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THE EFFECT OF A CONSTANT ELECTRIC FIELD ON THE COMBUSTION WAVE OF SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS. A MODEL OF A MEDIUM OF INTERACTING DIFFUSION PAIRS

I. M. Kotin

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The study was carried out to investigate the effect of a constant electric field (CEF) on the parameters of the combustion wave of self-propagating high-temperature synthesis. A model of a medium that consists of interacting diffusion pairs is used. It is found that the combustion rate increases with an increase in the CEF (Joule heat is neglected); the combustion temperature remains unchanged under the action of the CEF. The possibility of experimental detection of the effect of a CEF is discussed.

In self-propagating high-temperature synthesis (SHS) it is possible to obtain various kinds of materials such as metal borides, metal salicylides, intermetallides, high-temperature and ordinary superconductors, etc. It should be noted that the conditions of synthesis affect the structure and properties of the materials produced [1] and are characterized, in particular, by combustion temperatures and a combustion wave velocity. Various external actions (a magnetic field [2], ultrasonic vibrations [3], mass forces [4], etc.) affect these parameters of the combustion wave, thereby changing the synthesis conditions.

According to experimental results of [5], direct current that passes through a flat diffusion pair (DP) changes the absolute values and ratios of the thicknesses of phases that grow in the diffusion zone in comparison with the case without current, i.e., the current changes the growth rates of these phases. It is also found that the actions of currents of different directions are different. Using these data and the theoretical results of [6] on the effect of a constant electric field (CEF) on the kinetics of growth of the intermediate product in a single-phase system, in [7] we considered the effect of a CEF on the SHS combustion wave. Use was made of a medium consisting of independent flat DP. Diffusion pairs of only two orientations relative to the direction of the field were considered: 1) the field increases the diffusion mass transfer rate as much as possible (positive orientation) and 2) the field decreases the diffusion mass transfer rate as much as possible (negative orientation). The CEF was assumed to be generated by direct electric current that passed through a specimen; the Joule heat was neglected. It is found that there is a threshold value of the electric field up to which any increase in the CEF does not change the combustion temperature; after the threshold value is exceeded, the combustion temperature starts to decrease. This can be explained by incomplete reaction in negatively oriented DP. The combustion rate decreases as the CEF increases even at its pre-threshold values. Since the results given above are obtained within a model of a medium consisting of independent DP, while in real SHS mixtures the pairs certainly contact one another, it is necessary to consider a model of a medium of interacting DP.

The reaction medium is assumed to consist of first DP that are equal in size and composition and have only one of the two orientations mentioned above. DP of different orientations alternate and are tightly pressed to one another (see Fig. 1).

In the presence of a CEF in the medium, the system of equations that describes the propagation of a plane steady-state combustion wave has the following form (the Joule heat and thermoelectric effects are neglected) (see [7]):

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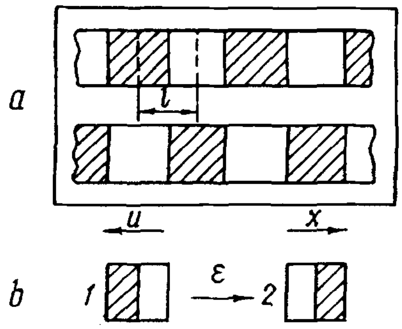

Fig. 1. Model of heterogeneous medium (a) and orientation of diffusion pairs (b): positive (1) and negative (2).

$$u\frac{dT}{dx} = \kappa\frac{d^2T}{dx^2} + \frac{Q}{2c\rho}u\frac{d}{dx}(\eta_+ + \eta_-)\,;$$

$$u\left(d\eta_+/dx\right) = k_0 \exp\left\{-E/RT\right\}\left[(1/\eta_+) + (T_e/T)\right]\,; \tag{1}$$

$$u\left(d\eta_-/dx\right) = k_0 \exp\left\{-E/RT\right\}\left[(1/\eta_-) - (T_e/T)\right]$$

with the boundary conditions: $x \to -\infty$: $T = T_0$, $\eta_+ = \eta_- = 0$; $x \to \infty$: $T = T_c$, $\eta_+ = \eta^*_-$, $\eta_- = \eta^*_-$. Here u is the combustion wave velocity; x is the coordinate (the axis x is opposite in direction to u and perpendicular to the plane of the wave front; $T_0(T_c)$ is the initial (maximum) temperature in the combustion wave; $T_e = |\mathcal{E}e^*|lc'/(k_B\Delta c)$; $\mathcal{E}$ is the CEF intensity; e^* is the effective charge of ions of the most mobile component in the intermediate phase [8]. It should be noted that here diffusion transfer of ions of components in the presence of electric current in the medium, i.e., electric diffusion, is meant. Electric current is predominantly caused by motion of electrons and holes in the medium. The effect of an electric field on diffusing ions is determined by two factors: the direct action of the field on the ion charge and the "electronic wind" force [8]. This force is caused by interaction of moving charge carriers with ions. For ions the presence of both factors is included phenomenologically by introduction of the effective charge e^*, which, as a rule, does not coincide with the true charge. The effective charge is either determined experimentally [9] or estimated theoretically [8].

Assuming that the thickness l of the pairs is small in comparison with the width of the heating zone, it can be stated that at any time, in the neighboring positive and negative pairs temperatures differ but slightly ($l|\nabla T| \ll T$). Therefore, it is assumed that in these pairs mass transfer and phase formation processes take place at the same temperature.

Since in the presence of a CEF in positive DP the growth rate of the product is higher in comparison with the case without a CEF, while in negative DP it is lower, a layer of the product from the positive DP passes through the formal boundary between the negative and positive pairs. Moreover, in a rather strong CEF, growth of the product in the negative DP is stopped, and the rest of the material in these pairs reacts due to the presence of contact with positive DP. Thus, in the adopted model of the medium, reactants are transformed completely at any value of the CEF. Therefore, in view of the last statement and the mentioned approximate equality of temperature conditions in neighboring positive and negative DP, satisfaction of the following conditions can be required

$$\eta^*_+ + \eta^*_- = 2\,. \tag{2}$$

It corresponds to cycling of neighboring positive and negative DP.

The first integral exists for the first equation in system (1):

$$\frac{dT}{dx} = \frac{u}{\kappa}\left[T - T_0 - \frac{Q}{2c\rho}(\eta_+ + \eta_-)\right]\,, \tag{3}$$

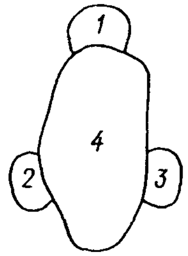

Fig. 2. Configuration of powder particles (see explanations in text).

whence, in view of the second boundary condition for systems (1) and (2), we obtain $T_c = T_0 + Q/(c\rho)$, i.e., the combustion temperature is independent of the value of the CEF.

In order to find the combustion rate, use will be made of an approximation of a narrow reaction zone. Then, with account of (3), the two last equations from (1) are written in the form:

$$d\eta_+/d\eta_- = [(1/\eta_+) + \alpha_e]/[(1/\eta_-) - \alpha_e]; \qquad (4)$$

$$\frac{u^2}{\kappa}(d\eta_+/dT)\left[T_c - T_0 - \frac{Q}{2c\rho}(\eta_+ + \eta_-)\right] = k_0 \exp\left\{-E/RT\right\}[(1/\eta_+) + \alpha_e]$$

with the boundary conditions: $T = T_0$: $\eta_+ = \eta_- = 0$; $T = T_c$: $\eta_+ = \eta_+^*$, $\eta_- = \eta_-^*$; here $\alpha_e = T_e/T_c$.

Solving system (4) with the boundary conditions, we obtain:

$$u^2(\alpha_e) = u_0^2 [I(\alpha_e)]^{-1},$$

$$I(\alpha_e) = 3\int_0^{\eta_-^*} \eta_-(2 - \eta_- - \eta_+)(1 - \alpha_e\eta_-)^{-1}\, d\eta_- = 6\alpha_e^{-2} \ln [\alpha_e^{-1} \operatorname{sh} \alpha_e].$$

In calculation of $I(\alpha_e)$ we took into consideration the first equation from (4) and the value $\eta_-^* = \alpha_1^{-1} + 2[1 - \exp(2\alpha_e)]^{-1}$, which is found from (2) and the solution of the first equation from (4) with the initial condition $\eta_+(\eta_- = 0) = 0$.

It can be shown that $I(\alpha_e)$ is a decreasing function and $I(\alpha_e = 0) = 1$, i.e., at a constant combustion temperature the combustion rate increases with the CEF. This can be explained by the CEF-induced increase in the reaction rate per unit volume of the mixture that consists of contacting DP of different orientations. At $0 < \alpha_e \ll 1$ we obtain $u^2 = u_0^2(1 + \alpha_e^2/30)$.

Discussion. Thus, for a model of a medium consisting of interacting DP with different orientations relative to the field, we obtained that a CEF does not change the combustion temperature or increase the combustion rate. As was mentioned above, in [7] for a model of a medium of independent DP, it is found that a CEF decreases the combustion rate by decreasing the reaction rate per unit volume of the medium by decreasing the diffusion rate by the CEF in negatively oriented DP. It is also found that starting from a certain threshold CEF, an increase in the CEF results in a decrease in the combustion temperature because of incomplete reaction in the negatively oriented DP.

We compare changes in the combustion rates in both models of the medium.

1. $0 < \alpha_e \ll 1$: $u^2 = u_0^2(1 + \alpha_e^2/30)$ for interacting DP and $u^2 = u_0^2(1 - 0.3\alpha_e^2)$ for independent DP [7];

2. $\alpha_e = 1$ (corresponds to the threshold value of the CEF from [7]): $u^2 = u_0^2[6 \ln(\operatorname{sh} 1)]^{-1} \simeq 1.03u_0^2$ for interacting DP and $u^2 = u_0^2[6(1 - \ln 2)]^{-1} \simeq 0.54u_0^2$ for independent DP [7].

It is worth mentioning that in the model of [7] the change (decrease) in the combustion rate is much greater than the change (increase) in the model of interacting DP. Therefore, in the presence of a CEF, even a rather small amount of independent negatively oriented DP that may be contained in a real mixture can lead to a decrease in the combustion rate (at least when $0 < \alpha_e \leq 1$).

In real SHS media that are a compressed mixture of powders, the size, shape, and orientation of DP depends on the size and shape of the powder particles as well as on the compression force, i.e., on the porosity of the medium. It can be suggested that a negatively oriented independent DP can occur, in particular, in the configuration of particles shown in Fig. 1. Here 1-3 are particles of the same reactant, and 4 is a particle of a different reactant. Pair 1-4 is oriented negatively and pairs 2-4 and 3-4 are oriented positively; in the figure the lower boundary is not in contact with anything. Then, the lower part of particle 4 and particles 2 and 3 can be a negatively oriented independent DP (screening of diffusion by electric current). It should be remembered that the Joule heat was neglected in (1). That this heat can be neglected is demonstrated in article [7], which contains numerical estimates that suggest that in experiments the CEF threshold value can be attained before initiation of an electrothermal explosion [10]. The threshold value of the CEF is defined by the relation

$$\mathcal{E}_{\text{th}} = T_c k_B \Delta c / (|e^*|\, l c') . \tag{5}$$

Since a real SHS mixture contains pairs of different sizes, generally speaking, the experimental $\mathcal{E}_{\text{th}}$ should be determined by independent negatively oriented DP of maximum size.

We estimate $\mathcal{E}_{\text{th}}$ for the intermetallide CuAl, since aluminides burn with a narrow reaction zone [11]. From the constitution diagram of the system Cu-Al [12] we find $c' \simeq 0.499$, $\Delta c \simeq 0.015$. According to [9], $e^*_{\text{Cu}} \simeq -7e$ and $e^*_{\text{Al}} \simeq -17e$ in the system Cu-Al (e is the electron charge); $e^* \simeq -10e$, $T_c \simeq 1073$ K [11], and $l \simeq 10^{-4}$ m are assumed. Then, from (5) we obtain $\mathcal{E}_{\text{th}} \simeq 2.78$ V/m.

This estimate can be considered tentative, since Cu-Al is a multiphase system and CuAl has a rather wide homogeneity region. The presence of a wide homogeneity region violates the condition of quasisteadiness that was used in [6] in analysis of phase growth in electric diffusion.

The results given above are obtained with the assumption that only one intermediate phase is formed in the diffusion zone and the CEF only changes the diffusion mass transfer rate. However, according to [5], when several intermediate phases are present in the system, the effect of the CEF is more complicated. In particular, in the presence of a CEF, in the diffusion zone at a certain temperature, phases can grow that are absent in a zero CEF at the same temperature. The inverse effect is also observed, when phases that grow without a CEF do not appear in the field. Thus, the CEF affects the formation of a certain phase in the system in which there is more than one intermediate phase; the formation of every phase is accompanied by its own thermal effect. Therefore, in the case of a multiphase system, in the presence of a CEF the heat source in the heat conduction equation should have a more complicated form as compared with the source used in the present work. Consequently, in systems that contain more than one intermediate phase, the effect of a CEF on the combustion wave should be rather diverse and requires a separate study. As the CEF affects the formation and growth of intermediate phases in multiphase systems, a CEF can be used as a parameter that controls the composition of the end product of SHS.

Conclusions. In the present work a model of a reaction medium is suggested that consists of interacting DP. This model includes the effect of a CEF on the combustion wave of SHS. It is also found that as the CEF increases, the combustion rate also increases, while the combustion temperature remains unchanged (the Joule heat is neglected). The present results are compared with the results of article [7], which considers a model of a medium consisting of independent DP. The experimental situation in the presence of a CEF is discussed on the basis of the results of a comparison. It is suggested to use the CEF as a parameter that controls the composition of the end SHS product in the case of a multiphase system.

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NOTATION

c', left-hand concentration boundary of intermediate phase; Δc, width of homogeneity region of intermediate phase; k_B, Boltzmann constant; T, temperature of medium; $\mathcal{E}_{\text{th}}$, threshold value of electric field; R, gas constant; l, thickness of diffusion pair; $\eta_+(\eta_-)$, degree of transformation in positive (negative) DP; k_0, preexponent; E, activation energy; u_0, combustion rate without CEP; κ, thermal diffusivity; Q, thermal effect of reaction per unit volume of medium; $c(\rho)$, specific heat capacity (density) of medium; $\eta^*_+(\eta^*_-)$, final transformation degree in positively (negatively) oriented DP; $I(\alpha_e)$, integral, that is a function of α_e. Subscripts: e refers to electric field; c refers to combustion temperature; th refers to threshold value of electric field.

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