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PROBLEM OF THE MECHANISM OF GASLESS COMBUSTION

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The conditions for gasless combustion with the formation of solid [1-4] and liquid products [5] are described in the literature.

In this paper, the more general case with respect to the state of aggregation is investigated experimentally. It includes not only the limiting cases mentioned above, but also the transition two-phase region.

The necessary condition for the experimental investigation is the measurement of the maximum temperature developing during combustion. The system Ni-Al of the equiatomic state formed during the combustion of nickel monoaluminide NiAl [6, 7] was chosen as the object of the investigation. Preliminary analysis showed that it is similar to the model for the solution of the problem posed.

EXPERIMENTAL METHOD

In the experiment we used powdered aluminide (ASD-4) with particle sizes of 1-5 μm and nickel (electrolytic) with particle sizes of less than 45 μm . Mixtures were prepared from the powders containing 68.5% Ni and 31.5% Al by weight (equiatomic composition) and mixtures diluted in the final product (NiAl) up to 46% by weight. The particle size of the diluent was less than 90 μm . The powders were mixed in a porcelain drum over 6-8 h and then cylindrical pellets with diameters of up to 40 mm and relative density of 0.6 were pressed from the mixture. The experiments were conducted in an argon medium at 1 abs. atm. The vertically standing sample was ignited with a thin tungsten spiral, which was burnt out by a transient electric pulse and ignited a powder mixture of the same composition poured onto the end of the pellet. At the lower end of the pellet, an opening with a diameter of 3-5 mm and a depth of 10-20 mm was drilled out and a thermocouple was inserted. The thermocouple junction was in contact with the sample. The thermocouple was welded from tungsten-rhenium wires (VR-5, VR-20) with a diameter of 100 μm .

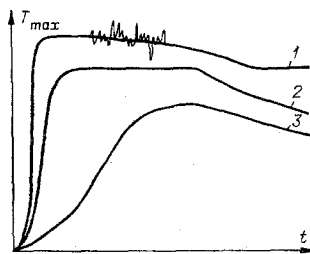


Fig. 1. Typical oscillograms obtained during the combustion of samples under different conditions.

1) $T_{\text{max}} > T_{\text{mp}}$; 2) $T_{\text{max}} = T_{\text{mp}}$; 3) $T_{\text{max}} < T_{\text{mp}}$.

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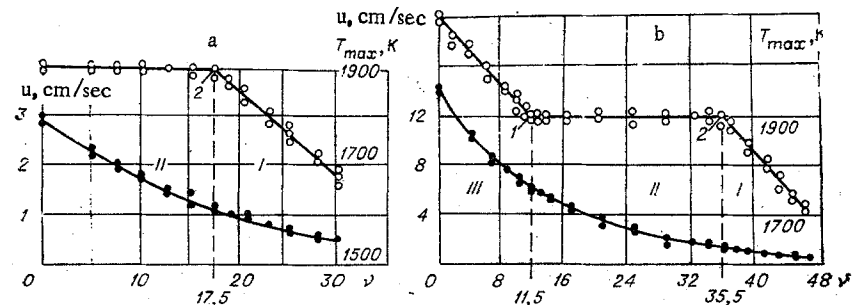


Fig. 2. Curve of combustion velocity u and maximum temperature T_{max} versus concentration of diluent ν . a) $T_i = 298^\circ K$; b) $T_i = 740^\circ K$.

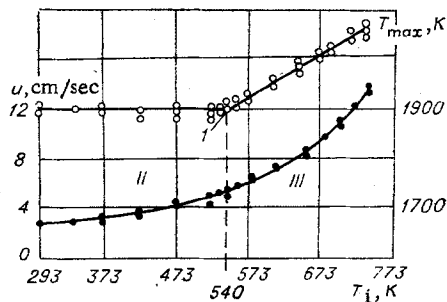


Fig. 3

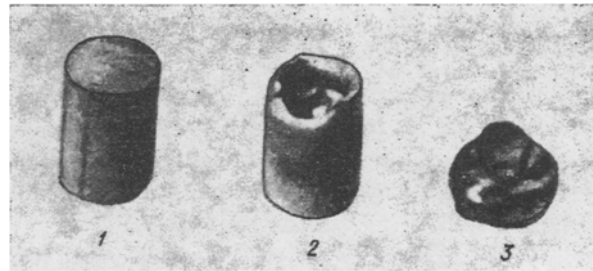


Fig. 4

Fig. 3. Curve of velocity and maximum temperature of combustion versus initial temperature ($\nu = 0$).

Fig. 4. Samples burnt when $\nu = 0$ and T_i is equal to $298^\circ K$ (1), $530^\circ K$ (2), and $540^\circ K$ (3).

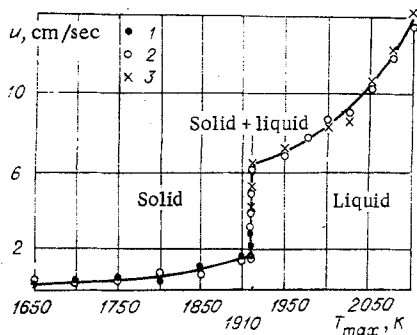


Fig. 5

Fig. 5. Dependence of combustion velocity on maximum temperature. 1) $T_i = 298^\circ K$, ν is variable; 2) $T_i = 740^\circ K$, ν is variable; 3) T_i is variable, $\nu = 0$.

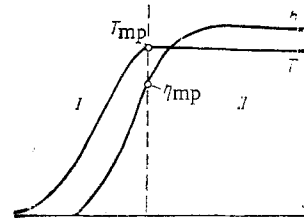


Fig. 6

Fig. 6. Structure of the adiabatic combustion wave ($T_c = T_{mp}$).

Since the main attention was to be paid to the maximum value of the combustion temperature, and not the temperature profile, the thickness of the thermocouple was of no particular importance. The temperature was recorded with an N-107 loop oscillograph with an MOO4-0.3 galvanometer. A thermocouple amplifier was installed in the thermocouple-oscillograph circuit. Simultaneously with the temperature measurement, the combustion velocity was measured by a photographic recording method. In some experiments, the sample was heated up prior to combustion. A cylindrical resistance furnace was used for this, with a narrow longitudinal slit for photographic recording. The combustion products were investigated by means of x-ray phase analysis.

In order to choose the conditions which would produce adiabatic combustion, the dependence of the combustion temperature on the diameter of the sample was investigated in the experiment. It was found that at a small dilution ($\sim 20\%$ NiAl), the combustion conditions can be assumed to be adiabatic if the diameter is equal to 20 mm and at stronger dilutions ($\sim 40\%$ NiAl), if the diameter is equal to 40 mm.

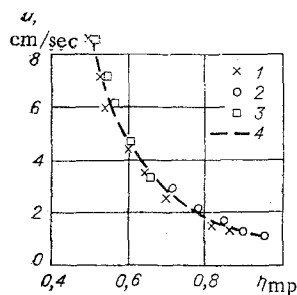


Fig. 7. Dependence of the combustion velocity on η_{mp} . 1) $T_i = 740^\circ\text{K}$, ν is variable; 2) $T_i = 298^\circ\text{K}$, ν is variable; 3) T_i is variable, $\nu = 0$; 4) $u = a\eta_s^{-m}$.

TABLE 1. Results of the Calculation of η_{mp}

T_i , K	ν	u , cm/sec	η_{mp}
740	5.75	8.7	0.48
	8.62	7.2	0.50
	11.5	6.0	0.53
	17.5	4.6	0.59
	21.0	3.6	0.63
	25.0	2.6	0.68
	33.5	1.6	0.81
	35.5	1.5	0.85
298	17.5	1.2	0.93
	15.0	1.3	0.90
	10.0	1.7	0.83
	5.0	2.3	0.76
	0	3.0	0.71
400	0	3.5	0.65
500	0	4.7	0.6
540	0	6.2	0.56
600	0	7.2	0.53
650	0	8.6	0.5

TABLE 2. Calculation of the Specific Heat of NiAl

Figure No.	Temperature range, $^\circ\text{K}$	$\bar{\alpha}$	$\bar{\beta}$	Phase	\bar{c} , (cal/mole·deg)
2, b	1910—2105	1695	—	Liquid	16.6
2, b	1710—1910	1904	—	Solid	14.7
2, a	1685—1910	1880	—	Solid	15.0
3	540—740	—	0.77	Solid	12.8

EXPERIMENTAL RESULTS

Figure 1 shows typical oscillograms obtained during the combustion of the samples; the origin of the time reading was chosen arbitrarily. In Fig. 1, curves 1 and 2, the horizontal parts can be seen, corresponding to melting and crystallization of the combustion products. In the case of melting of the samples ($T_c > T_{mp}$), distortions are frequently observed, cutting the thermogram traces; these are due, obviously, to the interaction of the molten product with the thermocouple. These distortions are observed, as a rule, after reaching T_{max} and are completely eliminated by using quartz capillaries. The relation between the combustion velocity u and T_{max} and the weight concentration of the diluent ν are plotted in Figs. 2 and 3 for $T_i = T_r$ and $T_i = 740^\circ\text{K}$, and also versus T_i when $\nu = 0$ (T_i is the initial temperature of the sample, and T_r is room temperature).

In order to illustrate melting, photographs of the samples are shown (Fig. 4), obtained under different conditions. Complete melting of the product is observed under conditions corresponding to the salient points 1 in Fig. 2b and Fig. 3. It should be noted that the phase state of the final product is almost unchanged and cor-

responds to the compound NiAl. Only in the case of strong dilution ($\nu \geq 30\%$) and with a small sample diameter (~ 15 mm) does a small amount of the Ni_2Al_3 phase appear (predominantly at the surface of the samples). Analysis of the experimental data leads to the following conclusions:

1. the combustion temperature of an equiatomic mixture of Ni + Al under normal conditions ($\nu = 0$, $T_i = T_r$) is equal to the melting temperature of NiAl (1910°K);
2. over a range of variation of ν and T_i , the combustion temperature is unchanged and remains equal to T_{mp} . Curves of the functions $T_c(\nu)$ and $T_c(T_i)$ have inflections and characteristic horizontal sections (with $T_c = T_{\text{mp}}$). At the point 1 (Figs. 2b and 3), the solid phase disappears and transition to the single-phase region (III) with a liquid combustion product is observed (this is confirmed also by a change of the exterior shape of the sample); at point 2 (Fig. 2a, b), the liquid phase disappears and transition to the single-phase region (I) with a solid product is observed; the intermediate region (II) is characterized by the presence of both a solid and a liquid product*;
3. the nature of the $u(\nu)$ and $u(T_i)$ dependences is smooth over the whole range of values of ν and T_i ;
4. the dependence of u on T_c (Fig. 5) bears an approximately universal nature, since the points for different values of ν and T_i lie on a single curve, which undergoes a sudden change when $T_c = T_{\text{mp}}$.

CHARACTERISTICS OF GASLESS COMBUSTION UNDER CONDITIONS CONDUCTIVE TO THE FORMATION OF SOLID AND LIQUID PRODUCTS

It will be most interesting in the result of the experiment to explain the region in which the combustion temperature is constant, but the combustion velocity is varying strongly (by a factor of several times). In the theory of gasless combustion, this case is not described. The experimental data and qualitative considerations lead to the following structure of the adiabatic combustion wave (Fig. 6). Two characteristic zones can be distinguished in it.

In zone I, self-heating of the substances up to T_{mp} occurs and only partial conversion of the substance takes place (with maximum value of the intensity of conversion η_{mp}). This zone determines the propagation velocity of the wave (in Fig. 6 the warmed-up layer is also referred to it).

Zone II is characterized by constant temperature, which is equal to T_{mp} . The chemical reaction in it is continued and proceeds intensely. However, the whole of the heat release† is expended on melting of the product formed in zone I. The processes taking place in this zone have no effect on the combustion velocity (in the same way, but of a different kind, as in the burn-out zones) [3, 4].

Thus, the model of the process being considered is related to a category of elementary combustion models of the species II, which characterize the incomplete conversion of the substance in the leading zone [8].

It follows from [8], that for this model

$$u^2 = \frac{\lambda}{Q\rho} \frac{RT_s^2}{E} k_0 e^{-E/RT_s} \varphi(\eta_s),$$

where T_s is the surface temperature; η_s is the conversion intensity at the surface; λ is the coefficient of thermal conductivity, cal/(cm·sec·deg); Q is the heat of formation of the product, kcal/mole; ρ is the density, g/cm³; E is the energy of activation, kcal/mole; and k_0 is the pre-exponent (1/sec for a reaction of zero order). The specific form of $\varphi(\eta_s)$ depends on the kinetic law of heat release during the lapse of the chemical reaction (for example, for a reaction of zero order, $\varphi(\eta_s) = 2\eta_s^{-1}$ [8]).

For the case being considered

$$T_s = T_{\text{mp}},$$

$$\eta_s = \eta_{\text{mp}} = \bar{c}(T_{\text{mp}} - T_i) / (1 - \nu) Q.$$

*The change of temperature only serves as the main confirmation of this; the amount of liquid and solid phases in the combustion product was not determined experimentally.

†The experimental results and the qualitative analysis refer to the case, however, when the heat losses to the surrounding medium are insignificant.

A more accurate value of η_{mp} should be determined from the expression

$$(1-\eta_{mp}) \{ [\Delta H_{Ni}(T_{mp}) - \Delta H_{Ni}(T_i)] + [\Delta H_{Al}(T_{mp}) - \Delta H_{Al}(T_i)] \} + (\eta_{mp} + m) [\Delta H_{NiAl}(T_{mp}) - \Delta H_{NiAl}(T_i)] = Q\eta_{mp} \quad (1)$$

[$m = \nu / (1 - \nu)$], taking into account the dependence of the specific heat of the mixture on ν and T . Since in Eq. (1) the function $c_p(T)$ for NiAl is unknown, the use of this expression also gives an approximate value for η_{mp} .

In finding η_{mp} , the data available in the literature on the heat content of the individual elements were used, and in order to determine the enthalpy of formation of nickel monoaluminide the expression $c_p = 11.64 + 1.23 \cdot 10^{-3}T$ was used. This relation was obtained through two points -293 and 1910°K . The specific heat of NiAl has been determined experimentally and is equal to 11.6 ± 0.3 cal/(g·mole). At the melting point (1910°K), the specific heat was assumed to be equal to $7n$ [10], where n is the number of atoms in the compound.

It can be seen from Table 1 that values of η_{mp} are close to unity (0.93) at the point of inflection 2 (see Fig. 2a). Using $u(\eta_{mp})$, the form of the function $\varphi(\eta_s)$ can be determined experimentally. The unambiguous dependence of u on η_s , which is valid for any values of ν and T_i occurring in η_s , can be used as the criterion of validity for the proposed combustion model. Table 1 shows the results of the calculation of η_s and Fig. 7 shows the dependence of u on η_s , which can be assumed and is represented by the formula

$$u = a\eta_s^{-m},$$

where $a = 1$ and $m = 3$.

We note that when constructing this curve, the experimental points were used, relating not only to the two-phase (solid + liquid) region, but also to the purely liquid-phase region ($T_i > 540^\circ\text{K}$, $\nu = 0$), since the model considered must be valid also over a certain range when $T_c > T_{mp}$. In this case, the flow of heat from the combustion product into the starting mixture is expended entirely on melting the solid product formed in zone I (see Fig. 6) and does not participate in heating up the mixture to T_{mp} , which determines the combustion velocity. The limiting conditions for purely liquid-phase combustion should be expected when $T_c \gg T_{mp}$.

DETERMINATION OF CERTAIN THERMODYNAMICAL PARAMETERS OF NICKEL MONOALUMINIDE FROM THE COMBUSTION EXPERIMENTS

The direct measurement in the experiments of the combustion temperature and its dependence on ν and T_i allows certain thermodynamic quantities to be determined, these characterizing the combustion product (NiAl). The temperature and the heat of fusion of NiAl can be determined from the experimental data. It has been mentioned already that $T_c = T_{mp}$. The value obtained $T_{mp} = 1910-1920^\circ\text{K}$ coincides well with the literature data ($T_{mp} = 1911^\circ\text{K}$) [11].

For the salient points 1 and 2 (see Fig. 2b), we can write

$$\int_{T_i}^{T_{mp}} c(T) dT = (1 - \nu'') Q,$$

$$\int_{T_i}^{T_{mp}} c(T) dT = (1 - \nu') Q - L_{mp},$$

where ν'' corresponds to the transition in the region of the solid phase (point 2); ν' corresponds to transition in the region of the liquid phase (point 1); L_{mp} is the heat of fusion of the products; and Q is the heat of formation of the product. Hence,

$$L_{mp} = (\nu'' - \nu') Q.$$

It follows from Fig. 2b that $\nu'' = 0.355$ and $\nu' = 0.115$. Assuming that $Q = 28.2$ kcal/mole [12], we obtain $L_{mp} = 6.7$ kcal/mole.

There are no data in the literature on the heat of fusion of the compound NiAl. However, in [11] it is shown that in the case of ordered compounds (to which NiAl also is related), to a first approximation L_{mp} can be assumed to be equal to the sum of the heats of fusion of the initial components. For NiAl, $L_{mp} = 6.7$ kcal/mole, which in accuracy is equal to the experimental value.

The mean values of the specific heats in the high temperature region can be determined also from the experimental data.

The basic thermodynamic relation for the combustion temperature has the form

$$\int_{T_i}^{T_c} c(T) dT = (1 - \nu)Q - \mu L_{mp},$$

where μ is the fraction of the liquid phase and $\mu = 0$ if $T_c < T_{mp}$; $\mu = 1$ if $T_c > T_{mp}$. Differentiating this expression with respect to ν or T_i , we can obtain

$$\alpha = \partial T_c / \partial \nu |_{T_i = \text{const}} = Q / c(T_c), \quad \beta = \partial T_c / \partial T_i |_{\nu = \text{const}} = c(T_i) / c(T_c).$$

By determining α and β from the experiments and specifying Q or $c(T_i)$ on the basis of the literature data, $c(T_c)$ can be determined, i.e., the temperature dependences of the specific heat in the region of high temperatures can be studied by the combustion method. Taking into account, however, the difficulties of the strict determination of the dependences of α and β on the temperature under the actual experimental conditions, we shall confine ourselves to finding the mean values of the specific heat.

The results of the calculations are shown in Table 2. The value $Q = 28.2$ kcal/mole [12] was used in the calculations. When processing Fig. 3, it was assumed that $c(T_c) = 16.6$ cal/(mole · deg), and the value of $c(T_i)$ was determined.

Data on the specific heat for nickel monoaluminide could not be found in the literature reference book. However, the data obtained coincide well with the theoretical values obtained by the formulas from [10]: when $T = T_{mp}$ is equal to $c_{solid} \gamma n = 14$ cal/(mole · deg); $c_{liquid} = 8n = 16$ cal/(mole · deg). According to theory, the specific heat in the liquid phase is almost independent of the temperature, and therefore the value determined from experiment has the significance of an accurate value and not an average quantity.

Thus, in this paper we have considered the problem concerning the effect of melting of the product on the mechanism of gasless combustion by the example of an equiatomic mixture of nickel with aluminum. This has permitted a new elementary model of combustion to be developed and certain thermophysical constants in the high-temperature region to be determined. The procedures proposed in the paper can be extended also to other systems, for which the combustion temperature is equal to the melting point of the product.

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