

## THERMODYNAMICS OF THE INTERACTION OF ALUMINUM, MAGNESIUM, AND ZIRCONIUM WITH COMPONENTS OF AN ELECTROLYTIC PLASMA

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For the idealized state of the gaseous components of an electrolytic plasma, we compute the thermodynamic parameters of their interaction with aluminum, magnesium, and zirconium (equilibrium constants and the characteristics of completeness of chemical reactions). It is shown that the process of synthesis of  $Al_2O$  in the electrolytic plasma includes several stages and passes through the formation intermediate compounds such as  $AlO$  and  $Al_2O_3$ . We indicate preferable reactions for the maximum output of the final product in the process of synthesis of  $Al_2O_3$  and  $ZrO_2$ . As pressure increases to 1 MPa, the temperature dependences of the output of the products of synthesis must shift toward higher temperatures.

The process of synthesis of oxides on rectifying metals in electrolytes in the presence of external electric fields includes several stages. The primary oxide film is formed according to the electrochemical mechanism [1] at voltages lower than the sparking voltage. Depending on the metal of the electrode and the composition of an electrolyte, the sparking voltage may vary within the range of several hundreds volts [2, 3]. In the second stage, the voltage becomes higher than the sparking voltage and this leads to the breakdown of the film and the appearance of discharge plasma channels [4] in which the temperature of plasma electrons can be higher than 7000°K [5]. The third stage is characterized by the gaseous-phase chemical reactions between the components of the metallic anode and plasma. At temperatures of about 7000°K, in plasmas formed by the dissociation and ionization of electrolytes with a degree of ionization of about  $10^{-5}$  [6], the partial pressures of atomic oxygen and hydrogen are sufficiently high for the intense chemical reactions with the metal of the anode [7]. On the "walls" of a discharge channel whose temperature is lower by several thousands of degrees, the partial pressure of OH radicals is also sufficient for chemical reactions. At this temperature, the partial pressures of all other components of the plasma are lower by several orders of magnitude. For a certain period of time, in the central part of the discharge channels, the plasma is quasi-perfect, nondegenerate, and equilibrium [6].

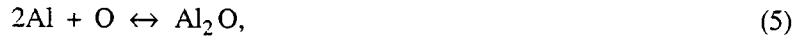
For the idealized state [8] of the gaseous components of plasmas, we determine the thermodynamic parameters of the interaction of metals (aluminum, magnesium, and zirconium) with components of the plasma (equilibrium constants and the characteristics of completeness of chemical reactions). According to the results presented in [9], this interaction can, generally speaking, be described by the following chemical reactions:



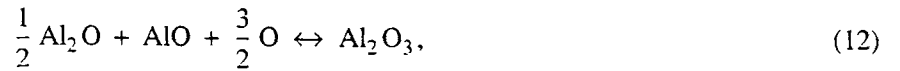
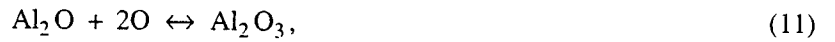
where  $Me_xO_y$  is either an intermediate product or the final product.

According to the Le Chatelier principle generalized by Onsager and Prigogine to the case of nonstationary irreversible processes, any increase in temperature promotes endothermic reactions in the system. At the same time, exothermic reactions in the system are facilitated as temperature decrease. The analysis of the total enthalpy of formation of intermediate compounds in the process of interaction of aluminum with atomic oxygen or OH according to reactions (1) and (2), which indirectly specifies the thermal effect, shows that  $AlO$ ,  $Al_2O$ , and  $AlO_2$  are, most probably, formed as a result of the following endothermic reactions [9]:

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and the final product can be regarded as formed in the following exothermic reactions:



For reactions (4)–(6), and (9), we compute the equilibrium concentrations and the output of compounds by the law of mass action. For reactions (7), (8), and (10)–(13), the same is done by the method of combined equilibria. We denote the output of compounds by  $nx$  and the number of source reagents by  $n(1-x)$ , where  $n$  are the corresponding coefficients in reactions. Following the method proposed in [8, 10], we determine the partial pressures of the source components and intermediate and final products as well as the equilibrium constants  $K^0$  of the analyzed reactions. As a result, we get

$$p_{\text{Al}} = \frac{1-x}{2-x} P, \quad p_{\text{O}} = \frac{1-x}{2-x} P, \quad p_{\text{AlO}} = \frac{x}{2-x} P, \quad \text{and} \quad K^0 = \frac{p_{\text{Al}} p_{\text{O}}}{p_{\text{AlO}}} = \frac{1-x^2}{x(2-x)} P$$

for reaction (4),

$$p_{\text{Al}} = \frac{2(1-x)}{3-2x} P, \quad p_{\text{O}} = \frac{1-x}{3-2x} P, \quad p_{\text{Al}_2\text{O}} = \frac{x}{3-2x} P, \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{O}}}{p_{\text{Al}_2\text{O}}} = \frac{4(1-x)^3}{x(3-2x)^2} P^2$$

for reaction (5),

$$p_{\text{Al}} = \frac{1-x}{3-2x} P, \quad p_{\text{O}} = \frac{2(1-x)^3}{3-2x} P, \quad p_{\text{AlO}_2} = \frac{x}{3-2x} P, \quad K^0 = \frac{p_{\text{Al}} p_{\text{O}}^2}{p_{\text{AlO}_2}} = \frac{4(1-x)^3}{x(3-2x)^2} P$$

for reaction (6),

$$p_{\text{Al}} = \frac{2(1-x)}{4-x} P, \quad p_{\text{OH}} = \frac{2(1-x)}{4-x} P, \quad p_{\text{AlO}} = \frac{2x}{4-x} P,$$

$$p_{\text{H}_2} = \frac{x^3}{4-x} P, \quad K^0 = \frac{p_{\text{Al}} p_{\text{OH}}}{p_{\text{AlO}}^{0.5} p_{\text{H}_2}} = \frac{2(1-x)^2}{x^{3/2} (4-x)^{1/2}} P^{0.5}$$

for reaction (7),

$$p_{\text{Al}} = \frac{2(1-x)}{3-1.5x} P, \quad p_{\text{OH}} = \frac{1-x^3}{3-1.5x} P,$$

$$p_{\text{Al}_2\text{O}} = \frac{x}{3-1.5x} P, \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{OH}}}{p_{\text{Al}_2\text{O}}^{1/2}} = \frac{4\sqrt{2}(1-x)^3}{(3x-1.5x^2)^{3/2}} P^{3/2}$$

for reaction (8),

$$p_{\text{Al}} = \frac{2(1-x)}{5-4x} P, \quad p_{\text{O}} = \frac{3(1-x)}{5-4x} P, \quad p_{\text{Al}_2\text{O}_3} = \frac{x}{5-4x} P, \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{O}}^3}{p_{\text{Al}_2\text{O}_3}} = \frac{36(1-x)^2}{x(5-4x)} P^4$$

for reaction (9) if it results in the formation of gaseous  $\text{Al}_2\text{O}_3$  or

$$p_{\text{Al}_2\text{O}_3} = 1 \quad \text{and} \quad K^0 = p_{\text{Al}}^2 p_{\text{O}}^3 = \frac{108(1-x)^5}{(5-4x)^5} P^5$$

if it results in the formation of liquid  $\text{Al}_2\text{O}_3$ ,

$$p_{\text{AlO}} = \frac{2(1-x)}{3-2x} P, \quad p_{\text{O}} = \frac{1-x}{3-2x} P, \quad p_{\text{Al}_2\text{O}_3} = \frac{x}{3-2x} P, \quad K^0 = \frac{p_{\text{AlO}}^2 p_{\text{O}}}{p_{\text{Al}_2\text{O}_3}} = \frac{4(1-x)^3}{x(3-2x)^2} P^2$$

for reaction (10) if it results in the formation of gaseous  $\text{Al}_2\text{O}_3$  or

$$p_{\text{Al}_2\text{O}_3} = 1 \quad \text{and} \quad K^0 = p_{\text{AlO}}^2 p_{\text{O}} = \frac{4(1-x)^3}{(3-2x)^3} P^3$$

if it results in the formation of liquid  $\text{Al}_2\text{O}_3$ ,

$$p_{\text{Al}_2\text{O}} = \frac{1-x}{3-2x} P, \quad p_{\text{O}} = \frac{2(1-x)}{3-2x} P, \quad p_{\text{Al}_2\text{O}_3} = \frac{x}{3-2x} P, \quad K^0 = \frac{p_{\text{Al}_2\text{O}}^2 p_{\text{O}}}{p_{\text{Al}_2\text{O}_3}} = \frac{4(1-x)^3}{x(3-2x)^2} P^2$$

for reaction (11) if it results in the formation of gaseous  $\text{Al}_2\text{O}_3$  or

$$p_{\text{Al}_2\text{O}_3} = 1 \quad \text{and} \quad K^0 = p_{\text{Al}_2\text{O}}^2 p_{\text{O}} = \frac{4(1-x)^3}{(3-2x)^3} P^3$$

if it results in the formation of liquid  $\text{Al}_2\text{O}_3$ ,

$$p_{\text{Al}_2\text{O}} = \frac{1-x}{2(3-2x)} P, \quad p_{\text{O}} = \frac{3(1-x)}{2(3-2x)} P, \quad p_{\text{AlO}} = \frac{1-x}{3-2x} P,$$

$$p_{\text{Al}_2\text{O}_3} = \frac{x}{3-2x} P, \quad K^0 = \frac{p_{\text{Al}_2\text{O}}^{1/2} p_{\text{AlO}} p_{\text{O}}^{3/2}}{p_{\text{Al}_2\text{O}_3}} = 1.304 \frac{1-x}{x(3-2x)^2} P^2$$

for reaction (12) if it results in the formation of gaseous  $\text{Al}_2\text{O}_3$  or

$$p_{\text{Al}_2\text{O}_3} = 1 \quad \text{and} \quad K^0 = p_{\text{Al}_2\text{O}}^{1/2} p_{\text{AlO}} p_{\text{O}}^{3/2} = 1.304 \frac{(1-x)^3}{(3-2x)^3} P^3$$

if it results in the formation of liquid  $\text{Al}_2\text{O}_3$ , and

$$p_{\text{Al}} = \frac{2(1-x)}{5-2.5x} P, \quad p_{\text{OH}} = \frac{3(1-x)}{5-2.5x} P, \quad p_{\text{H}_2} = \frac{3x}{2(5-2.5x)} P,$$

$$p_{\text{Al}_2\text{O}_3} = \frac{x}{5-2.5x} P, \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{OH}}^3}{p_{\text{Al}_2\text{O}_3} p_{\text{H}_2}^{3/2}} = \frac{58.8(1-x)^5}{x^{2.5}(5-2.5x)^{2.5}} P^{2.5}$$

for reaction (13) if it results in the formation of gaseous  $\text{Al}_2\text{O}_3$  or

$$p_{\text{Al}_2\text{O}_3} = 1 \quad \text{and} \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{OH}}^3}{p_{\text{H}_2}^{3/2}} = 58.8 \frac{(1-x)^5}{x^{1.5}(5-2.5x)^{3.5}} P^{3.5}$$

if it results in the formation of liquid  $\text{Al}_2\text{O}_3$ .

Parallel with  $\text{Al}_2\text{O}_3$ , small amounts of  $\text{AlOOH}$  were detected in the coatings. The formation of this compound is possible in the peripheral regions of the discharge channel as a result of the following reaction between the excess of  $\text{AlO}$  and  $\text{OH}$ :



For this reaction, we have

$$p_{\text{AlO}} = \frac{1-x}{2-x} P, \quad p_{\text{O}} = \frac{1-x}{2-x} P, \quad p_{\text{AlOOH}} = \frac{x}{2-x} P, \quad K^0 = \frac{p_{\text{AlO}} p_{\text{OH}}}{p_{\text{AlOOH}}} = \frac{(1-x)^2}{x(2-x)} P$$

if it results in the formation of gaseous  $\text{AlOOH}$  or

$$p_{\text{AlOOH}} = 1 \quad \text{and} \quad K^0 = p_{\text{AlO}} p_{\text{OH}} = \frac{(1-x)^2}{(2-x)^2} P^2$$

if it results in the formation of liquid  $\text{AlOOH}$ .

Although the probability of the reaction of aluminum with water is quite low, for the sake of comparison, we also consider the reaction



for which

$$p_{\text{Al}} = \frac{2(1-x)}{5-x} P, \quad p_{\text{H}_2\text{O}} = \frac{3(1-x)}{5-x} P, \quad p_{\text{H}_2} = \frac{3x}{5-x} P,$$

$$p_{\text{Al}_2\text{O}_3} = \frac{x}{5-x} P, \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{H}_2\text{O}}^3}{p_{\text{Al}_2\text{O}_3} p_{\text{H}_2}^3} = \frac{12(1-x)^5}{x^4(5-x)} P$$

if it results in the formation of gaseous  $\text{Al}_2\text{O}_3$  or

$$p_{\text{Al}_2\text{O}_3} = 1 \quad \text{and} \quad K^0 = \frac{p_{\text{Al}}^2 p_{\text{H}_2\text{O}}^3}{p_{\text{H}_2}^3} = \frac{12(1-x)^5}{x^3(5-x)^2} P^2$$

if it results in the formation of liquid  $\text{Al}_2\text{O}_3$ .

The analysis of the thermodynamic parameters of formation of the  $\text{AlH}$ ,  $\text{AlH}_2$ , and  $\text{AlH}_3$  hydrides shows [11] that the formation of  $\text{AlH}$  according to the reaction



should be regarded as the most probable. For this reaction, we have

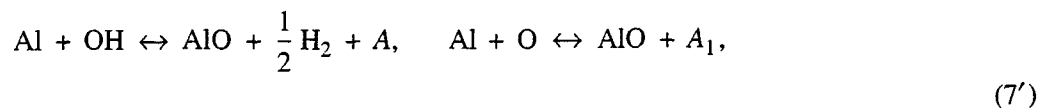
$$p_{\text{Al}} = \frac{1-x}{2-x} P, \quad p_{\text{H}} = \frac{1-x}{2-x} P, \quad p_{\text{AlH}} = \frac{x}{2-x} P, \quad K^0 = \frac{(1-x)^2}{2x-x^2} P^2$$

if it results in the formation of gaseous  $\text{AlH}$  or

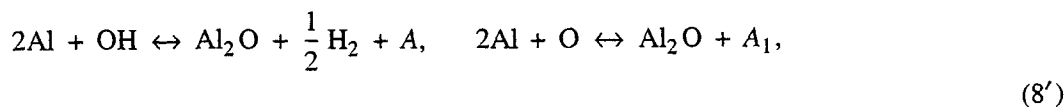
$$p_{\text{AlH}} = 1 \quad \text{and} \quad K^0 = \frac{(1-x)^2}{(2-x)^2} P^2$$

if it results in the formation of liquid  $\text{AlH}$ .

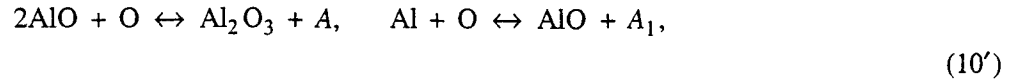
To determine the equilibrium constants and characteristics of completeness of the reaction by the method of combined equilibria, we represent the analyzed reaction as a sum or difference of reactions with known equilibrium constants. In this case, the required chemical affinity  $A$  is equal to the sum of the affinities  $A_1$  and  $A_2$  of the elementary reactions. If we add the affinities  $A$  for the same values of temperature and pressure, then the equilibrium constants are multiplied or divided because they appear under the logarithm sign. For reactions (7), (8), and (10)–(15), we obtain



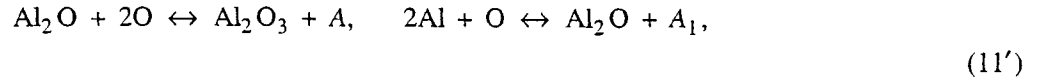
$$\text{O} + \text{H} \leftrightarrow \text{OH} + A_2, \quad K^0 = \frac{K_1^0}{K_2^0},$$



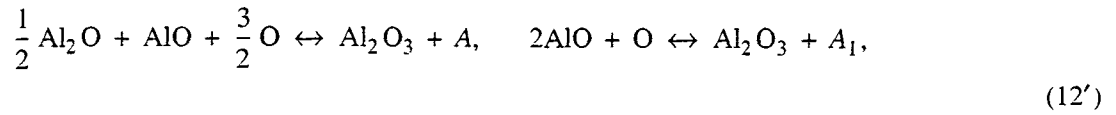
$$\text{O} + \text{H} \leftrightarrow \text{OH} + A_2, \quad K^0 = \frac{K_1^0}{K_2^0},$$



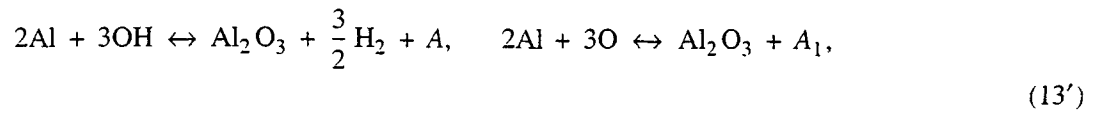
$$2\text{Al} + 3\text{O} \leftrightarrow \text{Al}_2\text{O}_3 + \text{A}_2, \quad K^0 = \frac{K_2^0}{K_1^0},$$



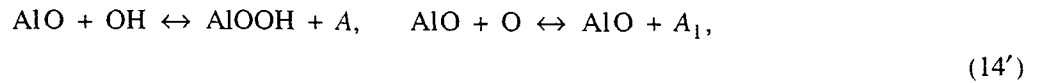
$$2\text{Al} + 3\text{O} \leftrightarrow \text{Al}_2\text{O}_3 + \text{A}_2, \quad K^0 = \frac{K_2^0}{K_1^0},$$



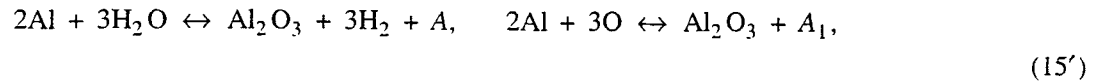
$$\text{Al}_2\text{O} + 2\text{O} \leftrightarrow \text{Al}_2\text{O}_3 + \text{A}_2, \quad K^0 = K_1^0 K_2^0,$$



$$\text{O} + \text{H} \leftrightarrow \text{OH} + \text{A}_2, \quad K^0 = \frac{K_1^0}{K_2^0},$$



$$\text{O} + \text{H} \leftrightarrow \text{OH} + \text{A}_2, \quad K^0 = K_1^0 K_2^0,$$



$$\text{O} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{A}_2, \quad K^0 = \frac{K_1^0}{K_2^0},$$

To determine the equilibrium constants and the characteristics of completeness of the reactions (Fig. 1), we use the tables of thermodynamic quantities for individual substances presented in [11, 14].

We consider the reaction of liquid aluminum with gaseous atomic oxygen resulting in the formation of liquid  $\text{Al}_2\text{O}_3$ :

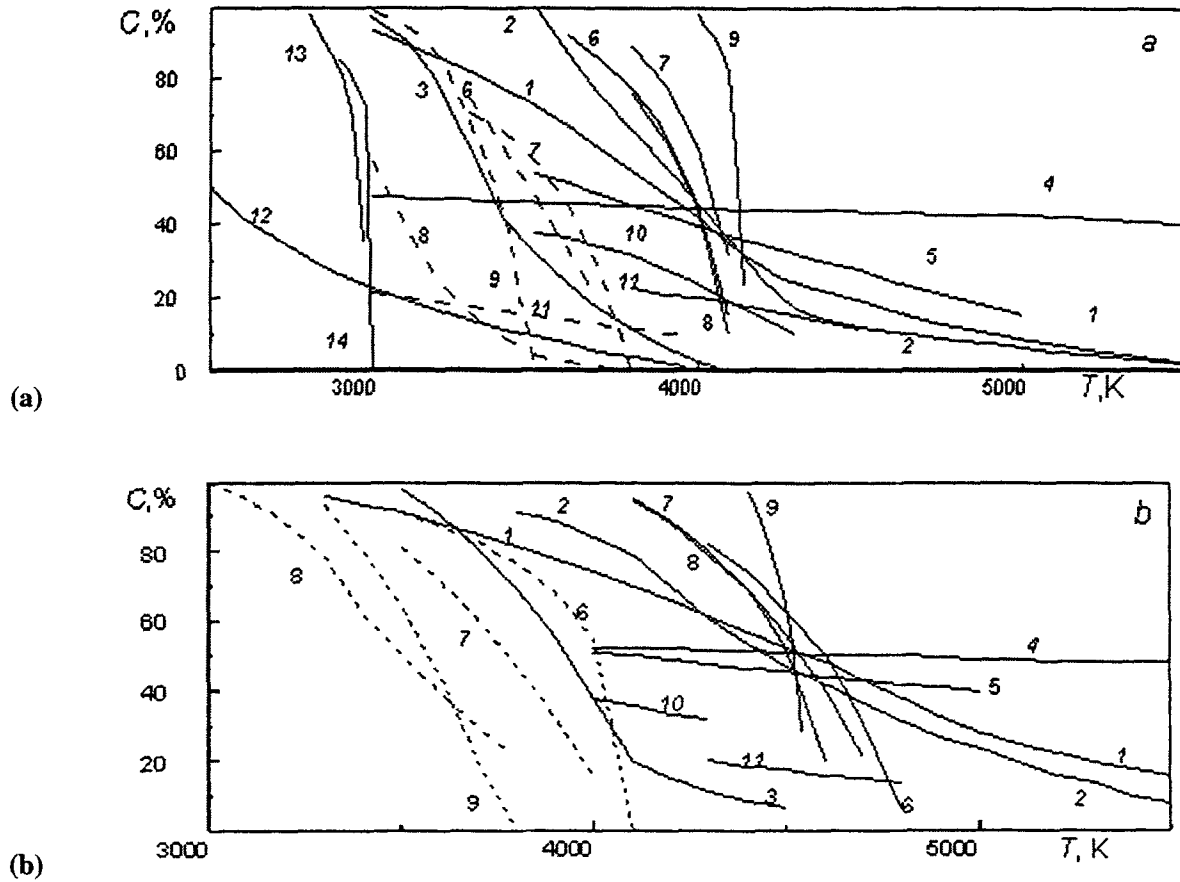


The equilibrium constants are computed by using the formula

$$R \ln K^0(i, T) = \Delta_r S^0(T) - \frac{\Delta_r H^0(0)}{T}, \quad (18)$$

where  $\Delta_r \Phi^0(T)$  is the increment of the reduced Gibbs energy,  $\Delta_r H^0$  is the increment of enthalpy, and  $R$  is the gas constant.

For substances in the condensed states, the equilibrium constant of the reactions of sublimation and evaporation accompanied by the formation of a gas of the same molecular composition as in the condensed phase is given by the formula



**Fig. 1.** Temperature dependences of the output of the products of synthesis under a pressure of 0.1 MPa (a) or 1 MPa (b) for the following reactions: (4) (curve 1), (3) (curve 2), (6) (curve 3), (7) (curve 4), (8) (curve 5), (9) (curve 6), (10) (curve 7), (11) (curve 8), (12) (curve 9), (13) (curve 10), (15) (curve 11), (16) (curve 12), (26.5) (curve 13), and (26.3) (curve 14). The dashed lines correspond to gaseous Al<sub>2</sub>O<sub>3</sub>.

$$R \ln K^0(i, T) = R \ln p(i, T) = \Phi^0(i, g, T) - \Phi^0(i, c, T) - \frac{\Delta_S H^0(0)}{T}, \quad (19)$$

where  $\Phi^0(i, g, T)$  and  $\Phi^0(i, c, T)$  are the values of reduced Gibbs energy for the  $i$ th substance in gaseous and condensed states and  $\Delta_S H^0(0)$  is the enthalpy of the reaction of sublimation at  $T = 0$ .

We compute the value of enthalpy via the known enthalpies  $\Delta_f H^0(0)$  of formation of all substances participating in the reaction under the standard conditions

$$\begin{aligned} \Delta_r H^0(T) = \Delta(\Delta_f H^0(A_i, T)) = & v'_1 \Delta_f H^0(A'_1, T) + v'_2 \Delta_f H^0(A'_2, T) + \dots \\ & - v_1 \Delta_f H^0(A_1, T) - v_2 \Delta_f H^0(A_2, T) - \dots, \quad (20) \end{aligned}$$

where  $v$  is the number of moles of the substance  $A_i$ . By using relations (18)–(20), we determine the equilibrium constant of reaction (17) as follows:

$$R \ln K^0 = \left[ \Phi^0(T)_{\text{Al}_2\text{O}_3} - \frac{\Delta_r H^0(0)_{\text{Al}_2\text{O}_3}}{T} \right] - 2 [\Phi^0(T)_{\text{Al},g,T} - \Phi^0(T)_{\text{Al},c,T}]$$

$$+ \frac{2\Delta_S H^0(0)_{Al}}{T} - 3 \left[ \Phi^0(T)_0 - \frac{\Delta_f H^0(0)_0}{T} \right]. \quad (21)$$

In view of the fact that, in the condensed state, the partial pressures of aluminum and its oxide can be set equal to one, we can write the following relation for the equilibrium constants and the characteristics of completeness of the reaction:

$$K^0 = 3 - \frac{3x}{5} - 4x. \quad (22)$$

It follows from relations (21) and (22) that  $K^0 = 0.27$ ,  $\log K^0 = -0.2566$ ,  $C_{Al} = 14.5\%$ ,  $C_O = 21.7\%$ , and  $C_{Al_2O_3} = 63.8\%$  for  $T = 3000^\circ\text{K}$  and  $K^0 = 0.6027$ ,  $\log K^0 = -0.02199$ ,  $C_{Al} = 39.2\%$ ,  $C_O = 58.9\%$ , and  $C_{Al_2O_3} = 1.9\%$  for  $T = 2900^\circ\text{K}$ .

Under the actual conditions of synthesis of oxidoceramic coatings, both aluminum and its  $Al_2O_3$  oxide are in the solid phase. Thus, we consider the reaction



We determine the thermodynamic equilibrium of this reaction by using the exact tabular method of Vladimirov [10] to compute the logarithms of the equilibrium constants by the formulas

$$\Delta Z_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T \int_{298}^T \frac{dT}{dT^2} \int_{298}^T \Delta C_P dT, \quad (24)$$

$$\log K = \frac{\Delta_f(\Delta H)}{T} + \Delta_f(\Delta S) + \Delta C_0 M_0 + \Delta C_1 M_1 + \Delta C_2 M_2 + \Delta C_{-2} M_{-2}, \quad (25)$$

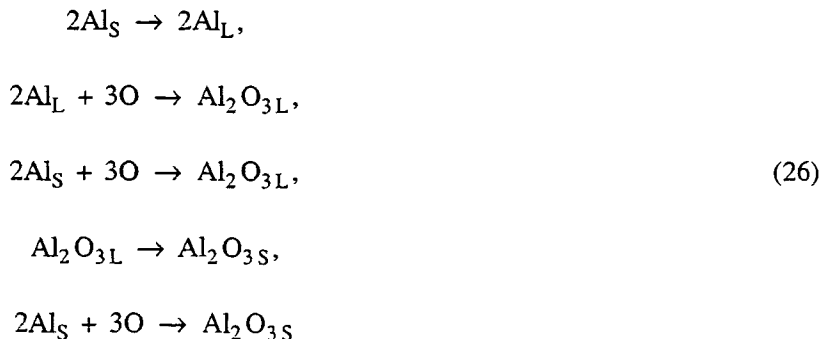
where

$$M_0 = \ln\left(\frac{T}{298.13}\right) + \frac{298.13}{T} - 1 \quad \text{and} \quad M_0 = \frac{(T - 298.16)^2}{2T}$$

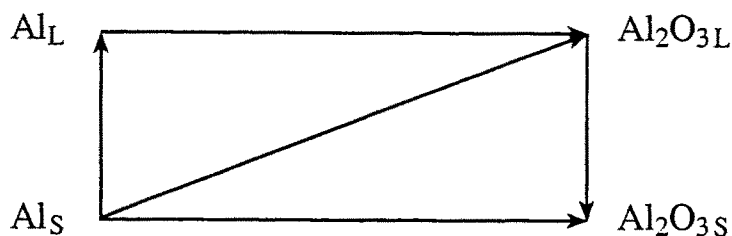
are functions of temperature. Each term of relation (24) is the algebraic sum of numerical values of one of the functions  $\Delta H$ ,  $\Delta S$ , or  $\Delta C_P$  for the corresponding reagent. The logarithm of the equilibrium constant of the reaction is the algebraic sum of all terms of this equation, which enables us to find it in the convenient tabular form. We determine the logarithm of the equilibrium constant by using this method as follows: We write the symbols of all reagents in a separate table arranging them in a column. The values of the molar coefficients for each reagent are presented together with its symbol. Then, by using the auxiliary tables presented in [10, 15] or, if necessary, performing special calculations, we determine the functions corresponding to each reagent in the order of their appearance in the table. Further, we add the functions thus obtained in each vertical column. The result denoted by  $\Delta f$  for the first column means the increment of the function  $\Delta H$  for the system under consideration, i.e.,  $\Delta_f(\Delta H)$ . For the second column, this result is equal to the increment of the function  $\Delta S$ , i.e.,  $\Delta_f(\Delta S)$ , etc. By using the auxiliary tables for the functions of temperature  $f(T)$  or finding them, we write these functions  $f(T)$  as a separate row in the same sequence with the exception of the second column where they are absent. After this, it is necessary to multiply the values of the functions in the last two rows  $[\Delta f \cdot f(T)]$  and enumerate the values obtained as a result in all columns. This gives the required logarithm of the equilibrium constant of the investigated reaction in the direct direction.



From the thermodynamic point of view, only the final result of the process is important but not the way of its attainment. Thus, the reaction (23) of oxidation of solid aluminum by atomic oxygen leading to the formation of solid alumina can be represented in the form of the following five reactions:



whose schematic representation is presented below.



We consider the first reaction in (26) but in the reverse direction despite the fact that for the evaluation of  $N$  and  $M$ , we pass from the standard state for solid aluminum to the nonstandard state for liquid aluminum. The latent heat of melting of 1 g-atom of aluminum is equal to 2520 cal. Therefore, for two moles, we have

$$M \cdot 10^{-3} = 10^{-3} \cdot \frac{\Delta H_{298}^0}{R} = -1.1016 \quad \text{and} \quad N = 0.21858 \cdot \Delta S_{298}^0 = 1.18.$$

The heat capacity of liquid aluminum is equal to 7. Thus, for two moles, it is equal to 14. This means that  $f(\Delta C_L) = 3.06$ . Thus, by using reactions (26), we determine the equilibrium constants for the first process at various temperatures (see Table 1). Indeed, the logarithm of the equilibrium constant  $\log K$  of the first reaction in (26), has the following values at different temperatures: 0.5329 for 2700°K, 0.5079 for 2800°K, 0.4821 for 2900°K, 0.4684 for 2950°K, and 0.4629 for 2970°K. For the second reaction in (26), these values are computed by using relation (21). This yields 3.591 for 2700°K, 1.9903 for 2800°K, 1.0914 for 2900°K, 0.6676 for 2950°K, and 0.5026 for 2970°K. The logarithm of the equilibrium constant of the third reaction in (26) is equal to the sum of the logarithms of the equilibrium constants of the first two reactions.

The value of  $\log K$  for the process of hardening of alumina is determined by using an approximate tabular method. The temperature of melting of alumina is 2303°K and the latent heat of melting is equal to 2600 cal/mole. Hence, for the process  $\text{Al}_2\text{O}_{3L} \rightarrow \text{Al}_2\text{O}_{3S}$ , we obtain  $M = -5683$  and  $N = 2.467$ .

The equation of aggregate transformation has the form

$$\log K = \frac{M}{T} + N. \tag{27}$$

By using this equation, we obtain the following values of  $\log K$  for the aggregate transformation at different temperatures:  $-0.3622$  for 2700°K,  $-0.4374$  for 2800°K,  $-0.5074$  for 2900°K,  $-0.5406$  for 2950°K, and  $-0.4629$  for 2970°K.

Table 1

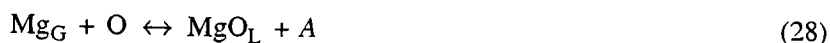
T, °K	Reagents	M · 10 <sup>-3</sup>	N	f(ΔC <sub>L</sub> )		log K <sup>0</sup>
				C <sub>0</sub>	C <sub>1</sub> · 10 <sup>-3</sup>	
	-2Al <sub>L</sub>	1.016	-1.18	-3.06		
	+2Al <sub>S</sub>	0	0	2.098	1.408	
	Δf	1.1016	-1.18	-0.962	1.408	
2800	f(T)	0.3571		1.3462	1.1177	
	Δf · f(T)	0.3934	-1.18	-1.295	1.5737	-0.5079
2700	f(T)	0.3704		1.3138	1.068	
	Δf · f(T)	0.408	-1.18	-1.2539	1.503	-0.5329
2900	f(T)	0.3448		1.3776	1.1672	
	Δf · f(T)	0.3798	-1.18	-1.3255	1.6434	-0.489
2950	f(T)	0.339		1.393	1.192	
	Δf · f(T)	0.3734	-1.18	-1.3401	1.6783	-0.4684
2970	f(T)	0.3367		1.3991	1.2018	
	Δf · f(T)	0.3709	-1.18	-1.3459	1.6921	-0.4629

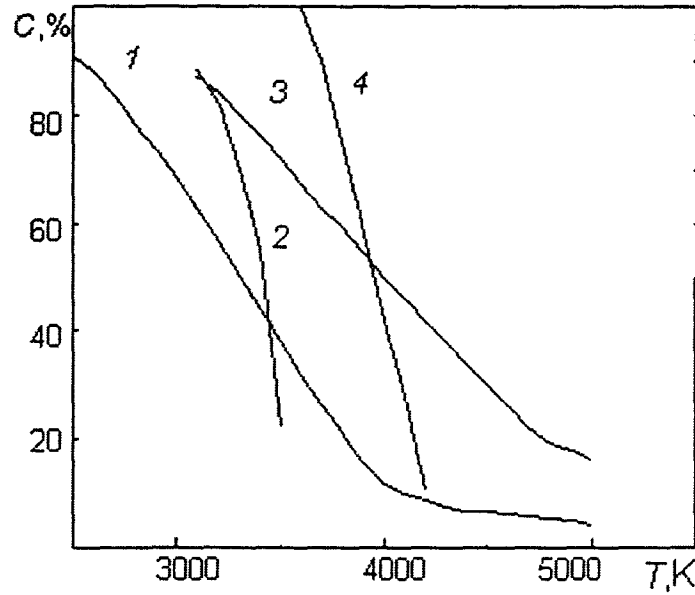
As a result, for the fifth reaction in (26), we obtain the following values of log K: 3.7617 for 2700°K, 2.0608 for 2800°K, 1.066 for 2900°K, 0.5954 for 2950°K, and 0.412 for 2970°K.

By using Eq. (22) and the fact that  $\log K^0 = -\log K$ , we determine the equivalent compositions of reaction (23) at different temperatures, namely, 100% Al<sub>2</sub>O<sub>3</sub> at 2700°K, 0.5% Al, 0.9% O, and 98.6% Al<sub>2</sub>O<sub>3</sub> at 2800°K, 5.7% Al, 8.6% O, and 85.7% Al<sub>2</sub>O<sub>3</sub> at 2900°K, 16.9% Al, 25.9% O, and 57.7% Al<sub>2</sub>O<sub>3</sub> at 2950°K, and 25.8% Al, 38.7% O, and 35.5% Al<sub>2</sub>O<sub>3</sub> at 2970°K.

Assume that there is no lack of atoms of aluminum and oxygen in the reaction zone. Then, at temperatures of 4000°K and higher, reactions (4), (5), and (12) are preferable for the output of Al<sub>2</sub>O<sub>3</sub>. As temperature decreases, the output of reactions (9)–(11) considerably increases. As the external pressure increases, the equilibrium in these reactions shifts to the right and, hence, the output of Al<sub>2</sub>O<sub>3</sub> at higher temperatures increases. In this case, the direct reaction (9) becomes preferable. At the same time, at temperatures below 4370°K, the output of the product in reactions (4), (5), and (12) increases (Fig. 1). The electronic vibrational transitions in AlO molecules were identified in [16]. This proves that the process of synthesis of Al<sub>2</sub>O<sub>3</sub> in the electrolytic plasma passes through several stages. At temperatures higher than 2700°K, the output of aluminum hydride is negligible (Fig. 1).

Unlike Al<sub>2</sub>O<sub>3</sub>, which decomposes in the process of heating at a certain temperature, the magnesium and zirconium oxides sublimate. This enables us to represent the reaction





**Fig. 2.** Temperature dependences of the output of MgO in reactions (28) and (30): (1) gaseous MgO,  $P = 0.1$  MPa. (2) liquid MgO,  $P = 0.1$  MPa, (3) gaseous MgO,  $P = 1$  MPa. (4) liquid MgO,  $P = 1$  MPa.

as the sum of the following reactions:



As a result, for the original reaction (28), we get

$$p_{\text{Mg}} = \frac{1-x}{2-x} P, \quad p_{\text{O}} = \frac{1-x}{2-x} P, \quad p_{\text{MgO}} = 1, \quad K^0 = K_1^0 K_2^0 = p_{\text{Mg}} p_{\text{O}} = \frac{(1-x)^2}{(2-x)^2} P^2$$

and, for reaction (29), we can write

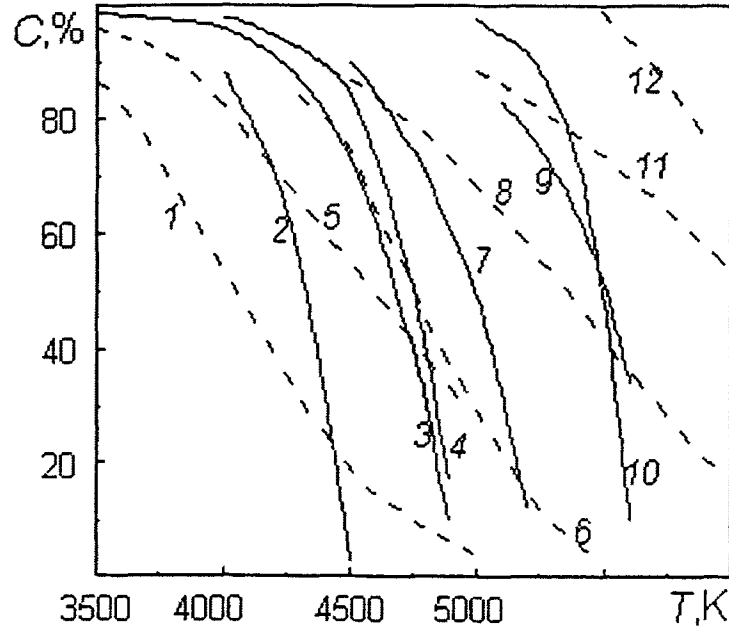
$$p_{\text{Mg}} = \frac{1-x}{2-x} P, \quad p_{\text{O}} = \frac{1-x}{2-x} P, \quad p_{\text{MgO}} = \frac{x}{2-x} P, \quad K^0 = \frac{p_{\text{Mg}} p_{\text{O}}}{p_{\text{MgO}}} = \frac{(1-x)^2}{x(2-x)} P,$$

where  $K_1^0$  and  $K_2^0$  are the equilibrium constants.

After necessary calculations, we arrive at the temperature dependences of the outputs of  $\text{MgO}_G$  and  $\text{MgO}_L$  under pressures of 0.1 and 1 MPa (Fig. 2). The temperature of formation of MgO according to reaction (28) increases with pressure. We do not analyze the reactions of formation of magnesium dioxide ( $\text{MgO}_2$ ) due to its quite low stability [11].

In the process of interaction of zirconium with oxygen, one may observe the formation of the gaseous and solid (liquid) phases of  $\text{ZrO}$  and  $\text{ZrO}_2$  [17]. We now consider the following chemical reactions of their formation:





**Fig. 3.** Temperature dependences of the output of gaseous  $ZrO_2$  (1, 5, 6, and 12), gaseous  $ZrO$  (8 and 11), and liquid  $ZrO_2$  (2, 7, 4, 9, 3, and 10) in reactions (31) (curves 8–10), (32) (curves 6, 12), (33) (curves 1, 5), (34) (curves 2, 7), (35) (curves 4, 5), and (36) (curves 3, 10) for  $P = 0.1$  MPa (curves 1–4, 6, 8) and  $P = 1$  MPa (curves 5, 7, 9–12).



Thus, we get

$$p_{Zr} = \frac{1-x}{2-x} P, \quad p_O = \frac{1-x}{2-x} P, \quad p_{ZrO} = \frac{x}{2-x} P, \quad K^0 = \frac{p_{Zr} p_O}{p_{ZrO}} = \frac{(1-x)^2}{x(2-x)} P$$

for reaction (31),

$$p_{ZrO_2} = \frac{x}{3-2x} P, \quad K^0 = \frac{p_{Zr} p_O}{p_{ZrO_2}} = \frac{4(1-x)^3}{x(3-2x)} P^2$$

for reaction (32),

$$p_{ZrO} = \frac{1-x}{2-x} P, \quad p_O = \frac{1-x}{2-x} P, \quad p_{ZrO_2} = \frac{x}{2-x} P, \quad K^0 = \frac{p_{Zr} p_O}{p_{ZrO_2}} = \frac{(1-x)^2}{x(2-x)} P$$

for reaction (33),

$$p_{Zr} = \frac{1-x}{3-2x} P, \quad p_O = \frac{2(1-x)}{3-2x} P, \quad p_{ZrO_2} = \frac{2(1-x)}{3-2x} P,$$

$$p_{\text{ZrO}_2} = 1, \quad K^0 = \frac{p_{\text{Zr}} p_{\text{O}}}{p_{\text{ZrO}_2}} = \frac{2(1-x)^2}{3-2x} P^2$$

for reaction (34), and

$$p_{\text{ZrO}} = \frac{1-x}{2-x} P, \quad p_{\text{O}} = \frac{1-x}{2-x} P, \quad p_{\text{ZrO}_2} = 1, \quad K^0 = p_{\text{Zr}} p_{\text{O}} = \frac{(1-x)^2}{(2-x)^2} P^2$$

for reaction (35).

For reaction (33),  $K^0$  is obtained by dividing its value for reaction (32) by its value for reaction (31). For reactions (34) and (35), the value of  $K^0$  is obtained by multiplying the corresponding values for reactions (32) and (33) by the value established for the reaction



By using the known values of the thermodynamic parameters [18] for reactions (31)–(35), we obtain the temperature dependences of the output of ZrO and ZrO<sub>2</sub> (Fig. 3). The maximum output of gaseous ZrO and ZrO<sub>2</sub> as temperature decreases under a pressure of 0.1 MPa is observed in reactions (31), (32), and (33). Under a pressure of 1 MPa, the same is true for reactions (32), (31), and (33). Thus, the maximum output of the final product of synthesis of ZrO<sub>2L</sub> under pressures of 0.1 and 1 MPa is guaranteed by the preferable coupled reactions (32), (36)–(31), and (35). The data of X-ray structural analysis show that the coating consists of the monoclinic phase of ZrO<sub>2</sub>. Some authors [19] indicate that it is, in principle, possible to obtain zirconium monoxides (ZrO) at high temperatures and under high pressures. As temperature decreases, these monoxides are oxidized to ZrO<sub>2</sub>.

## CONCLUSIONS

The results of our theoretical calculations and experimental investigations demonstrate that the process of synthesis of Al<sub>2</sub>O<sub>3</sub> in the electrolytic plasma passes through several stages and through the formation of intermediate compounds (AlO and Al<sub>2</sub>O). In this case, reactions (4), (5), and (12) are preferable from the viewpoint of the maximum output of the final product.

Reactions (32), (36) and (31), (35) prove to be preferable under the conditions of synthesis of ZrO<sub>2</sub>. It is shown that, as pressure increases to 1 MPa, the temperature dependences of the output of intermediate and final products of synthesis shift toward higher temperatures.

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