Production of Ferro Alloys from Wolframite Concentrate Using Pressure

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Abstract

The temperature of aluminotermic processes changes largely depending on appointment, structure and property of received products. Optimum conditions steal up for each concrete process. One of important practical questions is influence of temperature and external pressure upon extraction of restored elements in an ingot. In work concentration and high-speed limits of burning of system WO_3-Al are defined. Limits of burning of system (4,3 – 19,1 g/sm^3) are established at dilute from 10 to 300 % by a ballast. The factors influencing for speed of burning mixture from tungsten concentrate are investigated. Influence of superfluous pressure on fusion indicators is investigated at reception ferrotungsten from various raw materials. Modes of preparation of initial raw materials to process of fusion are defined and parametres of carrying out of process of reception ferrotungsten under pressure are established. It is shown that superfluous pressure does not shift balance of reaction of restoration of tungsten only suppresses disorder of a reacting mix and prevents ablation of a reacting mix that promotes increase in an exit of an alloy.

Introduction

To work on getting ferrotungsten surveyed the raw materials used to the possibility of his carrying out the process in spontaneous mode. SHS raw material was analyzed by quantitative content of oxides which would allow obtaining aluminothermy ferrotungsten required composition. Analysis of the quantitative content of components was performed by XRD.

The composition of wolframite:

WO_3 − 65 %; FeO − 16,77 %; MnO − 78 %;
SiO_2 − 1,6 %; CO − 0,12 %; Sn − 0,12 %;
MoO_3 − 1,08 %; S − 1,9-2,4 %.

Composition of low – wolframite %:

W − 20,39; Cu − 0,19; Co − 2,64; Fe − 1,68;
Ti − 1,05; Ca − 0,45; K − 0,038; Si − 26,34;
S − 0,065; Al − 1,44; Mg − 0,24.

X-ray analysis of wolframite showed that the main phase is wolframite (FeMn) WO_4. X-ray analysis of the poor of tungsten raw materials - the main phases of WO_3 and SiO_2 in the form of cristobalite.

As a secondary raw material used tungsten scrap and waste electric lamp production (a mixture of tungsten-molybdenum wire).

In laboratory studies often using the linear velocity V_h, cm/s, combustion exothermic compositions defined as the ratio of column height h to the charge of burning time. The method of measuring the linear velocity is very simple is fixed from time to fuse the charge prior to the sharp variations in the thermocouple mounted on the bottom of the crucible [1] and does not require complex calculations:

$$V_h = h/\tau \qquad (1)$$

For stoichiometric combustion temperature systems with 2460°C and above atmospheric pressure according to [2] the process proceeds explosively. This is due to the fact that the system creates a positive pressure in the evaporation of

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aluminum and the formation of volatile lower oxides of aluminum (AlO, AlO_2), sublimation of the oxides of manganese and tungsten [3].

In order to reduce the loss of metal and taking it to the alloy in a series of experiments to identify the emerging positive pressure during combustion of the charge on the basis of wolframite concentrate.

For the experiments we used wolframite concentrates of two kinds.

Analysis of raw materials was carried out by XRD. The composition of wolframite %:

a) WO_3 – 65 %, FeO – 16.47, MnO – 7.8, SiO_2 – 1.6, CuO – 0.12, Sn – 0.08, MoO_3 – 1.09;

b) WO_3 – 58 %, FeO – 21.2, MnO – 7.1, SiO_2 – 1.7, CuO – 0.12, Sn – 0.2, MoO_3 – 1.09, Bi – 0.02.

On the basis of raw materials was carried out calculations of the charge for ferrotungsten with tungsten content 70%.

In this paper the charge is calculated per 1 kg of wolframite based on an analysis of the concentrate. The calculation was performed on all aluminum oxides.

We give an example of calculating the amount of aluminum for the reduction reaction of tungsten trioxide to concentrate "B" for 1 kg of concentrate.

$$1000 \cdot 0{,}58 \cdot 54/232 = 135 \text{ g}$$

The total number of aluminum is 250 g.

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From 1 kg of smelt wolframite (1000 · 0,58 · 183/232) 457,5 g of tungsten, 163 g of iron, 37.9 g of manganese, 7.1 silicon. The percentage of tungsten will be 69 %.

Estimated amount of aluminum to concentrate on a 226 kg amount of iron to be added to the charge for ferrotungsten containing 70% tungsten according to the calculations – 40 g. Number of fluxing additives is taken at 15 % of the aluminum.

With the settlement of the charge and concentrate on the reference data the heats of reactions calculated specific heat of the process. To concentrate containing 65% tungsten oxide specific heat is calculated in the previous stages and is 140.9 kJ/g · atom. Process temperature is 3104 K.

For oxides of W, Mo, V, etc. determined by the formula:

$$T_{pr} = 11{,}6 \cdot \delta'H + 1400 \qquad (2)$$

For further calculation, the formula (2) must be converted to gram-atoms of the charge. The total number of gram-atoms is 4.95.

$$\delta H' = 2473 : 18.3 = 135.14 \text{ kJ / g} \cdot \text{atom}$$
$$T_{pr} = 11{,}6 \cdot \delta H' + 1400 = 2967 \text{ K}$$

This temperature is sufficient for the process because above the melting point of all oxides present in the mixture.

Study the influence of particle size distribution in the process of aluminothermic recovery

To obtain a high yield of metal melting furnace at you must carefully select the charge materials by size to ensure the fullest possible occurrence of reduction reactions.

The crushing burden materials is one of the most important factors determining the performance - furnace smelting. The size of the average oxide recovery, having, as a rule, a low melting temperature should not exceed 5 microns.

The size of the aluminum powder is selected depending on the size of the oxides and process conditions.

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To determine the effect size of the charge materials on the yield of the alloy used ferrotungsten concentrate with 58% tungsten oxide and aluminum powder. Both components have inhomogeneous particle size. Powders are sowing on the sieves of 100, 300, 400 and 500 microns. Then the charge was prepared from powders of identical and different sizes.

In all experiments, the output of the alloy was the highest in the case of the same size of wolframite and aluminum.

Used in the aluminum powder and wolframite concentrates are very heterogeneous in size and have similar grain-size composition. In these there are particles of aluminum and tungsten from 100 to 500 microns, iron trioxide and fluorspar 100 microns.

The choice of iron-containing component in the alloy depends on the content of iron oxide in the composition of wolframite concentrate. If the amount required in the calculation of the ratio of the alloy is sufficient the additional amount of iron is not introduced into the mixture.

Iron-containing component of the charge can be introduced into the mixture in the form of iron oxide or iron in the form of chips. The iron oxide mixed with aluminum is an additional source of heat and iron shavings acts as ballast and requires a flow of heat to melt it.

When using the concentrate "b" the introduction of additional amounts of iron in the charge does not require the calculation of iron oxide contained in concentrate enough to get the desired alloy composition.

Investigation of the nature of the influence of additives on the yield ballast alloy and metal extraction of raw materials

For high-thermite burning systems with high speed and spread, it is important to bring them in for a more relaxed mode and so reduce metal loss. Slow down the process and temperature can be an introduction to the charge of ballast additives. For each specific charge composition was chosen number ballast supplements.

As ballast additives used alumina and ground slag previous batches. The experiments were performed with the charge of concentrates with different contents of tungsten trioxide (Figure 1).

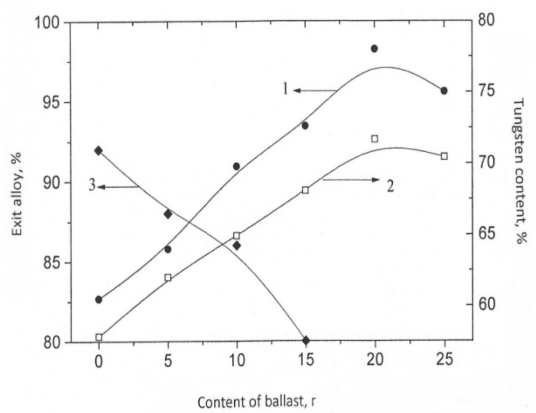

Fig. 1. Effect of additives on the yield ballast alloy and tungsten content in the alloy: 1 - yield an alloy of tungsten charge "a", 2 - tungsten content in the alloy, 3 - way out of an alloy mixture of wolframite "b"

The data presented in Figure 1 illustrate the positive impact ballast additives batch of concentrate containing tungsten oxide in 65%. With increasing additions to a certain size, for sample 300 g of concentrate, the optimal number of ballast wolframite is – 20, when the output of the alloy and tungsten content in the alloy is the highest. Introduce ballast in charge of the concentrate "b" is not necessary.

Selection of optimal process parameters under pressure

Various authors [2-4] noted the influence of external pressure on the rate of reaction front propagation for high aluminothermic steel.

The burning of WO_3 + Al and Fe_2O_3 +Al are accompanied by the rapid course of the process of reacting with a range of reagents. To suppress the spread and reduce the loss of the main alloying element experiments were conducted to identify the impact of excessive pressure on the yield of extraction of tungsten alloy.

For this purpose the crucible to ensure preservation of the emerging pressures. For the laboratory experiments used 2.5-liter crucible.

Based on the calculation of the charge, the experiments on the identification of ballast additives on the yield of the alloy was used charge of wolframite concentrates containing WO_3 - 65%.

Composition of the mixture in the experiments,%:

Wolframite concentrate – 73.2
Iron shavings – 3.0
Aluminum – 16.6
Ballast – 4.8
Fluorspar – 2.4.

In carrying out preliminary experiments for different pressures, it was found that the magnitude of emerging positive pressure depends on the composition of the reaction mixture and the scale factor. To obtain different pressure values used sample of the charge, g: 418, 703, 836, 1365, 2047.5.

Mixed components of the mixture with low weight covered in ceramic unfired reactor and placed in a crucible. When rigging charge is 1365 g, it poured directly into the crucible. At the bottom of the crucible was poured slag. Set fire to the charge we made with nichrome spiral by electrical pulse. The pressure was varied from normal up to 13 atm.

The results of experiments that are shown in table 1 show the influence of the excess pressure on the performance of the process.

Weight of all samples was the same pressure to 5 atm. For more high-pressure we increased weight of the samples.

Up to a certain increase in pressure values favorable effect on the output of the alloy and extraction pressure.

This quantity is equal to 5.7 atmospheres, a further increase in pressure leads to a decrease in the yield probably due to the change rate of the process downward.

In the experiments recorded as the time of combustion of the charge depending on the emerging of excess pressure. With increasing pressure to a pressure of 7 atmosphere burning time decreased at higher pressures up to 13 atmosphere, the rate of the fallen and at a pressure of 13 atmosphere is again a slight increase in burning rate but such a high increase in pressure is not desirable due to increased risk of carrying out the process in this mode.

Table 1
Effect of pressure on melting rates

№	Weight of the charge, g	Pressure, atm	The output of the alloy			Extraction of tungsten,%
			Calculated, g	The practical weight of the alloy, g	The output from the calculation,%	
1	1365	normal conditions	697,7	615,4	88,2	89
2	1365	1	697,7	626,8	89,8	90
3	1365	2	697,7	627,9	90,0	91,8
4	1365	3	697,7	640,0	91,8	92,8
5	1365	5	697,7	676,8	97,0	98,0
6	1365	7	697,7	683,7	98,0	98,5
7	2047,5	9	1046,5	1021,0	97,6	98,0
8	2047,5	12	1046,5	1020,5	97,4	98,0
9	2047,5	13	1046,5	1020,1	97,5	98,2
10	2047,5	14	1046,5	1021,0	97,6	98,7

Up to a certain increase in pressure values favorable effect on the output of the alloy and extraction pressure.

Using the results of experimental data, we determined the optimal conditions for obtaining aluminothermic ferrotungsten from concentrate containing WO_3 – 65%, ballast – 4.8 of the total composition of the charge (usually considered to be ballast on the amount of aluminum and are, in this case 28.8%), pressure 5.7 atmosphere. According to the parameters were given control fusion.

Results of the analysis (X-ray spectral analysis) of the samples of the alloy and slag are shown in Tables 2 and 3.

The increased amount of tungsten in the alloy, compared with an estimated due to the fact that some of the oxides (MnO, FeO, SiO_2, TiO, etc.) is not transferred to the alloy but remained in the slag.

According to information received the least amount of tungsten in the slag and the highest content in the alloy, it can be seen in experiments 1, 2, 4. The resulting alloy is corresponding to GOST 17293-82.

Table 2
Composition of wolframite concentrate ferrotungsten on the results of XRD,%

№	W	Mn	Fe	Ni	Cu	Sn	S	Al
1	74.42	0.9	13.97	0.11	0.3	0.09	0.07	6.14
2	74.84	0.6	11.91	0.16	0.28	0.08	0.06	5.78
3	70.58	0.7	16.71	0.14	0.4	0.1	0.07	5.8
4	74.28	0.8	14.20	0.14	0.49	0.08	0.07	6.0

Table 3
Composition of the slag,%

№	W	Fe	Si	Mn	Ti	Sn	Al	Ca	O
1	0.25	2.8	1.9	8.1	1.6	0.19	35.0	5.5	44.19
2	0.21	2.7	1.9	7.5	1.7	0.18	34.96	5.6	44.95
3	0.7	2.3	1.8	7.2	1.8	0.17	33.9	5.1	44.52
4	0.25	2.3	1.9	7.4	1.7	0.17	34.6	5.5	44.21

Effect of reducing the rate of melting of the charge

To determine the burning rate of the samples prepared with different contents of aluminum, from -10 % to 300% of the stoichiometric ratio. These experiments conducted in Table 4. Here are the results to determine the density of the resulting metal. The density of the metal is an important characteristic of the process, because it implicitly characterizes the composition of the metallic phase: the closer its value to the density of tungsten, the lower the impurities contained in the alloy.

From Table 4 and Figure 2 shows that the stoichiometric content of aluminum burning rate reaches its maximum value. In this case the reaction is explosive with a range of melt.

With further increase in aluminum velocity decreases and the process becomes more peaceful in nature. When the burning rate of 3,8-4,2 g/cm^2 ·s reaction products are object without phase separation. At intervals the deviation from stoichiometry (-10) - (+100) burning rate decreases to 10%. At 150 % it is reduced by almost 3 times and at 300% - in four.

The density of the alloy has a maximum value of 19.1 g/cm^3 with an excess of aluminum by 20%. Alloy density decreases with further increase of aluminum.

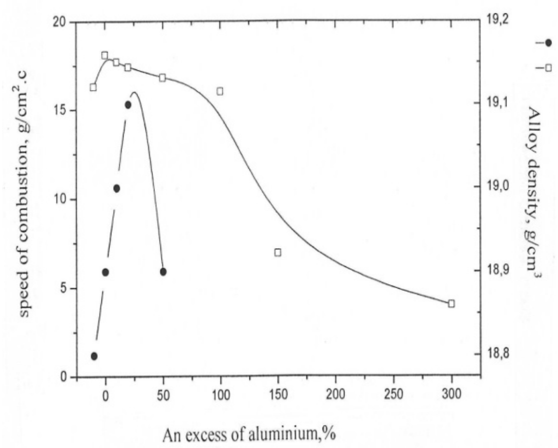

Fig. 2. Dependence of combustion rate and density of the alloy from an excess of aluminum:

(□) there is a sharp peak, indicating the existence of an optimal value of the deviation from the stoichiometric content of the additive ratio above which an adverse effect on the quality of the product of the reaction. For the combustion rate

(●) boundary conditions are less stringent ballast additives, however, to match the results obtained as the introduction of aluminum ballast additives rationally in an amount of from 10 to 20%. The velocity of combustion 17.4 g/cm^2 ·s and density of the metallic phase 19.1 g/cm^3, what is most relevant to pure tungsten (19,3-19,6 g/cm^3).

Table 4
Rate of combustion of tungsten trioxide

№	Charge, g		The excess of Al over stoichiometric concentration,%	The burning rate, g/cm^2 •sec	The density of the alloy, g/cm^3
	trioxide of tungsten	Aluminum			
1	250	52,2	-10	16,3	18,8
2	250	58,0	0	18,1	18,9
3	250	63,8	10	17,7	19,0
4	250	69,6	20	17,4	19,1
5	250	87,0	50	16,8	18,9
6	250	116	100	16,1	-
7	250	145	150	6,9	-
8	250	232	300	4,0	-

Particularly evident influence of aluminum as ballast additives on the parameters of the combustion process is presented in Figure 2. For the curve characterizing the change in density (Based on the results of combustion of tungsten trioxide with aluminum was investigated the possibility of obtaining ferrotungsten of wolframite concentrate.

Feedstock used to produce ferrotungsten is not tungsten monoxide and a mixture of oxides (WO_3; Fe_2O_3; MnO, etc.)

To determine the burning rate of the charge initially determined by the rate of combustion basic oxides contained in the concentrate - tungsten oxide and iron trioxide - depending on the amount of reducing agent and a mixture of WO_3 with Fe_2O_3 in the ratio required for ferrotungsten -70.

In the unfired ceramic reactor volume of 250 ml poured charge. One thermocouple was placed on the surface of the charge, the second at the bottom of the reactor.

Ignition was made of nichrome spiral electrical pulse. The beginning and end of combustion on the deviation of the thermocouple whose testimony is recorded loop oscilloscope NO114M brand.

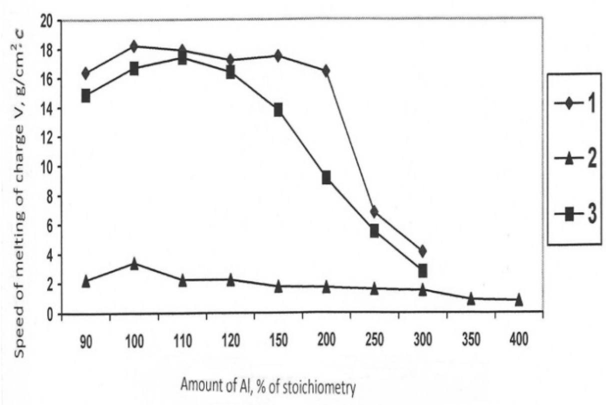

Fig. 3. Dependence of the burning rate of the charge on the amount of Aluminum: 1 - burning WO_3; 2 - burning Fe_2O_3; 3 - combustion system $WO_3 + Fe_2O_3$

Nature of the change rates of the aluminothermic reduction of oxides of tungsten and iron, depending on the concentration of aluminum in the reaction mixture systems is described by curves with a pronounced maximum. These experiments make it possible to draw conclusions about the kinetics of aluminothermic process, tungsten oxides and iron, and mixtures thereof.

The kinetics of these processes is determined mainly phenomenon of diffusion in complex melts. As the Kostfard [6], liquid oxides, apparently, are not an effective barrier to diffusion, and its speed is very high compared to diffusion in solids.

The processes that occur without significant or insignificant with the formation of vapor phase, the maximum velocity at the stoichiometric composition of reaction mixtures or close to it in Figure 3. For the boundary conditions of the burning rate content ballast additives, which serves as aluminum vary widely but for metal and alloy aluminum to efficiently introduce ballast from 10 to 20%. The velocity of combustion WO_3 - 17,2 - 17,9 g/cm^2 · sec. For Fe_2O_3 - 2,0 - 2,25 g/cm^2 · sec.

Conclusion

- The concentration and speed limits of combustion of WO_3-Al. Set the limits of combustion systems (4.3 - 19.1 g/cm^3) at a dilution of 10 to 300% of the ballast.
- The factors affecting the rate of combustion of the charge of wolframite concentrate.
- The effect of excess pressure on the melting rates when receiving ferrotungsten from different raw materials.
- Used modes of preparation of feedstock to the process of smelting.
- Used the parameters of the process of obtaining ferrotungsten under pressure.
- Found that the gauge pressure shifts the equilibrium of the reduction reaction of tungsten, only suppress the spread of the reaction mixture and prevents the entrainment of the reaction mixture which increases the output of the alloy.

References

1. J.L. Pliner, G.F. Ignatenko, E.A. Rubinstein Metallothermy. Proceedings Kliuchevskoi Ferroalloy Plant. Moscow: Metallurgiya, 1965, Vol. 2, p. 27-35.
2. Grump, I. Prentice, K. Kralutle. Gemb. Sci. And Tecuh, 1969, 1.205.
3. Maksimov E.P. and so on Combustion, Explosion, № 4, (1965).
4. Samsonov G.V., Chastyakov J.L. Metallothermic methods in chemistry and metallurgy. - Moscow: Progress of Chemistry, 1956.
5. A.F. Belyaev, Komkova L.D. // ZhFKh. 1950. - V.34 - Vyp.11. - S. 1302-1311.

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