Kinetics and modeling of diffusion phenomena occurring during the complete oxidation of zinc powder: influence of granulometry, temperature and relative humidity of the oxidizing fluid

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Abstract

The kinetics of the complete oxidation of zinc powder by oxygen or air has been investigated from thermogravimetric studies under isothermal conditions in the range 772–1107 K. Particles size and hygrometry were chosen in the 65–375 μm and 0–50% ranges, respectively. We have been able to carry out the powder oxidation above the zinc metal melting point without coalescence of the particles. A quantitative interpretation based on the diffusion of reactants through the oxide layer has been proposed. The activation energy calculated from the Arrhenius law is close to 130 kJ mol^{-1}. © 2000 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Zinc oxidation; Zinc powder; Arrhenius law; Kinetics

1. Introduction

This work enters the area of the perfection of a new process of production of ceramics based on the direct oxidation of a zinc alloy powder [1–4]. Doped zinc oxide ceramic blocks are used for the protection of electric or electronic devices against power surges. One of the weaknesses of the traditional procedures using a mixture of oxides is the difficulty in obtaining good chemical homogeneity. The new route studied is based on the principle that at high temperature a liquid solution is by its nature homogeneous and that a fast enough quench leads to a non-segregated solid usually as an alloy powder. Then the total oxidation of the powder produces agglomerates having the qualities desired for the manufacturing of ceramics [2]. The use of this new route requires the knowledge of the rate laws and oxidation mechanisms of zinc and of any added elements. This paper deals with the complete oxidation of pure zinc powders which do not sinter even above the melting temperature of the bulk metal zinc.

The mechanism controlling the oxidation of metals are not completely elucidated and are still the topics of numerous studies [5]. The results are hard to exploit because the majority focus entirely on the growth of thin layers, in order to study corrosion phenomena [5–11]. Our objective is the opposite because it concerns the total oxidation of the particles, as quickly as possible. The majority of the

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theories advanced apply to the surface oxidation of zinc, but very few models have been developed for the case of complete oxidation of metal powders.

Only Terem [12] treats oxidation from a perspective similar to ours. He states that isothermal oxidation of zinc particles follows a parabolic law. Nevertheless, results of this work could be defined with more accuracy, for instance the average particle size is not given. Moreover, Terem uses a discontinuous method that consists of periodically removing samples from the oven in order to follow the evolution of the bulk sample. We have reexamined this work by TGA in order to elaborate a kinetic model capable of quantitatively predicting the phenomena as a function of the temperature, particle size and relative humidity of the oxidizing fluid.

2. Experimental

The zinc is a product of Prolabo Normapur in granules of 99.9% purity. The other significant elements are: $Cu + Cd + Sn$ (10 ppm), Pb (50 ppm) and Fe (20 ppm). The production of a zinc powder is carried out as follows: zinc is melted under a reducing atmosphere in order to avoid premature oxidation. After cooling, the division of the plug is accomplished by cryogenic grinding (liquid air) on a rotating disc coated with SiC. The powder thus obtained is then sieved between 36 and 250 μm.
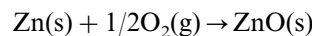
The variation of the mass of the sample as a function of temperature is followed by TGA using a Setaram B60 thermobalance. The gas is either pure oxygen or air. The hygrometry of the oxidizing fluid is held constant by passage through either a trap (relative humidity ratio $< 10\%$) or through a saturator thermostated to the highest values. It is defined by the relation $h_r = 10^2 \, p/p'$, where p and p' represent, for a given temperature, the vapor pressures of water and the vapor pressure at saturation, respectively. Under these conditions, $h_r = 0$ corresponds to completely dry air and $h_r = 100$ to saturated air.

The metallic powder is placed in a cylindrical silica container 10 mm in diameter and 12 mm long. The mass of the original metal sample weighed (accuracy up to 1/10 of a mg) is around 100 mg. The thickness of the powder bed is from 1.5 to 2 mm. The bed is not packed, in order to avoid any concentration gradient of the reactive gas in the reaction volume. The rising gas flow possesses sufficient intensity (4.5 l h^{-1}) to avoid any diminishment of oxygen level at the reaction interface.

3. Results and discussion

The experiments were conducted isothermally and in most cases at a temperature above the melting point of zinc at 692 K. The surface oxide prevents coalescence of the particles despite the presence of liquid in between the particles. The extent of the reaction:

$$Zn(s) + 1/2O_2(g) \rightarrow ZnO(s)$$

is defined by expression (1):

$$\alpha = [m^o_{Zn} - m^t_{Zn}]/m^o_{Zn} = [2 \, \delta m(t)M_{Zn}]/[m^o_{Zn}M_{O_2}] \qquad (1)$$

where m^o_{Zn}, m^t_{Zn} and $\delta m(t)$ are the initial mass, the mass and the experimental mass gain of the sample at time t, respectively. M_{Zn} and M_{O_2} are the molecular weights of zinc and oxygen. The isotherms were performed between 772 and 1107 K. Fig. 1 depicts the general appearance of an oxidation curve $\alpha = f(t)$. They are all parabolic in the studied temperature range.

In order to interpret and quantify these phenomena, let us consider the following general reaction: $v_A A(g) + v_B B(s) \rightarrow v_C C(s)$. We can approximate the particles B as spheres. Under these conditions, designating by r_0, r_B, r_C, the initial radius of B, of the reaction interface (metal/oxide) and of the oxide layer, respectively, we demonstrate the following relations:

$$r_B = r_0(1 - \alpha)^{1/3} \qquad (2)$$

$$r_C = r_0[1 + \alpha(\Delta - 1)]^{1/3} \qquad (3)$$

where $\Delta = v_C/[v^0_B - v_B]$ is the coefficient of Pilling and Bedworth [13]. As α is experimentally accessible, let us derive expression (1) with respect to time. Taking the reaction stoichiometry into account, it becomes:

$$\frac{d\alpha}{dt} = -\frac{1}{m^0_B} \frac{v_B}{v_A} \frac{dm_A}{dt} \qquad (4)$$

Assuming that the diffusion of the reactants through the thickness of the oxide layer is the limiting factor, application of Fick's law to reactant A leads to: $dm_A/dt = -D_A S_B \{dC_A/dr\}_{r = r_B}$, with $S_B = 4\pi r^2_B$, where D_A and $\{dC_A/dt\}_{r_B}$ are, respectively, the diffu-

sion coefficient and the local concentration gradient of A at the limit $r = r_B$. Substitution of this expression in Eq. (4) reduces to the following rate equation:

$$\frac{d\alpha}{dt} = \frac{1}{m_B^0} \frac{v_B}{v_A} D_A 4\pi r_B^0 \left\{ \frac{dC_A}{dr} \right\}_{r = r_B} \qquad (5)$$

This relation is integral if r_B and the concentration gradient at $r = r_B$ are expressed as functions of α. From the lack of accumulation of reactants in the reaction zone (steady-state hypothesis), one can deduce that at a given time t, the quantity of A which crosses a spherical surface of any thickness is equal to that consumed by the reaction, whence the equality: $4\pi r^2 D_A \{dC_A/dr\} = 4\pi r_B^2 \{dC_A/dr\}_{r = r_B}$

Taking into account the limiting conditions ($C_A = C_A^i = 0$ for $r = r_B$ and $C_A = C_A^e$ for $r = r_C$, where i and e stand for initial and equilibrium condition), respectively, one can write: $\int_{C_A^i}^{C_A^e} dc_A = r_B^2 (dc_A/dr)_{r = r_B} \int_{r_B}^{r_C} dr/r^2$ from which the expression of the gradient at $r = r_B$ can be linked to α via relations (2) and (3):

$$\left\{ \frac{dC_A}{dr} \right\}_{r = r_B} = \frac{r_C}{r_B(r_C - r_B)} C_A^e \qquad (6)$$

Substitution of relation (6) into expression (5) allows us to obtain a differential equation depending only on the variables α and t:

$$\frac{d\alpha}{dt} = \frac{v_B 4\pi D_A C_A^e}{v_A m_B^0} \left[\frac{1}{r_0(1 - \alpha)^{1/3}} - \frac{1}{r_0(1 - \alpha(\varDelta - 1))^{1/3}} \right]$$

which, after integration, leads to the following final equation:

$$\frac{\varDelta}{\varDelta - 1} - (1 - \alpha)^{2/3} - \frac{1}{\varDelta - 1} [1 + \alpha(\varDelta - 1)]^{2/3}$$
$$= \frac{v_B D_A C_A^e}{v_A 2 d_B r_0^2} \qquad (7)$$

(d_B being the density of B)

One can define:

$$k_{Zn}^0 = \frac{v_B D_A C_A^e}{v_A 2 d_B r_0^2} \qquad (8)$$

k_{Zn}^0 which is proportional to the diffusion constant, can be related to the observed rate constant of the reaction. For a fixed value of the particle size, temperature, and composition of fluid A, the constant k_{Zn}^0 can be experimentally determined at any time from the pair of points (α, t) and relation (7). In
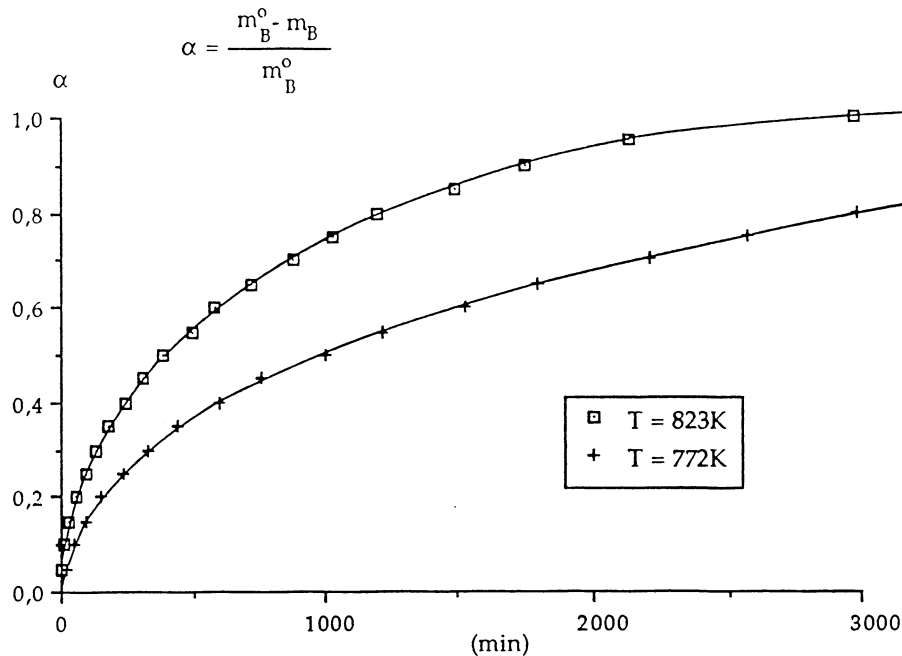

Fig. 1. Complete oxidation of powdered zinc. Progress of the reaction at 772 and 823 K. m_{Zn}^0 = initial mass of Zn; m_{Zn}^t = mass of Zn at time t.
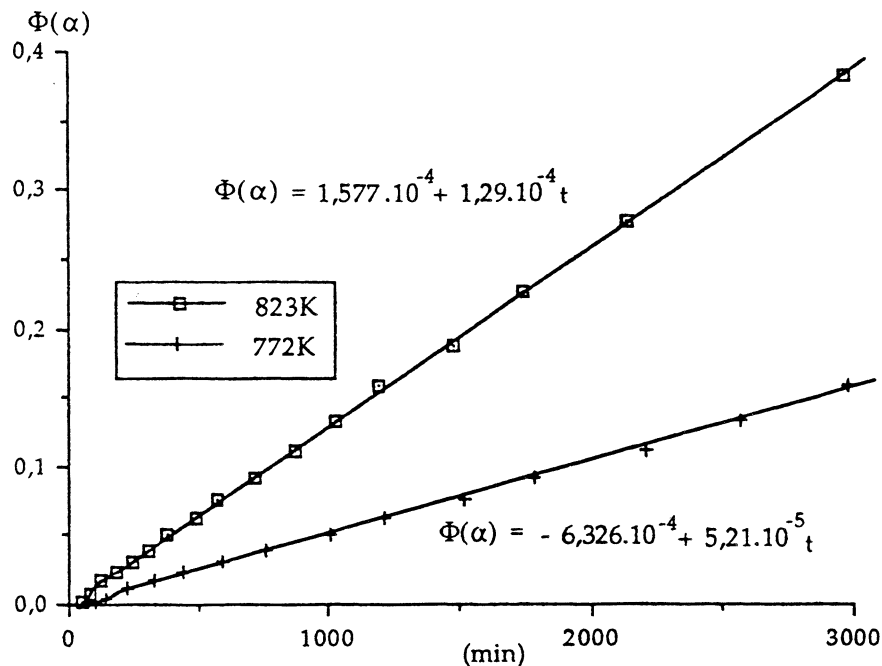
Fig. 2. Calculated kinetics of oxidation of zinc (diffusion law). {$m_0 = 100$ mg; $\Phi = 65$ μm; $h_r = 20\%$.

particular, the time necessary to totally consume the reactant B ($\alpha = 1$) is equal to:

$$\tau = \frac{1}{k_{Zn}^0} \frac{\Delta}{\Delta - 1} \left[1 - \frac{[1 + \alpha(\Delta - 1)]^{2/3}}{\Delta} \right]$$

Under these conditions, designating as $\Phi(\alpha)$ the first term of the equality (7), and replacing Δ with its numeric value ($\Delta = 1.57$), the equation describing zinc oxidation can be written:

$$\Phi(\alpha) = 2.75 - (1 - \alpha)^{2/3} - 1.75(1 + 0.57\alpha)^{2/3}$$
$$= k_{Zn}^0(r_0, T, C_A^e)t \tag{9}$$

Fig. 2 shows that the graph $\Phi(\alpha)$ versus time is a line passing through the origin with slope k_{Zn}^0 and a correlation coefficient of 0.99. The trials were undertaken using 100 mg of powder with an average particle size of 65 μm. The relative hygrometry of air at 298 K is fixed at 20%. At 772 and 823 K, the numeric values of k_{Zn}^0 are 5.21×10^{-5} and 1.29×10^{-4} min^{-1}, respectively. The weak deviation observed in the first few minutes is due to the establishment of equilibrium of the system and to the thermal inertia of the sample. Relation (9) is then verified for the rest of the reaction. The initial mass of the sample was held within an interval of 50–150 mg (Table 1).

3.1. Influence of particle size

In order to check the validity of the model, a series of measurements were carried out by varying the size of the particles from 65 to 375 μm. The trials

Table 1
Influence of the initial mass of the sample[a]

Initial weight (mg)	k_{Zn}^0 (min^{-1})
50	5.8×10^{-5}
80	5.6×10^{-5}
100	7.9×10^{-5}
150	5.4×10^{-5}

[a] $T = 772$ K, $\Phi = 65$ μm; $h_r = 20\%$.

Table 2
Influence of particle size powder on the oxidation rate constant at 823 K

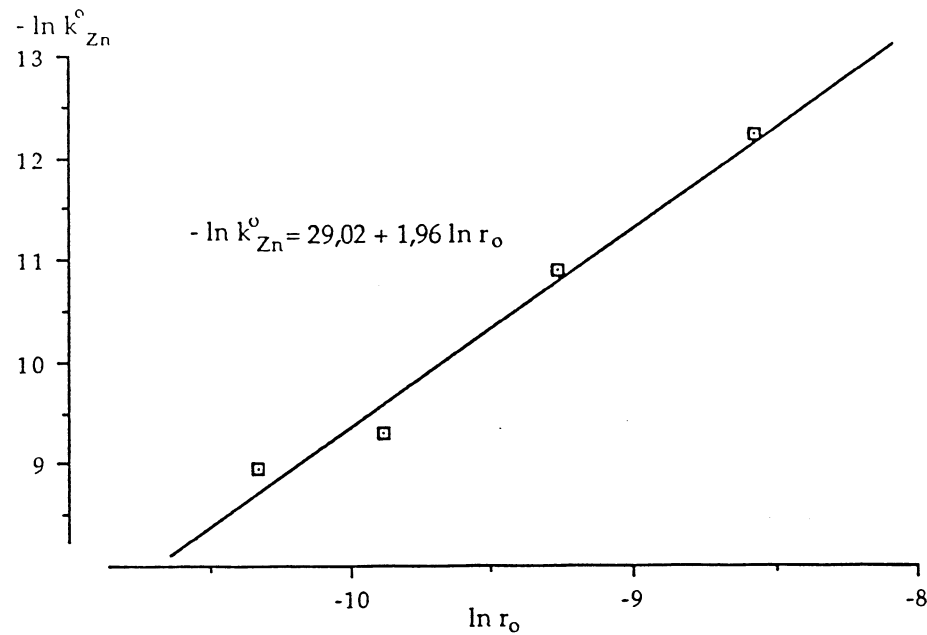| Φ (average) (μm)	r_0 (m)	k_{Zn}^0 (min^{-1})
375	1.87×10^{-4}	5.0×10^{-6}
187	9.35×10^{-5}	1.9×10^{-5}
102	5.10×10^{-5}	9.1×10^{-5}
65	3.25×10^{-5}	1.29×10^{-4}

Fig. 3. Study of the diffusion model. Change in the rate constant of zinc oxidation with the radius of the particles. ($T = 823$ K; $h_r = 20\%$; $3.25 \times 10^{-5} < r_0 < 1.87 \times 10^{-4}$ m).

Table 3
Determination of the activation energy for the zinc oxidation reaction

T (K)	772	823	897	996	1107
k_{Zn}^0 (min^{-1})	5.21×10^{-5}	1.29×10^{-4}	6.89×10^{-4}	3.91×10^{-3}	1.89×10^{-2}

were performed isothermally ($T = 823$ K) and a fixed humidity of 20% at 298 K. The results are collected in Table 2 and Fig. 3.

The slope close to 2 indicates that the rate constant varies linearly with $1/r_0^2$, which confirms the diffusion of the reactants in the solid phase at that temperature. A model in which the limiting factor is the oxygen–metal reaction or the diffusion of oxygen in the gas phase would correspond to a linear variation of k_{Zn}^0 with $1/r_0$.

3.2. Influence of temperature

The effect of temperature was studied between 773 and 1107 K using powder of a constant average particle size of 65μm. The results are tabulated in Table 3. The variation of k_{Zn}^0 as a function of temperature conforms to the Arrhenius law.

The curve $\ln k_{Zn}^0 = f(1/T)$ is a line with a slope $-W_{zn}$ and ordinate at the origin $\ln A_{Zn}$. W_{zn} and A_{Zn} represent the energy and the activation factor of the reaction, respectively. They have the following numeric values with a correlation coefficient of 0.997: $W_{zn} = 130$ kJ mol^{-1} and $A_{zn} = 3 \times 10^4$ min^{-1} (Fig. 4).

The value for the activation energy is in good agreement with those observed in the literature for the surface oxidation of bulk zinc. The result is however 10% higher than that of Terem [12] and Moore [13]. Moore reported results obtained under a pressure of 76–100 mmHg between 633 and 673 K without any other specifications concerning the experimental conditions such as relative humidity level or average particle size. The 10% misfit may therefore be caused by the difference in experimental protocols.
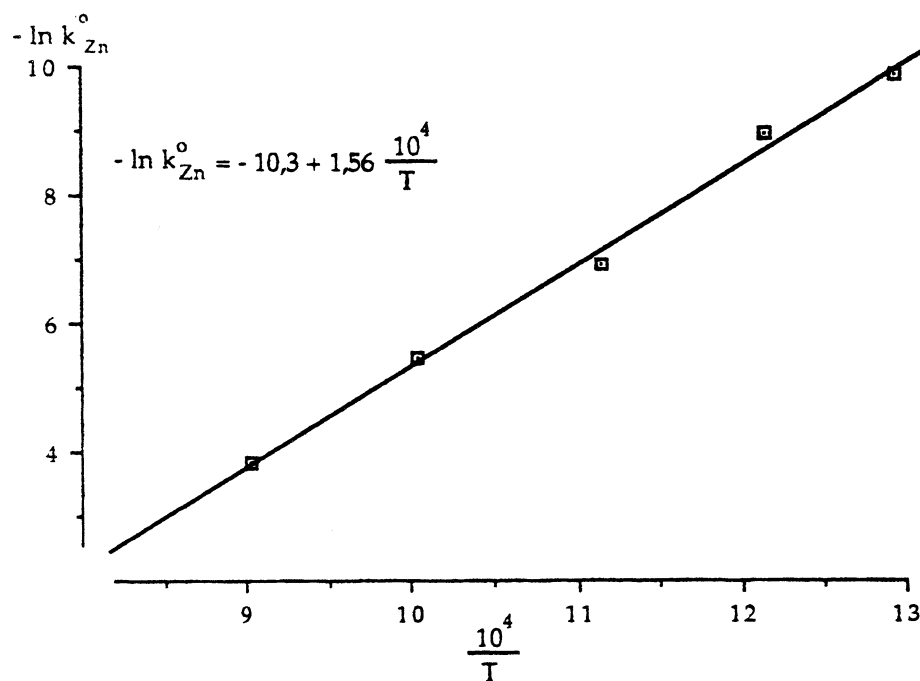
Fig. 4. Change in the rate constant of zinc oxidation with the temperature.

3.3. Influence of humidity level

We have studied the effect of air humidity on the rates of oxidation. The hygrometry was fixed between 0 and 100% at 298 K. The trials were performed at 773, 883, and 973 K on powders of an average particle size of 65 μm. For each temperature, three values of h_r were studied: 5, 20 and 50%. It was observed (Table 4) that the influence of humidity is negligible compared with that of temperature.

4. Conclusions

The complete oxidation of zinc powder is possible well above its melting point without particle coales-

cence. This phenomenon is linked to the presence of a thin layer ZnO which limits the vapor pressure of the metal inside the particle. The phenomenon may be quantified using Fick's law and the diffusion of reactants in the reaction zone. The observed effect of the powder particle size on the reaction rate confirms our model. For industrial development, the influence of the hygrometry level of the gas is negligible in view of the temperature effect, and air can be advantageously utilized on a fixed or fluidized bed. In particular, in the case of a 65 μm powder, the reaction time is 34 h ($\alpha = 0.99$) for an isotherm of 1107 K. Next it is necessary to study the intrinsic oxidation of dopants and their effect on the oxidation rate of the matrix. This work is presently being pursued.

Table 4
Change of the constant k_{Zn}^0 (min^{-1}) with temperature and the relative humidity level of the air used ($\Phi = 65$ μm)

h_r	773	883	973
5%	2.6×10^{-4}	3.6×10^{-3}	2.0×10^{-2}
20%	3.7×10^{-4}	4.9×10^{-3}	2.7×10^{-2}
50%	2.9×10^{-4}	4.3×10^{-3}	2.5×10^{-2}

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