Journal of Engineering Physics and Thermophysics, Vol. 65, No. 5, 1993

SOME FEATURES OF THE CHEMICAL TRANSFORMATION OF A HIGHLY EXOTHERMIC ORE CONCENTRATE-BASED MIXTURE IN A COMBUSTION WAVE

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UDC 536.46-57.04

Use of inexpensive ore concentrates as initial components in SHS metallurgy [1-3] brings about some specific features in the process and the properties of the materials obtained. Ore reagents contain a considerable amount of impurities (Al_2O_3, SiO_2, Fe_2O_3) that decrease the energetics of SHS systems and the temperature and the rate of combustion and create the limits of combustion and phase separation. In addition, the impurities participate in chemical reactions and enter the desired product. In many cases the presence of silicon, iron, and aluminum in a cast product does not prevent use of this product for practical purposes.

Use of ore concentrates broadens the resources of raw materials for SHS metallurgy and makes it possible to obtain less expensive synthesis products as compared to those synthesized from chemically pure raw materials.

The present work is devoted to investigation of specific features of SHS using ore concentrates. The chemical composition of the concentrates is given in Table 1. It is seen that SiO, Fe_2O_3, CaO are the main impurities of the ore concentrates. A characteristic property of the molybdenum concentrate is that a mixture of two oxides enters its composition.

Experimental Procedure. Experiments were conducted according to the following schemes of chemical reactions:

$$\nu MoO_3 \cdot MoO_2 + \nu Al \rightarrow \nu Mo + \nu Al_2O_3 ;$$

$$\nu MoO_3 \cdot MoO_2 + \nu Al + \nu Mg + \nu C \rightarrow \nu Mo_2C + \nu Al_2O_3 + \nu MgO ;$$

$$\nu MoO_3 \cdot MoO_2 + \nu Fe_3O_4 + \nu Al + \nu Mg \rightarrow \nu Mo_xFe_y + \nu Al_2O_3 + \nu MgO ;$$

$$\nu CrO_3 + \nu TiO_2 + \nu B_2O_3 + \nu Al \rightarrow CrB_2 \times TiB_2 + \nu Al_2O_3 ;$$

$$\nu MnO_2 + \nu Al \rightarrow \nu Mn + \nu Al_2O_3 ;$$

$$\nu MnO_2 + \nu Fe_3O_4 + \nu Al \rightarrow \nu Mn_xFe_y + \nu Al_2O_3 ;$$

$$\nu MnO_2 + \nu SiO_2 \,(Si) + \nu Al \rightarrow \nu Mn_xSi_y + \nu Al_2O_3 .$$

Combustion of the mixtures used here at atmospheric pressure is accompanied by partial and, sometimes, total spread-out of the reaction mass. Therefore all the experiments were conducted at an excess pressure of gas (argon, nitrogen) from 0.1 to 150 MPa.

Dependencing on the goals of the experiment we used two types of experimental setup: 1) a constant-pressure bomb and a high-pressure SHS apparatus for laboratory studies; 2) a general-purpose SHS-20 reactor for technological studies.

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TABLE 1. Chemical Content of Ore Concentrates

Chiaturskii manganese concentrate of the 1st grade (MnO_2) Mn, 48 wt.%	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	P
	9	2.6	1.5	1.2	1.2	0.17
Dashkesanskii magnetite (Fe_3O_4) Fe, 61 wt.%	SiO_2	CaO	Al_2O_3	MgO	MnO	P
	9-10	6-7	2-3	1	0.6-0.7	0.2-0.3
Vol'nogorskii rutile concentrate, TiO_2, 93 wt.%	SiO_2		Al_2O_3	Fe_2O_3	ZnO_2	P
	1.7		0.8	3.3	1.2	0.02
Molybdenum ore concentrate $MoO_3/MoO_2 = 60/40$ Mo, 66.4 wt.%	MgO	AS		CuO	S	P
	0.02	0.01		0.002	0.02	0.05
Mineral ore: quartzite SiO_2, 95 wt.%	Fe_2O_3, Al_2O_3					
	5					

A quartz or graphite mold filled with a mixture prepared in a batch was placed in a reaction volume. A tungsten or Ni-Cr alloy coil was terminated at the mixture surface. The experimental unit was pressurized and filled with gas up to the initial pressure. The batch was electric coil-fired. After cessation of synthesis and cooling of the product the gas was blown off, the experimental unit was depressurized and the synthesis products were extracted.

In the experiments, we measured the linear combustion rate u_0, the spread-out of the combustion mixture η_s, and the yield of the products in an ingot η_y.

The total yield (%) of the desired product was determined as the ratio of the ingot mass M_{in} of the desired product, obtained in the experiment, to the initial mixture mass M_0:

$$\eta_y = \frac{M_{in}}{M_0} \cdot 100\ \% .$$

The calculated total yield η_y^{cal} of the desired product from the initial batch was regarded as the ratio of the sum of the desired elements in the batch $(\sum_{i=1}^{N} m_i)$ to M_0 for the general case of chemical transformation:

$$\eta_y^{cal} = \frac{\sum_{i=1}^{N} m_i}{M_0} .$$

For quantitative characterization of the dispersion process of the reaction mass from the mold we calculated relative mass spread-out by the formula

$$\eta_s = \frac{\Delta M}{M_0} \cdot 100\ \% ,$$

where $\Delta M = M_b - M_e$ are the mass of the dispersed substance; M_b, M_e are the mass at the beginning and end of the synthesis, respectively.

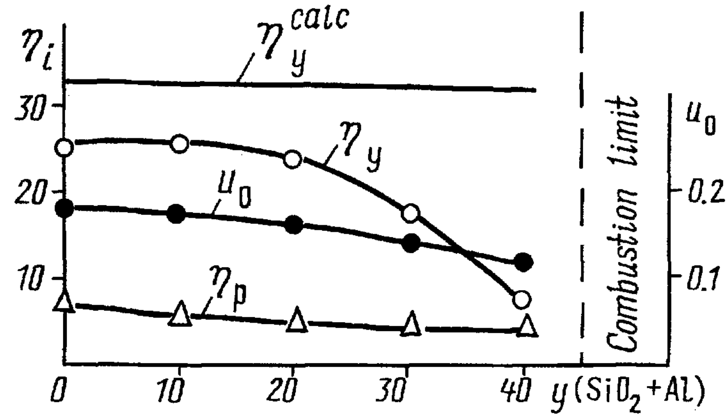

Fig. 1. Combustion rate, total yield, and mixture spread-out as a function of the compositions ratio in the initial mixture: x (MnO_2:Al) + y (SiO_2:Al), $x+y = 100\%$; η_i, y, wt.%; u_0, cm/sec.

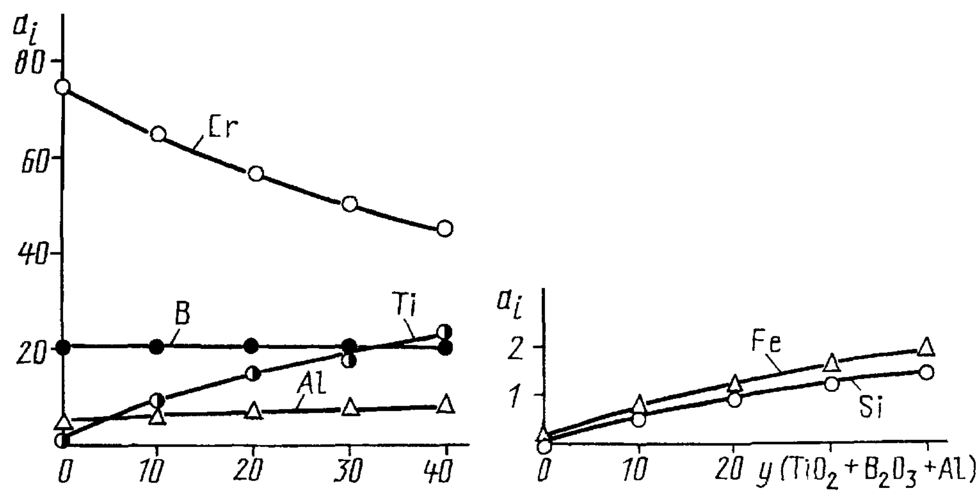

Fig. 2. Influence of the content of y(TiO_2+B_2O_3+Al), wt.%, in the batch on the chemical composition of the ingot a_i, wt.%.

The materials synthesized were analyzed by chemical, metallographic, and microprobe methods. Physicochemical and mechanical studies of the SHS materials were also made.

Experimental studies have shown that the systems burn in wide ranges of the reagent ratio and form cast products. As a rule, at a sufficiently large weight fraction of an ore reagent the combustion and phase separation limits are attained. For instance, the combustion limit for the MnO_2-SiO_2-Al system is attained when silicon makes up 45% of the mixture. Cessation of phase separation is explained by a decrease of specific heat in the process (Fig. 1).

Impurities in an ore raw material not only decrease the combustion temperature but also participate in chemical reactions. For instance, in the case of the CrO_3-B_2O_3-TiO_2-Al system, in addition to the desired elements Cr, B, Ti we have found Fe and Si in the ingot, which are contained in the rutile concentrate in the form of Fe_2O_3 and SiO_2 (Fig. 3). The fact that often a reducing agent (Al in the present case) passes into the desired product is noteworthy. However, optimizing the batch we have succeeded in decreasing its content to 3-5%.

The synthesis with participation of ore concentrates containing manganese is complicated by the volatility of the latter. Synthesis conducted at excess gas pressure makes its possible to suppress spread-out of combustion products, increase metallic manganese extraction from an ore concentrate into an ingot, and create an ecologically pure technology its production (see Fig. 3). An incomplete Mn yield into an ingot is explained by incomplete reduction of the initial oxides and sticking of metallic shot in the slag. As the batch mass increases, the content of the metal extracted increases substantially and attains 80%.

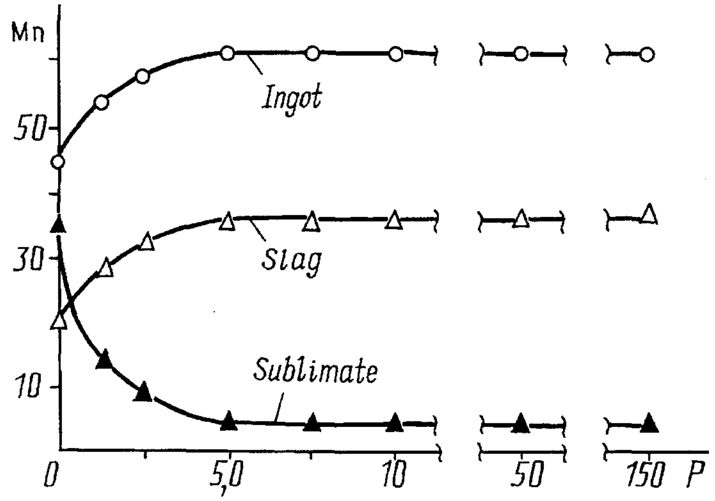

Fig. 3. Distribution of manganese between the ingot, the slag and the sublimate in the initial batch as a function of the initial pressure. The initial mixture: MnO_2-Fe_3O_4-Al. C_{Mn}, wt.%; P, MPa.

Similar investigations have been carried out with chemical compositions based on the rutile concentrate $MoO_3 \cdot MoO_2$. In the Mo-Fe system, alloys with a different Mo-to-Fe ratio in them and an impurity content of no more than 3 wt.% have been obtained. The content of nonmetals in the Mo-C system can be varied within wide ranges and such phases as Mo_2C, Mo_3C_2 can be obtained with an impurity content of no more than 0.45 wt.%.

Molybdenum carbide powders with small-size particles improve the homogeneity of titanium carbide-based solid alloys and increase the microhardness of the carbide grains.

Cast chromium-titanium boride is characterized by high wear resistance and microhardness (H_0 = 21,000-38,000). Tests have been made of $CrB_2 \cdot TiB_2$ as a solid-state component of welded-on electrodes, which have demonstrated its promising use for obtaining desired wear-resistant coatings.

REFERENCES

1. A. G. Merzhanov and I. P. Borovinskaya, Dokl. Akad. Nauk SSSR, **204**, No. 2, 366-369 (1972).
2. A. G. Merzhanov, V. I. Yukhvid, and I. P. Borovinskaya, Dokl. Akad. Nauk SSSR, **255**, No. 1, 120-124 (1980).
3. V. I. Yukhvid, Izv. Akad. Nauk SSSR, Metally, No. 6, 61-64 (1980).