A MODEL OF CoO OXIDATION

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A model of CoO oxidation was proposed which assumes the diffusion of cobalt atoms from the bulk of crystallite to its surface and the surface reaction of these atoms with surrounding oxygen. It depends on the comparison of expressions D/a_0^2 and kx_{ox}/a_0 to what extent these two processes will manifest themselves for the given temperature and oxygen mole fraction x_{ox}. The value of diffusivity D and its temperature dependence were estimated from the data in literature and the size of crystallites a_0 from roentgenographic measurements. The value of rate constant of surface reaction k and its energy of activation were evaluated from experimental data for CoO oxidation.

The rates of reoxidation of the reduced form (CoO) to the initial Co_3O_4 were measured for pure Co_3O_4 and Co_3O_4 with different doping ingredients in connection with the use of these substances as an active layer of catalysts for ammonium oxidation. Polycrystalline powders of grain size of about 5 . 10^{-5} m and porosity of about 0.3 were used. The oxidation was carried out at 700 °C with a mixture of inert gas (N_2 or He) and oxygen of linear velocity about 0.03 ml/s. It was calculated that under these conditions neither external nor internal mass transfer manifested itself[1]. It is reported[2] that the diffusion coefficient of oxygen in Co_3O_4 is two orders higher than the diffusion coefficient of cobalt atoms in Co_3O_4. Then on the assumption that the CoO grains are formed by non-porous crystallites, the following two processes may be effective in the CoO oxidation: the diffusion of cobalt atoms in crystallite and the surface reaction with oxygen.

The mechanism[2] proposed for the oxidation of CoO crystal and verified also for the polycrystalline CoO formed the basis for the CoO oxidation model, in which the diffusion of cobalt atoms in nonporous crystallite towards the surface and the subsequent reaction of these atoms with oxygen from the surrounding gas manifested themselves.

In accordance with this mechanism[2], the growth of Co_3O_4 layer on the initial CoO plane surface takes place in this way (see Fig. 1):

1. The s–s boundary is shifted towards the solid phase volume, and on this boundary, the reaction

$$4\,CoO \longrightarrow Co_3O_4 + Co \qquad (1)$$

takes place, the cobalt ions with the respective number of electrons diffusing simultaneously from the s–s boundary to the s–g boundary according to the mechanism[2]. For the sake of simplicity we consider further the diffusion of electroneutral cobalt atoms instead of the diffusion of the cobalt ions and the respective number of electrons.

2. A new layer of Co_3O_4 grows up on the s–g boundary by the reaction of these cobalt atoms with surrounding oxygen according to the reaction

$$3\,Co + 2\,O_2 \longrightarrow Co_3O_4 \qquad (2)$$

At that, the s–g boundary is shifted to the gas phase bulk, so in the opposite direction to the s–s boundary. It follows from the stoichiometry of these reactions that the ratio of Co_3O_4 amount in the new formed layer to the Co_3O_4 amount formed from the initial CoO is 1 : 3. However, it holds not until complete reacting up. In the course of reaction, this ratio would hold only in case that the cobalt atoms formed on the s–s boundary through reaction (*1*) were immediately displaced to the s–g boundary. Since the diffusion of cobalt atoms between the s–s and s–g boundaries takes place with a finite rate, there exists a time delay between the s–s boundary shift and the corresponding (for a plate equal to a third) shift of s–g boundary (see Fig. 1), the ratio 1 : 3 is therefore decreased. Authors[2,3] report at 800 °C the ratio of thickness of outer layer to the overall layer 0.22 – 0.23 (unlike 0.25 as it would correspond to the ratio 1 : 3), at 700 °C the values 0.11 – 0.13.

This apparent discrepancy when on the one hand, the diffusion is considered as infinitely rapid and on the other one as a controlling process, is removed in the proposed model.

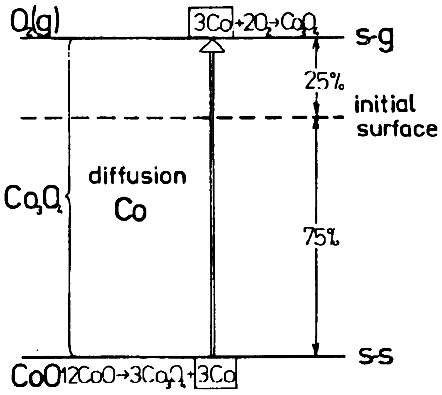

FIG. 1
Mechanism of Co_3O_4 layer growth on CoO single crystal according to ref.[2]

PROBLEM FORMULATION

We assume that CoO consists of nonporous tabular crystallites (both CoO and Co_3O_4 have cubic structure) of thickness $2a_0$ from which a plate of thickness $2a_0$ can be made up. The remaining two dimensions of the plate are much greater than the thickness, consequently an "infinite plate" is concerned.

The plate is surrounded on both sides with the gas phase with time and space unchanged oxygen concentration. Since the cobalt atom diffusion will take place in the plate symmetrically to both sides, we can consider only one half of plate, i.e., the plate of thickness a_0 surrounded by gas phase from one side (see Fig. 2).

We assume that the oxygen atoms form a tough lattice and that only cobalt atoms can diffuse, i.e., in the direction normal to the plate, into the region of the gas phase where the new layer grows up. From the initial CoO, where the ratio of number of cobalt atoms to oxygen ones was 1 : 1, becomes Co_3O_4 with its ratio of 3 : 4, the excessive cobalt atoms forming a new Co_3O_4 layer by the reaction with surrounding oxygen. The assumption of fixed lattice of oxygen atoms follows from the analogous structure of single crystals of CoO and Co_3O_4 where the oxygen ions are arranged in the face-centered cubic lattice. Whereas in case of CoO, the cobaltous ions fill up all octahedral positions, in case of Co_3O_4 with the spinel structure, the octahedral and tetrahedral positions are partly filled up with the cobaltic and cobaltous ions. Simultaneously, the oxygen atom distance in CoO and in Co_3O_4, i.e., the edge of the face-centered cubic lattice of oxygen atoms, is 0.4260 and 0.4042 nm (ref.[4]). On introducing the assumption of fixed lattice of oxygen atoms, the decrease of lattice is neglected which occurs in oxidation of CoO to Co_3O_4. This reduction is about 5% in length, i.e. about 17% in volume. On neglecting this contraction, we get, for the ratio of densities of CoO and Co_3O_4, the ratio of molar masses of 4 CoO and Co_3O_4, i.e., about 1.24. The actual ratio of densities is smaller, approximately by the above-mentioned 17%. The densities of

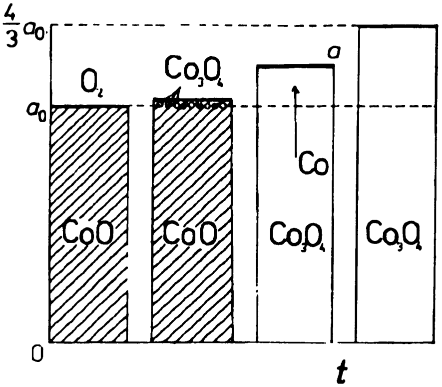

FIG. 2

Model of CoO crystallite oxidation: a_0 initial crystallite size, i.e., half the plate thickness, a instantaneous crystallite size single crystals of CoO and Co_3O_4 are 6.437 and 6.0547 g/cm^3 according to ref.[4] so that their ratio is 1.06.

On the plate surface, Co_3O_4 is formed by the reaction according to Eq. (*2*) and so the cobalt atom concentration is diminished in the surface layer. Owing to the concentration gradient, Co atoms diffuse which are in excess in CoO compared to Co_3O_4 stoichiometry, i.e., each fourth, to the surface which is designated s–g. Once some cobalt atom is missing in the CoO lattice, it is considered as Co_3O_4 and the cobalt atoms which are here in excess compared to stoichiometry, as diffusing cobalt ions. The reaction according to Eq. (*1*), i.e., the displacement of cobalt ions between the tetrahedral and octahedral positions and releasing the excessive cobalt atoms, is considered to be infinitely rapid. At time $t = 0$, all CoO is converted to Co_3O_4, and further the diffusion takes place between $x = 0$ and $x = a$, and, on the s–g boundary of coordinate a, the reaction according to Eq. (*2*) until all the excessive cobalt atoms diffuse out. A plate of thickness $4a_0/3$ formed because we assume that Co_3O_4 originating from the reaction according to Eq. (*2*) and Co_3O_4 forms from the initial CoO according to Eq. (*1*) have the same density and internal arrangement.

The balance of cobalt atoms diffusing between $x = 0$ and $x = a$ leads to the equation

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}\,. \qquad (3)$$

The concentration of diffusing Co atoms is designed by c. At the beginning of the reaction, in CoO, it corresponds to a quarter of the total cobalt atom concentration, and at the end of the reaction, in Co_3O_4, c is zero. In the course of reaction, c is a function of time and coordinate. Relation $V_M' = V_M/4$ holds between the molar volume of CoO, V_M', and the molar volume of Co_3O_4, V_M. Let us consider 1 mol CoO of volume V_M'. Then each fourth Co atom diffuses out of this volume; it remains 3/4 mol CoO and 1 mol O, therefore 1/4 mol Co_3O_4 of volume $V_M/4$. Concentration c in CoO is then $1/V_M$.

The rate of formation of Co_3O_4 according to Eq. (*2*) on the s–g boundary of coordinate a is expressed in this way:

$$\frac{\mathrm{d}n_{Co_3O_4}}{S\,\mathrm{d}t} = \frac{\mathrm{d}\left(\dfrac{\rho_{Co_3O_4}\,S\,a}{M_{Co_3O_4}}\right)}{S\,\mathrm{d}t} = \frac{1}{V_M}\,\frac{\mathrm{d}a}{\mathrm{d}t}\,. \qquad (4)$$

From the stoichiometry of Eq. (*2*) follows $\mathrm{d}n_{Co_3O_4}/\mathrm{d}n_{Co} = 1/3$. The molar flow of Co atoms through a unit area of s–g boundary is given by the relation

$$\frac{\mathrm{d}n_{Co}}{S\,\mathrm{d}t} = -D\left(\frac{\partial c}{\partial x}\right)_a\,.$$

The cobalt atoms passing through the s–g boundary, on the one hand react according to Eq. (*2*) forming new layer of Co_3O_4, on the other hand, in this new layer simultaneously form a certain concentration profile. We get the boundary condition on the s–g boundary with coordinate $x = a$:

$$-D\left(\frac{\partial c}{\partial x}\right)_a = \frac{3}{V_M}\frac{da}{dt} + c_a\frac{da}{dt} \,. \tag{5}$$

The boundary shift is given by the rate of formation of Co_3O_4. The rate of reaction according to Eq. (*2*) is considered proportional to the mole fraction of oxygen in the gas phase, x_{ox}, and to the concentration of cobalt atoms on the crystallite surface, c_a. The rate of Co_3O_4 formation is related to the surface area:

$$\frac{dn_{Co_3O_4}}{S\,dt} = R\,c_a\,, \qquad \text{where} \quad R = k\,x_{ox}$$

(k is the rate constant). On combining with Eq. (*4*), for the boundary shift holds the relation

$$\frac{da}{dt} = V_M R\,c_a\,. \tag{6}$$

It must hold for the symmetry reason that the diffusion flux in the plate centre is zero, then,

$$-D\left(\frac{\partial c}{\partial x}\right)_0 = 0\,,$$

hence we get the second boundary condition

$$\left(\frac{\partial c}{\partial x}\right)_0 = 0\,. \tag{7}$$

Consequently it is necessary to solve partial differential equation (*3*) with boundary condition (*5*) on the s–g boundary of coordinate a, the s–g boundary shift being described by Eq. (*6*). The second boundary condition is given by Eq. (*7*). The initial condition is

$$t = 0\,, \qquad a = a_0\,, \qquad c = 1/V_M \quad \text{for} \quad x \in \langle 0, a_0)\,. \tag{8}$$

The balance of total number of cobalt atoms during reoxidation, i.e., for changing layer thickness, leads to the equation (number of cobalt atom moles in the plate volume of unit area is balanced)

$$a_0 \frac{4}{V_\mathrm{M}} = a \frac{3}{V_\mathrm{M}} + \int_0^a c \, \mathrm{d}x \, .$$

The number of cobalt atoms in unit area of initial plate of thickness a_0 and total concentration $1/V_\mathrm{M}' = 4/V_\mathrm{M}$ is equal to the number of cobalt atoms in Co_3O_4 of layer thickness a and concentration $3/V_\mathrm{M}$, increased by the number of cobalt atoms diffusing between $x = 0$ and a. After rearranging we get

$$4 a_0 - 3 a = V_\mathrm{M} \int_0^a c \, \mathrm{d}x \, . \tag{9}$$

This balance equation is not independent. It holds here

$$\frac{\partial}{\partial t} \left(\int_0^a c \, \mathrm{d}x \right) = \int_0^a \frac{\partial c}{\partial t} \mathrm{d}x + c_a \frac{\mathrm{d}a}{\mathrm{d}t} \, .$$

The first term on the right-hand side is according to Eq. (3) and after rearranging and inserting from Eq. (5):

$$\int_0^a \frac{\partial c}{\partial t} \mathrm{d}x = D \int_0^a \frac{\partial^2 c}{\partial x^2} \mathrm{d}x = D \left(\left(\frac{\partial c}{\partial x} \right)_a - \left(\frac{\partial c}{\partial x} \right)_0 \right) =$$

$$= - \frac{3}{V_\mathrm{M}} \frac{\mathrm{d}a}{\mathrm{d}t} - c_a \frac{\mathrm{d}a}{\mathrm{d}t} - D \left(\frac{\partial c}{\partial x} \right)_0 \, .$$

We get

$$\frac{\partial}{\partial t} \left(\int_0^a c \, \mathrm{d}x \right) = - \frac{3}{V_\mathrm{M}} \frac{\mathrm{d}a}{\mathrm{d}t} \, .$$

After integrating

$$\int_0^a c \, \mathrm{d}x = - \frac{3}{V_\mathrm{M}} a + \mathrm{const}.$$

The value of the integration constant is obtained on inserting initial condition (*8*). So we get balance equation (*9*).

Provided $R \rightarrow \infty$, i.e., the surface reaction is infinitely rapid, $c_a = 0$, boundary condition (*5*) is simplified to the form

$$-D \left(\frac{\partial c}{\partial x} \right)_a = \frac{3}{V_\mathrm{M}} \frac{\mathrm{d}a}{\mathrm{d}t} \tag{10}$$

and simultaneously it describes also the boundary shift because Eq. (*6*) is not usable for the calculation.

Between coordinate a of the s–g boundary and conversion α there exists the relation

$$\alpha = \frac{a - a_0}{\frac{a_0}{3}} = 3 \left(\frac{a}{a_0} - 1 \right). \tag{11}$$

PROBLEM SOLUTION

A nonstationary problem is concerned. An analytical solution exists only on the assumption that the surface reaction is the controlling process. In this case the concentration in the plate is always constant for the given time moment and gradually decreases with time (see Fig. 3). For the whole time of the reaction course, $c(x,t) = c_a(t)$ holds. From Eqs (*6*) and (*9*) we get, after inserting for a according to Eq. (*11*), the relation for α

$$\frac{R}{a_0} t = - \frac{4}{9} \ln (1 - \alpha) - \frac{\alpha}{9},$$

from which it is possible to express the rate of reaction by the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{9R}{a_0} \frac{1 - \alpha}{3 + \alpha}. \tag{12}$$

For the numerical solution it is suitable to carry out the transformation to dimensionless quantities $C = c/(1/V_\mathrm{M})$, $X = x/a_0$, $A = a/a_0$. The equation

$$\frac{\partial C}{\partial t} = \frac{D}{a_0^2}\frac{\partial^2 C}{\partial X^2} \tag{13}$$

is solved with the boundary condition

$$-\frac{D}{a_0^2}\left(\frac{\partial C}{\partial X}\right)_A = 3\frac{\mathrm{d}A}{\mathrm{d}t} + C_A\frac{\mathrm{d}A}{\mathrm{d}t}\,, \tag{14}$$

along with the equation for the boundary shift

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{R}{a_0}C_A\,, \tag{15}$$

with the second boundary condition

$$\left(\frac{\partial C}{\partial X}\right)_{X=0} = 0 \tag{16}$$

and with the initial condition

$$t = 0\,, \qquad A = 1\,, \qquad C = 1\,. \tag{17}$$

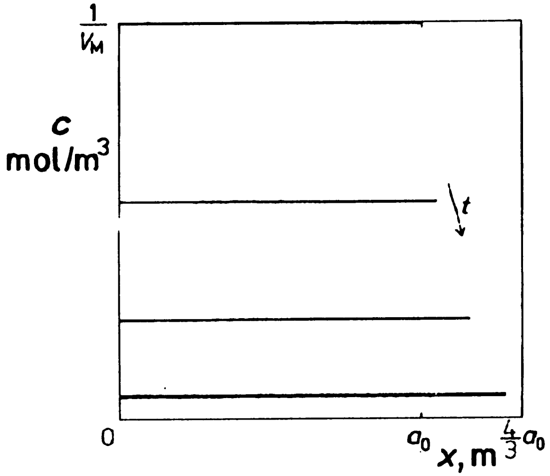

FIG. 3
Concentration profiles in case that surface reaction is controlling process

Therewith the observance of the balance

$$4 - 3A = \int_0^A C \, dX \qquad (18)$$

is checked. The partial differential equation of parabolic type with moving boundary is concerned. The solution is carried out by the implicit method[5]. Only the equation for the boundary shift (Eq. (*15*)) is expressed explicitly. The spatial step was chosen equidistantly 0.01, i.e., one begins with division 100, further divisions 0.01 are added so that the last division is generally nonequidistant. The implicit method leads then to the solution of tridiagonal matrix. The time step is chosen with respect to the magnitude of D/a_0^2. At the beginning (for $t = 0$) the step change of concentration from 0 to 1 is assumed at point $X = 1$. For single time steps, the fulfilment of balance (*18*) is always checked. Integration is carried out by the Simpson rule. The integration error is maximally 4%. The error in C is found by calculating for double spatial step. Its maximum values are for initial profiles and amount to about 0.02.

For the controlling process of diffusion, $C_A = 0$. In Eq. (*14*) there will not be the second term on the right-hand side, and the equation is not applicable. Transformation $T = Dt/a_0^2$ is carried out. The problem

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial T^2}$$

is then solved with the boundary conditions

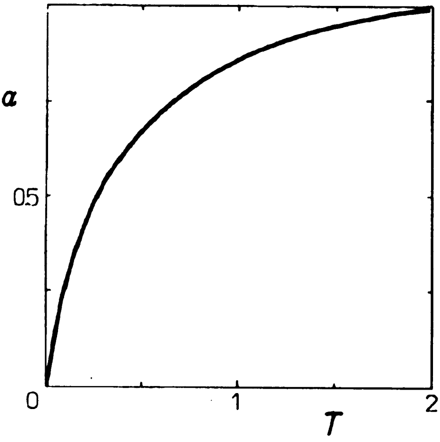

FIG. 4
Dependence of conversion α in reoxidation on quantity $T = Dt/a_0^2$ in case that diffusion is controlling process

$$\left(\frac{\partial C}{\partial X}\right)_A = 3\frac{dA}{dt} ,$$

$$\left(\frac{\partial C}{\partial X}\right)_0 = 0$$

and with the initial condition $T = 0$, $A = 1$, $C = 1$.

In coordinates C, T, the solution will be identical for different D and a_0. In Figs 4 and 5, the dependence of conversion on T and concentration profiles in different times can be seen.

In case that values of D/a_0^2 and R/a_0 are comparable, both diffusion and surface reaction are effective in reoxidation. The parameters of the model a_0, D and R have the following values:

1. The crystallite size in Co_3O_4 was calculated from the broadening of difraction lines and, on the average, has the value of 6 . 10^{-8} m. From this a_0 = 3 . 10^{-8} m.

2. The diffusion coefficient of cobalt ions in Co_3O_4 crystal at 800 °C equal 3 . 10^{-12} cm^2/s was determined in ref.[2]. The activation energy of ion diffusion in spinels is according to ref.[6] equal 250 – 350 kJ/mol. For the average value of 300 kJ/mol it is possible to calculate the diffusivity at 700 °C to be D = 1 . 10^{-17} m^2/s.

3. The assumption was introduced for the direct reoxidation that the surface reaction is the controlling process. Then the rate of reoxidation can be expressed by Eq. (*12*). The mean value of $k/a_0 = 1.25 \pm 0.14$ s^{-1} was calculated from the experimental values

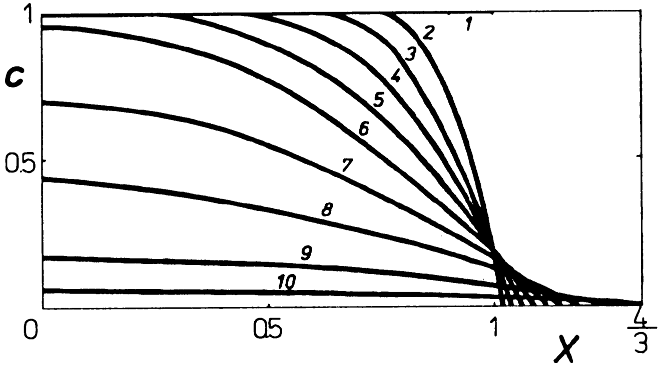

FIG. 5

Concentration profiles of diffusing cobalt atoms in crystallite in case that diffusion is controlling process of reoxidation; $T = Dt/a_0^2$: *1* 0.0000, *2* 0.0056, *3* 0.0111, *4* 0.0278, *5* 0.0556, *6* 0.1111, *7* 0.2778, *8* 0.5556, *9* 1.1111, *10* 2.2222 for direct reoxidation[7]. Inasmuch as x_{ox} for direct reoxidation varies within $1 \,.\, 10^{-3}$ – $2 \,.\, 10^{-3}$, value $R/a_0 = 0.00125 - 0.0025$ s^{-1} and with this $D/a_0^2 = 0.0111$ s^{-1}. The assumption of controlling process of surface reaction has been therefore justified. The value of R for oxygen ($x_{ox} = 1$) is about $4 \,.\, 10^{-8}$ m/s, for air about $8 \,.\, 10^{-9}$ m/s, which corresponds to the values of R/a_0 1.25 and 0.26 s^{-1}. It is in comparison with D/a_0 = 0.0111 s^{-1} high values. In this case, diffusion is therefore the controlling process of reoxidation.

For comparable values of D/a_0^2 and R/a_0, there is the time dependence of conversion in Fig. 6, and for comparison the time dependences of conversion are given as well for the cases when the controlling process is diffusion with the same D/a_0^2 or surface reaction with identical R/a_0. It can be seen that provided diffusion and surface reaction are efficient simultaneously, the reoxidation is a slower process than in case when the controlling process is diffusion with the same value of D/a_0^2 or surface reaction with the same value of R/a_0. In Fig. 7 there are the concentration profiles in several time intervals for the case of action of diffusion and surface reaction.

DISCUSSION

As it has been said above, the comparison of expressions D/a_0^2 and R/a_0 at the given temperature and O_2 concentration at the crystallite surface predetermine the degree of contribution of cobalt atom diffusion to the crystallite surface and the degree of contribution of reaction or cobalt atoms on the crystallite surface with surrounding oxygen, i.e., the controlling process of CoO reoxidation.

The activation energy of metal ions in spinels is known (250 – 350 kJ/mol), and we also know[2] the value of diffusion coefficient at the temperature of 800 °C ($3 \,.\, 10^{-16}$ m^2/s). It is therefore possible to describe the temperature dependence of diffusion coef-

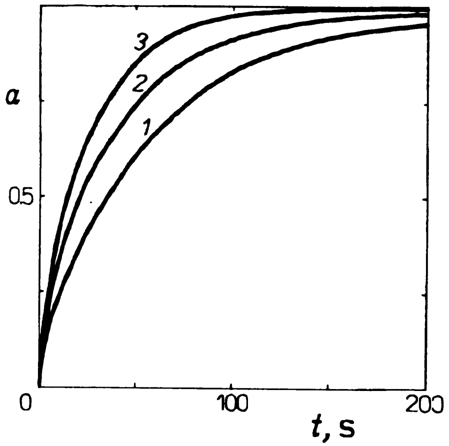

FIG. 6
Time dependence of conversion in reoxidation for different controlling processes (D/a_0^2 = 0.0139 s^{-1}, R/a_0 = 0.0167 s^{-1}): *1* both diffusion and surface reaction contribute, *2* diffusion is controlling process, *3* surface reaction is controlling process

ficient of cobalt atoms in Co_3O_4, $D(T)$. The size of crystallites, a_0, is considered to be temperature independent.

Quantity R is given as a product of the rate constant of surface reaction, k, and mole fraction of O_2 at the crystallite surface, x_{ox}. To do so, k/a_0 was evaluated experimentally at 700 °C and amounted to 1.25 s^{-1} for the crystallites with average value $a_0 = 3 \,.\, 10^{-8}$ m. The activation energy of surface reaction is about 100 kJ/mol (ref.[7]). The temperature dependence of $D(T)$ and $k(T)$ have then the forms

$$D(T) = 3 \,.\, 10^{-16} \exp\left(- \frac{3 \,.\, 10^5}{R} \left(\frac{1}{1\,073} - \frac{1}{T} \right) \right) ,$$

$$k(T) = 1.25 \,.\, 3 \,.\, 10^{-8} \exp\left(\frac{1 \,.\, 10^5}{R} \left(\frac{1}{973} - \frac{1}{T} \right) \right) .$$

(In these two equations, R denotes gas constant.) After inserting we obtain, e.g., for the controlling process of surface reaction, the nonequality

$$\frac{k(T)\, x_{ox}}{a_0} << \frac{D(T)}{a_0^2} ,$$

consequently

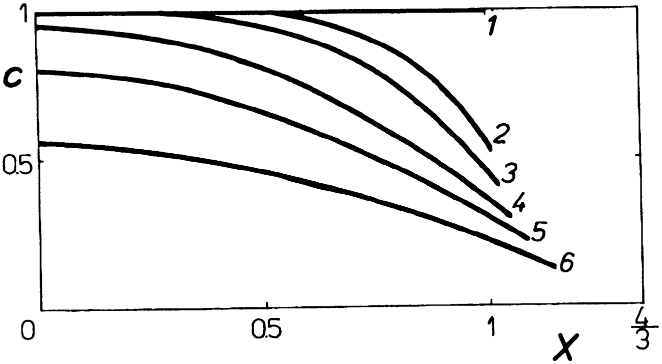

FIG. 7
Concentration profiles for simultaneous effect of diffusion and surface reaction (D/a_0^2 = 0.0139 s^{-1}, R/a_0 = 0.0167 s^{-1}) for time t (s): *1* 0, *2* 2, *3* 4, *4* 10, *5* 20, *6* 40

$$x_{ox} \ll \frac{D(T)}{a_0\, k(T)} = x_{ox}^{eq} ,$$

where x_{ox}^{eq} is such a mole fraction of O_2 at which for the given temperature just the equality between D/a_0^2 and R/a_0 holds. In Fig. 8 are plotted the dependences of x_{ox}^{eq} on temperature for different values of crystallite size a_0. The region of temperatures and x_{ox} is depicted in the diagram as well in which CoO is thermodynamically stable[8]. The more is remoted a point in the diagram with coordinates T, x_{ox} to the left from the dividing curve $x_{ox}^{eq}(T)$ for the given a_0, the more manifests itself diffusion as a controlling process of reoxidation at this temperature. The more is remoted to the right, the more manifests itself surface reaction. In the neighbourhood of dependence $x_{ox}^{eq}(T)$, the expressions D/a_0^2 and R/a_0 are comparable, and both the diffusion and surface reaction play a role in reoxidation.

Further one can see, for instance, in the diagram that for the given temperature and x_{ox}, the diffusion manifests itself the more, the larger are the crystallites. Or for the given temperature and crystallite size, the diffusion manifests itself the more, the higher x_{ox} is. For the given x_{ox} and crystallite size, then the more, the lower is temperature because owing to different activation energies, the rate of diffusion is slowed down with decreasing temperature more expressively than the rate of surface reaction.

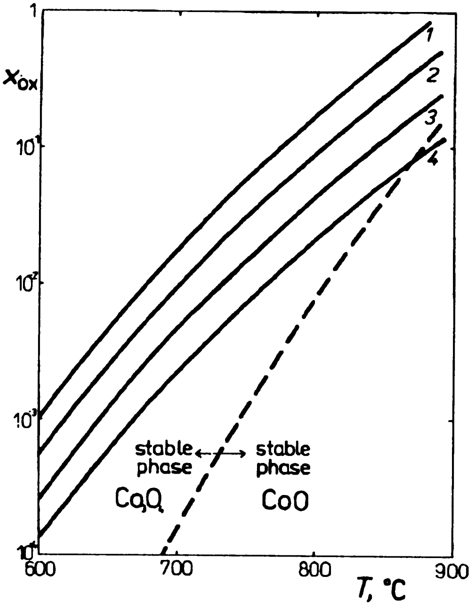

FIG. 8

Effect of diffusion and surface reaction in oxidation of CoO crystallites as a function of temperature and oxygen mole fraction, x_{ox}; crystallite size a_0 (m): *1* 1.5 . 10^{-8}, *2* 3 . 10^{-8}, *3* 6 . 10^{-8}, *4* 12 . 10^{-8}; dashed curve is the temperature dependence of oxygen equilibrium pressure for thermal decomposition of Co_3O_4 to CoO

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