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A Modified Model of the Ignition of a Magnesium Particle

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Abstract—A model of the ignition of an isolated magnesium particle in an oxidative atmosphere is suggested. The model takes into account the nonstationary character of the heat flux onto the surface of the particle and the nonuniformity of temperature distribution inside the particle. Calculations were performed to demonstrate the influence of these factors on the macrokinetic parameters of the empirical law of the oxidation of magnesium particles and the time characteristics of their ignition in hot air at atmospheric pressure.

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INTRODUCTION

The problem of the ignition and combustion of magnesium particles is of great importance for many applications, including the aerospace industry. For instance, magnesium is considered a promising rocket fuel component for Mars missions. The ignition and combustion of isolated magnesium particles have been the object of many studies directed toward the experimental determination of critical conditions [1–4] and the mechanisms of chemical reactions [5–8] and the development of mathematical models of the process [9–15].

An analysis of the literature data shows that several problems have remained unsolved. One of the key problems is the absence of a clear understanding of the mechanism of the preflame oxidation of magnesium, which hinders the construction of a correct model of the ignition of a particle. The problem of determining the effective kinetic parameters of empirical oxidation laws is no less important. According to [3, 9, 11, 12, 14], the effective activation energy obtained by comparing calculation results with experimental data [1, 2] can be from 18 to 48 kcal/mol.

According to [5], magnesium is ignited under kinetic control conditions over the whole range of air temperatures of importance for practical applications irrespective of the intensity of heat exchange. This is related to the loose structure of the oxide film, which does not hinder the diffusion of oxygen to the metal. It was, however, observed [6, 7] that, at the initial stage of particle heating, a dense oxide layer was formed on its surface (this layer was called “black oxide film” [7]), which cracks upon the attainment of a certain critical thickness. The critical thickness of the oxide layer is determined by the temperature of the medium, the content of oxygen in it, and the size of the particle [7]. It follows that the active oxidation of the metal can only begin after the cracking of the black oxide film; that is,

it depends on particle temperature changes during its heating.

Nonstationary heat exchange with the surrounding gas is as a rule modeled using the Newton heat transfer law [15], which is only valid for steady-state heat exchange. The admissibility of the application of the Newton law to the nonstationary problem of heat exchange between a spherical particle and gas was checked in [16] by comparative calculations for three models, standard, conjugated, and modified. The standard model used the Newton law. Calculations according to the conjugated model involved solving heat conduction equations in the gas phase and particle followed by joining the solutions together on the surface of the particle. The modified model approximately took into account the time dependences of the heat transfer coefficient and the temperature of the surface of the particle. A comparison of the standard model with the numerical solution of the conjugated problem showed [16] that the use of the standard model led to substantial errors in the calculated time dependence of the mean temperature of the particle. For instance, according to the standard model, the temperature of a spherical magnesium particle of diameter 70 μm placed into air heated to 1600 K increases from 293 to 723 K in 4 ms. The latter temperature is close to the so-called transition temperature considered [17] to be the minimum possible for the ignition of a magnesium particle in air. According to the conjugated and modified models, the temperature of the same magnesium particle under the same conditions only increases to 536 K. This error in calculations by the standard model (187 K!) can influence the time characteristics of ignition even if the simplest linear oxidation law [12] is used, which ignores the influence of oxide film growth on the mean particle temperature.

To determine the effective kinetic parameters of the law of metal particle oxidation using the best fit of calculation results to experimental data as a criterion, we

must know the heat transfer coefficient [15]. It follows from [16] that the heat transfer coefficient for a nonstationary process can be substantially different from the value used in the Newton law. It follows that the effective kinetic parameters obtained without taking into account the nonstationary character of the process must be refined.

The purpose of this work was to create a new mathematical model of the ignition of a magnesium particle in air with the inclusion of nonstationary heat exchange and inhomogeneous temperature distribution inside the particle and to apply this model for solving the direct and inverse problems of magnesium particle ignition.

PROBLEM STATEMENT

Standard Model

The standard model of the ignition of an immobile spherical magnesium particle in air at rest [14, 15] is based on the equations

$$cm \frac{d\bar{T}}{dt} = \alpha S (T_{g\infty} - \bar{T}) + Sq\rho_{ox} \frac{dh}{dt}, \quad \bar{T}(0) = T_0, \quad (1)$$

$$\frac{dh}{dt} = K \exp\left(-\frac{E}{R_{Mg}\bar{T}}\right), \quad h(0) = 0, \quad (2)$$

where t is the time, \bar{T} is the mean particle temperature, $T_{g\infty}$ is the temperature of air, $\alpha = Nu\lambda_g/d$ is the heat transfer coefficient, $Nu = 2$ is the Nusselt number, λ_g is the heat conductivity coefficient of air, $d = 2R$ is the diameter of the particle, R is the radius of the particle, S is the surface area of the particle, m is the mass of the particle, c is the heat capacity of the material of the particle, h is the oxide film thickness, q is the heat effect of the reaction per unit mass of magnesium oxide, ρ_{ox} is the oxide film density, K is the effective preexponential factor, E is the effective activation energy, T_0 is the initial temperature of the particle, $R_{Mg} = R_u/\mu_{Mg}$ is the gas constant for magnesium, R_u is the universal gas constant, and μ_{Mg} is the molecular weight of magnesium.

In oxidation law (2), the rate of oxide film growth is independent of its thickness. Model (1), (2) therefore reduces to one equation for the mean temperature of the particle,

$$cm \frac{d\bar{T}}{dt} = \alpha S (T_{g\infty} - \bar{T}) + Sq\rho_{ox} K \exp\left(-\frac{E}{R_{Mg}\bar{T}}\right), \quad (3)$$

$$\bar{T}(0) = T_0.$$

Modified Model

The modified model of heat exchange between metal and gas suggested in [16] can easily be extended

to the problem of the ignition of a spherical magnesium particle in air. Equation (1) is then replaced with

$$cm \frac{d\bar{T}}{dt} = \alpha_{ef} S (T_{g\infty} - T_i) + Sq\rho_{ox} \frac{dh}{dt}, \quad \bar{T}(0) = T_0, \quad (4)$$

where

$$\alpha_{ef} = \lambda_g [1 + (R^2/\pi a_g t)^{1/2}] R^{-1}$$

is the effective heat transfer coefficient depending on time, $a_g = \lambda_g(T_i)R_g T_i/c_p(T_i)p_0$ is the thermal diffusivity of air, $\lambda_g = \sum_{j=0}^2 g_j T_i^j$ is the heat conductivity coefficient of air ($g_0 = 0.003401$, $g_1 = 8.225e-5$, and $g_2 = -1.633e-8$), $c_p = 945.2 + 0.186T_i$ (J/(kg K)) is the isobaric heat capacity of air, T_i is the particle surface temperature (K), R_g is the gas constant of air, and p_0 is the atmospheric pressure. Note that the equation for α_{eff} is based on the analytic solution to the nonstationary spherical heat conductivity problem in a semilimited medium with $a_g = \text{const}$, $T_i = \text{const}$, and $T_{g\infty} = \text{const}$. This solution was successfully used in [16] to approximately solve the problem of heat exchange between a metallic particle and air taking into account thermo-physical property variations at $T_i \neq \text{const}$ and $T_{g\infty} = \text{const}$. The equation for λ_g was obtained by approximating the tabulated data [18].

Equation (4) is augmented by Eq. (2) for oxide film growth written as [11]

$$\frac{dh}{dt} = K \bar{c}_{ox}^n \exp\left(-\frac{E}{R_{Mg}T_i}\right), \quad (5)$$

where \bar{c}_{ox} is the weight fraction of oxygen in air ($\bar{c}_{ox} = 0.23$) and n is the order of the reaction of magnesium oxidation with respect to oxygen ($n = 1$).

Note three important differences between (4), (5) and (1), (2). First, the α heat transfer coefficient is replaced in (4) and (5) by the α_{eff} effective heat transfer coefficient. Next, instead of the $T_{g\infty} - \bar{T}$ difference, the $T_{g\infty} - T_i$ difference is used, which includes the particle surface temperature T_i . Lastly, the \bar{c}_{ox} oxygen concentration in air is explicitly included in (5) [15].

By analogy with (1), (2), system (4), (5) can be reduced to one differential equation,

$$cm \frac{d\bar{T}}{dt} = \alpha_{ef} S (T_{g\infty} - T_i) + Sq\rho_{ox} K \bar{c}_{ox}^n \exp\left(-\frac{E}{R_{Mg}T_i}\right), \quad (6)$$

$$\bar{T}(0) = T_0.$$

Equation (6) must be augmented by the following approximate equation for calculating the dimensionless particle surface temperature $\Theta_i = T_i/T_0$ [16]:

$$\Theta_i = \sum_{j=0}^3 b_j \bar{\Theta}^j, \quad (7)$$

Table 1. Thermophysical properties and ignition constants [14]

Substance	λ , W/(m K)	c , J/(kg K)	ρ , kg/m ³	Reaction	q , MJ/kg	K , m/s	E , MJ/kg
Mg	100.0	1100.0	1700	Mg + O ₂	49	0.103	4.288
MgO	58.0	803.0	3600				
Air*	0.0257	999.7**	1.2				

*At $T_0 = 293.15$ K.

**Isobaric heat capacity.

where $\bar{\Theta} = \bar{T}/T_0$ is the dimensionless mean temperature of the particle and b_j denotes the coefficients of the polynomial obtained in [16] by processing the results of the numerical solution to the conjugated heat exchange problem. To use (7) in the problem of the ignition of a magnesium particle, the applicability range of this equation was extended to $\bar{\Theta} \approx 7$. The following b_j values were obtained: $b_0 = 0.018809312$, $b_1 = 0.9888$, $b_2 = 2.311276682 \times 10^{-3}$, and $b_3 = -1.585948717 \times 10^{-4}$.

DIRECT PROBLEM

Model (6), (7) was checked by solving the problem of the ignition of a spherical magnesium particle ($R = 22 \mu\text{m}$) at atmospheric pressure and various air temperatures $T_{g\infty}$. The thermophysical characteristics of magnesium and magnesium oxide and the effective kinetic parameters of the law of oxidation [14] used in the calculations are listed in Table 1.

The calculations were performed for two models, modified (Eqs. (6) and (7)) and standard (Eq. (3)). For

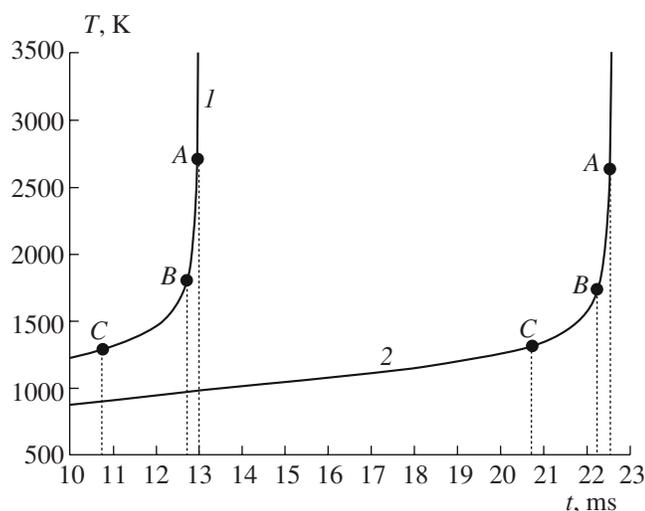


Fig. 1. Calculated time dependences of the mean temperature of magnesium particles at $R = 22 \mu\text{m}$ and $T_{g\infty} = 1323$ K; curves 1 and 2 correspond to the modified and standard models, respectively; A, $d\bar{T}/dt \approx 10^7$ K/s; B, $d\bar{T}/dt \approx 10^6$ K/s; and C, $d\bar{T}/dt \approx 10^5$ K/s.

the standard model, the problem was solved at a constant air heat conductivity coefficient ($\lambda_g = 0.0257$ W/(m K) [14]) and at a variable coefficient taking into account its dependence on the temperature $(\bar{T} + T_{g\infty})/2$ [15]. During calculations, we tracked changes in the mean particle temperature and determined the ignition lag t_{ign} .

The calculated time dependences of the mean particle temperature at $T_{g\infty} = 1323$ K obtained using the modified (curve 1) and standard (curve 2) models are by way of example shown in Fig. 1. The ignition lag was conventionally understood as the time moment at which the calculated rate of the growth of the mean particle temperature $d\bar{T}/dt$ reached the “critical” value 10^7 K/s. This ignition criterion was selected because, at higher critical $d\bar{T}/dt$ values, the ignition lag value remained almost unchanged. For instance, for curve 1, the criterion $d\bar{T}/dt = 10^7$ K/s gave $t_{ign} \approx 13$ ms. A decrease in the critical $d\bar{T}/dt$ value by one and two orders of magnitude (to $d\bar{T}/dt = 10^6$ and 10^5 K/s, respectively) changed the ignition lag by 2 and 14%, respectively. It follows from Fig. 1 that, at $T_{g\infty} = 1323$ K, the ignition lags calculated by the modified and standard models differed by almost two times.

Note that, for magnesium particles, Eq. (7) gave a mean particle temperature \bar{T} that differed only insignificantly from the surface temperature T_i . For instance, under the conditions of curve 1 in Fig. 1, the largest difference between these temperatures was 2–3 K.

The dependences of the ignition lag on the temperature of air obtained using the standard (curves 1 and 2) and modified (curve 3) models are shown in Fig. 2. The calculations showed that the inclusion of nonstationary heat exchange between the particle and gas influenced the ignition lag in a complex way. At high air temperatures, the new model predicts much shorter ignition delay times, whereas, at low temperatures, it increases ignition lags substantially compared with the standard model (curves 1 and 3). In the new model, the highest air temperature at which magnesium particle ignition was not observed was higher by about 20 K (1053 K) than in the standard model (1023 K).

These special features of the new model are well seen in Fig. 3, which displays the time dependences of the summed heat flux density onto the surface of a mag-

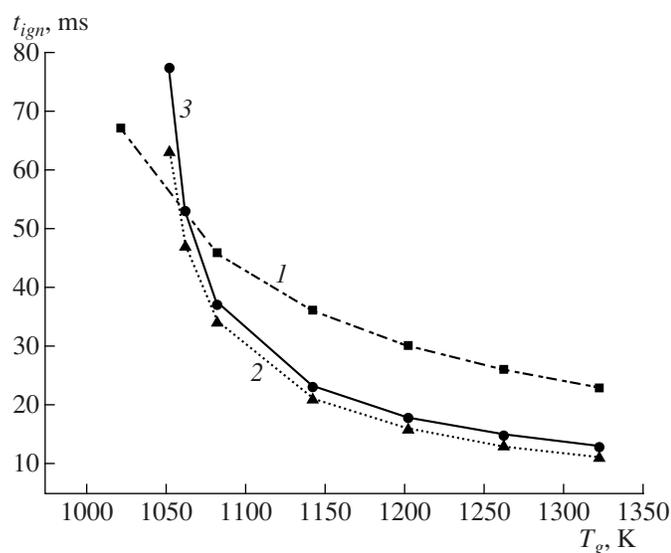


Fig. 2. Calculated dependences of ignition lag for spherical Mg particles on air temperature at atmospheric pressure ($R = 22 \mu\text{m}$): (1) standard model, $\lambda_g = \text{const}$; (2) standard model, $\lambda_g = f([\bar{T} + T_{g\infty}]/2)$; and (3) new model.

nesium particle q_Σ (the right-hand sides of (3) and (6) reduced to unit particle surface area) calculated using the new and standard models. Unlike the standard model, the new model predicts nonmonotonic changes in the total heat flux onto the surface of a particle during the initial period of heating, and the $q_\Sigma(t)$ curves contain local maxima (Fig. 3, curves 1 and 1'). The presence of the local maxima is explained by the nonmonotonic time dependence of the α_{eff} effective heat transfer coefficient (Fig. 4). After passing a maximum, the q_Σ value in Fig. 3 decreases for some time largely because of particle heating (a decrease in the $T_{g\infty} - T_i$ temperature difference) and then grows because of a progressing increase in the rate of the chemical reaction, which leads to particle ignition. Curve 1 (Fig. 3) does not contain a $q_\Sigma(t)$ increase stage. An analysis showed that, in this case, the direction of heat exchange between gas and the particle changed. The particle surface temperature became higher than the gas temperature ($T_i > T_{g\infty}$), and heat transfer from the particle into the environment balanced the second term on the right-hand side of (6). Such a situation can be classified as the absence of ignition. The possibility of such stationary states was noted in [19].

Ignition lags calculated according to the standard model with a variable heat conductivity coefficient ($\lambda_g = f([\bar{T} + T_{g\infty}]/2)$) more closely agree with the ignition lags calculated according to the new model (see Fig. 1) than calculations by the standard model with a constant heat conductivity. However, note that the use of variable λ_g contradicts the assumption $\text{Nu} = \text{const} = 2$, which implies that the α heat transfer coefficient is constant.

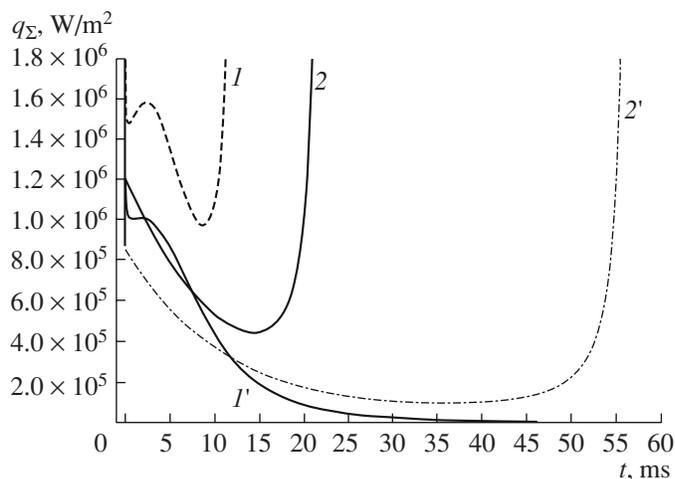


Fig. 3. Calculated time dependences of the total heat flux density onto the surface of a spherical magnesium particle for ignition in air: (1) new model, $T_{g\infty} = 1323 \text{ K}$; (1') new model, $T_{g\infty} = 1023 \text{ K}$; (2) standard model, $T_{g\infty} = 1323 \text{ K}$; and (2') standard model, $T_{g\infty} = 1023 \text{ K}$.

INVERSE PROBLEM

The new model of the ignition of magnesium particles in air can be used to determine the effective kinetic parameters of the law of the oxidation of a metal particle by fitting the calculation results to the experimental data, for instance, from [1] (Table 2). The kinetic parameters of the law of metal oxidation were calculated as follows:

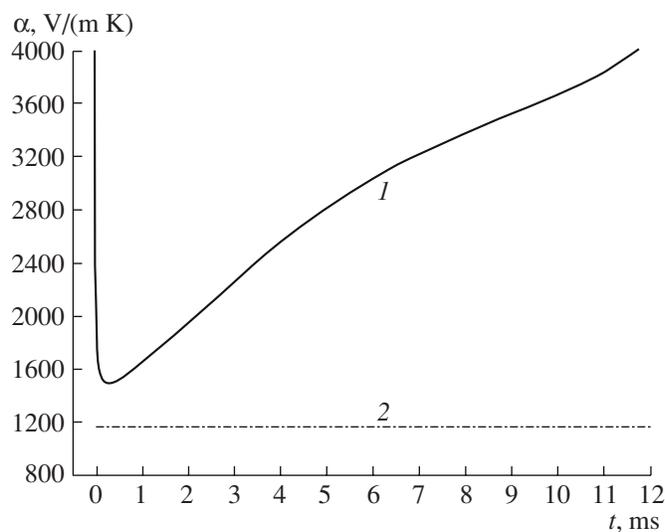


Fig. 4. Time dependences of heat transfer coefficient α for the ignition of a magnesium particle in air ($T_{g\infty} = 1323 \text{ K}$) calculated using the (1) new ($\alpha = \alpha_{\text{eff}}$) and (2) standard ($\alpha = \lambda_g/R = \text{const}$) models.

Table 2. Limiting ignition temperature of magnesium particles [1]

No.	$d, \mu\text{m}$	T_{gl}, K
1	15	1055
2	20	1014
3	25	986
4	30	969
5	36	953
6	40	942
7	46	932
8	50	924
9	56	919

Table 3. Effective kinetic parameters E and K for the ignition of isolated magnesium particles in hot air

$K, \text{m/s}$	$E, \text{MJ/kg}$	$\pm\Delta E, \text{MJ/kg}$	Source
0.103	4.288	–	[14]
1.391	4.345	0.114	this work

(1) For all pairs of experimental values i, j from Table 2, the E_{ij} effective activation energy was calculated by the equation [15]

$$E_{ij} = \frac{R_{\text{Mg}} T_{gl_i} T_{gl_j}}{T_{gl_i} - T_{gl_j}} \ln \left(\frac{\alpha_{ef_i}(T_{s_i}, t(T_{s_i})) T_{gl_i}^2}{\alpha_{ef_j}(T_{s_j}, t(T_{s_j})) T_{gl_j}^2} \right), \quad (8)$$

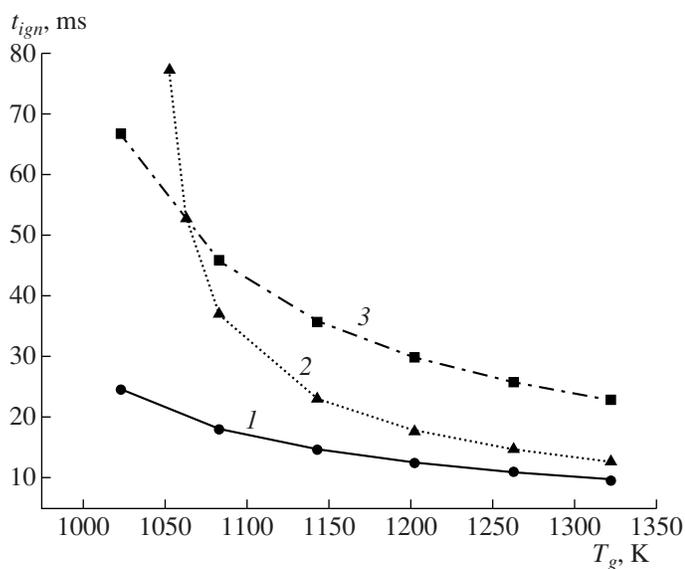


Fig. 5. Time dependences of Mg particle ignition lag ($R = 22 \mu\text{m}$): (1) new model with refined E and K (Table 3), (2) standard model with E and K from [14], and (3) new model with E and K from [14].

where T_{gl} is the air temperature at the ignition limit (Table 2), $T_s = T_{gl} + (R_{\text{Mg}} T_{gl}^2 / E_{ij})$ is the particle surface temperature at the ignition limit, and $t(T_s)$ is the time of the attainment of temperature T_s , which is represented in the form

$$t(T_s) = (\Theta_s - 1) \left(\sum_{k=0}^l p_k \Theta_s^k \right). \quad (9)$$

Here, l is the degree of the polynomial, p_k denotes its coefficients, and $\Theta_s = T_s / T_0$ is the dimensionless temperature of the surface of the particle at the ignition limit. System (8), (9) was solved by the method of successive approximations.

(2) The mean effective activation energy E was found as the mathematical expectation of the array of E_{ij} values.

(3) The root-mean-square deviation from the mean activation energy ΔE was determined.

(4) The mean effective activation energy found and an arbitrary experimental air temperature value (Table 2) were used to determine the effective preexponential factor K as

$$K = \frac{\alpha_{eff} R_{\text{Mg}} T_i^2}{q \rho_{ox} \bar{c}_{ox}^n E} \exp \left(\frac{E}{R_{\text{Mg}} T_i} - 1 \right). \quad (10)$$

The p_k coefficients were found using the numerical solution to the conjugated problem of conductive heat exchange between metal and other material particles and air under various initial conditions [16]. The calculations showed that the approximation of the numerical solution by Eq. (9) gave satisfactory accuracy (no worse than 3%) when a second-degree polynomial ($l = 2$) with the coefficients $p_0 = 0.045$, $p_1 = -0.012$, and $p_2 = 0.0009134$ was used.

Table 3 contains the effective kinetic parameters E and K characterizing the ignition of isolated magnesium particles in heated air. These parameters were calculated using the procedure described above. We see that the effective activation energy is close to the value obtained in [14]. The effective preexponential factor K is, however, an order of magnitude larger than in [14]. Even if we take into account that an explicit dependence of the rate of oxidation on the \bar{c}_{ox} concentration of oxygen is introduced into the new model, the K values remain different (by a factor of about 3).

DIRECT PROBLEM WITH REFINED PARAMETERS

The calculated dependences of the ignition lag on the temperature of air are shown in Fig. 5. These dependences were obtained using the new model and the

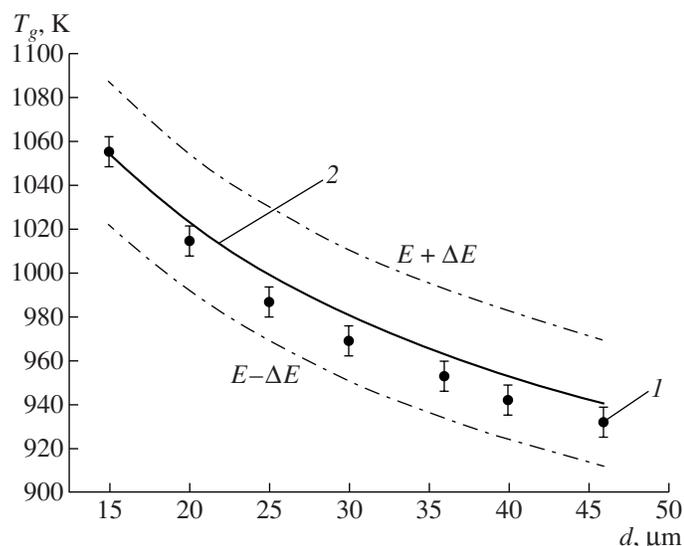


Fig. 6. Comparison of calculated and measured [1] limiting ignition temperatures of spherical magnesium particles of different sizes: (1) experiment [1] and (2) new model with refined E and K values (Table 3).

refined E and K parameters from Table 3 (curve 1). For comparison, curves 2 and 3 obtained for the standard and new models, respectively, with the kinetic parameters from [14] are also given (also see Table 3). Figure 5 shows that the refinement of the kinetic parameters considerably decreased the ignition lag of magnesium particles at comparatively low temperatures (1025–1150 K).

Unfortunately, data of direct measurements of ignition lags for magnesium particles in air are unavailable. There are only the experimental data [1] on the limiting temperature of ignition of particles of various sizes (see Table 2). Although the experimental results obtained in [1] were used to determine the refined kinetic parameters, we deemed it reasonable to directly compare the results of calculations by the new model with the data from [1]. Such a comparison is presented in Fig. 6. The solid curve corresponds to calculations with the refined E and K values, and symbols, to the experimental data from [1]. The band between the dot-and-dash lines in Fig. 6 corresponds to the uncertainty of the calculated limiting ignition temperatures caused by the root-mean-square deviation ($\pm\Delta E$) of the effective activation energy (see Table 3). We see that the results obtained using the new model with the refined effective kinetic parameters satisfactorily agree with the experimental data [1].

CONCLUSIONS

We comparatively studied two models of the ignition of spherical magnesium particles, the standard model [14] based on an ordinary differential equation for the mean temperature of particles and the Newton

heat transfer law and the new model. The main distinguishing features of the new model are the use of the effective heat transfer coefficient and particle surface temperature in the Newton law and the particle surface temperature in the macrokinetic law of the oxidation of metals. A comparison of the results of calculations according to the new model with the available experimental data was performed to refine the effective kinetic parameters, the preexponential multiplier K and activation energy E , in the law of magnesium oxidation, $K = 1.391$ m/s and $E = 4.345 \pm 0.114$ MJ/kg. Calculations of ignition lags for spherical magnesium particles 44 μm in diameter at various air temperatures and atmospheric pressure showed that the new model with the refined kinetic parameters predicted substantially shorter (by 2.4–2.7 times) ignition lags compared with the standard model over the temperature range 1023–1323 K. The new model of the ignition of magnesium particles can be readily used in multidimensional calculations of rocket engine combustion chambers.

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