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Validation of a kinetic model of diffusion for complete oxidation of bismuth powder: influence of granulometry and temperature

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Abstract

The kinetics of complete oxidation of bismuth powder by air has been investigated by thermogravimetric studies under isothermal conditions in the range 729–968 K. Particles size was chosen in the 35–375-μm range. We have been able to carry out the full oxidation of the powder far above the bismuth metal melting point (544.3 K) 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 139 kJ mol^{-1}. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

This work reports on a new process for the production of ceramics based on the direct oxidation of an 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 to obtain 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, especially of bismuth, which is an essential additive for ZnO varistances. This paper deals with the complete oxidation of pure bismuth powders, which do not sinter even above the melting temperature of the bulk metal bismuth.

Few studies deal with the full oxidation of metals; the works are mainly focus on the growth of thin layers, in order to study corrosion phenomena [5–8]. In contrast, our objective concerns the total oxidation of the particles, as quickly as possible. The majority of the theories advanced apply to the surface oxidation of metal but very few models have been developed for the case of complete oxidation of metal powders [8].

We have studied this case by TG in order to elaborate a kinetic model capable of quantitatively

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predicting the phenomena as a function of the temperature and particle size.

2. Experimental section

The powder used for this work is obtained by atomisation. The bulk metal is a product of Aldrich Chemicals of 99.999% purity. The production of bismuth powder is as follows: the metal is melted under a neutral atmosphere (Argon) to avoid premature oxidation. The system of atomisation is an annular nozzle; the liquid metal flows into the nozzle and is pulverized by nitrogen with determined pressure and flow. The spray of liquid metal droplets is then cooled into liquid nitrogen. The particles are then sieved between 35 and 375 μm.

The variation of mass of the sample as a function of temperature is followed by TG using a LINSEIS L81 thermobalance. The oxidizing gas is air.

The metallic powder is placed in a curved silica container of 25-mm length and 20-mm diameter. The mass of the original metal sample weighed (accuracy up 1/10 of a mg) is around 50 mg. These conditions allow the formation of a monolayer of particles on the container. The rising gas flow possesses sufficient intensity ($3\ \mathrm{l\ h^{-1}}$) 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 bismuth at 544.3 K. The surface oxide prevents coalescence of the particles despite the presence of liquid within the particles. The extent of the reaction

$$3/2\mathrm{O_2(g)} + 2\mathrm{Bi(l)} \rightarrow \mathrm{Bi_2O_3(s)}$$

is defined by:

$$\alpha = [m^{\circ}_{\mathrm{Bi}} - m^{t}_{\mathrm{Bi}}]/m^{\circ}_{\mathrm{Bi}} = [4/3\delta m(t) M_{\mathrm{Bi}}]/[m^{\circ}_{\mathrm{Bi}} M_{\mathrm{O_2}}] \qquad \text{(i)}$$

where m°_{Bi}, m^{t}_{Bi} and $\delta m(t)$, respectively, are the initial mass, the mass and the mass gain (obtained by TG experimental measurements) of the sample at time t. M_{Bi} and $M_{\mathrm{O_2}}$ are the molecular weights of bismuth and oxygen. The isotherms were performed between 729 and 968 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: $\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(l)} \rightarrow \nu_C \mathrm{C(s)}$.

The preservation of the spherical shape of the starting particles during the full oxidation allows us to name by r_0, r_B, r_C, respectively, the initial radius of

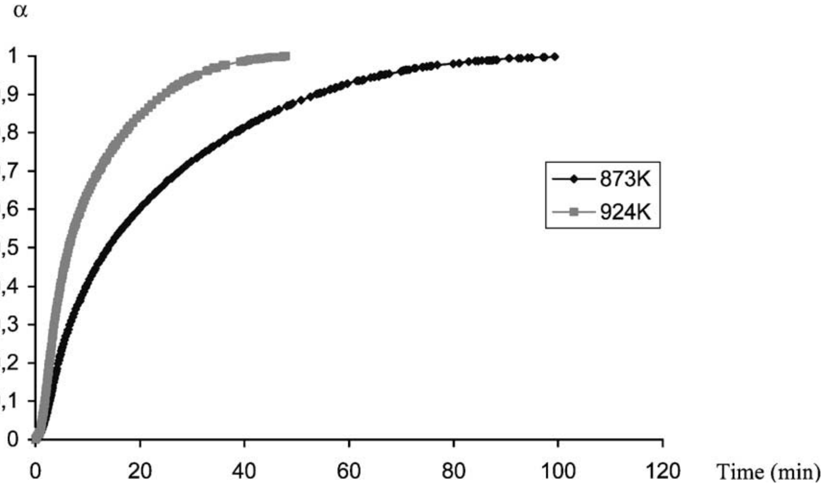

Fig. 1. Complete oxidation of powdered bismuth. Progress of the reaction at 873 and 924 K.

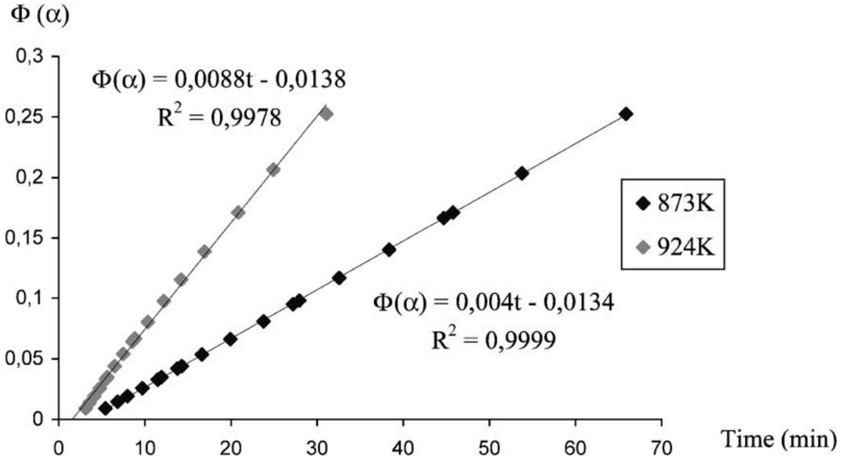

Fig. 2. Oxidation kinetics of bismuth: diffusion law ($m_0 = 50$ mg and $\phi = 71$ μm). (R^2 being the correlation coefficient).

B, of the reaction interface (metal/oxide) and of the oxide layer. We demonstrate the following relations:

$$r_B = r_0(1-\alpha)^{1/3} \tag{ii}$$

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

where $\Delta = V_C/[V^{\circ}_B - V_B]$ is the coefficient of Pilling and Bedworth [5].

As α is experimentally accessible, let us derive expression (i) with respect to time. Taking the reaction stoichiometry into account, it becomes:

$$\frac{d\alpha}{dt} = -\frac{1}{m^0_B}\frac{\nu_B}{\nu_A}\frac{dm_A}{dt}. \tag{iv}$$

Assuming that the diffusion of the reactants through the thickness of the oxide layer is the limiting factor and that the diffusivity of component B in the crystal lattice of the component C is negligible in the comparison with the diffusivity of component A, application of Fick's law to reactant A leads to: $\frac{dm_A}{dt} = -D_A S_B \left\{\frac{dC_A}{dr}\right\}_{r=r_B}$, with $S_B = 4\pi {r_B}^2$, where D_A and $\left\{\frac{dC_A}{dr}\right\}_{r_B}$ are, respectively, the diffusion coefficient and the local concentration gradient of A at $r = r_B$.

Substitution of this expression in Eq. (iv) reduces to the following rate equation:

$$\frac{d\alpha}{dt} = \frac{1}{m^0_B}\frac{\nu_B}{\nu_A} D_A 4\pi r_B^2 \left\{\frac{dC_A}{dr}\right\}_{r=r_B}. \tag{v}$$

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:

$$4\pi r^2 D_A \left\{\frac{dC_A}{dr}\right\}_r = 4\pi r_B^2 D_A \left\{\frac{dC_A}{dr}\right\}_{r=r_B}.$$

Taking into account the limiting conditions ($C_A = C^i_A = 0$ for $r = r_B$ and $C_A = C^e_A$ for $r = r_C$, where i and e stand, respectively, for initial and equilibrium condition), one can write:

$$\int_{C^i_A}^{C^e_A} dC_A = r_B^2 \left\{\frac{dC_A}{dr}\right\}_{r=r_B} \int_{r_B}^{r_C} \frac{dr}{r^2}$$

from which the expression of the gradient at $r = r_B$ can be linked to α via relations (ii) and (iii):

$$\left\{\frac{dC_A}{dr}\right\}_{r=r_B} = \frac{r_C}{r_B(r_C - r_B)} C^e_A \tag{vi}$$

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

$$\frac{d\alpha}{dt} = \frac{\nu_B}{\nu_A}\frac{4\pi D_A C^e_A}{m^0_B}\left[\frac{1}{r_0(1-\alpha)^{1/3}} - \frac{1}{r^0[1+\alpha(\Delta-1)]^{1/3}}\right]^{-1}$$

Table 1
Influence of particles size powder on the oxidation rate constant at 873 K

ϕ(average, μm)	r_o (m)	k(min^{-1})
375	1.87×10^{-4}	4×10^{-4}
187.5	9.37×10^{-5}	9×10^{-4}
102.5	5.12×10^{-5}	2.1×10^{-3}
71.5	3.57×10^{-5}	4×10^{-3}
51.5	2.57×10^{-5}	8.9×10^{-3}
35	1.75×10^{-5}	1.6×10^{-2}

ϕ: average diameter of the particles, $r_0=\phi/2$, k: kinetic constant of the oxidation reaction $Bi(l)+3/2O_2\rightarrow Bi_2O_3(s)$.

Table 2
Kinetic constant of the oxidation reaction with temperature

k(min^{-1})	T(K)
0.06×10^{-3}	729
0.3×10^{-3}	785
1.7×10^{-3}	830
4×10^{-3}	873
8.8×10^{-3}	924
15.6×10^{-3}	968

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

$$\frac{\Delta}{\Delta-1}-(1-\alpha)^{2/3}-\frac{1}{\Delta-1}[1+\alpha(\Delta-1)]^{2/3}=\frac{\nu_B D_A C_A^e}{\nu_A 2 d_B r_0^2}t \quad \text{(vii)}$$

(d_B being the density of B)

One can define: $$k=\frac{\nu_B D_A C_A^e}{\nu_A 2 d_B r_0^2} \quad \text{(viii)}$$

where k stands for the experimental observed rate constant of the reaction.

For a fixed value of the particle size, temperature, and composition of fluid A, the constant k can be experimentally determined at any time from the pair of points (α,t) and relation (vii). In particular, the time necessary to totally consume the reactant B ($\alpha=1$) is equal to: $\tau=\frac{1}{k}\frac{\Delta}{\Delta-1}\left[1-\frac{[1+(\Delta-1)]^{2/3}}{\Delta}\right]$.

Under these conditions, designating as $\Phi(\alpha)$ the first term of the equality (vii), and replacing Δ with its numeric value ($\Delta=1.23$), the equation describing bismuth oxidation can be written:

$$\begin{aligned}\Phi(\alpha)&=5.35-(1-\alpha)^{2/3}-4.35(1+0.23\alpha)^{2/3}\\&=k(r_0,\,T,\,C_A^e)t \qquad (ix)\end{aligned}$$

Fig. 2 shows that the graph $\Phi(\alpha)$ versus time is a line passing through the origin with slope k and a correlation coefficient better than 0.99. The trials were

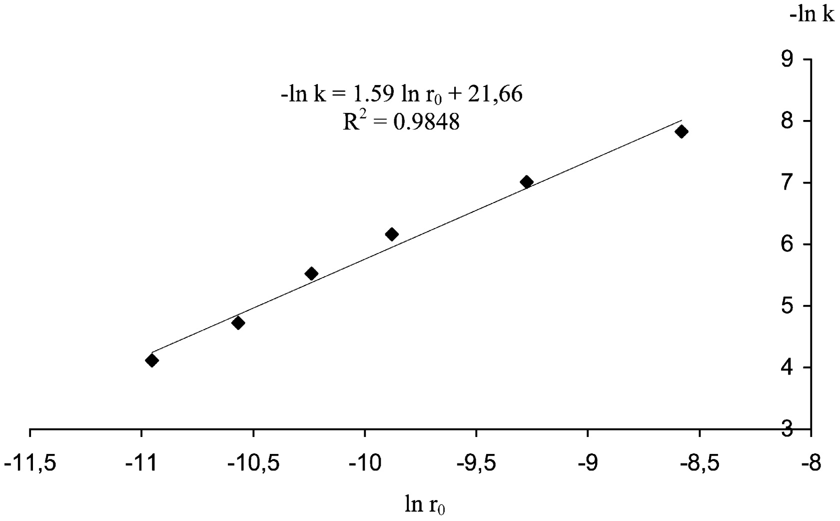

Fig. 3. Study of the diffusion model. The rate constant of bismuth oxidation as a function of the particles radius ($T=873$ K) (R^2 being the correlation coefficient).

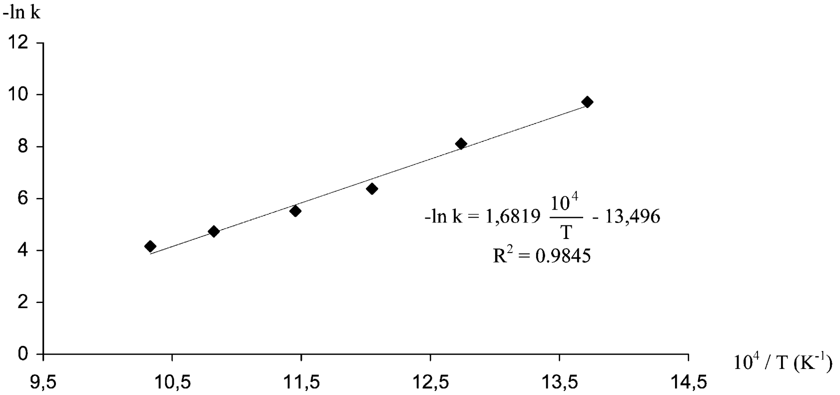

Fig. 4. Rate constant of bismuth oxidation as a function of the temperature (R^2 being the correlation coefficient).

undertaken using 50 mg of powder with an average particle diameter of 71 μm. At 873 and 924 K, the numeric values of $k$are 4×10^{-3} and 8.8×10^{-3} $\min^{-1}$, respectively.

4. 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 35 to 375 μm. The trials were performed isothermally ($T = 873$ K). The results are collected in Table 1 and Fig. 3.

The slope near 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 with $1/r_0$.

5. Influence of temperature

The effect of temperature was studied between 729 and 968 K using powder an average particle size of 71 μm. The results are tabulated in Table 2. The variation of k as a function of temperature conforms to the Arrhenius law.

The curve $\ln k = f(1/T)$ is a straight line. W and A, respectively, represent the energy and the activation factor of the reaction. They have the following numeric values with a correlation coefficient of 0.98: $W = 139$ kJ mol^{-1} and $A = 7 \times 10^5$ $\min^{-1}$ (Fig. 4).

The value for the activation energy is in good agreement with those observed in the literature for the surface oxidation of bulk bismuth [6].

6. Conclusion

The complete oxidation of bismuth powder is possible well above its melting point without particle coalescence. This phenomenon is linked to the presence of a thin Bi_2O_3 layer which confines the liquid metal in the particles and limits the vapour 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. Next, it is necessary to study the intrinsic oxidation of alloys containing bismuth and zinc and the effect of the bismuth dopant on the oxidation rate of the matrix. This work is presently being pursued.

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