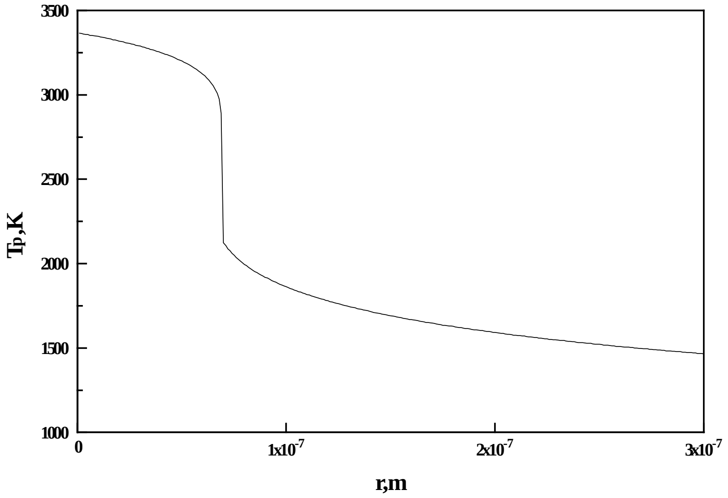

Fig.2. The dependence of the equilibrium particle temperature T_p upon the particle size *r*.

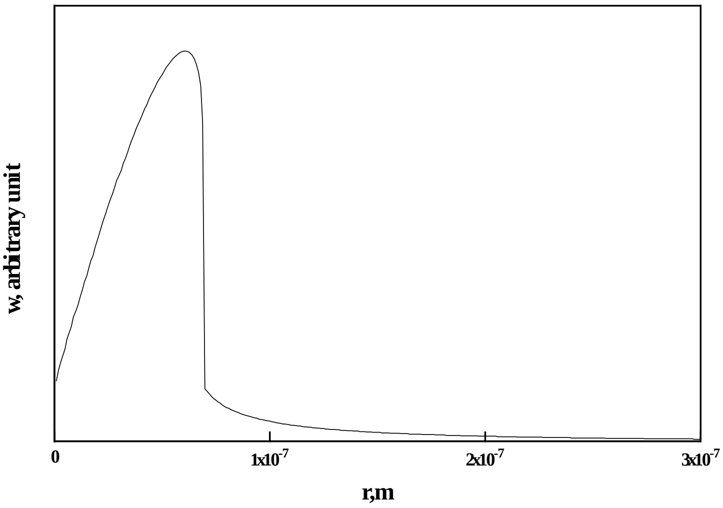

Fig.3. The dependence of the rate of the particle growth *w* upon the particle size *r*.