

Preparation of α -Bi₂O₃ from bismuth powders through low-temperature oxidation

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Abstract: α -Bi₂O₃ powders were prepared from nanometer Bi powders through low-temperature oxidation at less than 873.15 K. XRD, SEM, TEM and HRTEM were used to characterize the structure and morphology of Bi powders and Bi₂O₃ particles. Kinetic studies on the bismuth oxidation at low-temperatures were carried out by TGA method. The results show that bismuth beads should be reunited and oxidized to become irregular Bi₂O₃ powders. The bismuth oxidation follows shrinking core model, and its controlling mechanism varies at different reaction time. Within 0–10 min, the kinetics is controlled by chemical reaction, after that it is controlled by O₂ diffusion in the solid α -Bi₂O₃ layer. The apparent activation energy is determined as 55.19 kJ/mol in liquid-phase oxidation.

Key words: bismuth powder; low-temperature oxidation; α -Bi₂O₃; oxidation kinetics

1 Introduction

Bi₂O₃ has been used widely in the fields of catalysis [1,2], functional ceramics [3–7], special glass and optical materials [8–11], medicine synthesis [12], energy materials [13,14] and superconductor materials [15,16] owing to its special properties of wide band gap, dielectric permittivity, high refractive index, photoluminescence and photoconductivity. Many methods such as high-temperature oxidation of bismuth metal [17–19], pyrolysis of bismuth compound [20,21], hydro-chemical method [22–25] and solid state reaction [26] have been reported to prepare Bi₂O₃ powders. High-temperature oxidation of bismuth metal is also dividable into vapor-oxidation and spray-oxidation. Beta- and alpha- phase Bi₂O₃ nanoparticles could be formed through high-temperature vapor-oxidation of Bi metal at 1278 K [17]. It was difficult to oxidize bismuth completely to form Bi₂O₃ through spray-oxidation due to short retention time in air and kinetics limit at 1073 K [19]. Bi₂O₃ particles with hollow and well-defined morphology could be synthesized through spray-pyrolysis process with change of pyrolysis temperature using Bi(NO₃)₃·5H₂O as raw materials.

However, some above mentioned methods have disadvantages like higher energy consumption, complicated equipments and processing method, and the others produce toxic waste like N_xO_y gas.

Preparation of Bi₂O₃ at less than 873 K was investigated using metallic bismuth as raw materials. The reaction temperature can be controlled lower than 873 K in low-temperature oxidation process. Consequently, energy consumption and equipment cost obviously decrease. Moreover, low-temperature oxidation method could avoid producing air-borne emissions in spray-pyrolysis and reduce the waste water discharge in hydro-chemical method. The present work aims at investigating the kinetics of bismuth oxidation at a low temperature and characterizing the structure of Bi₂O₃ powders obtained from this method. The studies are a useful guideline on preparing Bi₂O₃ powders at less than 873.15 K, understanding the oxidation mechanism of bismuth and increasing the yield of Bi₂O₃ particles through low-temperature oxidation process.

2 Experimental

The bismuth powders with particle size of 20 nm were prepared through fusion spraying method.

Oxidation of bismuth at a low temperature was conducted by a Q600 differential thermal analyzer (TA, USA). Bismuth powders were put into the thermal analyzer and treated at a predetermined temperature for 30 min in N₂ flow with a heating rate of 3 °C/min, and then, switched from N₂ flow to air flow. The mass change of bismuth powder was recorded and the oxidation ratio of bismuth powders was calculated according to equation (1).

$$\alpha = (2 \times 208.9804 \times \Delta m) / (3 \times 15.9994 \times m) = 8.7075 \times \Delta m / m \quad (1)$$

where α denotes the fraction of oxidized bismuth, m is the initial mass of bismuth powders, and Δm represents the increased mass of the bismuth powders after oxidation reaction at different temperatures. The chemical compositions of Bi powders and as-synthesized Bi₂O₃ are listed in Table 1, which were analyzed by ICP-AES.

Table 1 Chemical compositions of bismuth powders and Bi₂O₃

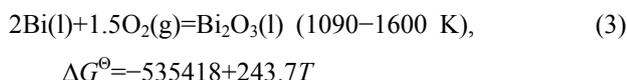
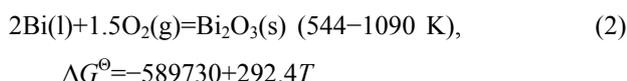
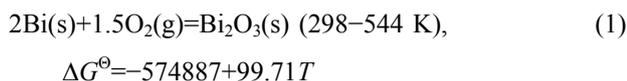
Sample	w(Ag)/ %	w(Cu)/ %	w(Pb)/ %	w(Sb)/ %	w(Fe)/ %
Raw material (w(Bi)≥99.99%)	0.0008	0.0008	0.0007	<0.001	<0.001
As-synthesized Bi ₂ O ₃ (w(Bi ₂ O ₃)≥99.92%)	0.0007	0.0007	0.0006	<0.001	<0.001

The X-ray diffraction (XRD) of the sample was recorded on a D/max 2550 (Rigaku, Japan) with Cu K_α radiation ($\lambda=0.1548$ nm) from 10°~80°(2 θ) at a scanning step of 0.25 (°)/s. The morphologies of the samples were characterized by a high-resolution transmission electron microscope (Tecnai G² 20, FEI, USA). Particle size distribution was detected by Mastersizer 2000 (Malvern, England).

3 Results and discussion

3.1 Effect of oxidation temperature on formation of Bi₂O₃

The bismuth-oxidation reaction can be presented as:



According to equations (1), (2), and (3), the Gibbs free energy is minus in the temperature range of 200–1600 K, which means the bismuth oxidation reaction is thermodynamically spontaneous.

Figure 1 shows the effect of oxidation time on yield of bismuth oxide at different temperatures under the conditions of particle size of 20 nm and air flow of 35 mL/min. The results demonstrate that the oxidation rate of bismuth powder increases with the increase of temperature. At 450 °C, the oxidation rate of bismuth is only 83.17% after 187 min. At 600 °C, however, the bismuth is completely transferred to Bi₂O₃ even through the reaction time is only 15 min. The possible reasons for these phenomena may be as follows: the O₂ diffusion coefficient in the gas film and solid Bi₂O₃ layer increases with the increase of temperature. Consequently, the oxygen molecules can rapidly pass through the gas film and solid Bi₂O₃ layer and transfer to the surface of un-reacted bismuth core. Sufficient oxygen molecules are supplied for the oxidation of bismuth powders.

The results propose that oxidation process of bismuth is controlled by gaseous and liquid oxidation, and gaseous oxidation contributes to improving oxidation rate. The relationship between vapor pressure of melting Bi and temperature is as follows [27]:

$$\lg p = -10051/T + 8.462 \quad (4)$$

where p denotes the vapor pressure of melting Bi, and T is the thermodynamic temperature.

According to Eq. (4), the vapor pressures of Bi are 90.18 Pa at 873.15 K, 18.03 Pa at 823.15 K, 2.92 Pa at 773.15 K, 0.37 Pa at 723.15 K, respectively. Higher vapor pressure can destroy the film outside of the bismuth bead and benefit diffusion of O₂ molecules from atmosphere to surface of bismuth bead.

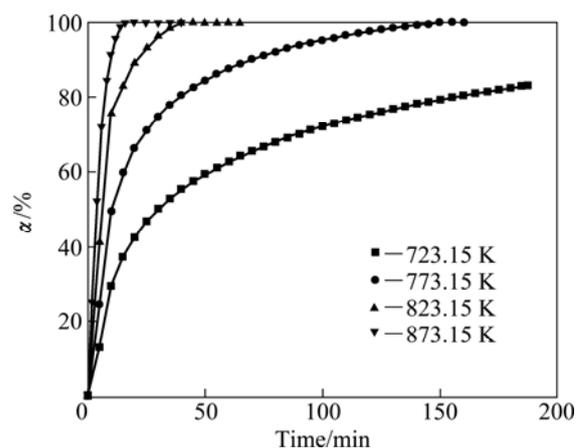


Fig. 1 Effect of oxidation time on yield of bismuth oxide at different temperatures

3.2 Particle size distribution and crystal structure of Bi₂O₃

The XRD pattern of as-prepared Bi₂O₃ is shown in Fig. 2. Three characteristic peaks are indexed as (120), (200) and ($\bar{1}$ 21), indicating that monoclinic Bi₂O₃ (PDF# 65–2366, P21/c(14)) has come into being. The

XRD results demonstrate that there are no impurities existing in powders.

Laser particle analysis shows that particle size distribution ranging from 10 to 70 μm is the dominating size characteristic, and a few particle sizes are less than 100 nm (see Fig. 3).

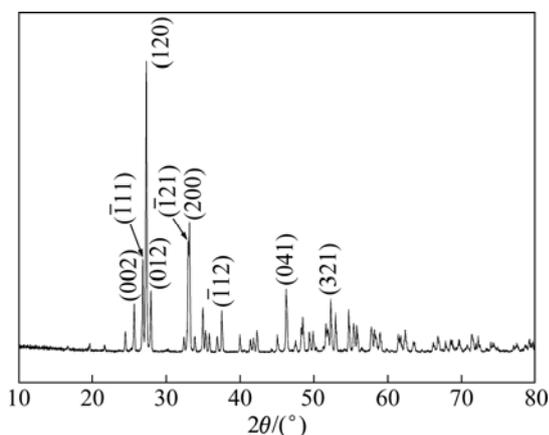


Fig. 2 XRD pattern of as-synthesized Bi_2O_3

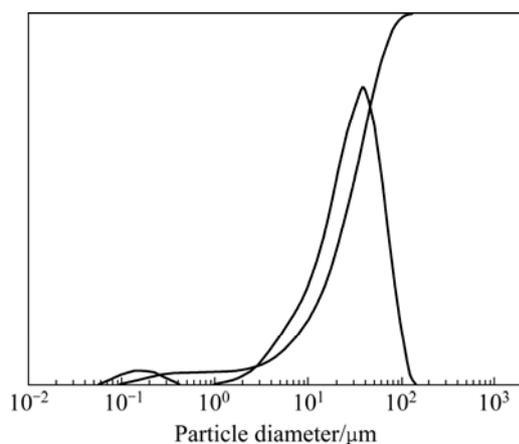


Fig. 3 Laser particle size distribution analysis of as-synthesized Bi_2O_3

To understand the structure of as-synthesized α - Bi_2O_3 and oxidation mechanism of Bi particles better, the TEM images of Bi particles, SEM and HRTEM images of α - Bi_2O_3 powders are shown in Fig. 4.

Figure 4(a) shows that raw materials of Bi powders are nano-particles with regular shape. Melting bismuth will become spherical at a high temperature due to surface tension. The shape of α - Bi_2O_3 would be spherical if oxidation process in-situ could occur. However, the SEM image of α - Bi_2O_3 powders shows that the shape is irregular (see Fig. 4(b)). Particles reunite each other, and some small narrow particles cohere to large size α - Bi_2O_3 powders. Results propose further that oxidation of bismuth involves two types of processes namely vapor-phase and liquid-phase. The latter dominates the whole process while the former controls the shape of

cohered α - Bi_2O_3 powders.

Figure 4(c) shows a HRTEM image with inset of FFT from a α - Bi_2O_3 particle. This image clearly displays that the lattice fringes of as-synthesized α - Bi_2O_3 have no defect appearance. The observed HRTEM image shows a lattice spacing of 0.268 nm and 0.325 nm, corresponding to that of (200) plane and (120) of α - Bi_2O_3 . The FFT image of HRTEM shows a set of diffraction pots with typical monoclinic structure. The result further confirms that the powders are α - Bi_2O_3 crystalline.

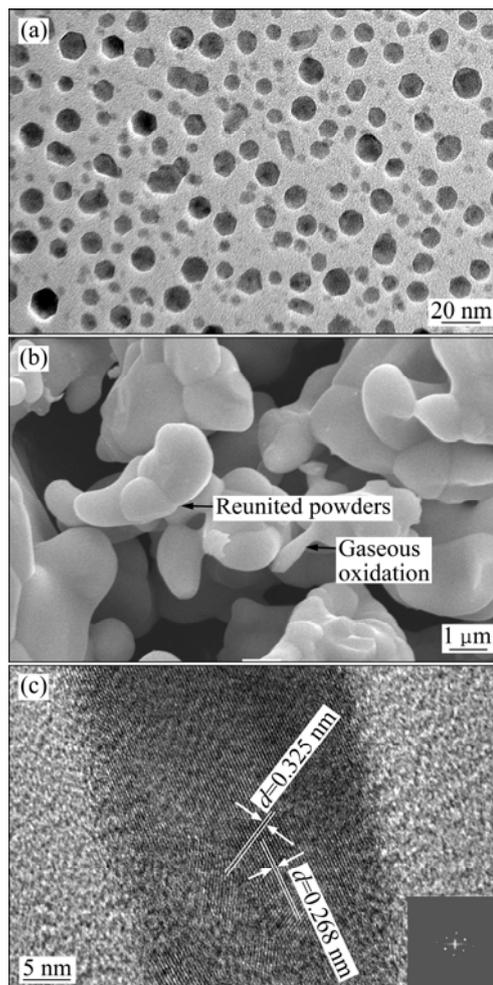


Fig. 4 TEM image of Bi powders (a), SEM image (b) and HRTEM image (c) of as-synthesized α - Bi_2O_3 (Inset of (c) is FFT image of HRTEM)

3.3 Kinetics of bismuth oxidation at low temperature

The process was dominated by liquid-phase oxidation. The mechanism of bismuth oxidation is demonstrated in Fig. 5, and the formation of α - Bi_2O_3 at a low temperature can be divided into four steps.

1) Solid bismuth powders fuse to form bismuth beads, and bismuth beads reunite each other. Oxygen molecules in air flow diffuse into gas film which covers the surface of bismuth beads. After passing through the gas film, the oxygen molecules absorb on the surface of bismuth beads.

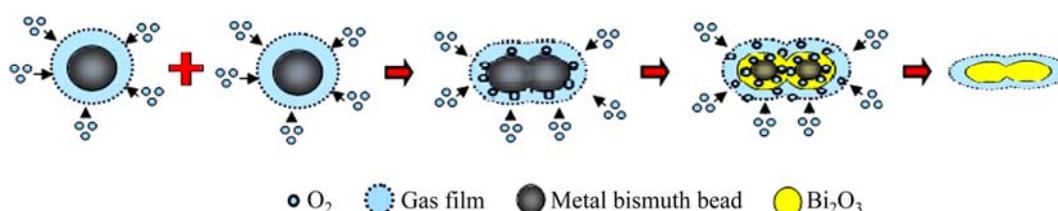


Fig. 5 Schematic representation of oxidation mechanism of bismuth powders

2) Oxygen molecules absorbing on the bismuth beads crack into O atoms, and then react with bismuth to form Bi₂O₃, which covers the un-reacted bismuth core to form solid-state layer.

3) Oxygen molecules continue diffusing through the gas film and solid Bi₂O₃ layer in turn, and react with liquid bismuth beads. Consequently, the volume of un-reacted bismuth core shrinks continuously.

4) Oxidation reaction of bismuth powders is finished, and the bismuth beads convert into solid Bi₂O₃ completely.

Since the whole process mentioned above is similar to the chemical reaction between compact solid particle and gas, the un-reacted shrinking core model can be used to describe the formation of Bi₂O₃. The reaction controlling steps during formation of Bi₂O₃ at a low temperature are as follows.

1) If the reaction rate is controlled by O₂ diffusion in the gas film, the kinetic equation is $\alpha=kt$.

2) If the reaction rate is controlled by O₂ diffusion in the Bi₂O₃ layer, the kinetic equation can be presented as $1-3(1-\alpha)^{2/3}+2(1-\alpha)=kt$.

3) If the reaction rate is controlled by chemical reaction, the kinetic equation is $1-(1-\alpha)^{1/3}=kt$.

4) If the reaction rate is the mixture controlling of chemical reaction and solid phase diffusion, the kinetic equation can be presented as $t=[1-3(1-\alpha)^{2/3}+2(1-\alpha)]/k_2+[1-(1-\alpha)^{1/3}]/k_3$.

The linear fitting of oxidation curve of bismuth powder at different temperatures is presented in Fig. 6 and Fig. 7. In the temperature range of 450–600 °C, a linear relationship between $1-(1-\alpha)^{1/3}$ and reaction time (t) is obtained within 0–10 min (see Fig. 6). After 10 min, a plot of $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ versus reaction time (t) shows another perfect linear relationship (see Fig. 7). It indicates that the bismuth oxidation follows shrinking core model, and its controlling mechanism is variable at different reaction time. Within 0–10 min, the kinetics is controlled by the chemical reaction, and then with the oxidation reaction proceeding, it is controlled by O₂ diffusion in the solid Bi₂O₃ layer.

However, the oxidation mechanism does not correspond to the above kinetics equation when the

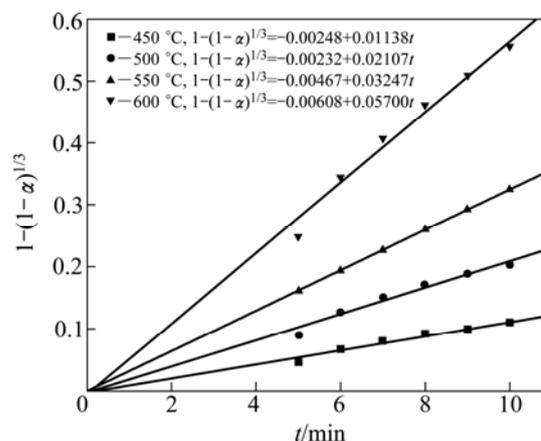


Fig. 6 Linear relationship between $1-(1-\alpha)^{1/3}$ and t within 0–10 min at different temperatures

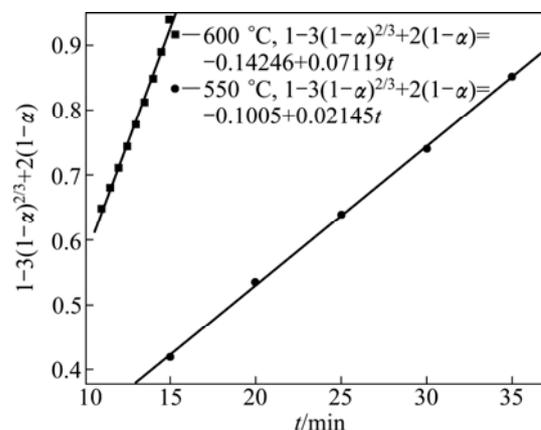
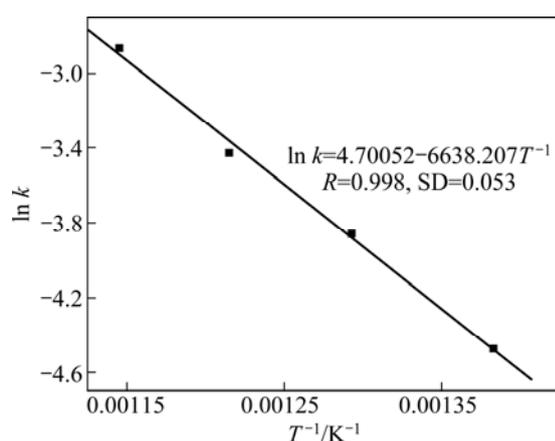


Fig. 7 Linear relationship between $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ and t at different temperatures after 10 min

oxidation process occurs at 823.15 K and 873.15 K after 10 min. These phenomena confirm that more complex kinetics mechanism exists in oxidation reaction of Bi powders at a higher temperature. The oxidation reaction rate constants of bismuth powders at different temperatures are listed in Table 2. It shows that the oxidation rate constant increases sharply with the increase of temperature during the chemical reaction controlling period. As shown in Fig. 8, a plot of the $\ln k$ versus T^{-1} displays a perfect linear relationship, and the apparent activation energy is determined to be 55.19 kJ/mol according to Arrhenius equation.

Table 2 Oxidation reaction rate constants of bismuth powders at different temperatures

T/K	$T^{-1}/10^{-3}K^{-1}$	Chemical reaction control		Internal diffusion control	
		Rate constant (k)/ 10^{-2}	$\ln k$	Rate constant (k)/ 10^{-2}	$\ln k$
723.15	1.383	1.138	-4.4759	—	—
773.15	1.293	2.107	-3.85991	—	—
823.15	1.215	3.247	-3.42744	2.145	-3.84203
873.15	1.145	5.700	-2.8647	7.119	-2.6424

**Fig. 8** Linear relationship between $\ln k$ and T^{-1}

4 Conclusions

1) α - Bi_2O_3 powders were prepared from nano Bi powders through low-temperature oxidation at less than 873.15 K. The conversion of Bi is 100% after oxidation at 823.15 K for 40 min. Microstructural results of Bi_2O_3 powders show that bismuth beads should be reunited and oxidized to become irregular Bi_2O_3 powders. Oxidation of bismuth involves two types of processes, namely vapor-phase and liquid-phase. The latter dominates the whole process while the former controls the shape of cohered α - Bi_2O_3 powders.

2) Kinetic experimental results indicate that the bismuth oxidation follows the shrinking core model, and its controlling mechanism is variable at different reaction time. Within 0–10 min, the kinetics is controlled by chemical reaction, and then with the oxidation reaction proceeding, it is controlled by O_2 diffusion in the solid Bi_2O_3 layer. The oxidation rate constant increases sharply with the increase of temperature during chemical reaction controlling period, and the apparent activation energy is determined to be 55.19 kJ/mol.

3) The low-temperature oxidation process can prepare Bi_2O_3 . The contents of Bi_2O_3 and Ca, Fe, Si and Sb and other impurity elements are up to industrial standards for electronic-grade bismuth oxide.

References

[1] JIN Sheng-ming, TANG Mo-tang, YANG Wei-jun. Preparation of

catalyst for ammoxidation of propylene in chlorination salts systems (II)—Catalytic activity rating of Bi containing catalyst [J]. Journal of Central South University of Technology: Natural Science, 2001, 32(4): 247–250. (in Chinese)

- [2] YANG Han-pei, FAN Yi-ning, LIN Ming, XU Bo-lian, CHEN Yi. Structure and catalytic properties of Bi–Mo composite oxide catalyst for selective oxidation of propane [J]. Chinese Journal of Catalysis, 2002, 60(6): 1006–1010. (in Chinese)
- [3] LAZAREVIĆ Z, STOJANOVIĆ B D, VARELA J A. An approach to analyzing synthesis, structure and properties of bismuth titanate ceramics [J]. Science of Sintering, 2005, 37(3): 199–216.
- [4] PAVLOVIC NIKOLINA, SRDIC VLADIMIR V. Synthesis and structural characterization of Ce-doped bismuth titanate [J]. Materials Research Bulletin, 2009, 44(4): 860–864.
- [5] LAURENT K, WANG G Y, TUSSEAU-NENEZ S, LEPRINCE-WANG Y. Structure and conductivity studies of electrodeposited δ - Bi_2O_3 [J]. Solid State Ionics: Diffusion and Reactions, 2008, 178(33): 1735–1739.
- [6] SHAO Zong-ping, XIONG Guo-xing, YANG Wei-shen. Progress in bismuth-contained mixed conducting oxide membranes [J]. Journal of Inorganic Materials, 2001, 16(1): 23–31.
- [7] SUNARSO J, LIU S, LIN Y S, da COSTA J C D. Oxygen permeation performance of BaBiO_3 - δ ceramic membranes [J]. Journal of Membrane Science, 2009, 344(1–2): 281–287.
- [8] CHEN Dan-ping, JIANG Xiong-wei, ZHU Cong-shan. Study on the structure of Bi_2O_3 - Li_2O glass [J]. Journal of Inorganic Materials, 2002, 17(2): 202–209.
- [9] YANG Jian-hu, DAI Shi-xun, WEN Lei, LIU Zhu-ping, HU Li-li, JIANG Zhong-hong. Spectroscopic properties and thermal stability of a new erbium-doped bismuth-based glass [J]. Acta Physica Sinica, 2003, 52(3): 508–514.
- [10] LEONTIE L, CARAMAN M, DELIBAS M, RUSU G I. Optical properties of bismuth trioxide thin films [J]. Materials Research Bulletin, 2001, 36(9): 1629–1637.
- [11] HASEGAWA T, NAGASHIMA T, SUGIMOTO N. Determination of nonlinear coefficient and group-velocity-dispersion of bismuth-based high nonlinear optical fiber by four-wave-mixing [J]. Optics Communications, 2008, 281(4): 782–787.
- [12] YANG Nan, SUN Hong-zhe. Biocoordination chemistry of bismuth: Recent advances [J]. Coordination Chemistry Reviews, 2007, 25(17–20): 2354–2366
- [13] JIANG Zhi-yi, ZHANG Lei, CAI Li-li, XIA Chang-rong. Bismuth oxide-coated (La,Sr) MnO_3 cathodes for intermediate temperature solid oxide fuel cells with yttria-stabilized zirconia electrolytes [J]. Electrochimica Acta, 2009, 54(11): 3059–3065.
- [14] SMIRNOVA A, SARAT S, SAMMES N. Bismuth oxide doped scandia-stabilized zirconia electrolyte for the intermediate temperature solid oxide fuel cells [J]. Journal of Power Sources, 2006, 160(2): 892–896.
- [15] LIN Yu-bao, LIN Liang-zhen, XIAO Li-ye. Development of bismuth-base high temperature superconducting DC cable [J]. Physics, 2001, 30(7): 389–391.
- [16] MAKAROVA M V, KAZIN P E, TRETYAKOV YU D, JANSEN M, REISSNER M, STEINER W. Zr, Hf, Mo and W-containing oxide

- phases as pinning additives in Bi-2212 superconductor [J]. *Physica C*, 2005, 419(1): 61–69.
- [17] HU Han-xiang, QIU Ke-qiang, XU Guo-fu. Preparation of nanometer δ - and β -bismuth trioxide by vacuum vapor-phase oxidation [J]. *Transactions of Nonferrous Metals Society of China*, 2006, 16(1): 173–177.
- [18] MARTIROSYAN K S, WANG L, VICENT A, LUSS D. Synthesis and performance of bismuth trioxide nanoparticles for high energy gas generator use[J]. *Nanotechnology*, 2009, 20(40): 405–412.
- [19] KRÜGER J, WINKLER P, LU'DERITZ E, LÜCK M, WOLF H U. Bismuth, bismuth alloys, and bismuth compounds, Ullmann's encyclopedia of industrial chemistry [M]. Weinheim, Germany: Wiley-VCH Verlag GmbH, 2000.
- [20] MÄDIER L, PRATSINIS S E. Bismuth oxide nano-particles by flame spray pyrolysis [J]. *Journal of American Ceramic Society*, 2002, 85(7): 1713–1718.
- [21] JUNGK H, FELDMANN C F. Polymediated synthesis of submicrometer Bi_2O_3 particles [J]. *Journal of Material Science*, 2001, 36(1): 297–299.
- [22] HE Wei-ming, ZHEN Qiang, PAN Qing-yi, LIU Jian-qiang. Study on preparation of ultra-fine bismuth oxide powder by reversing-titration method [J]. *Journal of Functional Materials*, 2003, 34(6): 702–706. (in Chinese)
- [23] LI Wei. Preparation of monodisperse nanometer Bi_2O_3 powder[J]. *Journal of Central South University: Science and Technology*, 2005, 36(2): 175–178. (in Chinese)
- [24] ZHENG Bo, REN Zhi-gang, TONG Jian-ying, GU Jian-sheng. Preparation of ultrafine bismuth oxide by electrochemical method [J]. *Chemical Research and Application*, 2004, 16(3): 411–412.
- [25] ZHENG Bo, PANG Ai-hong, GU Jian-sheng. Synthesis of ultrafine γ - Bi_2O_3 powder at low temperature [J]. *Chemical Journal of Chinese Universities*, 2005, 26(4): 628–630.
- [26] HONG Wei-liang, ZHAO Feng-qi, LIU Jian-hong, TIAN De-yu. Synthesis of nanometer PbO , Bi_2O_3 and their effect on burning properties of solid propellants [J]. *Chinese Journal of Explosives & Propellants*, 2001, 24(3): 7–9. (in Chinese)
- [27] ENDEBROCK R W, ENGLE P M. Separation of polonium from bismuth by distillation[R]. AECD-4146, 1953–08–01.

铋粉低温氧化制备 α - Bi_2O_3

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摘要: 纳米金属铋粉在低于 873.15 K 的温度下被氧化而制备成 α - Bi_2O_3 粉体, 采用 XRD、SEM、TEM 和 HRTEM 等技术表征 α - Bi_2O_3 粉体的晶体结构和形貌, 通过 TGA 技术研究铋粉的低温氧化动力学行为。结果表明, 纳米铋粉在较低的温度下熔融成铋珠, 铋珠结合长大并氧化生成不规则的 Bi_2O_3 粉体, 铋珠氧化机理符合核收缩模型; 动力学控制步骤随着氧化时间的变化而变化, 在 0~10 min 内, 铋珠氧化动力学表现为化学反应控制, 然后转化为 O_2 内扩散控制, 低温氧化表观反应活化能为 55.19 kJ/mol。

关键词: 铋粉; 低温氧化; α - Bi_2O_3 ; 氧化动力学

(Edited by LI Xiang-qun)