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Interaction of oxides of 3d transition metals with boron

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Abstract

Differential thermal analysis and X-ray phase analysis were used to investigate the preparation conditions and composition of products of the borothermal reduction of oxides of 3d transition metals (titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc) at 50–1350 °C. The intermediate stages of the borothermal reduction were investigated. Identification of the products obtained at different stages of the interaction between oxides and boron is given.

1. Introduction

The borothermal reduction of oxides by elemental boron is one of the main methods for obtaining borides of transition metals. In these processes, in addition to the main product, boron oxide is formed. However, opinions differ as to the composition of the oxide [1, 2]: some authors state that B_2O_2 is formed, others B_2O_3. Besides, the different stages of these processes are not at all clear. The present investigation is aimed at obtaining more complete information about these reactions.

2. Experimental details

The experiments were conducted on pressed mixtures of powder-like oxides and amorphous boron. Pyrolitic amorphous boron with a purity of 99.6% and powders of oxides (TiO_2, V_2O_5, Cr_2O_3, MnO_2, Co_3O_4, NiO, CuO, ZnO) with a purity of no less than 99.5% and a dispersity of 5–20 μm were used to obtain metal diborides and boron suboxide (B_6O).

After mixing and compacting under a pressure of 100 MPa, the mixtures were put into quartz ampules and heated in an atmosphere of argon with a purity of 99.999% under a pressure of 0.1 MPa. The chemical interaction in the mixtures was studied by differential thermal analysis (DTA) and X-ray phase analysis (XPA). DTA curves were obtained in the temperature range 25–1350 °C, the rate of heating being 10 °C min^{-1}. XPA was conducted with Cu Kα and Fe Kα irradiation. The decoding of diffractograms was done with the help of standard tables of interplane distances [3].

3. Results and discussion

3.1. Titanium(IV) oxide

The thermogram obtained by heating a mixture of TiO_2 and amorphous boron is shown in Fig. 1 (curve 1). As a result of the interaction of TiO_2 with boron (mole ratio 1:14) the DTA curve shows three exothermic effects, starting at 684, 796 and 1250 °C respectively. The XPA data enable us to state that the oxide Ti_3O_5 and titanium borate ($TiBO_3$) are the products of the chemical reaction accompanying the first exothermic effect. The samples are a light blue colour, which also indicates the presence of Ti_3O_5 since this has the same colour. On the basis of these data the reaction can be presented in the form

$$4TiO_2 + B \longrightarrow TiBO_3 + Ti_3O_5 \tag{1}$$

The samples quenched after the second exothermic effect contain neither borate nor Ti_3O_5. Instead they exhibit titanium diboride (TiB_2) and boron oxide (B_2O_3). The presence of the latter is confirmed by the reflexes on X-ray patterns of boric acid (H_3BO_3) formed at the stage of preparation of the samples under XPA in a moist atmosphere. Thus the second exothermic effect can be caused by two reactions:

$$TiBO_3 + 3B \longrightarrow TiB_2 + B_2O_3 \tag{2}$$

$$3Ti_3O_5 + 28B \longrightarrow 9TiB_2 + 5B_2O_3 \tag{3}$$

The samples quenched after the third exothermic effect contain TiB_2 and B_6O. Consequently, this effect is caused by the reaction

$$B_2O_3 + 16B \longrightarrow 3B_6O \tag{4}$$

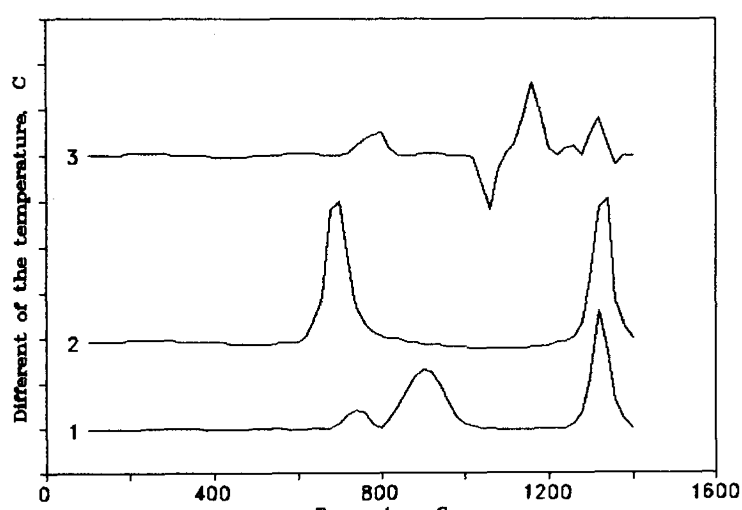

Fig. 1. DTA results for reaction of amorphous boron with 3d transition metal oxides: 1, TiO_2; 2, V_2O_5; 3, Cr_2O_3.

This is also confirmed by the initial temperature of the effect (1250 °C). It is at this temperature (to an accuracy of 5 °C) that earlier [4] the formation of a suboxide in the above-mentioned substances was recorded.

On the basis of the above results it is possible to present the total reaction of reduction of TiO_2 by amorphous boron in the form

$$TiO_2 + 14B \longrightarrow TiB_2 + 2B_6O \tag{5}$$

3.2. Vanadium(V) oxide

Figure 1 (curve 2) shows the thermogram obtained by heating V_2O_5 with boron (mole ratio 1:34). The DTA curve has two exothermic effects which, according to XPA, can be interpreted as originating from the reactions

$$3V_2O_5 + 4B \longrightarrow 3V_2O_3 + 2B_2O_3 \tag{6}$$

$$V_2O_3 + 22B \longrightarrow 2VB_2 + 3B_6O \tag{7}$$

The total reaction of the process can be presented in the form

$$V_2O_5 + 34B \longrightarrow 2VB_2 + 5B_6O \tag{8}$$

3.3. Chromium(III) oxide

The thermogram obtained by heating a mixture of Cr_2O_3 and amorphous boron is shown in Fig. 1 (curve 3). The interaction of Cr_2O_3 with boron (mole ratio 1:22) results in five effects on the DTA curve, four effects being exothermic and the fifth one endothermic. It was not possible to establish unambiguously the nature of the first exothermic effect at 717 °C. By XPA of samples, in addition to the starting substances, a small quantity of orthoboric acid was found. The appearance of the latter is probably connected with a partial oxidation of amorphous boron by oxygen contained in Cr_2O_3, which leads to an exothermic effect as in the case of the borothermal reduction of MnO_2 (see below).

In the sample quenched after the endothermic effect (1020 °C) boron oxide (B_2O_3) and the boride Cr_5B_3 were found. Since the temperature of melting (softening) of B_2O_3 is much lower than the starting temperature of the reaction, the B_2O_3 formed should be in a molten state and should evaporate partially, absorbing heat. Therefore this effect is endothermic and the chemical reaction causing it can be written as

$$5Cr_2O_3 + 16B \longrightarrow 2Cr_5B_3 + 5B_2O_3 \tag{9}$$

The second exothermic effect is produced by the reaction

$$Cr_5B_3 + 2B \longrightarrow 5CrB \tag{10}$$

The third exothermic effect is caused by the reaction

$$CrB + B \longrightarrow CrB_2 \tag{11}$$

Finally, the last effect is produced by reaction (4). Thus the total reaction has the form

$$Cr_2O_3 + 22B \longrightarrow 2CrB_2 + 3B_6O \tag{12}$$

3.4. Manganese(IV) oxide

The thermogram obtained by heating a mixture of MnO_2 and amorphous boron is shown in Fig. 2 (curve 1). The interaction of MnO_2 with boron (mole ratio 1:14) results in seven exothermic effects on the DTA curve. Diffractograms of the starting mixture before and after the first effect (80 °C) hardly differ. At the same time this effect is not observed on the DTA curves of either boron or MnO_2 alone. Consequently, it is caused by the joint presence of the components. It was noted that preliminary annealing of MnO_2 results in a decrease in the effect, while heating the mixture in an oxygen atmosphere leads to an increase. This last fact proves that heating the mixture of boron and MnO_2 to 80 °C leads to oxidation of one of the components. The results of spectral X-ray analysis of mixtures heated to 100 °C in an oxygen atmosphere show that in such samples the B—O bond is clearly manifest, while there is practically no such bond in samples which were not subjected to thermal treatment. The data obtained show that the first exothermic effect with a starting temperature of 80 °C is caused by the oxidation of elemental boron. This result is unexpected since it is well known that elemental boron starts to oxidize at above 300 °C [5]. Obviously, the oxygen absorbed by MnO_2 (a compound with a deficient structure, which is a good adsorbent of gases) favours the oxidation of boron.

The second exothermic effect accompanies the reaction of formation of Mn_3O_4. The volume of gas evolved in the reaction corresponds to 98.8% of

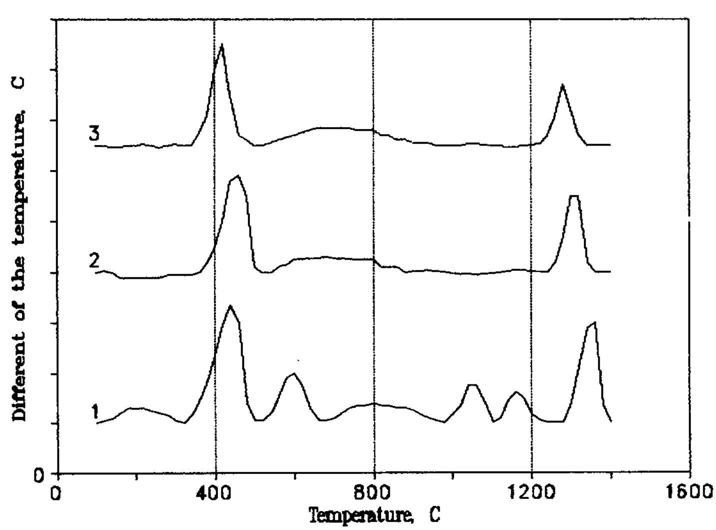

Fig. 2. DTA results for reaction of amorphous boron with 3d transition metal oxides: 1, MnO_2; 2, Fe_2O_3; 3, Co_3O_4.

the theoretical value calculated for B_2O_2. Consequently, the second exothermic effect is due to the reaction

$$3MnO_2 + 2B \longrightarrow Mn_3O_4 + B_2O_2 \tag{13}$$

The third exothermic effect resulted in the appearance of MnO and the borate $Mn_3(BO_3)_2$ in the reaction mixture. In the process of interaction of boron with the lowest oxides and $Mn_3(BO_3)_2$ practically no gas is evolved. Therefore the reaction which caused the appearance of the third exothermic effect can be written as

$$3Mn_3O_4 + 2B \longrightarrow Mn_3(BO_3)_2 + 6MnO \tag{14}$$

The products of the fourth reaction (MnB, $Mn_3(BO_3)_2$) can be obtained by the interaction of boron with both MnO and $Mn_3(BO_3)_2$. The results of DTA for these substances with boron show that the interaction of MnO with boron starts at 670 °C and of $Mn_3(BO_3)_2$ at 970 °C. In the first case MnB and $Mn_3(BO_3)_2$ are the products of the reaction and in the second case Mn_2B and B_2O_3. Therefore the reactions producing the fourth and fifth exothermic effects can be presented in the form

$$6MnO + 5B \longrightarrow MnB + Mn_3(BO_3)_2 \tag{15}$$

$$2Mn_3(BO_3)_2 + 7B \longrightarrow 3Mn_2B + 4B_2O_3 \tag{16}$$

The sixth exothermic effect is caused by the interaction of Mn_2B with boron:

$$Mn_2B + B \longrightarrow 2MnB \tag{17}$$

The last exothermic effect is connected with reaction (4). If we consider the total process, we can write the summary equation as

$$MnO_2 + 8B \longrightarrow MnB + B_6O + \tfrac{1}{2}B_2O_2 \tag{18}$$

3.5. *Iron(III) oxide*

Figure 2 (curve 2) shows the thermogram obtained by heating a mixture of α-Fe_2O_3 with amorphous boron. The interaction of α-Fe_2O_3 with boron (mole ratio 1:22) results in three thermal effects on the DTA curve. On the basis of the XPA data the thermal effects observed are caused by the reactions

$$\text{I. } Fe_2O_3 + 2B \longrightarrow 2Fe + B_2O_3 \tag{19}$$

$$\text{II. } Fe + B \longrightarrow FeB \tag{20}$$

$$\text{III. } B_2O_3 + 16B \longrightarrow 3B_6O$$

The total reaction for this process has the form

$$Fe_2O_3 + 20B \longrightarrow 2FeB + 3B_6O \tag{21}$$

3.6. *Cobalt(II–III) oxide*

The thermogram obtained by heating a mixture of Co_3O_4 and boron is given in Fig. 2 (curve 3). The interaction of Co_3O_4 with amorphous boron (mole ratio 1:30) results in three exothermic effects on the DTA curve. On the basis of the XPA data the thermal effects observed are caused by the reactions

$$\text{I. } 3Co_3O_4 + 8B \longrightarrow 9Co + 4B_2O_3 \tag{22}$$

$$\text{II. } Co + B \longrightarrow CoB \tag{23}$$

$$\text{III. } B_2O_3 + 16B \longrightarrow 3B_6O$$

The total reaction has the form:

$$Co_3O_4 + 27B \longrightarrow 3CoB + 4B_6O \tag{24}$$

3.7. Nickel(II) oxide

Figure 3 (curve 1) presents the thermogram obtained by heating a mixture of NiO with amorphous boron. There are four exothermic effects on the DTA curve resulting from the interaction of NiO with boron (mole ratio 1:8). The following reactions produced the thermal effects observed (on the basis of the XPA data):

$$\text{I. } NiO + B \longrightarrow Ni + B_2O_3 + n(2NiO \cdot B_2O_3) \tag{25}$$

$$\text{II. } 4Ni + 3B \longrightarrow Ni_4B_3 \tag{26}$$

$$\text{III. } Ni_4B_3 + B \longrightarrow 4NiB \tag{27}$$

$$Ni + B \longrightarrow NiB \tag{28}$$

$$\text{IV. } B_2O_3 + 16B \longrightarrow 3B_6O$$

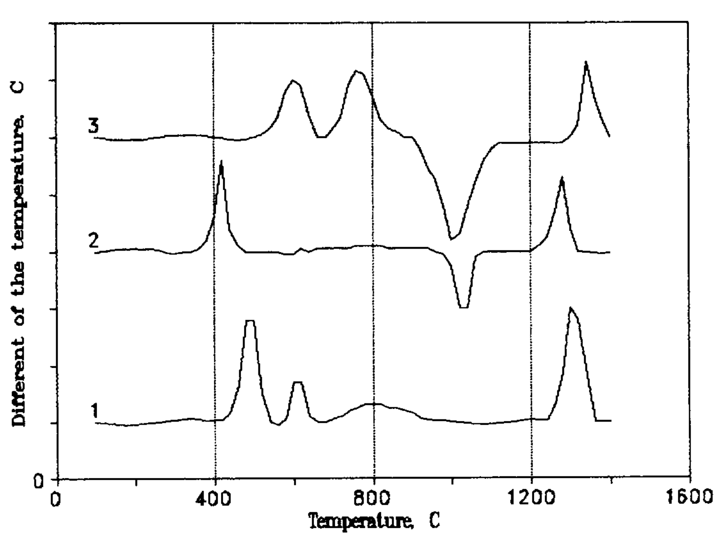

Fig. 3. DTA results for reaction of amorphous boron with 3d transition metal oxides: 1, NiO; 2, CuO; 3, ZnO.

If we consider the whole process, we can write the equation of the total reaction as

$$NiO + 7B \longrightarrow NiB + B_6O + n(2NiO \cdot B_2O_3) \tag{29}$$

where $n < 1$.

3.8. Copper(II) oxide

The thermogram obtained by heating a mixture of CuO and boron is presented in Fig. 3 (curve 2). The interaction of CuO with amorphous boron (mole ratio 1:8) results in three thermal effects on the DTA curve. One of them is endothermic and the other two are exothermic. The following reactions produced the thermal effects observed (on the basis of the XPA data):

$$\text{I. } 3CuO + 2B \longrightarrow 3Cu + B_2O_3 \tag{30}$$

II. Melting of the eutectic mixture containing solid solutions of boron in copper and of copper in boron.

$$\text{III. } B_2O_3 + 16B \longrightarrow 3B_6O$$

The total reaction has the form

$$CuO + 6B \longrightarrow Cu + B_6O \tag{31}$$

3.9. Zinc(II) oxide

Concerning the borothermal reduction of ZnO, it is well known that it proceeds with the formation of metallic zinc and B_6O [6]. It was interesting to follow the step-by-step development of this process. The thermogram obtained by heating a mixture of ZnO and amorphous boron (mole ratio 1:8) is shown in Fig. 3 (curve 3). As in the case of chromium and manganese oxides, there are no noticeable changes in the phase composition of the mixture after the first effect. It is possible that here the thermal effect is also caused by a partial boron oxidation. The second exothermic effect is produced by the reaction of formation of B_2O_3 and metallic zinc. The latter boils at 907 °C. This process is accompanied by absorption of heat, which is observed on the thermogram in the form of an endothermic effect. Finally, the last effect is due to the interaction of boron with B_2O_3 in accordance with reaction (4). The total reaction of the process can be presented in the form

$$ZnO + 6B \longrightarrow Zn + B_6O \tag{32}$$

4. Conclusions

As a rule, the reactions under consideration proceed via sequential stages of the reduction of metal oxides from the highest to the lowest and then via the formation of mixed metal–boron–oxygen phases. Borides are formed in the last stages. As byproducts, amorphous B_2O_3 occurs at low temperatures and crystalline B_6O at high temperatures.

The total reactions of the borothermal reduction of oxides of 3d transition metals can be described in the form of a single chemical equation:

$$Me_xO_y + (mx + 6y)B \longrightarrow xMeB_m + yB_6O \qquad (33)$$

If the oxide-forming metals have d shells with an increasing number of unpaired electrons (Ti–Cr), the reduction of their oxides proceeds until diborides are formed ($m = 2$). With a decrease in the number of unpaired d electrons (Mn–Ni) the formation of borides is hindered and the reduction reactions proceed until monoborides appear ($m = 1$). Finally, in the case of copper and zinc oxides, whose d electrons are all paired, borides are not synthesized at all and the reduction proceeds until the metals themselves are obtained ($m = 0$).

The process of the reduction of MnO_2 is an exception to the general rule. In this process, in addition to MnB and B_6O, the oxide B_2O_2 is formed. Another exception to the general rule is the process of the reduction of NiO, where, in addition to NiB and B_6O, the borate $Ni_2B_2O_5$ is formed. The latter does not interact with boron in the range of temperatures under consideration.

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