COMPARATIVE THERMODYNAMIC ANALYSIS OF PLASMOCHEMICAL SYNTHESIS OF ALUMINUM AND YTTRIUM OXIDES

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A thermodynamic calculation of the dependence of the end-product yield and specific enthalpy on the pressure and temperature is performed for the plasmochemical synthesis of aluminum and yttrium oxides.

The synthesis of such refractory compounds as aluminum and yttrium oxides and aluminum—yttrium garnet in a high-frequency plasma is very promising, since it has a whole series of advantages over traditional methods of synthesis. In this connection, investigation of the thermodynamics of plasmochemical synthesis of these compounds is an important problem. Such investigations may serve to provide preliminary information on the process parameters, in the absence of which the practical realization of such processes would be difficult.

In the present work, results of calculations for aluminum oxide are compared with results of analogous calculations for yttrium oxide [1], which allows both general laws and distinctive characteristics of plasmochemical synthesis for these refractory compounds to be established, and allows useful information to be obtained on the synthesis conditions for yttrium—aluminum garnet. This is particularly important, since the absence of many thermodynamic characteristics of yttrium—aluminum garnet means that direct thermodynamic investigation of the synthesis characteristics of this compound is impossible.

The mixture composition and the process parameters for synthesis were determined numerically using a numerical calculation program for the composition and thermodynamic functions of a multicomponent heterogeneous mixture. The program is written in Fortran for the Minsk-32 computer [1], on the basis of the method of minimizing the isobaric—isothermal potential [2, 3]. In the calculations it was assumed that the gaseous components of the mixture constitute an ideal gas. The total isobaric—isothermal potential of the condensed components was assumed to be independent of pressure. In the case of aluminum-oxide synthesis, 35 possible components were considered, consisting of five chemical elements. It was assumed that the synthesis was performed by introducing aqueous $AlCl_3$ solution in an oxygen—argon plasma. The reduced isobaric—isothermal potentials of the components were taken from [4]. The calculations were performed for variation of the flow rates of the plasma-forming gas in the range 10-100 liter/min and of the aqueous solution in the range 1-10 g/sec. Note that the dependences considered below did not change qualitatively over the given flow-rate ranges.

In the present work, results are given for the following flow-rate values: 60 liter/min O_2; 30 liter/min Ar; 5 g/sec 33% aqueous $AlCl_3$ solution. These flow rates are typical for practical aluminum-oxide synthesis. In the case of yttrium-oxide synthesis, the results are given for the flow rates cited in [1]. The input temperature of the initial materials was taken to be 20°C.

The temperature dependence of the aluminum oxide yield $\eta = m/m_0$ at 1-atm pressure is shown in Fig. 1 in comparison with the analogous dependence for yttrium oxide. It is evident from Fig. 1 that for aluminum oxide, in contrast to yttrium oxide, there is no lower bound on the region of maximum yield. The upper temperature limit T_2 of the region of existence is approximately 1000°K lower for aluminum oxide than for yttrium oxide. In Fig. 2 the dependence of T_2 on the pressure is shown. It is seen that for aluminum oxide this dependence is almost unchanged with change in pressure at high pressures. The difference in T_2 for the two oxides decreases with drop in pressure. From Figs. 1 and 2 the temperature range in which the yields of both aluminum and yttrium oxides is unity may be determined.

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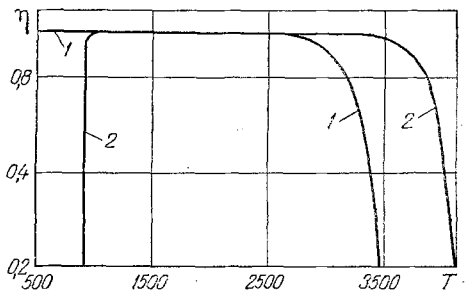

Fig. 1

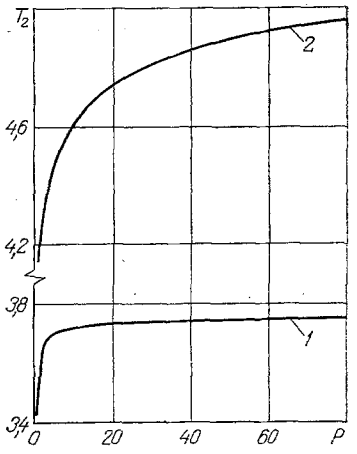

Fig. 2

Fig. 1. Temperature dependence of end-product yield: 1) Al_2O_3; 2) Y_2O_3.

Fig. 2. Pressure dependence of upper temperature bound on region of end-product existence: 1) Al_2O_3; 2) Y_2O_3. $T_2 \cdot 10^{-3}$.

At 1-atm pressure this interval falls between 940 and 2400°K. It is in this temperature range that the synthesis of yttrium and aluminum oxides, and in particular yttrium–aluminum garnet, should be performed.

An important parameter of plasmochemical synthesis, characterizing the energy consumption per unit mass of end product, is the specific enthalpy, $E = (H - H_0)/m$. The specific enthalpy of aluminum oxide synthesis, as for yttrium oxide synthesis [1], increases linearly with rise in pressure. The pressure and temperature dependences of the specific enthalpy are well approximated by the function

$$E(T, P) \approx f(T, P) = f_1(T)P + f_2(T), \quad (1)$$

where

$$f_1(T) = \exp\ (2.920 + 5.218t - 2.400t^2 + 0.475t^3 - 0.026t^4);\ f_2(T) = \exp\ (8.241 + 0.281t + 0.565t^2 - 0.349t^3 - 0.065t^4);\ t = T \cdot 10^{-4}.$$

For aluminum oxide, in contrast to yttrium oxide [1], no deviation in the specific-enthalpy behavior from the function f(T, P) at low temperatures is observed. At low pressures and high temperatures, as for yttrium oxide, the true function E(T, P) for aluminum oxide differs from f(T, P) in that the isotherms of E(T, P) have a minimum (Fig. 3). In Fig. 4, the temperature dependence of the pressure P_{min} at which the specific enthalpy has a minimum is shown. Since the upper bound on the region of existence is 1000° lower for aluminum oxide than for yttrium oxide, the difference in the temperatures corresponding to the same P_{min} would be expected to be approximately the same. However, it is evident from Fig. 4 that this difference is considerably less and, with decrease in Pmin, the curves for the two compounds become closer together. The explanation for this is that the slope of the straight line approximating E(P) is several times larger for aluminum oxide than for yttrium oxide, and at low pressure, instead of the expected minima, reduction in the rate of growth of E(P) is observed. The curves in Fig. 4 define the optimal pressure for conducting plasmochemical synthesis, corresponding to this reaction temperature.

NOTATION

η, end-product yield; m, end-product mass, kg; m_0, maximum possible end-product mass, kg; E, specific enthalpy, kcal/kg; H, enthalpy, kcal; H_0, enthalpy of initial-material formation at input temperature, kcal; T, temperature, °K; P, pressure, atm; P_{min}, pressure corresponding to minimum of E(P), atm; f(T, P), function approximating specific enthalpy, kcal/kg; T_2, upper temperature bound on region of end-product existence, °K.

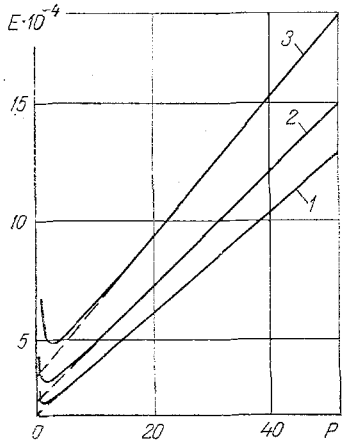

Fig. 3

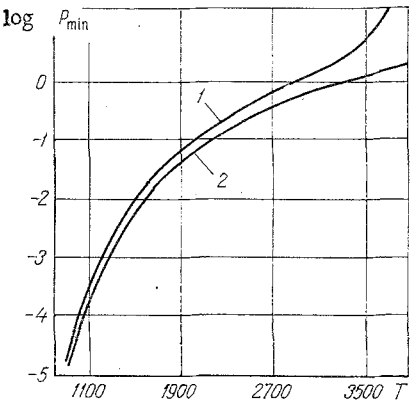

Fig. 4

Fig. 3. Pressure dependence of specific enthalpy of aluminum oxide synthesis; the dashed curve corresponds to Eq. (1): 1) T = 2900°K; 2) 3100°K; 3) 3300°K. E, kcal/kg; P, atm.

Fig. 4. Temperature dependence of optimal pressure: 1) Al_2O_3; 2) Y_2O_3.

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