Preparation of $\alpha$-Bi$_2$O$_3$ from bismuth powders through low-temperature oxidation

XIA Ji-yong$^1$, TANG Mo-tang$^1$, CHEN Cui$^1$, JIN Sheng-ming$^2$, CHEN Yong-ming$^1$

1. School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China;
2. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 23 September 2011; accepted 5 January 2012

Abstract: $\alpha$-Bi$_2$O$_3$ 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 Bi$_2$O$_3$ 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 Bi$_2$O$_3$ 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 O$_2$ diffusion in the solid $\alpha$-Bi$_2$O$_3$ layer. The apparent activation energy is determined as 55.19 kJ/mol in liquid-phase oxidation.

Key words: bismuth powder; low-temperature oxidation; $\alpha$-Bi$_2$O$_3$; oxidation kinetics

1 Introduction

Bi$_2$O$_3$ 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 Bi$_2$O$_3$ powders. High-temperature oxidation of bismuth metal is also dividable into vapor-oxidation and spray-oxidation. Beta-and alpha-phase Bi$_2$O$_3$ 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 Bi$_2$O$_3$ through spray-oxidation due to short retention time in air and kinetics limit at 1073 K [19]. Bi$_2$O$_3$ particles with hollow and well-defined morphology could be synthesized through spray-pyrolysis process with change of pyrolysis temperature using Bi(NO$_3$)$_3$·5H$_2$O 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$_x$O$_y$ gas.

Preparation of Bi$_2$O$_3$ 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 Bi$_2$O$_3$ powders obtained from this method. The studies are a useful guideline on preparing Bi$_2$O$_3$ powders at less than 873.15 K, understanding the oxidation mechanism of bismuth and increasing the yield of Bi$_2$O$_3$ 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).

\[ \alpha = \frac{2 \times 208.9804 \times \Delta m}{3 \times 15.9994 \times m} = 8.7075 \times \frac{\Delta m}{m} \]  

where \( \alpha \) denotes the fraction of oxidized bismuth, \( m \) is the initial mass of bismuth powders, and \( \Delta m \) 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>
<thead>
<tr>
<th>Sample</th>
<th>( w(\text{Ag})/% )</th>
<th>( w(\text{Cu})/% )</th>
<th>( w(\text{Pb})/% )</th>
<th>( w(\text{Sb})/% )</th>
<th>( w(\text{Fe})/% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>0.0008</td>
<td>0.0008</td>
<td>0.0007</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>(( w(\text{Bi}) \geq 99.99% ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-synthesized Bi₂O₃</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.0006</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>(( w(\text{Bi₂O₃}) \geq 99.92% ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The X-ray diffraction (XRD) of the sample was recorded on a D/max 2550 (Rigaku, Japan) with Cu Kα radiation (\( \lambda = 0.1548 \) nm) from 10°~80°(2θ) 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:

\[ 2\text{Bi}(s) + 1.5\text{O}_2(g) = \text{Bi}_2\text{O}_3(s) \quad (298–544 \text{ K}) \]  

\[ \Delta G^0 = -574887 + 99.71 T \]  

\[ 2\text{Bi}(l) + 1.5\text{O}_2(g) = \text{Bi}_2\text{O}_3(s) \quad (544–1090 \text{ K}) \]  

\[ \Delta G^0 = -589730 + 292.4 T \]  

\[ 2\text{Bi}(l) + 1.5\text{O}_2(g) = \text{Bi}_2\text{O}_3(l) \quad (1090–1600 \text{ K}) \]  

\[ \Delta G^0 = -535418 + 243.7 T \]  

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]:

\[ \lg p = -10051/T + 8.462 \]  

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.

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 (121), 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$_2$O$_3$](image)

![Fig. 3 Laser particle size distribution analysis of as-synthesized Bi$_2$O$_3$](image)

To understand the structure of as-synthesized α-Bi$_2$O$_3$ and oxidation mechanism of Bi particles better, the TEM images of Bi particles, SEM and HRTEM images of α-Bi$_2$O$_3$ 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$_2$O$_3$ would be spherical if oxidation process in-situ could occur. However, the SEM image of α-Bi$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ powders.

Figure 4(c) shows a HRTEM image with inset of FFT from a α-Bi$_2$O$_3$ particle. This image clearly displays that the lattice fringes of as-synthesized α-Bi$_2$O$_3$ 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$_2$O$_3$. 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$_2$O$_3$ crystalline.

![Fig. 4 TEM image of Bi powders (a), SEM image (b) and HRTEM image (c) of as-synthesized α-Bi$_2$O$_3$ (Inset of (c) is FFT image of HRTEM)](image)

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$_2$O$_3$ 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.
2) Oxygen molecules absorbing on the bismuth beads crack into O atoms, and then react with bismuth to form Bi$_2$O$_3$, which covers the un-reacted bismuth core to form solid-state layer.

3) Oxygen molecules continue diffusing through the gas film and solid Bi$_2$O$_3$ 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 Bi$_2$O$_3$ 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 Bi$_2$O$_3$. The reaction controlling steps during formation of Bi$_2$O$_3$ at a low temperature are as follows.

1) If the reaction rate is controlled by O$_2$ diffusion in the gas film, the kinetic equation is $\alpha=kt$.

2) If the reaction rate is controlled by O$_2$ diffusion in the Bi$_2$O$_3$ 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 O$_2$ diffusion in the solid Bi$_2$O$_3$ layer.

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

<table>
<thead>
<tr>
<th>T/K</th>
<th>T⁻¹/10¹³K⁻¹</th>
<th>Chemical reaction control</th>
<th>Internal diffusion control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rate constant (k) x 10⁻²</td>
<td>lnk</td>
</tr>
<tr>
<td>723.15</td>
<td>1.383</td>
<td>1.138</td>
<td>-4.4754</td>
</tr>
<tr>
<td>773.15</td>
<td>1.293</td>
<td>2.107</td>
<td>-3.85991</td>
</tr>
<tr>
<td>873.15</td>
<td>1.145</td>
<td>5.700</td>
<td>-2.8647</td>
</tr>
</tbody>
</table>

Fig. 8 Linear relationship between lnk and T⁻¹

4 Conclusions

1) α-Bi₂O₃ 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 Bi₂O₃ powders show that bismuth beads should be reunited and oxidized to become irregular Bi₂O₃ 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-Bi₂O₃ 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 O₂ diffusion in the solid Bi₂O₃ 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 Bi₂O₃. The contents of Bi₂O₃ and Ca, Fe, Si and Sb and other impurity elements are up to industrial standards for electronic-grade bismuth oxide.

References

[16] MAKAROVA M V, KAZIN P E, TRETYYAKOV YU D, JANSEN M, REISSNER M, STEINER W. Zr, Hf, Mo and W-containing oxide
铋粉低温氧化制备 $\alpha$-Bi$_2$O$_3$

夏纪勇$^1$, 唐谟堂$^1$, 陈萃$^1$, 金胜明$^2$, 陈永明$^1$

1. 中南大学 冶金科学与工程学院, 长沙 410083；
2. 中南大学 资源加工与生物工程学院, 长沙 410083

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 $\alpha$-Bi$_2$O$_3$ 粉体, 采用 XRD、SEM、TEM 和 HRTEM 等技术表征 $\alpha$-Bi$_2$O$_3$ 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$_2$O$_3$ 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; $\alpha$-Bi$_2$O$_3$; 氧化动力学

Edited by LI Xiang-qun