

THERMOCHEMISTRY AND MECHANISM ON THE PROCESS OF PREPARING POWDER OF Bi_2O_3 USING MELT-ATOMIZING-COMBUSTION METHOD^①

Zhou Naijun, Yin Zhimin[†], Chen Shizhu[†]

Department of Applied Physics & Thermoenergy Engineering,

† Department of Materials Science and Engineering,

Central South University of Technology, Changsha 410083

ABSTRACT Based on the experimental results concerning preparing nanometer powder of pure Bi_2O_3 using the melt atomizing combustion method, the thermochemistry and reaction mechanism of the process of melt atomizing combustion were studied. The results showed that, first, the specific heat capacity of gaseous Bi_2O_3 at temperature higher than 1 097 K is $105.324 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and its latent heat of evaporation at 2 163 K is $276.896 \text{ kJ} \cdot \text{mol}^{-1}$; second, the cause for obtaining small powder size and high powder purity is that the processes of preparing powder could proceed upon a model as “atomization—vaporization—combustion—coacervation”, finally, reasonable process parameters of preparing powder of pure Bi_2O_3 should be melt temperature 900~1 000 °C, mole ratio of excess oxygen 2~2.5, and cooling intensity of reactor 80~100 kW.

Key words bismuth trioxide nanometer powder atomizing combustion thermochemistry

1 INTRODUCTION

A new method called as melt-atomizing-combustion of preparing metal oxide powder has been invented^[1]. Compared with traditional methods of Bi_2O_3 preparation, the new method has a lot of advantages, for example, its technological process is simpler, and the cost is lower, the productive efficiency is higher, the particle size of powder is finer and the purity is purer, especially the whole process is no pollution^[2]. In this paper, based on the experiments obtaining successfully pure bismuth trioxide (Bi_2O_3) nanometer powder by this method, the authors will analyze thermochemical characterization and reaction mechanism on the process of melt atomizing combustion, and conduct the optimal process parameters.

2 EXPERIMENT AND RESULTS

In the experiment, refined bismuth heated

to melting and overheated to a given temperature was flowed into the reactor through the leak pipe of a leak vessel, and was sprayed into fine melt droplets by atomizing gas (industry oxygen with high pressure). While the reaction conditions being satisfied, the melt droplets would be oxidized strongly to burning, and then formed into Bi_2O_3 . The reaction products (Bi_2O_3) went through cooling—gathering—filtering—drying, then Bi_2O_3 powder was gotten.

Main control parameters in the experiment are that the quantity of refined bismuth which is put into the reactor at one time, G_1 , with 2.5 kg; the overheated temperature of melt, T_{01} , at about 1 200 K; the pressure of atomizing medium, P_0 , with 0.8 MPa (absolute pressure); and the total reaction time, τ , in about 45 s. The Bi_2O_3 product gained finally is yellow spherical or similar spherical shaped powder, the range of its particle size is 20~200 nm, and its phase structure is $\alpha - \text{Bi}_2\text{O}_3$ with pseudoorthorhombic form^[2].

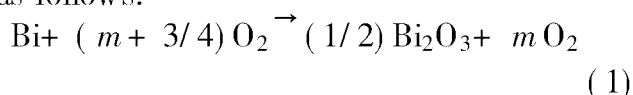
① Supported by the Natural Science Foundation of Hunan Province

Received Jun. 14, 1996; accepted Oct. 16, 1996

The experimental results show that in order to enable the melt to be atomized very well and to react sufficiently, the overheated temperature of melt, the pressure and flow rate of atomizing medium should be selected and controlled very well. Higher overheated temperature of melt and smaller flux of oxygen could increase reaction intensity, increase reaction temperature and lead to damaging of nozzle. However, lower overheated temperature and bigger flux would not enable the reaction to fulfill sufficiently. Therefore, in order to give appropriate process parameters, it is necessary to make analysis on thermochemistry and reaction mechanism of the melt atomizing combustion process.

3 THERMOCHEMISTRY OF THE REACTION PROCESS

Provided the reaction equation can be written as follows:



here m is quantity of excess oxygen corresponding to 1 mole of bismuth in the reaction (i. e. a ratio of excess oxygen).

In this section, in order to approach further on reaction mechanism and to select the process parameters, we will deduce out the relationship between the reaction temperature and the ratio of excess oxygen.

While, in order to simplify the expression, units in all of equations will be omitted. The SI unit will be adopted, i. e. the unit of enthalpy H or heat Q is $\text{J} \cdot \text{mol}^{-1}$, specific heat capacity C_p , $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, temperature T , K , pressure P , kPa . It is necessary to point out specially that the data given in various references are some different, and the data adopted in present paper are taken from reference [3] and [4].

3.1 Basic data and equations of enthalpy

From reference [3] we can get the data about specific heat capacity and latent heat of Bi, O_2 and Bi_2O_3 . With retreating and calculating the data given in the reference, we can get the equations of enthalpy of these substances: en-

thalpy of oxygen in the range of 298.15 K to 3000 K:

$$H_{\text{O}_2}(T) = -9679 + 29.957T + 2.092 \times 10^{-3}T^2 + 1.674 \times 10^5T^{-1} \quad (2)$$

Enthalpy of bismuth within 298.15~544 K:

$$H_{\text{Bi}}(T) = -3510 + 11.849T + 15.234 \times 10^{-3}T^2 - 4.105 \times 10^5T^{-1} \quad (3)$$

within 544~1200 K:

$$H_{\text{Bi}}(T) = 10137 + 19.016T + 5.186 \times 10^{-3}T^2 - 20.740 \times 10^5T^{-1} - 1.326 \times 10^{-6}T^3 \quad (4)$$

Moreover, the melting point of bismuth is 544 K, the boiling point is 1835 K; and the latent heat of fusion at melting point, ΔH_{Bi} , is 11300 $\text{J} \cdot \text{mol}^{-1}$. The melting point of Bi_2O_3 is 1097 K, the boiling point is 2163 K, the enthalpy of formation at standard state (298.15 K) is $\Delta H^0 = -570700 \text{ J} \cdot \text{mol}^{-1}$; and the specific heat capacity at liquid (within 1097~1800 K), C_{pl} , is 152.716 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Therefore, the enthalpy of Bi_2O_3 liquid within 1097~1800 K is

$$H_{\text{Bi}_2\text{O}_3}(T) = 51531 + 152.716T \quad (5)$$

However, while temperature is over 1800 K, there are no available data up to date. In order to obtain the enthalpy equation to be able to applied beyond 1800 K, we will adopt following method to deduce the specific heat capacity of gaseous Bi_2O_3 and its latent heat of evaporation.

3.2 The specific heat capacity of gaseous Bi_2O_3 and its latent heat of evaporation

A saturated vapor pressure equation of Bi_2O_3 within 1098~1835 K was already given by reference [4]:

$$\log(P) = -19818T^{-1} - 5.70\log T + 26.805 \quad (6)$$

Having taken derivative of equation (6) with respect to T and reorganized, we can get

$$dP/dT = (45633 - 5.70T)/T^2 \times P \quad (7)$$

On the other hand, assuming Bi_2O_3 gas to be a perfect gas, according to Claperon-Clausius

equation, there is the following result:

$$dP/dT = (\Delta H / RT^2) \cdot P \quad (8)$$

here, ΔH is the latent heat of evaporation at temperature T . Compared equation (7) with (8), we have

$$\begin{aligned} \Delta H &= R \cdot (45\,633 - 5.70\,T) \\ &= 8.3143 \times (45\,633 - 5.70\,T) \\ &= 379\,403 - 47.392\,T \end{aligned} \quad (9)$$

We suppose that equation (9) could be applied till boiling point of Bi₂O₃ (2163 K)^①. Then it can be calculated out from equation (9) that the latent heat of evaporation of Bi₂O₃ at 2163 K is $\Delta H_b = 276\,896\,\text{J} \cdot \text{mol}^{-1}$.

Provided Bi₂O₃ melt has been reaching two phase equilibrium at two various temperatures, T_1 or T_2 , respectively, when there is no difference in phase structure at the same physical state while temperature is changed, then when the molecules of Bi₂O₃ have converted from liquid at temperature T_1 to gas at temperature T_2 along two various routes illustrated as Fig. 1, their enthalpy values should be satisfied with

$$\Delta H_1 + \Delta H_g = \Delta H_1 + \Delta H_2 \quad (10)$$

i. e.

$$\begin{aligned} &(379\,403 - 47.392\,T_1) + \int_{T_1}^{T_2} C_{pg} dT \\ &= \int_{T_1}^{T_2} C_{pl} dT + (379\,403 - 47.392\,T_2) \end{aligned} \quad (11)$$

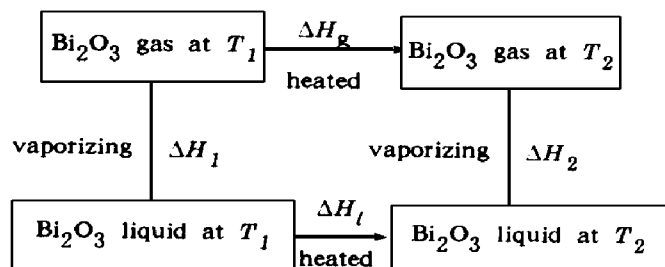


Fig. 1 A scheme that liquid converted into gas

In this equation, the specific heat capacity of liquid Bi₂O₃, $C_{pl} = 152.324\,\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, may be thought as a constant not to vary with temperature. Owing to T_1 and T_2 being two temperatures given arbitrarily, it can be got

from the equation (11) that the specific heat capacity of gaseous Bi₂O₃ is $C_{pg} = 105.324\,\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Such as that mentioned above, we suppose that the results can be applied till or above the boiling point of Bi₂O₃^②. Then we can write as follow: within 1097~2163 K:

$$H_{\text{Bi}_2\text{O}_3}(T) = 51\,531 + 152.716\,T \quad (12)$$

when $T > 2163\,\text{K}$:

$$H_{\text{Bi}_2\text{O}_3}(T) = 430\,935 + 105.324\,T \quad (13)$$

3.3 Theoretical reaction temperature and mixing temperature of reactants

If without consideration of heat losses, according to energy conservation equation we have

$$\begin{aligned} H_{\text{Bi}}(T_{01}) + (m + 3/4)H_{\text{O}_2}(T_{02}) - \\ (1/2)\Delta H^0 = (1/2)H_{\text{Bi}_2\text{O}_3}(T_m) + \\ mH_{\text{O}_2}(T_m) \end{aligned} \quad (14)$$

Here, T_{01} and T_{02} are initial temperatures of the melt and oxygen entering the reactor, respectively. Applied the enthalpy values of various substances obtained above, the theoretical reaction temperature (i. e. the highest temperature reached possibly during the melt atomizing combustion), T_m , can be found out from equation (14), and the results are shown in Table 1 for various m values (In the Table 1, we has taken $T_{01} = 1200\,\text{K}$, $T_{02} = 298.15\,\text{K}$).

Similarly, the mixing temperature of reactants, T_h , will be able to be found out from equation (15) for various m values, and the results are also shown in Table 1.

$$\begin{aligned} H_{\text{Bi}}(T_{01}) + (m + 3/4)H_{\text{O}_2}(T_{02}) \\ = H_{\text{Bi}}(T_h) + (m + 3/4)H_{\text{O}_2}(T_h) \end{aligned} \quad (15)$$

3.4 Heat of reaction

Provided products of reaction will be cooled to 298.15 K, according to heat equilibrium of reaction, we have

$$\begin{aligned} Q = G_1 \times (1/209) \times H_{\text{Bi}}(T_{01}) + \\ G_2 \times (1/32) \times H_{\text{O}_2}(T_{02}) - \\ (1/2) \times G_1 \times (1/209) \times \Delta H^0 \end{aligned} \quad (16)$$

Replacing the experimental data and the en-

① According to examination what the author did using Bi, H₂O, Bi₂O₃ etc., this supposition is acceptable.

thalpies into this equation (here, the second item at right side will be zero), we can calculate out that the heat of reaction, Q , is 3 848 kJ, then the intensity of heat of reaction is $3848\text{kJ}/45\text{s}=85.5\text{kW}$, which will be related to the cooling intensity of the reactor.

Table 1 Relationship of the ratio of excess oxygen with theoretical temperature and mixed temperature of reactants

m	T_m	n	T_h	$1 - n^0$
0.00	2163	0.945	768	1.000
0.50	2163	0.710	670	1.000
1.00	2163	0.476	604	1.000
1.50	2163	0.241	558	1.000
1.69	2163	0.096	544	1.000
2.00	2163	0.006	544	0.793
2.013	2163	0.000	544	0.784
2.205	2086	0.0	544	0.656
2.50	1980	0.0	544	0.456
3.00	1828	0.0	544	0.117
3.188	1770	0.0	544	0.000
5.00	1426	0.0	479	0.0
8.20	1098	0.0	420	0.0

(n is a rate of gasified Bi_2O_3 , n^0 is a rate of condensed Bi)

4 MECHANISM OF REACTION AND OPTIMAL PROCESS PARAMETERS

In the process of powder preparing, oxygen entering into the reactor is not only atomizing medium but also oxidant. In order to enable reaction to fulfill sufficiently, oxygen must be excessive. And in order to ensure efficiency of atomizing, the velocity at outlet of nozzle should be high enough. However, the outlet velocity of atomizing medium will be confined by the pressure at the outlet of nozzle. For a convergent nozzle, when the area of outlet is fixed, the outlet velocity will increase with increasing of the pressure at the inlet of nozzle, but the highest outlet velocity will not beyond local velocity of sound^[5], therefore, for a given nozzle, the flow rate of oxygen will exist a maximum, i. e. m value will exist a maximum. For the nozzle adopted by the authors in the experiment, the

maximum of m is 2.205 via calculating and analyzing. Under the conditions of experiment, m already reaches actually this maximum.

When $m = 2.205$, it can be seen from Table 1 that, if oxygen could mix sufficiently with melt, the mixing temperature of reactants would be at melting point of Bismuth by chance, and there would be liquid bismuth about 34.4 percent to be condensed into solid. However, the mixing could not be sufficient in the experiment, and actually, the atomizing, mixing and combustion could proceed simultaneously in the powder preparing process. Only if the reaction occurs, the heat produced by oxidizing reaction would heat the melt and oxygen, so the temperature of the melt droplets could be higher than the melting point of bismuth (544 K), the condensation would not occur in fact. Therefore, it is sure that the melt droplets are at liquid state during the reaction.

On the other hand, it can be seen from Table 1 that, with increasing of m value, the theoretical reaction temperature drops, and the rate of gasified Bi_2O_3 reduces. The m value (2.205) under the experimental conditions is greater than m value (2.013) which enable produced Bi_2O_3 not to gasify, but is far less than m value (8.2) which enable produced Bi_2O_3 not to condense into solid. Actually, the reaction temperature corresponding to $m = 2.205$, T_m , is 2086 K, and it is little lower than the boiling point of Bi_2O_3 (2163 K) but far higher than melting point of Bi_2O_3 (1097 K). Therefore, even if considering the heat losses, the actual reaction temperature would be greater than 1097 K. From this, it is sure that the product of reaction would be liquid Bi_2O_3 before cooled by the following cooling process.

The theoretical reaction temperature, $T_m = 2086\text{K}$, already is higher than the boiling point of bismuth (1835 K). For a melt droplet at the front of flame, its temperature will be far higher than the melting point of bismuth (544 K). In the experiment, owing to the temperature of flame being approximately equal to T_m , the temperature around the melt droplet (i. e. the temperature of flame front) would be higher than

the boiling point of bismuth (1 835 K). Therefore, for a melt droplet of Bismuth which is proceeding oxidized reaction, there would be an evaporation process at its surface, and the actual reaction would be that molecules of O_2 combine with gaseous molecules of bismuth and form gaseous molecules of Bi_2O_3 . However, from above analysis, it is known that the heat produced by reaction would not be enough to maintain Bi_2O_3 molecules being gas. Therefore, the Bi_2O_3 molecules would be cooled instantly by atmosphere and coacervate into liquid droplets of Bi_2O_3 . Finally, the liquid droplets are condensed into solid powders by cooler. Fig. 2 illustrates these processes.

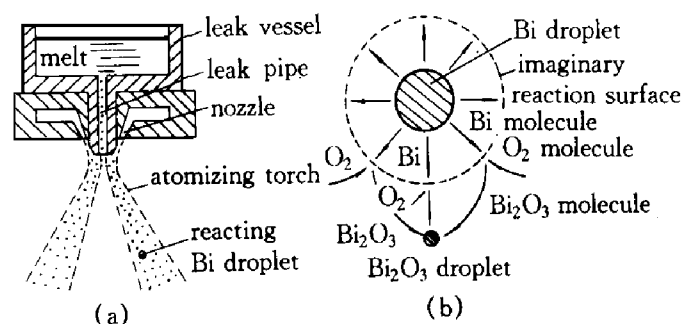


Fig. 2 A scheme on the processes of atomizing and burning

- (a) —the atomizing process of the melt;
 (b) —the process with evaporating,
 reacting and coacervating

Since the final powders of Bi_2O_3 are formed from liquid droplets which gaseous Bi_2O_3 molecules are coacervated into, their particle size could be far less than that of the melt droplets formed by atomizing, and with order of nanometer. It also indicated that, each particle of Bi_2O_3 would not contain impurity such as metal bismuth. On the other hand, during the melt atomizing combustion, impurities such as K, Na in refined bismuth would be turned into corresponding oxides resolved easily into water, but Bi_2O_3 is not resolvable, therefore they would be taken out easily. So the contents of impurity in the Bi_2O_3 product could be lower than that of refined bismuth. This is the reason that the Bi_2O_3 powder produced by this method has finer diam-

eter and higher purity.

As mentioned above, in the process of preparing pure nanometer powder of metal oxide, appropriate process conditions should be that oxygen must be excessive and the outlet velocity must be high enough so as to ensure high atomizing efficiency and enable the melt to mix with oxygen sufficiently. But the quantity of excess oxygen can not be too great, otherwise, it could lead that the mixing temperature is over low, and the reaction could not fulfill sufficiently. Actually, when the mixing temperature is lower than the burning point of bismuth, the burning will not occur. However, the quantity of excess oxygen is not sole affecting factor. The overheated temperature of melt also is one of the important factors affecting the melt atomizing combustion process. In addition, the flow rate of the melt, the method and intensity of cooling applied to process of preparing powder would also lead some effects. Therefore, all of them should be selected or controlled very well. The present research shows that the reasonable range of process parameters should be that the ratio of excess oxygen is within 2~ 2.5, the overheated (or preheated) temperature of the melt is within 900~ 1 000 $^{\circ}\text{C}$, and the intensity of cooling is within 80~ 100 kW. To reach these conditions, the process of preparing powder would proceed upon a model as “atomizing—vaporization—combustion—coacervation”, and pure Bi_2O_3 nanometer powder would be prepared.

REFERENCE

- 1 Yin Zhimin, Chen Shizhu *et al.* CN92107155. 8. 1994.
- 2 Yin Zhimin, Chen Shizhu, *et al.* The Chinese Journal of Nonferrous Metals, (in Chinese), 1994, 4(4): 62.
- 3 Liang Yingjiao *et al.* Handbook on Thermodynamic Properties of Inorganic Substances. Shenyang: NEUT Press, 1993: 79– 81, 281.
- 4 Knacke O, Kubaschewski O, Hesselmann K. Thermochemical Properties of Inorganic Substances. Second Edition. Springer-Verlag, Berlin, Heidelberg, New York: 1991: 252, 147, 236, 810.
- 5 Mei Chi. Principle of Transport Processes in Metallurgy. Changsha: CSUT Press, 1987: 110– 113.

(Edited by Zhu Zhongguo)