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Abstract

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A Manganothermic Method for Obtaining the Intermetallic Compound Manganese–Bismuth

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Many intermetallic compounds based on manganese possess valuable semiconductor and ferromagnetic properties, especially in the highly dispersed state. In this respect, the intermetallic compound MnBi deserves attention ([1]). The known methods for obtaining this compound are based on the fusion of bismuth and manganese at high temperature in an inert atmosphere in a rotating furnace, or on the sintering of a pressed mixture of powders of these metals in an inert medium ([2], [3]). Recently, a method has also been published for obtaining the indicated compound based on mixing mercury amalgams of bismuth and manganese, followed by distillation of the mercury from the intermetallic compound formed under these conditions ([4]).

All these methods are cumbersome and require complex equipment. In addition, the formation of the indicated intermetallic compound does not proceed to completion, regardless of the initial ratio between the components. As for the method employing mercury amalgams, it requires additional measures to ensure production safety. In connection with this, we proposed an electrolytic method for obtaining the intermetallic compound manganese–bismuth, which is described in detail in work ([5]).

In this communication we present the results of a study of the process of formation of the intermetallic compound manganese–bismuth during the metallothermic reduction of bismuth oxide by highly dispersed metallic manganese powder. In this process, powders of bismuth oxide and metallic manganese, after thorough mixing and sieving, are heated in an inert atmosphere until the reaction begins:

$$\mathrm{Bi_2O_3} + 5\mathrm{Mn} = 2\mathrm{MnBi} + 3\mathrm{MnO} + 134 \text{ kcal.}$$

In the present case, a typical metallothermic process takes place. By analogy with the aluminothermic method, this method may be called manganothermic.

However, the manganothermic method has its own special features, which are mainly determined by the chemical nature of manganese, its ability to form a whole series of oxides with sharply different thermal effects. Thus, for example, the amount of heat released upon the addition of 1 gram-atom of oxygen to manganese is, in the case of formation of MnO, 184 kcal; Mn_3O_4, 165.7 kcal; Mn_2O_3, 154 kcal; and MnO_2, 124 kcal. This property of manganese must be taken into account in establishing the optimal conditions for the reduction of bismuth oxide by highly dispersed metallic manganese.

This method for obtaining the intermetallic compound manganese—bismuth has been applied by us for the first time. The literature contains no indications whatever on the characteristics of the processes of reduction of metal oxides by highly dispersed metallic manganese.

However, the results of investigations on general questions of metallothermy, systematized in a number of works (^{6}-^{9}), enabled us to outline concrete ways of studying this process.

Conditions for the Reduction of Bismuth Oxide by Metallic Manganese

Preliminarily dried powders of bismuth oxide and metallic manganese, sifted through a silk sieve (200 mesh), were mixed in various weight ratios

Table 1

Component ratio in the charge, molar Bi_2O_3 : Mn	Component ratio in the charge, atomic Bi : Mn	Component ratio in the charge, by weight Bi_2O_3 : Mn	Reaction duration, sec	Temperature difference, °C	Component ratio in the charge, molar Bi_2O_3 : Mn	Component ratio in the charge, atomic Bi : Mn	Component ratio in the charge, by weight Bi_2O_3 : Mn	Reaction duration, sec	Temperature difference, °C
2 : 1	4 : 1	17 : 1	17.35	75	1 : 5	2 : 5	8.5 : 5	2.00	525
1 : 1	2 : 1	8.5 : 1	12.4	125	1 : 6	2 : 6	8.5 : 6	2.2	375
1 : 2	2 : 2	8.5 : 2	4.2	400	1 : 7	2 : 7	8.5 : 7	3.9	325
1 : 3	2 : 3	8.5 : 3	4.00	425	1 : 8	2 : 8	8.5 : 8	4.05	275
1 : 4	2 : 4	8.5 : 4	2.5	425					

(Table 1). The mixtures obtained were again sifted through a silk sieve for the most uniform distribution of the charge components and placed in refractory test tubes 40–50 cm high and 2–2.5 cm in diameter.

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Fig. 1. Dependence of the specific thermal effect of the reaction on the ratio of components in the charge

Fig. 2. Curves of the specific thermal effect of the reaction.
1 –calculated, 2 –obtained experimentally

The openings of the test tubes were closed with thick-walled rubber tubes with plugs and oblique cuts, which served as safety valves for the release of gases during the reaction and isolated the reaction products from atmospheric oxygen.

The reaction was carried out in an electric furnace at an initial temperature of 600°. The experiments were conducted under completely identical conditions; therefore it may be assumed that the thermograms obtained fully characterize the initial and final temperatures, as well as the rate of the reduction reaction.

bismuth oxide with highly dispersed metallic manganese, depending on the atomic ratio of the interacting components in the charge. The error in temperature measurement was +15°.

As is known, during a metallothermic reaction the temperature of the reacting substances rises sharply, and correspondingly the reaction rate increases; the reaction proceeds mainly by a chain mechanism.

In the present case it is impossible to calculate theoretically the rate of the interaction reaction between bismuth oxide and metallic manganese, since simultaneously with this reaction there proceeds the reaction of formation of the intermetallic compound manganese–bismuth.

The special difficulties in theoretically calculating the rate of the indicated reaction are further explained by the fact that it proceeds at the phase boundary, and its rate is determined mainly by the magnitude of the surface of separation of these phases and by their mutual diffusion, as well as by the ratio of the reacting components of the charge and the density of the latter. In this connection, thermograms (Fig. 1) are of interest, giving a direct idea of the rate of the simultaneous processes of reduction of bismuth oxide by metallic manganese and interaction of the latter with the reduced bismuth.

In calculating the thermograms we took into account that the points $a_1, \dots, a_8$ correspond to the temperature at the beginning of the reaction, and the points $b_1, \dots, b_8$ to the temperature at the end of the reaction. The increase in the temperature of the system from a to b occurs due to the evolution of the heat of reaction, which proceeds during the time interval $\tau_2 - \tau_1$, which was readily determined graphically from the speed of motion of the tape, which in this case was 1 mm/sec. The results of these calculations are given in Table 1 and shown graphically in Fig. 2.

As can be seen from Fig. 2, the maximum of the calculated specific thermal effect does not coincide with that established experimentally. For the reaction $Bi_2O_3 + 3Mn = 2Bi + 3MnO$, the calculated maximum (point A) corresponds to the ratio $Bi_2O_3 : Mn = 1 : 3$, whereas the experimentally established maximum corresponds to the ratio $1 : 5$. This displacement of the maximum is caused by the evolution of heat during the formation of the intermetallic compound MnBi. If the reduction reaction of Bi_2O_3 ended at the stage of formation of pure Bi, then the maxima of curves 1 and 2 would coincide at a charge-component ratio of $1 : 3$. During formation of MnBi, 76.4 cal of heat is evolved per 1 g of charge. Since the yield of the magnetic fraction relative to the charge is only 37.7%, the formation of 1 g-mol of MnBi (i.e., 263.9 g) releases 4 kcal/g-mol.

The reaction products were ground in a roller mill, and the powders were sieved through a silk sieve. The resulting fine powder fraction was introduced into the rotating magnetic field of a permanent magnet, and magnetic particles were separated from nonmagnetic ones. The yield of the magnetic fraction was determined by the gravimetric method. An attempt at chemical separation of Mn oxides from the magnetic fraction gave no positive results. After treatment of the powder with aqueous or alcoholic solutions of acids (acetic, oleic, and butyric—) powder acquired a dark-brown coloration and lost its magnetic properties. Evidently, in the process of dissolving MnO in organic acids, the manganese that is part of the intermetallic compound also dissolves, and thus the crystalline structure of the powder is disrupted; moreover, a system close to the Bi—MnBi eutectic is formed, possessing very low magnetic properties.

Table 2

No.	Ratio of components in the charge, molar $Bi_2O_3 : Mn$	Ratio of components in the charge, atomic $Bi : Mn$	Yield of magnetic fraction, %
1	2 : 1	4 : 1	
2	1 : 1	2 : 1	1.5
3	1 : 2	2 : 2	6.0
4	1 : 3	2 : 3	15.0
5	1 : 4	2 : 4	31.9
6	1 : 5	2 : 5	37.5
7	1 : 6	2 : 6	30.1
8	1 : 7	2 : 7	28.2
9	1 : 8	2 : 8	20.4

As can be seen from Table 2, the optimal conditions for the formation of the intermetallic compound correspond to a charge composition with a ratio of the reacting substances $Bi_2O_3 : Mn = 1 : 5$, at which the maximum yield of the magnetic fraction is observed.

According to the equation $Bi_2O_3 + 5Mn = 2MnBi + 3MnO$, after the reaction the charge should contain 71.5% of the magnetic fraction, i.e., MnBi. However, because during the reaction other products are also formed (manganese oxides, pure bismuth, the Bi—MnBi eutectic), the practical yield of ferromagnetic powder is considerably smaller (see Table 2).

The properties of MnBi powders obtained by the manganothermic method proved to be as follows:

Property	Value
Optimal charge composition (mol.)	$Bi_2O_3 : 5Mn$
Yield of magnetic fraction (wt.%)	37.5
Chemical composition of the magnetic fraction (wt.%)	Bi 78.5; Mn 20.45
Microhardness under a load of 50 g (kg/mm^2)*	148
Thermal coefficient of electrical resistance	$4.56 \cdot 10^{-3}$
Crystal-lattice constants (Å)	$a = 4.26$; $c = 6.15$
Coercive force (oersteds)	700

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REFERENCES

1. Hilpert, T. Diekmann, *Ber.*, **44**, 283 (1911).
2. E. Adams, V. Hubbard, A. M. Sayles, *Problems of Modern Metallurgy*, No. 3, 114 (1953).
3. A. B. Altman, *Physics of Metals and Metallography*, **6**, No. 1, 46 (1958).
4. A. Goldmann, G. J. Post, *J. Appl. Phys.*, **30**, No. 4, 204 (1959).
5. E. M. Natanson, N. N. Kozachek, V. V. Bushin, *Doklady AN*, **135**, No. 1, 137 (1960).
6. G. V. Samsonov, Yu. D. Chistyakov, *Uspekhi Khimii*, **25**, issue 10, 1223 (1956).
7. N. N. Murach, U. D. Veryatin, *Introduction to Metallurgy*, Moscow, 1956.

8. S. A. Pogodin, A. N. Zelikman, *Izv. sekt. fiz.-khim. anal. IONKh AN SSSR*, No. 16, 1 (1943).

9. V. P. Elyutin, Yu. A. Pavlov, B. E. Levin, *Ferroalloys*, Moscow, 1950.

* Microhardness was determined in an alloy of the reaction products on a PMT-3 instrument.

Note: Figure translations are in progress. See original paper for figures.

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