Microstructure evolution of the full transition of bismuth metal to a bismuth oxide particulate

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Abstract

A morphological study is presented showing the evolution of a bismuth particle during its full oxidation and above its melting temperature at 873 K. The results are in good agreement with the theoretical data obtained by solving the Fick's equation relative to the steady diffusion of a reactant through an oxide layer.
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Keywords: Bi_2O_3; Powder; Diffusion; Oxidation

1. Introduction

Sintering ZnO with about 5 wt.% of various metal oxide dopants results in a polycrystalline ceramic with nonlinear current–voltage characteristics commonly known as the varistor effect.[1,2]

There is a continuous need to improve the protection level against transient surge voltages, i.e. a surge suppressor such as a varistor should offer reduced residual voltage, better energy absorption capability and lower leakage currents. The proper physico-chemical characteristics of the initial ceramic powders are very important to achieve a good varistor.

The atomization process remains a good choice among the different methods of metal powder production due to its versatility and the quality and purity of the resulting powders; the control of their properties and the potential for tonnage production. The atomization process of molten metals, as considered in the present paper, is the starting step in a new production process for oxide ceramic powders. This new route known as direct oxidation of a precursory alloy (DOPA) leads to a ceramic powder by total oxidation of a metallic alloy powder obtained by atomization. The oxide powder can then be pressed and sintered to obtain a bulk ceramic. The precursor metal alloy powders need to be accurately controlled in terms of chemical purity, morphology and particle size distribution. The aim of this study was to further the understanding of the oxidation process as a basis for subsequent work to develop and optimize the DOPA process. The DOPA process of course, can be applied to the preparation of single elemental metal powders which is the case for the present work where bismuth is studied.

Preliminary details on the complete oxidation of bismuth and zinc powder well above their melting point without particle coalescence taking place have already been published.[3,4] This phenomenon was explained by the surface tension and/or the presence of a thin oxide layer which confines the liquid metal in the particles and limits the vapour pressure of the metal inside the particles.

The purpose of this paper is to report on the microstructure evolution of the composite metal–ceramic (Bi–Bi_2O_3) particles obtained during the oxidation process carried out subsequently to the molten metal atomization.

2. Experimental procedure

The powder used for this work is obtained by the atomization of a molten metal or alloy. The bulk bismuth 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

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  E-mail address: metz@univ-lyon1.fr (R. Metz).

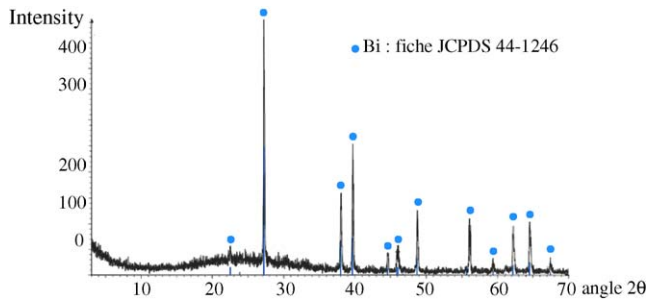Fig. 1. X-ray diffraction diagram of an atomized bismuth powder.

Fig. 2. Scheme of a cross-section diffusion.

atmosphere (Argon) to avoid premature oxidation. The system of atomization is based on an annular nozzle. The liquid metal flows into the nozzle where it is pulverized by nitrogen with determined pressure and flow rate. The spray of liquid metal droplets is then dropped into liquid nitrogen for quick cooling. The particles are then sieved between a 63 and 80 μm mesh.

Particles were embedded in a polymer resin. After it became harder, the form was polished down until it reached a fair planar surface. Characterization of the powder morphology was carried out using a scanning electron microscope (SEM) Hitachi S800.

Elemental mapping was performed using a Cameca Camebax electron probe microanalyser (EMPA) with an energy dispersive spectrometer. Mapping was performed for resin mounted specimens. This technique was used to evaluate bismuth and oxygen dispersion thorough the diameter of the particles. The relation between composition and microstructure of the resulting materials was investigated by a combination of EPMA and SEM.

The phases present in the powders were identified by powder X-ray diffractometry (PXRD). The X-ray measurements were conducted in a Siemens diffractometer model using Cu Kα1 radiation with a wavelength $\lambda = 0.154$ nm. PXRD were determined in the $2\theta = 5$–$90°$ range with a resolution of $0.02°$ and a time step of 1 s.

3. Experimental results and discussion

X-ray diffraction analysis has been carried out to check the absence of foreign phases. Contamination could indeed arise from the interaction between the molten metal and the atomizing gas or the quenching media (cold water or liquid nitrogen) inducing the formation of nitrides or oxides. Fig. 1 shows a typical PXRD pattern. Since the detection limit of the PXRD was 2%, it was not possible to detect any by-product as a consequence of a reaction between molten bismuth and its surrounding.

The oxidation phenomenon may be quantified using Fick's law and the diffusion of oxygen through the growing oxide layer (Fig. 2). The kinetic model of the parabolic diffusion is expressed by the expression:[3]

$$\text{oxidation } (\xi) = \frac{\Delta}{\Delta - 1} - (1 - \xi)^{2/3}$$

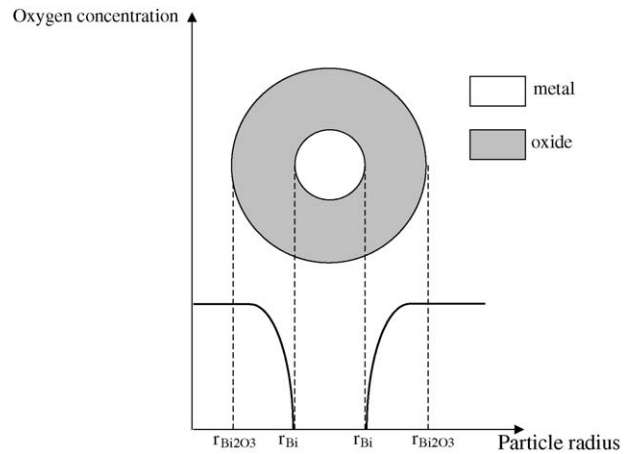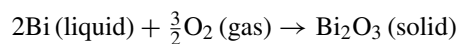$$- \frac{1}{\Delta - 1}[1 + \xi(\Delta - 1)]^{2/3} = kt \qquad (1)$$

where Δ is the transformation expansion coefficient between the oxide and the metal and ξ the extent of the heterogeneous oxidation reaction. To interpret and quantify these phenomena, we consider the reaction:

$$2\text{Bi (liquid)} + \tfrac{3}{2}\text{O}_2 \text{ (gas)} \rightarrow \text{Bi}_2\text{O}_3 \text{ (solid)}$$

with $\xi = [4/3(m_0 - m_t) M_{\text{Bi}}]/[m_0 M_{\text{O}_2}]$ where m_0 and m_t, respectively, are the initial mass of bismuth and the mass of the sample at the time t. M_{Bi} and M_{O_2} are the molecular weights of bismuth and oxygen, respectively. The expression (i) is perfectly validated from $\xi = 0$ to 1 in the range 729–928 K as shown in Fig. 3.

The partially oxidized particles as well as those fully oxidized keep a spherical shape and smoothness (Fig. 4). SEM pictures
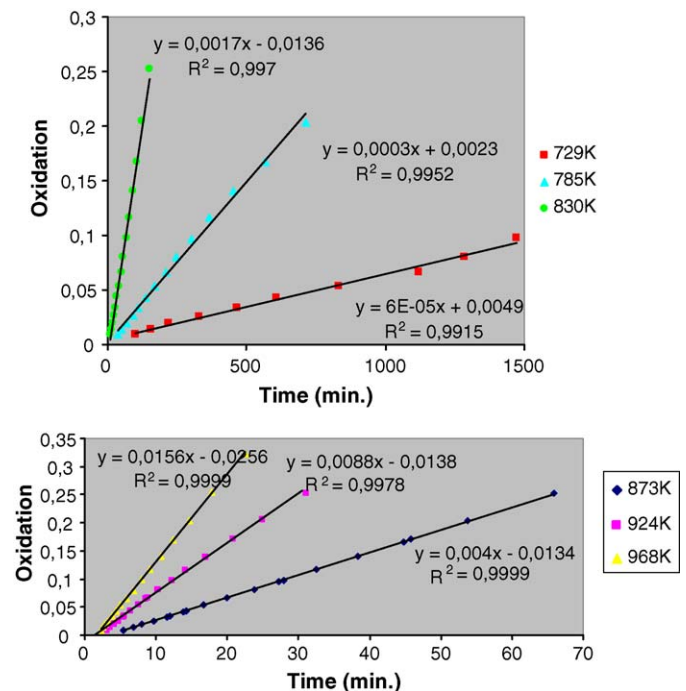

Fig. 3. Oxidation kinetics of bismuth: diffusion law ($m_0 \sim 50$ mg and the particle diameter is about 71 μm) (R^2 being the correlation coefficient).
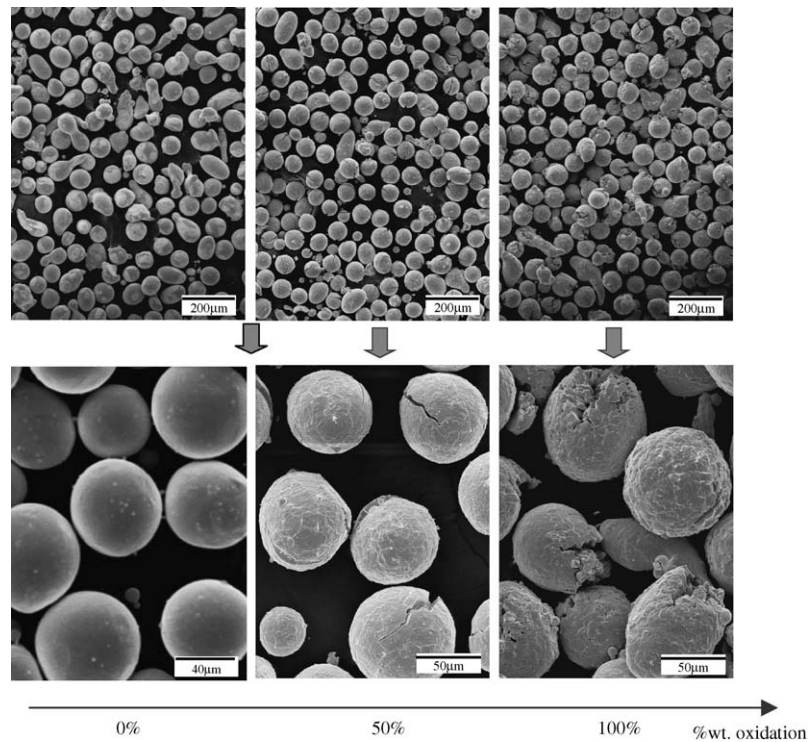
Fig. 4. SEM pictures of bismuth particles, 50 and 100 wt.% oxidized (isotherm 873 K).

of the original metal particles confirm the absence of particle coalesence despite the oxidation temperature being above the melting temperature of bismuth metal. The microstructural change at 873 K is illustrated in Fig. 5. The first layer of oxide around the metal powder exhibits several cracks which result from the difference between the oxide and the metal expansion coefficient. Kinetics are realized at temperatures far above the melting temperature of bismuth (544 K). At this temperature, Bi is melt and the fracture observed at room temperature might result from the cooling of the powders.

A polished cross-section of these metal particles has been examined to assess the powder internal densification. The powder particles were mounted into a polymeric resin and the resin was polished until the particles are cut around the middle. An example of a SEM image is shown in Fig. 6. The surface of this cross-section presents some scratches due to polishing. It can be noticed that the particle is fully densified and does not show any apparent macroscopic porosity.

After 50% of oxidation, the particles present two differentiated area. A metallic core of bismuth and a Bi_2O_3 ring around it are observed by X-ay mapping relative to oxygen and bismuth (Fig. 6). The metal–ceramic interface does not show any apparent cracks.

A cross-analysis along the particle diameter shows the profile depicted in Fig. 6. The center of the particles is composed of pure bismuth. The border of the particle is composed of both bismuth and oxygen. The ratio Bi/O agrees with the composition: Bi_2O_3 ($\%m_{theory}(Bi) = 89.7\%$ and $\%m_{theory}(O) = 10.3\%$). A profile was measured through the diameter of the particle. It appears that the bismuth/oxygen ratio is fairly stable in the oxide layer and decreases drastically at the Bi–Bi_2O_3 interface. The relatively large error bars on $\%wt_i$ are a consequence of the small number of transversal analysis that could be examined in a reproducible manner. Nevertheless, we observe a slightly curve profile witnessing the diffusion of oxygen out of the particle and accumulation at the interface.
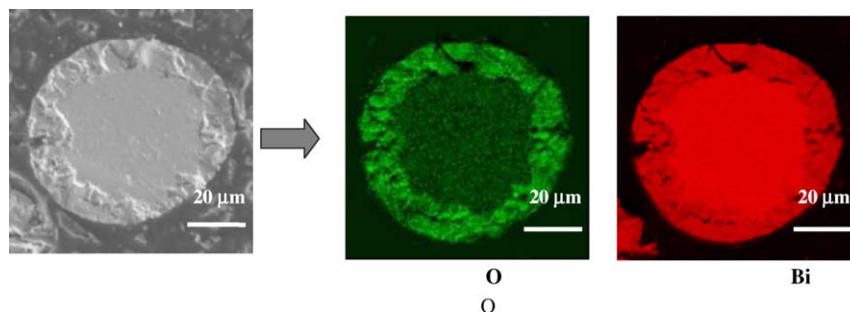

Fig. 5. Elemental mapping of a cross-section of a Bi particle oxidized at 50 wt.% (O map and Bi map).
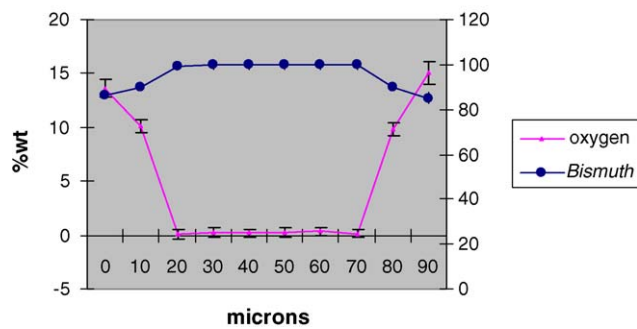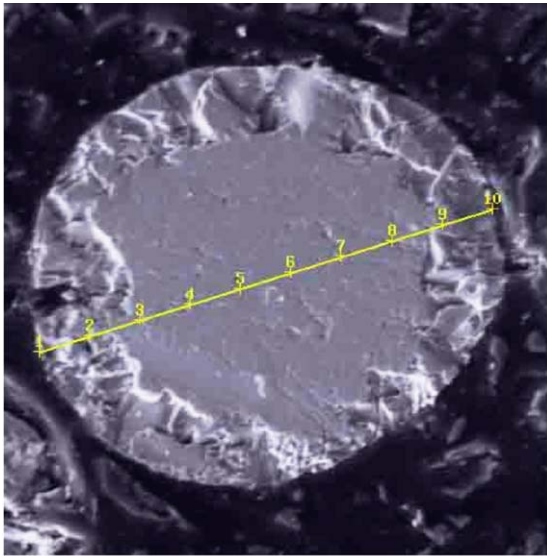
4. Conclusion

The study of the microstructure transition from a bismuth metal particle to a bismuth oxide ceramic particle confirms the theoretical model as expressed in equation (i) assuming the diffusion of oxygen (or bismuth) through a growing layer of oxide.

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Fig. 6. Elemental analysis along the diameter of a bismuth particle oxidized at 50 wt.%.