SINTERING OF A FINE FRACTION FROM "GRANCHARITSA" DEPOSIT IN LABORATORY CONDITIONS

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ABSTRACT

The possibilities for sintering a fine scheelite concentrate containing a significant amount of tungsten in the form of calcium tungstate ($CaWO_{\downarrow}$) were considered. Scheelite originates from the Grncharitsa deposit, located near the town of Velingrad, Bulgaria The scheelite fine fraction was obtained after numerous technological and transport operations of the coarse fraction, as well as after flotation treatment of scheelite raw material. Experimentation is at the laboratory level. The influence of flux on the agglomeration process was established. Studies without flux have been also done. High-temperature metallurgical equipment was used, through which it is possible to follow the results of the process of thermal coagulation (sintering) of the charge materials. The used methodology of conducting the experiments is close to that of the classic agglomeration process in terms of thermal partial melting of the particles of the charge, by burning soot carbon, but without permeation of air through the layer of the charge (laboratory crucibles have a relatively small working volume and it was assumed that air in and above the charge will be sufficient). The main goal is to obtain a qualitative sinter and to draw conclusions regarding the processing of the scheelite fine fraction in a larger-scale apparatus, for example agglomeration.

Keywords: tungsten concentrate (sheelite), agglomeration, sinter product, coke fines, high-temperature equipment.

INTRODUCTION

Tungsten, used in the form of ferrotungsten, is one of the most important alloying elements in the production of special steels. By arresting grain growth when heated and creating a fine-grained structure, tungsten increases the steel's hardness, strength limit and ductility. 15 different minerals of tungsten are known, but two minerals are mainly of industrial importance - wolframite and scheelite. Wolframite is a solid solution of iron and manganese tungstates (Fe, Mn)WO₄. Scheelite contains calcium tungstate CaWO₄. The rich tungsten ores contain from 0.2 to 2.0 % WO₃ [1 - 4]. Currently, ferrotungsten is not produced in our country. When alloying to obtain quality steels, an imported one is used.

On the other hand, our country is home to one of the richest tungsten deposits in Europe - the Grncharitsa deposit near the Velingrad village of Krastava, Bulgaria. In recent years, it has been the object of investment interest, with a developed project and planned investments in the amount of about BGN 150 million. According to the project, the tungsten raw material will be mined underground. The mineral to be mined is scheelite (CaWO₄). It is a combination of calcium oxide and tungsten trioxide (CaO.WO₂), the latter being a raw material for obtaining ferrotungsten. Also according to the project, processing will take place after transportation to an existing factory in the village of Elshitsa. The project was developed jointly with the Austrian company Wolfram, which has experience in mining tungsten raw material in the city of Kitzbühel, Austria [5 - 7]. Due to the numerous technological and transport operations during the implementation of the tungsten concentrate mining project, a large volume of fine fractions will be obtained. These fractions together with the fractions from the flotation treatment are expected to be over 15 % of the total yield. Such fractions, on the one hand, contain a high percentage of tungsten raw material, and on the other hand, if they are not utilized, they will pollute the environment.

EXPERIMENTAL

General characteristics of the scheelite raw material and determination of the amount of fuel

A general view of a piece of the scheelite mineral from the Grancharitsa deposit is illustrated in Fig. 1.

Table 1 shows the chemical composition of scheelite after flotation treatment.

The presence of MoO₃ gives a dark color to the tungsten raw material.

Tungsten fines from scheelite concentrate after flotation treatment is presented in Fig. 2.

Until now, in our country, no experiments have been conducted in terms of agglomeration of scheelite concentrate. The worldwide information is mainly in the area of pre-treatment of tungsten concentrates, by briquetting. During briquetting, a solid product is obtained, but without a fuel element in it, because such a product is then directly reduced by a carbothermal or metallothermal method to obtain metallic tungsten or ferrotungsten. This feature makes it difficult to estimate the initial amount of fuel when using another method of concreting, for example, sintering by burning coke fines inside the charge or sintering by agglomeration method. Therefore, the percentage of fuel confirmed in the agro-practice of solidification of iron-containing raw materials for obtaining iron and its alloys is set as the initial amount of fuel [8 - 13]. This percentage is usually in the range of 6 to 10 % (average about 8 %), depending on the preliminary agglomeration calculations. At the beginning of the experiment it is convenient to double the amount of fuel, i.e. about 16 %, because of the significant heat losses that can be expected during a purely laboratory agglomeration process, as well as because of the relatively higher initial melting temperature of WO₂, accordingly with its thermodinamic line compared to that of iron oxides [14 - 16, 18].

Sintering of scheelite fine fraction with flux

As a result of the determined amount of fuel, experiments were conducted to obtain an agglomerate product from scheelite fines with and without the addition of flux [3, 4, 14, 17]. The fluxed charge consists of tungsten scheelite concentrate, limestone and coke fines. For this purpose, a high-temperature superkanthal furnace and crucibles, each with a working volume of 71.22 cm³, were used.



Fig. 1. Scheelite from the Grancharitsa deposit.

Table 1. Chemical composition of scheelite from the Grancharitsa deposit after flotation.

Chemical composition, %						
WO ₃	FeO	CaO	SiO ₂	As	MoO ₃	others
68.78	1.30	21.17	3.88	0.01	3.39	1.46



Fig. 2. Tungsten concentrate (fines) after flotation originating from the Grncharitsa deposit.

A sieve analysis was performed of the charge materials. The limestone is pre-ground to a coarse fineness from the tungsten deposit during its extraction. This is for the purpose of more intense contact between the individual particles in the sintering process. The fractional composition of the two ingredients is as follows:

- fraction over 1 mm 10 %;
- fraction 0.1 mm 1.0 mm 70 %;
- fraction below 0.1 mm 20 %.

The coke fines are selected with a larger size in order to ensure the necessary porosity of the charge with a view to the optimal combustion process. Its fractional composition is:

- fraction below 1 mm 25 %;
- fraction 1.0 mm 5.0 mm 50 %;
- fraction over 5.0 mm 25 %.

The amount of the charge was calculated, relatively to the volume of the crucibles used. For safer handling, they are filled to a maximum of 75 % of their working volume or 53.42 cm³.

Thus, for experiment No. 1 (E1), the amount of the charge is obtained:

$$m_{ch} = m_{t.c.} + m_{lim.} + m_{c.f.}$$
 (1)

where: $m_{ch.}$ - total mass of the charge, g; $m_{t.c.}$ - amount of tungsten concentrate, g;

 $m_{lim.}$ - amount of limestone, g; $m_{c.f.}$ - amount of coke fines, g.

The amount of tungsten scheelite concentrate $(m_{t.c.})$ is calculated by the formula:

$$m_{t.c.} = (\frac{V_{c.} \cdot M_{t.c.}}{100}) \rho_{t.c.}$$
 (2)

where: $V_{c.}$ - working volume of the crucible (53.42), cm³; $M_{t.c.}$ - amount of tungsten in the charge compared to the rest of the components, %; $\rho_{t.c.}$ - bulk density of tungsten concentrate (6.00), g/cm³.

The amount of limestone is calculated using the formula:

$$m_{lim.} = (\frac{V_{c.} \cdot M_{lim.}}{100}) \rho_{lim.}$$
 (3)

where: V_c - working volume of the crucible (53.42), cm³; $M_{lim.}$ - amount of limestone in the charge relative to the other components, %; $\rho_{lim.}$ - bulk density of limestone (2.00), g/cm³.

The amount of coke fines is calculated by the formula:

$$m_{c.f.} = (\frac{V_{c.}.M_{c.f.}}{100})\rho_{c.f.}$$
 (4)

where: V_c - working volume of the crucible (53.42), cm³; $M_{c.f.}$ - amount of coke fines in the charge compared to other components, %; $\rho_{c.f.}$ - bulk density of coke fines (0.80), g/cm³.

After substitution and calculation, it turns out that: Tungsten scheelite concentrate - 76 % or 243.60 g; Limestone - 8 % or 8.54 g; Coke fines - 16 % or 6.84 g. The charge for E1 has a total weight of - $m_{ch.}$ = 258.98 g.

The next operation is its drying in a dryer at a temperature of 150°C and holding for 15 min. After



Fig. 3. Top view of a dried charge crucible.

removing the moisture, the charge is ready for loading into a crucible and subsequent high-temperature agglomerate processing.

A crucible with a charge loaded into it after preliminary low-temperature treatment is shown in Fig. 3. After high-temperature processing and reaching a temperature of 1200°C, the crucible was held for 20 min. After removing it from the furnace and cooling it, an inspection and sieve analysis of the sinter was made. The result of the sieve analysis is that the fractional composition of the mixture in the crucible is identical to that of the charge before the high-temperature sintering, i.e. the charge does not agglomerate.

This made it necessary to envisage several more experiments analogous to the first one, without changing the flux, but with an increased amount of fuel in steps of 5 %, in accordance with well-established agglomerating practices worldwide and dependencies (1 - 4). Thus, the charge for experiments No. 2 - 5 (E2, E3, E4 and E5) has the composition indicated below:

For E2: Tungsten scheelite concentrate - 71 % or 227.57 g; limestone - 8% or 8.54 g; coke fines -21 % or 8.98 g. The charge for E2 has a total weight of - $m_{ch.}$ = 245.09 g.

For E3: Tungsten scheelite concentrate - 66 % or 211.54 g; limestone - 8% or 8.54 g; coke fines - 26 % or 11.11 g. The charge for E3 has a total weight of - $m_{ch.}$ = 231.19 g.

For E4: Tungsten scheelite concentrate - 61 % or 195.52 g; limestone - 8% or 8.54 g; coke fines - 31 % or 13.25 g. The charge for E4 has a total weight of - $m_{ch.}$ = 217.31 g.

For E5: Tungsten scheelite concentrate -56% or 179.49 g; limestone - 8% or 8.54 g; coke fines - 36 % or 15.39g. The charge for E5 has a total weight of - $m_{ch.}$ = 203.42 g.

After the completion of the experiments, despite the increased amount of fuel and maintaining the same temperature regime, the results for E2, E3, E4 and E5 are of the same nature as for E1. The resulting brittle structures retain a fluid appearance similar to the starting charge. After weight analysis the percentages of solid and gas phases are:

For E1: solid phase - 94.29 %; gas phase - 5.71 %. For E2: solid phase - 90.67 %; gas phase - 9.33 %. For E3: solid phase - 87.05%; gas phase - 12.95 %. For E4: solid phase - 83.43 %; gas phase - 16.57 %. For E5: solid phase - 79.81 %; gas phase - 20.19 %.

Sintering of tungsten concentrate fine fraction without flux

As a result of the unsatisfactory results of the experiments with fluxed charge, five more experiments were conducted without fluxing the charge. The same temperature conditions, technical equipment, technological management of the process and characteristics of the charge materials are preserved [3, 4, 14, 17]. In accordance with the predetermined fuel, the step of increasing the amount of coke fines in the charge was also maintained for the individual experiments, similar to the flux experiments.

Thus, for E6, the amount of the charge is: Tungsten scheelite concentrate - 84 % or 269.24 g; coke fines - 16 % or 6.84 g. The charge for E6 has a total weight of - m_{ch} = 276.08 g.

For E7: Tungsten scheelite concentrate - 79 % or 253.21 g; coke fines - 21 % or 8.98 g. The charge for E7 has a total weight of - $m_{ch} = 262.19$ g.

For E8: Tungsten scheelite concentrate - 74 % or 237.19 g; coke fines - 26 % or 11.11 g. The charge for E8 has a total weight of - m_{ch} = 248.30 g.

For E9: Tungsten scheelite concentrate - 69 % or 221.16 g; coke fines - 31 % or 13.25 g. The charge for E9 has a total weight of - m_{ch} = 234.41 g.

For E10: Tungsten scheelite concentrate - 64 % or 205.13 g; coke fines - 36 % or 15.39 g. The charge for E10 has a total weight of - m_{ch} = 220.52 g.

A total of five experiments were performed for the five calculated charges (Fig. 4), the crucibles were removed from the furnace and cooled to room temperature, Fig. 5.

The resulting annealed products for experiments E6 and E7 are shown in Figs. 6 and 7, respectively. The resulting product of E9 and E10 is approximately the same as that of E8 (Fig. 8).

Fractional analysis was performed on the five sinter



Fig. 4. Moment from E6.



Fig. 5. Cooling of unfluxed sinter after E10.



Fig. 6. Sinter from E6.



Fig. 7. Sinter from E7.



Fig. 8. Sinter from E8.

products. After determination of the weight of the individual fractions was calculated their percentages shown below.

For E6:

- fraction below 5.0 mm 55 %;
- fraction 5.0 mm 20.0 mm 5 %;
- fraction over 20.0 mm 40 %. For E7:
- fraction below 5.0 mm 5 %;
- fraction 5.0 mm 20.0 mm 5 %;
- fraction over 20.0 mm 90 %. For E8:
- fraction below 5.0 mm 3 %;
- fraction 5.0 mm 20.0 mm 2 %;
- fraction over 20.0 mm 95 %. For E9:
- fraction below 5.0 mm 2 %;
- fraction 5.0 mm 20.0 mm 2 %;
- fraction over 20.0 mm 96 %. For E10:
- fraction below 5.0 mm 1 %;
- fraction 5.0 mm 20.0 mm 1 %;
- fraction over 20.0 mm 98 %.

According to the obtained products and their fractional composition, it can be considered that the E7 sinter is the optimal for subsequent processing to metal. In the agglomerated products of E8, E9 and E10, fraction +20 mm, a glass phase composed mainly of calcium silicates is observed.

The obtained products were analyzed by weight. The percentage amounts of the solid and gas phases are as follows:

For E6: solid phase - 94.98 %; gas phase - 5.02 %. For E7: solid phase - 91.90 %; gas phase - 8.10 %. For E8: solid phase - 88.96 %; gas phase - 11.04 %. For E9: solid phase - 86.81 %; gas phase - 13.19 %. For E10: solid phase - 84.93 %; gas phase - 15.07 %.

RESULTS AND DISCUSSION

The choice of temperature regime during the experiments is consistent with the agglomeration practice in the agglomeration of iron-containing charges. The optimum temperature of 1200°C is sufficient to obtain an agglomerated sinter of scheelite tungsten concentrate in the no-flux experiments. A subsequent increase can lead to an intense reduction of the FeO contained in the charge, as well as the formation of iron silicates, which would lead to excessive wetting of the rest of the charge subjected to agglomeration. This, in turn, will not lead to an energy-efficient process in obtaining liquid metal from the sinter.

The obtained solid phase in experiments without flux is within the expected amount - for E6 it is 94.98 %, for E7 it is 91.90 %, for E8 it is 88.96 %, for E9 it is 86.81 %, for E10 it is 84.93 %. The gas phase was formed primarily by the smoldering of the coke fines, as well as by minimal flaming of the coke carbon observed during the experiments. This process is a consequence of partial coagulation of coke particles during the mixing to form the starting charge. It is primarily due to an insufficiently dried charge, which gives reason to increase the drying time of the charge, which is the same in all experiments. In experiments with the addition of limestone, the gas phase is more abundant, due to the dissociation of CaCO₃ and release of CO₂.

Fig. 8 clearly shows the formation, apart from the optimally obtained sinter, of a glass phase of the type of calcium silicates. It is determined by the presence of a certain percentage of SiO₂ in the scheelite, as well as

a significant amount of natural CaO. This suggests that dissociation of CaO from CaWO₄ takes place, passing into the slag phase together with SiO₂. The temperature of such separation has not yet been specified. Another factor for obtaining calcium silicate is the increased amount of fuel compared to experiments

E6 and E7, which leads to a more intensive formation of silicate compounds. In this way, the processed to agglomerated sinter charges from experiments E8, E9 and E10 are rather unsuitable for obtaining metal from them. This is because the glass phase is generally better not to be produced in such a large quantity while creating the agglomerated product. It is better to obtain this phase during high-temperature processing of sinter to metal so that it can be the main part of the slag. With E6, the charge, according to the fractional analysis, will also not be suitable for further processing, due to the large amount of relatively fine solid phase.

From the research done, E7 turns out to be the experiment with the relatively optimal final result. In further experiments, the chemical composition and strength indicators will be established, after obtaining a sufficient amount of product using the E7 technology.

CONCLUSIONS

As a result of the experiments, the following conclusions can be made:

- Sintering with a flux charge does not give a significant result. Subsequent experiments on obtaining a fluxed sinter must be conducted after preliminary consideration of CaO from tungsten concentrate, through which the sinter self-fluxed to some extent.
- The processing of an unfluxed charge leads to the production of an agglomerated product with an optimal fractional composition. The sinter is suitable for subsequent processing to metal.
- The selected temperature regime during the sintering of a fluxless charge is sufficient to ensure the production of a sintering product. The temperature mode of drying the charge should be slightly changed in subsequent experiments in the direction of increasing the retention time of the drying charge at a temperature of 150°C.
- An actual amount of fuel of 21 % in the charge was determined to obtain an agglomerated product, with

- an optimal amount of glass phase and a suitable fractional composition.
- The obtained results are the basis for conducting a large-scale agglomeration process of the scheelite raw material.

REFERENCES

- 1. L. Genov, M. Maneva, Neorganichna himia II, Sofia., Nauka i izkustvo, 1990, (in Bulgarian).
- 2. https://bg.wikipedia.org/wiki/
- 3. H. Erinin, A. Avramov, Metalurgia na ferosplavite, Sofia, Tehnika, 1979, (in Bulgarian).
- 4. M. Gasik, N. Liakishev, B. Emlin, Teoria I tehnologia proizvodstva ferosplavav, Moskva, Metalurgia, 1988, (in Russian).
- https://www.me.government.bg/bg/themes/vaprosotnosno-ikonomicheskata-ocenka-na-proekt-zarazrabotka-na-volframovo-nahodishte-v-raiona-naveli-1493-0.html
- https://dv.parliament.bg/DVWeb/showMaterialDV. jsp;jsessionid=6F9A5D971EEBC3BA99BE781D7 1680362?idMat=21069
- 7. https://obuch.info/na-resurs-1-ad-za-izvrshvane-na-detajlno-doprouchvane-na-volfr.html?page=7
- 8. M. Rais, Proizvodstva ferosplavav, Moskva, Metalurgia, 1985, (in Russian).
- 9. A. Balevski, Metaloznanie, Sofia, Tehnika, 1988, (in Bulgarian).
- 10. https://www.iico.ru
- 11. https://www.vtorlomet.ru/ferrovolfram
- 12. https://www.asianmetal.com
- 13.http://www.mgu.bg/drugi/ebooks/mt/mineralogia_62-257.pdf
- 14. I. Valchev, Ts. Tsanev, Rakovodstvo za uprazhnenia po metalurgia na chuguna, Sofia, Tehnika, 1979, (in Bulgarian).
- 15.L. Belianchikov, I. Mokrov, Posobie po razchetu materialnova teplova balansov plavki pri proizvodstve ferosplavav, Moskva, MISiS, 1980, (in Russian).
- 16. U. Usfin, N. Pashkov, Metalurgii zheleza, Moskva, Akademkniga, 2007, (in Russian).
- 17. A. Stroganov, M. Rais, Proizvodstvastali i ferosplavav, Moskva, Metalurgia, 1979, (in Russian).
- 18.S. Bratchikov, Teplotehnika okuskavania zhelezorudnova sairia, Moskva, Metalurgia, 1970, (in Russian).