FERROTUNGSTEN PRODUCTION FROM WOLFRAMITE CONCENTRATE BY ALUMINOTHERMAL METHOD

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ABSTRACT

In this article of the present of the results limits end the burning rate the system WO_3+Al at a mixture weakening by excess of aluminium. Heat effects and temperatures of processes for deriving ferrotungsten from a concentrate are calculated. Agency of the ballasting component on an output of an alloy and extraction of target metal is displayed.

Keywords: metallothermic, ferro-alloies

INTRODUCTION

The modern production process, despite of utilization of novel specie of metal products, closely related with a introduction in production of high-quality, special steel alloys and alloys, with new operational characteristics that is impossible without production of ferro-alloies. Having all aspects of minerals which one is necessary for production of ferro-alloies, in economics of Kazakhstan there is an obvious dominance of raw material direction and phases of finishing production are rather weakly developed. On presence of a rich source of raw materials of production of ferro-alloies it is introduced only two large enterprise, which receive ferro-alloies by an electric furnace mode. The fundamental raw for deriving a tungsten and ferrotungsten are the scheelite and concentrates of a tungsten. Carbon, aluminum and ferrosilicon-75 may be used as reducing agents. Current technology of ferrotungsten production of the following grades: "FeW 70, FeW 70-B and FeW 65" are available through reduction of the concentrates by use of carbon and silicon. The alloys' other grades are melted out by use of the alumino-silicothermal or aluminothermal methods.

ACCOUNT AND EXPERIMENTAL RESEARCH OF METHODS OF INTENSIFICATION AND OPTIMIZATION OF PROCESS OF SMELTING OF FERROTUNGSTEN OUTSIDE OF A FURNACE VODE

The smelting of ferrotungsten from used raw (wolframite) requires an individual approach at account of a charge makeup. It is necessary to allow for burning behavior of easily reconstituted oxides. Presence in structure of a blend of oxides and aluminium result to stormy flow and of a response to metal loss. Losses happen and to evaporation of oxide of a tungsten. Following measures were made for optimization of process of deriving of ferrotungsten from wolframite: speed reduction and combustion temperatures.

Indispensable specific heat of process:

$$\delta H'_i = 116 \text{ кJoule/g atom}$$

Actual heat of process at combustion of 300 g of a concentrate of a tungsten $\delta H'_a = 140,9$ кJoule / g atom.

At such heat of process reaction temperature:

$$T_p = 11,6 \cdot 140,9 + 1400 = 3034 \text{ К.}$$

At heat of a blend on each 100 0C the specific heat of process is increase by 0,567 kcal/g atom. It is necessary to introduce such quantity of a ballast for which at melting spend heat of process and the temperature go down. For this purpose it is necessary to expend 3,402 кJoule / g mole [8].

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For this purpose as a ballast the aluminium powder of mark ПА4, a particle size 150 micrometer. Excess of aluminium in system plays a role of a flame retardant.

Heat effect of a response of aluminothermic reduction WO_3:

$$2/3\ WO_3 + ¾\ Al = 2/3\ W + 2/3\ Al_2O_3$$
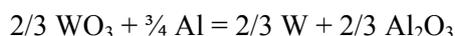
constitutes 559 ± 8 кJoule /mole [2].

For realization of experiments samples with the various contents of aluminium - from 10 % up to 300 %.

The composition history of a blend positively has influenced evolution of process of combustion. Outcomes of experiments have displayed efficiency of injection of the additive of aluminium over a stoichiometry for exchange of detonation of process of stationary.

Combustion speed was determined a tungsten of rhenium by thermoelectric couple. The combustion time consider by formula:

$$\tau = \frac{l}{v},\qquad(1)$$

where l - spacing interval between top and bottom points of indication of thermoelectric couples, sm;

v - speed of movement of paper in the oscillating detector, sm/sec.

The combustion speed was determined from following expression:

$$S = \frac{l_1 \cdot g}{V \cdot \tau},\qquad(2)$$

where l_1 - indication of thermoelectric couples;

g - weight of a blend, g;

V - volume of a blend, sm^2;

τ - time, sec.

Data of experiments are tabulated (Tab. 1). From table 1 it is see, that at the stoichiometric contents of aluminium the combustion speed reaches the maximal value. Thus the response goes detonating, with scatter of a melt. At the further increase of aluminium of speed of decrease and process have quiet character. At a combustion speed of 3,8 - 4,2 g/sm^2s reaction products sinter without stages of separation. In intervals (-10) - (+100) combustion speed is descended within the limits of 10 %. At 150 % she is descended almost in 3 times, and at 300 % - in four. Thus the density of an alloy has the maximal value of 19,1 g/sm^3 at excess of aluminium on 20 %. At the further increase of aluminium the density of an alloy is decrease.

Table 1. Combustion speed of aluminium depending on the contents in a blend of aluminium

№	fusion mixture, г.		overflow of quantity Al above stoichiometric concentration, %	combistion speed, $g/sm^2 \cdot s$	density alloy, g/sm^3
	wolframium trioxide	aluminium			
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	-

Effect of aluminium as the of ballast of additive on arguments of process of combustion is introduced in a figure 1. On a curve of density change the acute maximum testifying to existence of a best value of a deflection of the contents of the additive from a stoichiometric relationship is watched. Injection of aluminium as the ballast additive rationally in quantity from 10 up to 20 %. Thus the combustion speed of 17,4 $g/sm^2 \cdot s$ and density of a metallical phase of 19,1 g/sm^3, that to the greatest degree matches to a clean tungsten (19,3-19,6 g/sm^3).
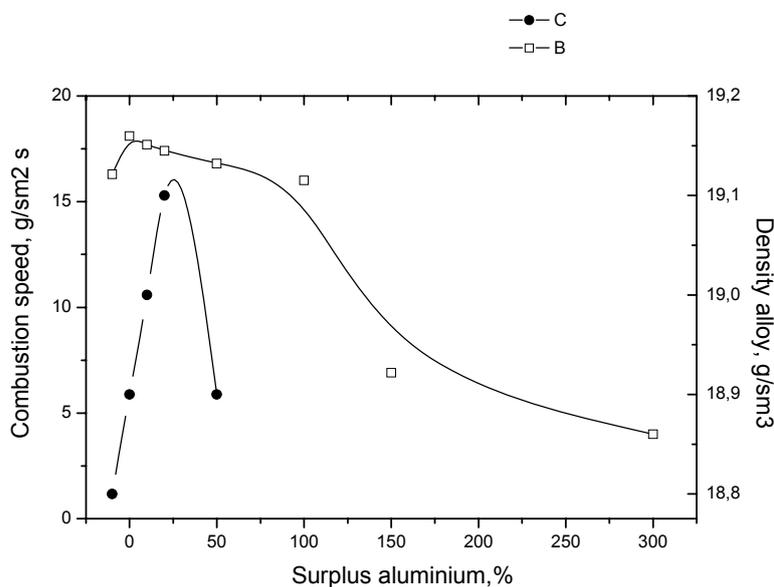
Fig. 1. Dependence of a combustion speed and densities of an alloy from surplus of aliminium

On the basis of the received outcomes of process of combustion of tungsten trioxide with aluminium the possibility of deriving of ferrotungsten from a concentrate wolframite was explored.

DERIVING OF FERROTUNGSTEN FROM CONCENTRATE OF WOLFRAMITE

In this the work use wolframite a concentrate of a following content: WO_3 - 65 %, FeO - 16,47 %, MnO - 7,8 %, SiO_2 - 1,6 %, Cu - 0,12 %, Sn - 0,08 %, MoO_3 - 1,09 %, S - 1,9-2,4 %.

For a desulfurization a concentrate exposed a roast at 750-780 ^{0}C.

The blend consider on 300 g of a concentrate of wolframite. During aluminium of thermal deriving of ferrotungsten of exothermic reactions of recovery will:

$$WO_3 + 2\,Al = W + Al_2O_3 \qquad (3)$$

$$3\,FeO + 2\,Al = 3\,Fe + Al_2O_3 \qquad (4)$$

$$MoO_3 + 2\,Al = Mo + Al_2O_3 \qquad (5)$$

$$3\,SnO_2 + 4\,Al = 3\,Sn + 2\,Al_2O_3 \qquad (6)$$

$$3\,SiO_2 + 4\,Al = 3\,Si + 2\,Al_2O_3 \qquad (7)$$

$$3\,CuO + 2\,Al = 3\,Cu + Al_2O_3 \qquad (8)$$

$$3\,MnO + 2\,Al = 3\,Mn + Al_2O_3 \qquad (9)$$
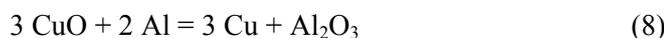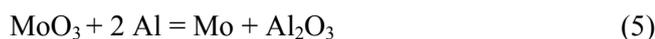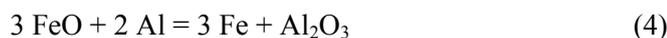
The concentrate of wolframite has a grain size 250 - 300 $\mu\kappa$.

Account of quantity of aluminium for a response was conducted as follows:

in 300 g of wolframite is contained - 195 g WO_3. Molecular weight WO_3 is peer 232 g. On recovery of one molecula WO_3 of 2 moleculas of aluminium, i.e. 54 g of aluminium are indispensable. In 300 g of wolframite 65 % WO_3, that is 195 g are contained. Therefore, the indispensable quantity of aluminium is constituted 195· 54/232 = 45,4 g.

Calculated quantity of aluminium at a shot of a concentrate of wolframite of 300 g 68 g constitutes. Quantity of a parulis (blue john) took at the rate of 15 % of a weight from aluminium. The quantity of iron in a blend was equated 12 g.

The specific heat and operating temperature of smelting aluminiumthermal ferrotungsten for a concentrate of wolframite have been determined. At a response give off heat quantity Q in (kcal) is:

$$WO_3 \rightarrow W \quad 300 \cdot 0,65 \cdot 865 = 168675$$

$$MoO_3 \rightarrow Mo \quad 300 \cdot 0,0109 \cdot 1515 = 4954,0$$

$$SiO_2 \rightarrow Si \quad 300 \cdot 0,016 \cdot 973 = 4670,4$$

$$FeO \rightarrow Fe \quad 300 \cdot 0,1647 \cdot 956 = 47326$$

$$MnO \rightarrow Mn \quad 300 \cdot 0,078 \cdot 875 = 20475$$

total: Q – 246010 kcal

On the basis of these data the specific heat of process by formula has been calculated:

$$\delta H = \frac{Q}{m} \qquad (10)$$

$$\delta H = \frac{246010}{300 + 75 + 12} = 636 \quad \text{(kcal/g or 2661 kJoule/g)},$$

where 246010 - an exotherm, 300 g - a weight вольфрамитового a concentrate, 75 g - a weight of aluminium, 12 g - a weight of iron.

For determination of temperature of combustion of process of (T_p) used thermic coefficient V.A.Bogolyubov [9] which one is peer 0,32.

$$T_{пр} = \delta H / 0,32. \qquad (11)$$

The received value of operating temperature T_p = 1986 ^{0}C considerably below temperature metered by means of a tungsten-rhenium thermoelectric couple (2450 - 2500 ^{0}C) [10, 13].

Proceeding from quantity of gram-atoms of a blend, the specific heat and an operating temperature have been calculated:

$$\delta H' = 140,9 \text{ kJoule/g atom,}$$

$$T_p = 11,6 \cdot \delta H' + 1400 = 3104 \text{ K}$$

Using literary data [4] we shall receive:

$$Lg\, Q' = \frac{T_{ox}}{3770} + 2,95 = 3,412, \qquad (12)$$

where T_{oxide} = 1743 K.

At the same time Q - the specific heat of aluminothermic process referred to 1 kg of a blend, is peer:

$$Q = 2930 \text{ kJoule/kg.}$$

At such value of specific heat Q the system is heated up up to higher temperature, than a fusion point of oxides and iron ($T_f \rightarrow WO_3$ - 1743 K, FeO - 1644 K, Mo_3 - 1068 K, MnO - 1923 K, SiO - 1986 K, Fe - 1802 K) [14].

Burden constituents carefully intermixed, insert in the reactor from not roasted porcelain and pressed together. Burn of admixtures made nickel-chrom a spiral. Very stormy combustion with spread of a melt was watched. The output of an alloy constituted the little more than 80 %. As the ballast component used an aluminium oxide.

In a table 2 outcomes of experiments is shown and in a fig. 2 of influence of quantity of a ballast on an output of an alloy is shown. Injection of a ballast already in quantity of 10 g contributes in gain in yield of an alloy almost on 7,0 %. Tall outcomes are received on additive in a blend of an aluminium oxide of 20 g.

Table 2. Influence of quantity of ballasting component Al$_2$O$_3$ on an output of an alloy

№	charge makeup, g					weight alloy, g	settlement weight alloy, g	yield. %
	concentrate	Fe	Al	blue john	aluminium oxide			
1	300	12	75	11	-	174,2	217	80,3
2	300	12	75	11	10	187,0	217	86,6
3	300	12	75	11	15	195,0	217	89,4
4	300	12	75	11	20	200,9	217	92,6
5	300	12	75	11	25	198,5	217	91,5

Further as a ballast used milled scoria from the previous smelts. In table 3 outcomes of calculation of a composition of an alloy and masses of an ingot. The contents of a tungsten in a an actual ingot and scoria determined method of X-ray analysis.
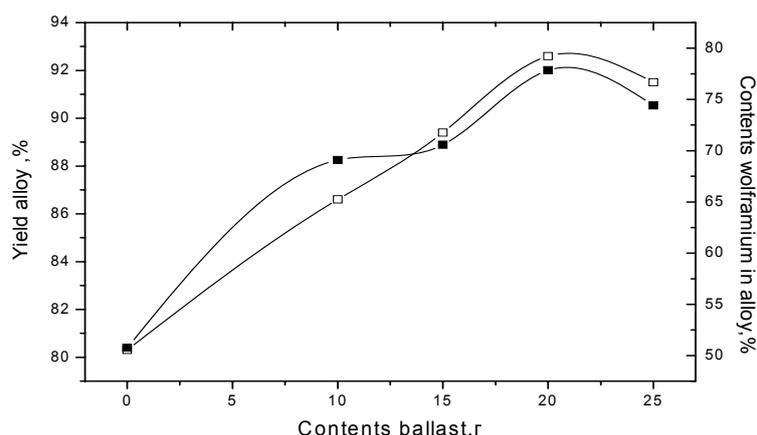
Fig. 2 - Influence of quantity of ballasting component Al$_2$O$_3$ on an output alloy and the contents of a wolframium in an alloy

In table 3 dependence of the contents of a wolframium in scoria and an alloy from quantity of ballasting introduced into a blend. Both experiments are yielded with higher indexes of process.

Table 3. Influence of quantity of a ballast on the contents of a wolframium in an alloy

№	charge makeup, g					weight alloy, g	settlement weight ingot, g	settlement weight alloy, %		The contents in an scoria, %	The contents W in an alloy, %
	Fe	concentrate	Al	blue john	scoria			W	Fe		
1	12	300	75	11	-	174	217	73	27	2,4	50,75
2	12	300	75	11	10	187	217	73	27	1,89	69,08
3	12	300	75	11	15	195	217	73	27	1,07	70,58
4	12	300	75	11	20	200	217	73	27	0,3	77,86
5	12	300	75	11	25	198	217	73	27	0,9	74,42

At injection of a ballast of 10 g the contents of a tungsten in scoria is descended on 21 %, and in an alloy is increase by 26,5 %. It show build-down of losses of deficient both cost intensive metal and economic benefit of utilization of ballastings material. It is fixed, that the increase of the additive over 20 g is led to build-down of an output of an alloy and extraction of metal (Table 4).

Table 4. Charge makeup

№	charge makeup, %							Output of an alloy, %	Contents W in an alloy, %
	raw material contained wolframium	Fe_2O_3	NH_4NO_3	KNO_3	$NaNO_3$	Al	blue john		
1	58,4	9,2	–	–	–	28,2	4,2	–	–
2	59,2	2,8	17,8	–	–	17,3	2,9	50	32
3	54,55	2,4	–	21,8	–	18,2	3,05	96	36-43
4	54,55	2,4	–	–	21,8	18,2	3,05	93	36-43

It is revealed, that at reduction responses in system there was a chilling effect of combustion of a blend. A reason in heat waste on heat up and a melting of a great quantity of a ballast at enough high speed of process.

The received alloys analysed on a x-ray spectrometer (Table 5).

Table 5. Composition of alloys

№*	elements, %									
	Al	Si	Ti	Cr	Mn	Fe	Co	Mo	Cu	W
3	3,18	27,97	2,47	0,18	0,13	17,35	5,19	0,28	0,54	36,61
4	1,57	27,00	2,67	0,23	0,21	16,59	6,32	1,47	0,27	43,27

*Numbers in table 6 match to numbers of experiments in table 4.

CONCLUSIONS

1. Limits and a combustion speed of system WO_3+Al are determined at a mixture weakening by excess of aluminium (table 1, figure 1).

2. Heat effects and temperatures of processes for deriving ferrotungsten from a concentrate are calculated.

3. Charge makeup from various raw material are calculated.

4. Experiments on the calculated charge makeup (tables 2, 4) are make.

5. Influence of the ballasting additive on an output of an alloy and extraction of target metal (table 3, figure 2) is establish.

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