



Direct Oxidation of an Alloy Precursor Complete Oxidation of Bismuth and Zinc Powder

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Submitted July 3, 2003; Revised November 14, 2003; Accepted November 25, 2003

Abstract. This work reports on a process (DOPA: Direct Oxidation of a Precursory Alloy) of preparation of ceramics used as varistors for the electric protection against power surges. This new route has been applied for the production of ZnO varistors doped with Bi₂O₃, Sb₂O₃ and other oxides. One important stage of this process is the total conversion of an alloy into the corresponding mixed oxide. We have reported here the studies of the full conversions metal-ceramic powders of the main components of these varistors: zinc and bismuth.

Keywords: zinc, bismuth, oxidation, ceramic-metal conversion

Introduction

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. A novel procedure, has been carried out for ceramic powder production: Direct Oxidation of a Precursor Alloy (DOPA) [1]. A melt of the component metals is propelled through a nozzle with hot compressed air and quenched. The resulting product is a homogeneous alloy powder which is oxidized in air under a carefully-controlled sequence of reaction steps that produces oxide powder of controlled stoichiometry. The ceramic powder obtained can be processed in order to convert green discs to sintered parts at high temperature and to obtain well densified ceramics usable as surge arrestors. One important stage of this

process is the total conversion of an alloy into the corresponding multiple elements oxide. We have reported here the studies of the full conversions metal-ceramic powders of the main components of these varistors: zinc and bismuth.

Experimental Methods

Zinc is in granules from Prolabo Normapur—99.9% purity, the bulk bismuth metal is a product of Aldrich Chemicals of 99.999% purity. The production of powders is as follows: the metals are 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. Resulting powder of size varying between 500 and 10 μm were sieved into 500, 250, 125, 80, 63, 40, 30, 20 and 10 μm to ensure narrow particle size distribution. Secondary electron microscopy observation shows that particles shapes were not well defined for the fractions above 80 μm. However the particles had a rather spherical shape below 80 μm.

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

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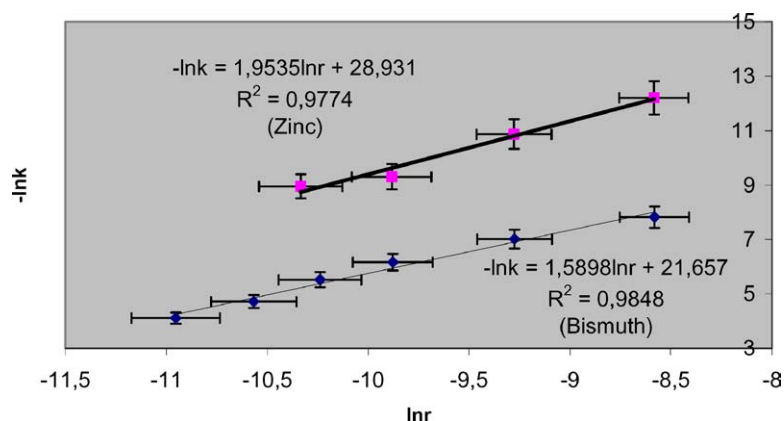


Fig. 1. Study of the diffusion model. Change in the rate constant of zinc and bismuth oxidation with the radius of particles. ($T = 823$ K and 873 K respectively). (R^2 being the correlation coefficient).

gas is air. The metallic powder is placed in a curved silica container of 25 mm long and 20 mm large. 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 powder on the container. The rising gas flow possesses sufficient intensity (3 Lh^{-1}) to avoid any diminishment of oxygen level at the reaction interface.

Results and Discussion

The experiments were conducted isothermally and in all cases at a temperature above the melting point of zinc and bismuth at 692 and 544.3 K respectively. The surface oxide prevents coalescence of the particles despite the presence of liquid in-between the particles.

The kinetic model of the parabolic diffusion of oxygen through an oxide layer can be expressed by the expression:

$$\frac{\Delta}{\Delta - 1} - (1 - \alpha)^{2/3} - \frac{1}{\Delta - 1} [1 + \alpha(\Delta - 1)]^{2/3} = kt$$

where $\Delta = V_{\text{oxide}}/[V_{\text{metal}}^{\circ} - V_{\text{metal}}]$ is the coefficient of Pilling and Bedworth [4] ($\Delta_{\text{Zn}} = 1.57$ and $\Delta_{\text{Bi}} = 1.23$), α is the extent of the heterogeneous oxidation reactions expressed as $[m_{\text{metal}}^{\circ} - m_{\text{metal}}^t]/m_{\text{metal}}^{\circ}$ where m_{metal}° is the initial mass of metal and m_{metal}^t is the mass of the metal at time t .

In order to check the validity of the model, several measurements were carried out by varying the size of

the particles from 35 to 375 μm . The trials were performed isothermally at 823 and 873 K respectively. The results are collected in Fig. 1.

The slope near to 2 indicates that the rate constant varies linearly with $1/r^2$, r being the mean radius of the particles, which confirms the diffusion of the reactants in the solid phase at that temperature.

The evolution of the kinetic with the temperature for zinc and bismuth particles depicted in Fig. 2 allow us to get the activation energy of both metals:

$$E_{\text{zn}} = 130 \text{ kJmol}^{-1},$$

$$E_{\text{Bi}} = 139 \text{ kJmol}^{-1}.$$

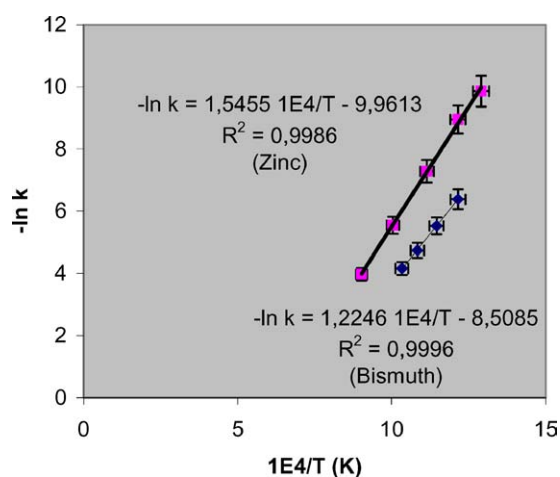


Fig. 2. Change in the rate constant of zinc and bismuth oxidation with the temperature. (R^2 being the correlation coefficient).

The result is however 10% higher than that of TEREM [5] and MOORE [6]. Reported results obtained with multiple weighed between 633 and 673 K using both a furnace and a balance. The 10% misfit may therefore be caused by the difference in experimental protocols.

Data on the oxidation of bismuth particles were not found. However, the value for the activation energy is in good agreement with those observed in the literature for the surface oxidation of bulk bismuth [7].

The complete oxidation of zinc and bismuth powders is possible well above their melting point without particle coalescence. This phenomenon is linked to the presence of a thin ZnO or Bi₂O₃ layer which confines the liquid metal in the particles and limits the vapor pressure of the metal inside the particle or the surface tensile of the liquid metal which keep the particle spherical. The phenomenon may be quantified using Fick's law and the diffusion of reactants in the reaction zone.

Acknowledgments

This work was supported by the Fond d'Incitation au Transfert Technologique (FITT) de la région Rhône Alpes. Gratitude is expressed to Anvar Rhône Alpes, Research Direction of university Lyon-1 and EZUS.

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