Physicochemical Simulation of the Combustion of Materials with the Total Endothermal Effect

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Received December 27, 2006

Abstract—A new type of combustion, namely, the combustion of materials without heating of the environment, is described, and the conditions under which this process can occur are analyzed. It is demonstrated that the possibility of occurring the process under consideration depends substantially on the microstructure of the material. The characteristics of the material for which the liquid-phase combustion takes place without an increase in the temperature of the melt are determined using the interaction of a material based on iron and aluminum oxides with the Fe–Zr–O melt as an example.

DOI: 10.1134/S1087659607050112

INTRODUCTION

In our earlier works [1–3], we analyzed a special case of the interaction between oxide materials and melts with a high reducing power. The study of this process has been of considerable practical interest for the development of so-called sacrificial materials used in the passive safety system of nuclear reactors [4, 5]. It was shown that the kinetics of the interaction between these materials and the melt simulating the core melt of the nuclear reactor can be described in the framework of the combustion theory [6]. The specific feature of the process under consideration is that, despite the high exothermal effect characteristic of oxidation of melt components upon their interaction with some components of the oxide material (combustion), the total thermal effect of the interaction between the melt and the material provided a decrease in the temperature of the melt. Since the combustion of the material proceeded in the course of the interaction with the melt, the resulting reaction products were, at least in part, in the liquid state. Consequently, this type of combustion, according to the classification proposed in [7], was assigned to the liquid-phase combustion. It should be noted that, most likely, the combustion of the compounds without an increase in the temperature of the environment and, in particular, with the total endothermal effect can be observed for other types of chemical interactions between solids and melts and, hence, can cover a wider range of chemical processes and a wider field of practical applications. Thus, the investigation into the mechanism of these processes and the conditions of their occurrence is an important problem.

PHYSICOCHEMICAL SIMULATION AND CALCULATIONS

The interaction of a material with a melt in the combustion regime, i.e., when the chemical reaction proceeds at the solid–liquid interface and leads to an increase in the temperature at the interaction front and, hence, to an increase in the rate of the chemical reaction, is schematically illustrated in Fig. 1. The combustion rate (the velocity of propagation of the combustion front) can be limited by the heating rate of the material to the temperature corresponding to the initiation of the chemical interaction, the rate of addition of the reagents
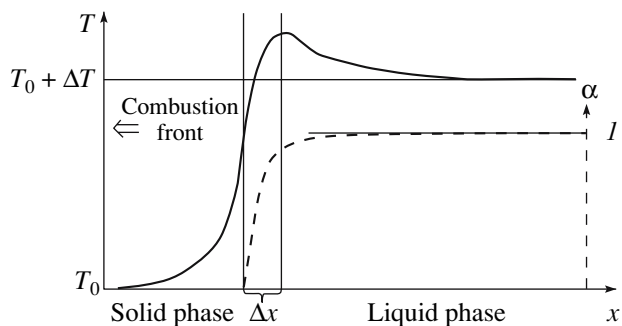

Fig. 1. Characteristic variations (for the combustion process) in the temperature and the fractional conversion of reagents (dashed line) in the region of their active interaction (Δx) and the adjacent solid and liquid phases. Designations: T_0 is the initial temperature of the material, $T_0 + \Delta T$ is the mean temperature to which the components of the material are heated during the interaction with the melt, and x is the spatial coordinate.

from the liquid phase, the rate of removal of the products from the reaction zone, or the rate of the chemical reactions themselves in the combustion zone (Fig. 1). The regimes of combustion limited by the above processes are described in numerous works (see, for example, [6, 8–13]). All variants of the combustion process are characterized by a stationary propagation of the combustion front (including a self-oscillation regime, as is the case with the thermodynamics of nonequilibrium processes [14]) and an increase in the temperature of the environment due the exothermal effect of the process. As was noted above, in a number of cases, it is necessary to perform the chemical reaction between materials and melts with a reaction front propagation characteristic of combustion but without an increase in the temperature of the environment.

According to the general principle of combustion with the total endothermal effect, two processes, namely, one exothermal process (ΔH_{exo}) and one endothermal process (ΔH_{endo}), should occur in the zone of the combustion front so that the total thermal effect should satisfy the condition

$$\Delta H_{exo} + \Delta H_{endo} > 0. \qquad (1)$$

If the exothermal process somewhat leads the endothermal process due to the kinetic factors, it can be expected that the front of the interaction between the material and the melt will propagate in the regime typical of combustion. A rapid addition of reagents and a rapid removal of products are important conditions for the occurrence of the process under consideration. For the interaction of materials with melts, these conditions mean that the products of the chemical interaction should be in the liquid or dispersed form.

The aforementioned conditions can occur, for example, in a ternary system presented in Fig. 2, in the range of the temperature T_0. In this case, the material consisting of the components A and B is in the solid state, because the temperature T_0 of the system is below the eutectic temperature: $T_0 < T_{e(A-B)}$ (Fig. 2). If the contact of the melt based on the component C with the phase A at the temperature T_0 leads to the formation of the solid solution $C_{1-x}A_x$ (Fig. 2), which prevents further interaction between the components, the contact of the component C with the phase B results in the formation of the low-melting compound B_nC_m, which passes into the melt and virtually does not hinder further interaction between the components B and C. In the cases where the reaction

$$nB + mC = B_nC_m \qquad (2)$$
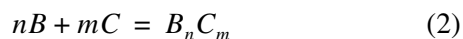
is exothermal and proceeds rapidly while the component A rather slowly passes into the melt according to the eutectic mechanism with an endothermal effect, in the zone of the chemical interaction (Fig. 3a, zone *II*) there can arises a local increase in the temperature, which results in the interaction of the melt with the material in the combustion regime. As was noted above,
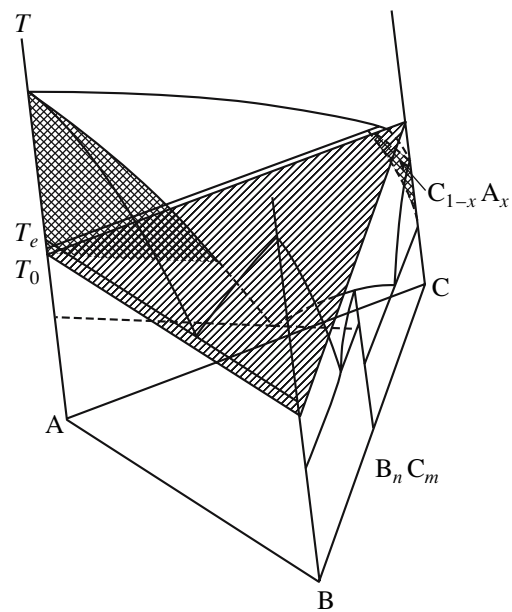

Fig. 2. Phase diagram of the *A–B–C* hypothetical system in which the combustion regime can occur without an increase in the temperature of the environment.

the transfer of the component A to the melt, which after occurrence of the exothermal reaction consists of the components B_nC_m and C, is the endothermal process. Therefore, the temperature decreases in zones *III* and *IV* of the interaction between the material and the melt. At a particular ratio between the components A and B in the material, condition (1) is satisfied and the total temperature in the system decreases to the initial temperature or even below (Fig. 3a). It should be noted that the total decrease in the temperature of the environment, i.e., the melt interacting with the material, can be partially associated with the heat loss for heating of the material (the heat removal from the system in the given case is disregarded).

The necessary rates [for maintaining reaction (2)] of addition of the reagents (the component C) and removal of the reaction products (the compound B_nC_m) from the reaction zone can be reached not only at particular diffusion coefficients or other parameters characterizing the mobility of the components in the melt (if they are contained in the melt in the form of the dispersed phase) but also at a specific ratio between the geometric parameters, in particular, at a specific ratio $\bar{d}/\bar{l}$ (Fig. 3a). In turn, this ratio depends on the microstructural parameters of the material and the ratio between the velocity of propagation of the combustion front (the front of the interaction of the components B and C) and the rate of transfer of the component A to the melt.

The role of the microstructure of the material in providing the possibility of occurring its interaction with the melt in the combustion regime is clearly illustrated in Fig. 3b. In this case, the ratio between the compo-
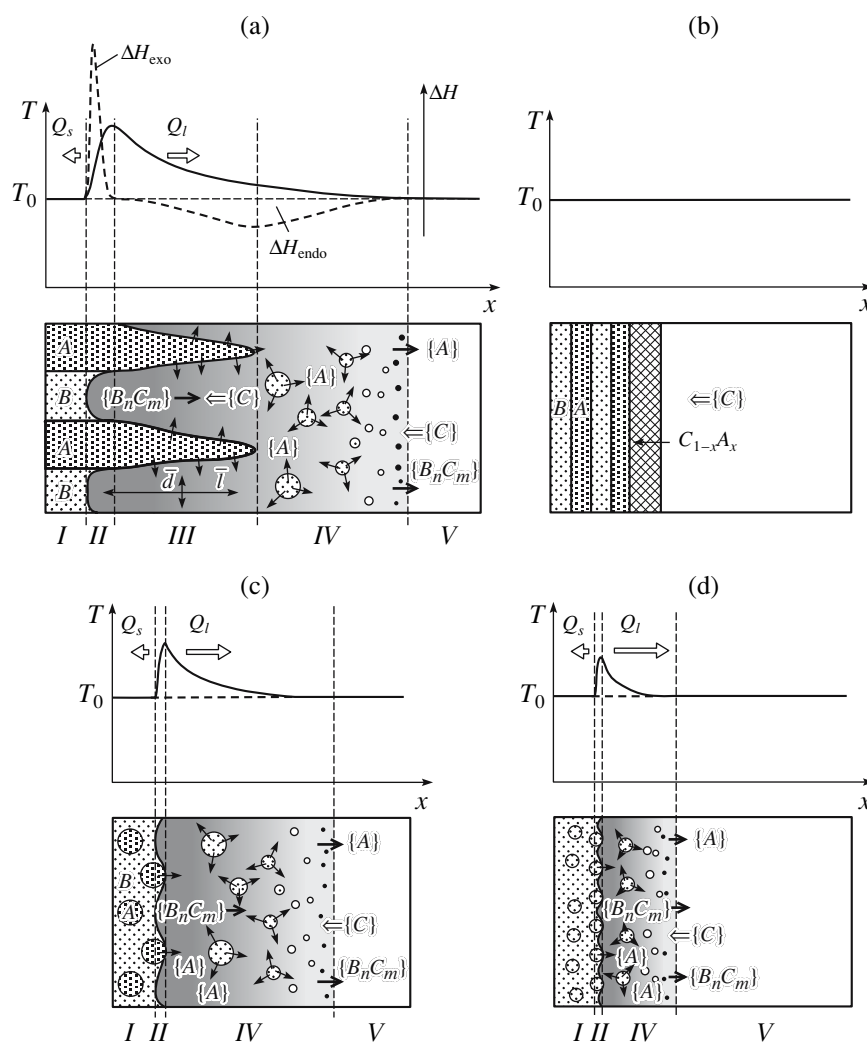
Fig. 3. Possible variants of the interaction between the material and the melt for different microstructural parameters of the material: (a) the components A and B can participate equally in the interaction, (b) the access to the component A can be limited, and (c, d) the component A is uniformly distributed in the matrix B. Designations: I is the initial material, II is the zone of the chemical interaction with the exothermal effect, III and IV are the zones of the interaction with the endothermal effect, V is the initial melt, $\bar{d}$ is the mean width of the zone of dissolution of the component B in the material, $\bar{l}$ is the mean dynamic depth of dissolution of the component B in the material, Q_s is the heat transfer to the material, Q_l is the heat removal to the melt, $\Leftarrow$ is the addition of the melt components to the interaction zone, $\longrightarrow$ is the removal of the reaction products from the interaction zone to the melt, $\rightarrow$ is the addition of the components of the material to the interaction zone, and $\{\dots\}$ are components.

nents A and B in the material is identical to that in the variant shown in Fig. 3a but the arrangement of the phases with respect to the boundary of contact with the melt is different. As a result, the solid solution $C_{1-x}A_x$ formed at the material–melt interface prevents a further interaction between the components of the material and the melt.

When the ratio between the components A and B ensuring the fulfillment of inequality (1) is so that the component A can be distributed in the form of inclusions in the matrix based on the component B, the interaction zone III degenerates and zone IV is located immediately after the combustion front (Fig. 3c, 3d).

This variant of the microstructure of the material substantially facilitates the addition of the reagents to the reaction zone and the removal of the reaction products from it. In the given case, the size of particles composed of the component A substantially affects the interaction of the material with the melt. A decrease in the size of particles of the phase A leads to a narrowing of the zone in which the component A passes into the melt with the endothermal effect. This leads to an improvement of mass transfer of the components and, hence, to a potential increase in the velocity of propagation of the combustion front, on the one hand, and to a decrease in the temperature in the zone of the exothermal interaction due to an increase in the flux of heat removed from the

combustion front to the melt (Fig. 3d), i.e., to a potential decrease in the velocity of propagation of the combustion front, on the other hand.

It should be noted that the exothermal reaction (2) and the eutectic interaction of the component *A* with the melt (Fig. 2) are considered as an example. The combustion process under investigation can be provided using any chemical reactions that satisfy three conditions: (1) the reactions should be exothermal, (2) the reaction products should be dissolved or/and dispersed in the initial melt in the form of droplets of the second liquid or solid particles so that the addition of the melt components to the reaction zone should not be hindered, and (3) the reaction products should not prevent transfer of other components of the material to the melt with an endothermal effect. Apart from the components interacting with the melt with an exothermal effect, the material should contain the components that fulfill the following conditions: (1) the components should chemically interact with the melt, undergo melting, dissolve, evaporate, or be dispersed in the melt with the formation a two-component (multiphase) system with an endothermal effect; (2) the rate of transformation of these components should be lower than the rate of interaction that proceeds between the components and the melt with the exothermal effect in order to ensure a local increase in the temperature providing the combustion regime in the material at the interaction front; and (3) the components under consideration or the products of their interaction with the melt should dissolve, be dispersed, or precipitate from the melt and, thus, provide a sufficiently high rate of the removal of the interaction products and the addition of the reagents to the combustion front.

When the components of the material satisfy the aforementioned conditions, the interaction between the material and the melt will proceed through the combustion mechanism, i.e., with an increase in the temperature in the reaction zone and a reaction front propagation characteristic of the combustion reaction, but the total thermal effect of all processes can be zero or endothermal.

Therefore, the performed analysis of the above processes indicates that the range of conditions ensuring the possibility of occurring the combustion process with the total endothermal effect is substantially wider than that considered in [1–3].

In the general case, the phases *A* and *B* forming the material can be complex compounds. The melt can also consist of several components but, as follows from the above analysis, should contain at least one compound *C*, which interacts, for example, with the phase *B* with an exothermal effect; that is,

$$B + a_0 C = \sum_{i=1}^{k} a_i P_i. \tag{3}$$
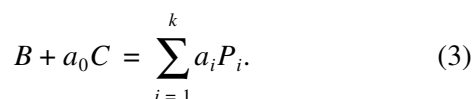
Here, P_i ($i = 1, \ldots, k$) are the products of reaction (3) and a_i ($i = 1, \ldots, k$) are the stoichiometric coefficients of reaction (3). In the specific case $i = 1$, the number of products can be equal to unity, as is the case with reaction (2).

The endothermal transformation with the thermal effect ΔH_{endo} is associated both with the transfer of the compound *A* to the melt (melting) or to the gas phase (evaporation) and with the possible chemical reactions between the melt components, including the products of reaction (3) and the components of the compound *A* transforming into the liquid state. With due regard for the aforementioned processes, the overall transformation of the compound *A* with the endothermal effect ΔH_{endo} can be conventionally written in the form

$$[A]_s \longrightarrow [A]_{l(gas)}, \tag{4}$$

where the subscripts indicate the state of aggregation of the phases (solid, liquid, gaseous) of the components of the compound *A* before and after its interaction with the melt.

With some degree of conventionality, the boundary between zones *I* and *II* (Fig. 3), whose temperature corresponds to the eutectic temperature of the *A–B* system (Fig. 2), can be considered a boundary surface of the interaction between the material and the melt. The propagation of the interaction front can be described by a system of equations of heat and mass transfer with allowance made for the chemical reactions (3), phase transformations (4), and the corresponding thermal effects [15], as was done, for example, in our previous paper [1].

It should be noted that the narrow-reaction zone approximation, which was proposed by Zel'dovich [16, 17] in the theory of flame propagation and which made it possible to obtain the approximate analytical solution for the combustion rate, cannot be used in our case primarily due to the extension of the liquid-phase combustion of materials with the total endothermal effect along the coordinate parallel to the direction of propagation of the combustion front (Fig. 3). In this respect, in the case of combustion of materials under investigation, it is necessary either to develop new approaches to search for the analytical solution or to use numerical methods for solving the system of nonlinear differential equations with a moving boundary. In our earlier paper [18], we demonstrated that the cellular automaton method is a promising approach to the solution of the problem under consideration.

According to the aforementioned physicochemical model of the process, we performed the numerical calculations of the interaction between the material based on the FeO–Al_2O_3 system and the melt based on the Fe–Zr–O system. In this case, the temperature of the melt was taken equal to 1800°C and the temperature of the material was varied from 200°C to the temperature of the melt. The results of the calculations in the form of the region that indicates the compositions of the
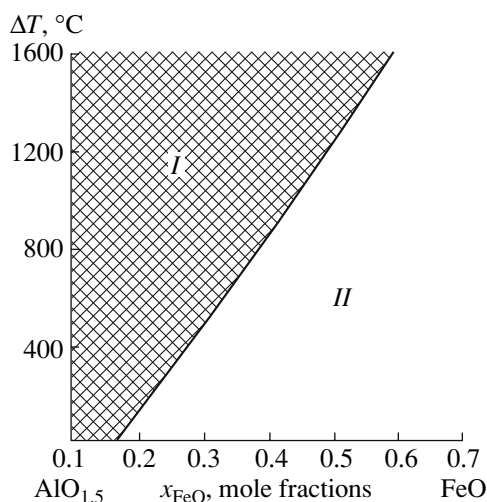
Fig. 4. Effect of the composition and the initial temperature of the material on the possibility of occurring its interaction with the melt in the combustion regime without heating of the melt (region *I*) and with an increase in the temperature of the melt (region *II*). The designation ΔT is the same as in Fig. 1.

material and the combustion conditions at which the liquid-phase combustion of the material can occur without an increase in the temperature of the melt are presented in Fig. 4.

RESULTS AND DISCUSSION

The analysis of the results of the calculations of the interaction between the material based on the FeO and Al_2O_3 oxides and the melt based on the Fe–Zr–O system (Fig. 4) demonstrates that, at specific ratios of the components and initial temperatures of the material and the melt, the solid and liquid phases can interact in the regime characteristic of combustion, i.e., with heat release due to the exothermal redox reaction of the iron oxide with zirconium at the material–melt interface and, hence, with a local increase in the temperature. However, the total thermal effect of the interaction between the material and the melt at $x_{FeO} < 0.13$ mole fractions will be endothermal (Fig. 4), because the melting of aluminum oxide is an endothermal process. Since the melting of aluminum oxide at specific sizes of aluminum oxide particles occurs more slowly than the exothermal chemical reaction of reduction of iron ions with zirconium, the thickness of the front of interaction between the material and the melt will increase and the processes with different signs of the thermal effect can appear to be spatially separated (Fig. 3a). This separation in combination with the total thermal effect of the processes provides conditions for the liquid-phase combustion of the materials with the total endothermal effect. Now, we examine the situation when the material and the melt in the initial state have different temperatures. As follows from the calculated data pre-

sented in Fig. 4, the region of compositions of the material that can participate in the liquid-phase combustion without an increase in the temperature of the melt extends considerably. It should be noted that experimental investigations of the interaction between the material similar in composition to the material under consideration and melts containing uranium and zirconium [1–3] confirm the validity of the inference that the liquid-phase combustion can proceed without an increase in the temperature of the melt.

CONCLUSIONS

Thus, it has been theoretically demonstrated that, as a result of the occurrence of several processes that initiate each other and exhibit thermal effects differing in sign in the reaction zone, the total thermal effect can appear endothermal although the reaction proceeds in the combustion regime. The revealed possibility of occurring, in principle, liquid-phase combustion of materials without an increase in the temperature of the environment is validated experimentally. The conclusions drawn from a physicochemical analysis of the process of liquid-phase combustion of materials are confirmed by the calculations using the example of the system "a melt based on the Fe–Zr–O system and a material based on iron and aluminum oxides." It is shown that, even in the case where the material and the melt have an equal temperature, the total effect in the reaction zone will remain endothermal to a FeO content of 0.13 mole fractions. The inclusion of the quantity of heat required to warm up the material to the temperature of the melt considerably extends the composition region in which the process of liquid-phase combustion can occur without an increase in the temperature of the melt.

ACKNOWLEDGMENTS

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