THERMODYNAMIC ANALYSIS OF THE CHARACTERISTICS OF THE PLASMOCHEMICAL SYNTHESIS OF YTTRIUM OXIDE

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The nonmonotoneity of the dependence of the end product yield and the specific enthalpy on the pressure and temperature during plasmochemical synthesis of yttrium oxide is established. Optimal pressures are determined.

At present, a great deal of attention is paid to the investigation of the plasmochemical synthesis of refractory inorganic compounds. Of special interest is plasmochemical synthesis in a high-frequency (HF) plasma since obtaining the end product with the least quantity of impurities is hence assured. Studies of HF plasmas [1] have shown that the processes in a plasma are almost in equilibrium for pressures of 1 atm and higher. Hence, it is expedient to investigate the plasmochemical synthesis by performing thermodynamic analyses whose purpose is to determine the composition of the multicomponent heterogeneous mixture and to find the pressure and temperature corresponding to the optimal process parameters. Among such parameters might be the end product yield $\eta = m/m_0$ and the specific energy consumption $E_0 = Q/m$.

In place of the specific energy consumption the specific enthalpy

$$E = \frac{H - H_0}{m} = E_0(1 - \alpha) \tag{1}$$

is investigated theoretically in this paper.

It is easier to determine the quantity E than E_0 by starting from these computations, and it is independent of the parameter α to be determined experimentally. All the regularities obtained for the quantity E are certainly qualitatively valid for the specific energy consumption as well.

The thermodynamic computations performed are based on the method of minimizing the isobaric–isothermal potential [2]. By using the algorithm proposed in [3], the system of equations for the composition of the multicomponent heterogeneous mixture consisting of k components containing m elements was reduced to a system of m nonlinear equations with m unknowns which can be solved numerically by using successive approximations [3]. A general

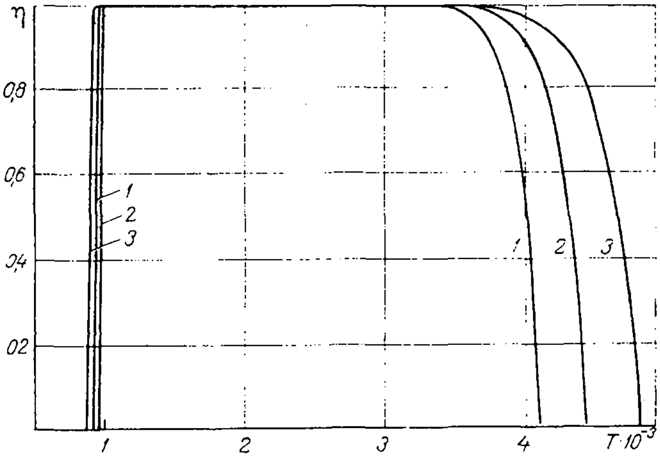

Fig. 1. Dependence of the yield of Y_2O_3 on the tempeature: 1) p = 1; 2) 4; 3) 30 atm; T, °K.

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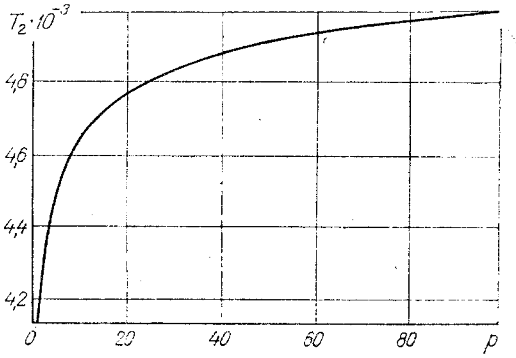

Fig. 2. Dependence of the upper temperature boundary of the domain of Y_2O_3 existence on the pressure; T_2, °K; p, atm.

purpose program to compute the composition and thermodynamic functions of a multicomponent heterogeneous mixture, compiled in FORTRAN for the "Minsk-32" electronic computer, was produced on the basis of the method mentioned, and is convenient for the description of the thermodynamics of processes occurring during plasmochemical synthesis. The program permits performing computations for $k \leqslant 200$ and $m \leqslant 10$.

To compute the composition of a multicomponent mixture, the reduced isobaric—isothermal potentials of the components proposed must be known for different temperatures. Values of the reduced potentials were taken from [4, 5] and were approximated by using the least-squares method in the form of seven-term polynomials of the form [6, 7]

$$\Phi = a_1T^{-2} + a_2T^{-1} + a_3 + a_4 \ln T + a_5T + a_6T^2 + a_7T^3. \tag{2}$$

For components for which there are no reduced potentials in [4, 5], approximate computations were performed by using data from [9-12].

Let us formulate the results of a theoretical investigation of the dependence of the quantities η and E on the pressure p and temperature T for the case of plasmochemical synthesis of yttrium oxide, producible by inserting an aqueous solution of yttrium chloride into the plasma. It is assumed that the following substances are introduced into the plasma: O_2 with a 60-liters/min consumption, Ar with a 30-liters/min consumption, and a 63% aqueous solution of YCl_3 with a 5-g/sec consumption. Therefore, the number of elements was m = 5, and 25 possible components were examined. The range of pressures considered was 1-100 atm and of temperatures was 300-5000°K. The characteristic feature of the system under consideration is the multiple excess oxygen as compared to yttrium.

The curves (Fig. 1) show the dependence of $\eta(T)$ for some values of the pressure. It is seen that the end product Y_2O_3 exists ($\eta \neq 0$) in a limited temperature band. The lowest boundary T_1 hence varies with the change in pressure from 870 to 920°K. For $T < T_1$ the element Y is contained in YOCl. The upper boundary depends more strongly on the pressure. The dependence $T_2(p)$ is represented in Fig. 2, from which it is seen that the compound Y_2O_3 can be stable at higher temperatures as the pressure rises. For $T > T_2$, Y_2O_3 decomposes and the decomposition products into which the element Y enters are Y and YO. The dependences $\eta(T)$ (Fig. 1) are typical for any values of the pressure.

The quantity E is a linear function of the pressure in a large pressure range. The dependence of E on the pressure and temperature for Y_2O_3 is approximated well by the function

$$E(T,\ p) \approx f(T,\ p) = f_1(T)\,p + f_2(T), \tag{3}$$

where

$$f_1(T) = 10^2\,(-0.082 + 4.861t + 168.540t^2 - 602.598t^3 + 833.189t^4),$$
$$f_2(T) = \exp(6.752 + 11.245t + 53.708t^2 + 156.262t^3 - 110.132t^4),$$
$$t = T\cdot 10^{-4}.$$

Formula (3) is valid for $T_1 < T < T_2$. The function f(T, p) is increasing in both variables. The true function E(T, p) differs from f(T, p) in certain sections of the (T, p) space. Two kinds of deviations of the function E(T, p) from f(T, p) can be isolated. The deviations of the first kind include the presence of provisional minimums of the functions E(T, p) corresponding to isobars in the low-temperature domain (Fig. 3). The appearance of these minimums is explained by the abrupt diminution in the yield of Y_2O_3 in the low-temperature domain (Fig. 1), where the yttrium oxychloride turns out to be considerably more

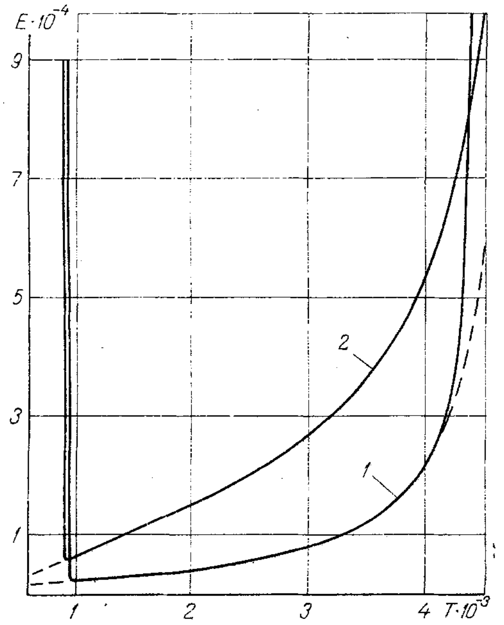

Fig. 3

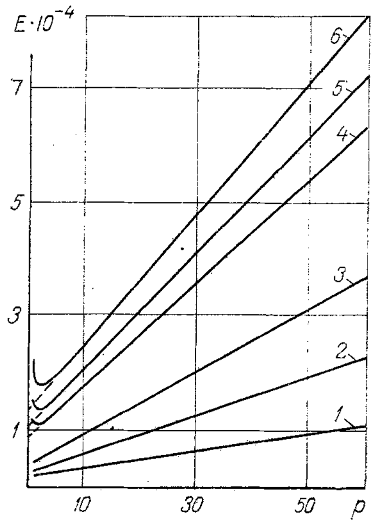

Fig. 4

Fig. 3. Isobars of the function E(T, p): dashed lines correspond to the dependence (3): 1) p = 4; 2) 30 atm; E, kcal/kg; T, °K.

Fig. 4. Isotherms of the function E(T, p): dashed lines correspond to the dependence (3): 1) T = 960°K; 2) 1700; 3) 2500; 4) 3500; 5) 3700; 6) 3900°K; E, kcal/kg; p, atm.

stable thermodynamically than the yttrium oxide. The minimum of the dependence E(T) hence occurs at a temperature close to the lower boundary T_1 of the domain of Y_2O_3 existence. For $T < T_1$, $E \to \infty$.

Deviations of the second kind are the presence of provisional minimums in the function E(T, p) corresponding to isotherms in the low-pressure domain. For sufficiently high temperatures these minimums are reached at pressures greater than 1 atm (Fig. 4). The appearance of such minimums is associated with the dependence of the upper boundary T_2 of the domain of Y_2O_3 existence on the pressure: for $p < p_{min}$ we go over into the domain $T > T_2$.

The growth of E with the rise in temperature that follows from (3) is natural, i.e., from the thermodynamic viewpoint, the least energy consumption is assured if the reaction proceeds at a temperature close to T_1. In this case, in conformity with (3), the function E(T, p) grows with the rise in pressure in practically the whole range of pressures under consideration; hence it is most expedient to set up a synthesis mode corresponding to the least pressure at a temperature close to the least-temperature boundary of the domain of Y_2O_3 existence. But, as is known, as the temperature drops, the chemical reaction rates are reduced, and one of the advantages of plasmochemical synthesis is the possibility of realizing reactions at high temperatures when the reaction rates are high. Therefore, from the kinetic viewpoint a temperature rise is expedient. Hence it is impossible to solve the problem of the optimal temperature by using just a thermodynamic method. A thermodynamic analysis only permits the determination of the optimal pressures corresponding to a given reaction temperature. These pressures do indeed determine the points of the minimums of the function E(T, p) for T = const (Fig. 4).

NOTATION

η, is the end product yield; m, end product mass, kg; m_0, greatest possible mass of end product, kg; Q, energy consumption, kcal; E_0, specific energy consumption, kcal/kg; H, enthalpy, kcal; E, specific enthalpy, kcal/kg; α, coefficient characterizing the energy loss by radiation, heat conduction, and other losses; H_0, enthalpy of formation of the initial substances at the insertion temperature, kcal; Φ, reduced isobaric—isothermal potential, kcal/°K; T, temperature, °K; p, pressure, atm; f(T, p), a function approximating the specific enthalpy, kcal/kg; T_1, T_2, upper and lower temperature boundaries of the domain of Y_2O_3 existence, °K.

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DEVICE FOR MEASUREMENT OF HEAT CAPACITY OF SMALL SPECIMENS IN THE RANGE 10-20°K

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The construction of a calorimeter for rapid measurement of heat capacity by the cooling method is described.

In the technology of producing materials with certain properties (i.e., superconductors) the need often arises for rapid low-temperature measurements of the heat capacity of a large number of small specimens no more than 0.05 cm^3 in volume. One of the methods which may be used is that of continuous cooling of the specimen. In this method the decrease in specimen enthalpy per unit time is equal to the thermal flux through the heat sink. The equation describing the cooling process has the form

$$C(T)\dot{T} = -W(T, T_0). \tag{1}$$

The heat power $W(T, T_0)$ may be determined in individual measurements. In experiment the temperature of the cooling specimen is measured as a function of time. The rate of temperature change is found by numerical differentiation. The literature describes the use of such a method for measurement of heat capacity at temperatures below4.4°K [1, 2].

Heat capacity may also be measured during the process of continuous heating [3]. However, the cooling method is more easily realizable, since it does not require total adiabatization of the specimen; the only requirement is constancy of heat sink conditions from experiment to experiment. The experimental point density with the cooling method can be made extremely high (up to 100 points per degree).

A block diagram of the device which realizes the cooling method is shown in Fig. 1. The specimen is heated to a temperature T and heating is terminated, so that the specimen cools through the heat sink to the"bath" temperature T_0. The voltage across the resistance

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