



Article

Physical and Chemical Studies of Smelting Products of Calcinated Composite Pellets Produced from Chromium Production Waste

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Abstract: This study presents the results of the enlarged laboratory research on the melting of calcined composite pellets for ferrochrome obtained from fine-dispersed conditioned chrome concentrate containing 50.3% Cr_2O_3 . This is a product of the gravitational beneficiation of waste sludge tailings from the Dubersay tailings dump at the Donskoy Mining and Processing Plant (DMPP) of JSC “TNC Kazchrome”. The composition of the charge for obtaining composite pellets consisted of 88.5% of chrome concentrate, 3% of mineral part of refined ferrochrome slag (RFC), 4% of ferruginous diatomite, 3% of coke and 1.5% of liquid glass. The initial charge was pelletized on a laboratory pelletizer to a size of 6–10 mm, dried at room temperature for 24 h and fired at 1200 °C for 60 min at a heating rate of 15 deg/min. On the basis of the developed composite annealed pellets, studies on the production of high-carbon ferrochrome at different melting temperatures were carried out. The results showed that with an increase in temperature from 1750 to 1850 °C, the iron–chromium phase in the composition of the alloy increases from 45.2 to 50.1%, the chromium carbide phase decreases from 23.7 to 11.3% and the chromium–iron phase increases from 7 to 11.2%. The carbon content in the alloys at temperatures from 1750 to 1850 °C varies from 7.2 to 8.94%, respectively. The maximum chromium content of the alloy is 64.82% with a melting point of 1850 °C; this alloy can be classified as FeCr60C90LP grade ferrochrome according to the international Chinese standard, which has no more than 0.03% phosphorus and no more than 0.1% sulfur.

Keywords: chromium production waste; chromium concentrate; compositional pellets; smelting; ferrochromium; slag



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1. Introduction

Long-term development of ore deposits associated with mining, beneficiation and metallurgical smelting leads to the accumulation of a large amount of waste in the form of stockpiled beneficiation tailings and metallurgical slags, dumps of substandard ores, industrial effluents, forming large-scale dumps and water settler-storers and technogenic mineral formations [1].

In Kazakhstan, this problem is of particular concern due to the resource extraction and processing orientation of the industrial complex, accompanied by significant volumes of waste generation [2].

The accumulated reserves of valuable components in tailings are comparable in terms of the volume of accumulation and the content of valuable components with natural deposits, which determine the expediency of classifying them as man-made deposits. Mining wastes (overburden dumps, mill tailings, smelter slags and sludge and ash from thermal power plants) are often of high industrial value. Production from mining waste is two–four times cheaper than from a natural deposit, and the payback on capital investment usually does not exceed 1–2 years [3]. Technogenic wastes have passed all stages of

extraction and beneficiation and are stored in tailings ponds so that they do not incur additional costs for extraction, operation of an open pit or mine and ore preparation (crushing and grinding), which is the economic feasibility of processing this raw material.

The main area of chromium and ferrochromium application is the smelting of alloyed steels, chromium bronzes and cast irons of special alloys. Corrosion-resistant steels and alloys can contain up to 30–40% Cr. The addition of up to 3% Cr to conventional carbon steels significantly improves their mechanical properties [4–6]. Steels containing 5–6% Cr are characterized by increased corrosion resistance. Steels undertake high corrosion resistance at 10% chromium content.

Kazakhstan ranks second in terms of quantities of the raw material base. Its contribution to the world production of commercial chrome ores is 15–20%. The most significant part of Kazakhstan's chromite reserves is explored in the Kempirsay massif deposits. The average content of Cr_2O_3 in these ores reaches 50%, and the content of iron and harmful impurities (phosphorus and sulphur) is very low. According to a report from the U.S. Geological Survey, the world's chromium resources are concentrated in Kazakhstan, South Africa and India, which produce the bulk of the world's ferrochromium. The analysis of prices for ferrochrome suggests that all grades of ferrochromium are in demand and their prices are growing at a fairly high rate [7,8].

The current state of research in the field of ferroalloy production technologies, as well as the environmental aspects of their production, are discussed in [9–11].

The ferroalloy production concepts have been analysed with the involvement of new data on thermodynamics, kinetics and mechanisms of reduction melting processes. An overview of the sources of chromium raw materials and methods for the reduction of chromium with carbon, silicon and aluminium is given.

An increase in the dispersion of chromium concentrates during electric arc melting of raw materials in alternating current furnaces leads to a decrease in the technical and economic indicators of the processes. To solve this problem, preliminary agglomeration of raw materials is required to obtain a product for melting in electric arc furnaces [12–14].

The main technologies for agglomeration of chrome raw materials include agglomeration, briquetting and granulation. All these technologies were implemented on an industrial scale at the enterprises of TNC Kazchrome JSC (Transnational Company Kazakhstan Chrome) at different times; however, the planned indicators have not been achieved. Also, a high extraction of Cr_2O_3 from the feedstock (no more than 66%) has not been achieved due to inefficient equipment used for gravity enrichment of fine fractions of raw materials.

Technologies for agglomeration of finely dispersed chromium raw materials were introduced, and technologies for roasting "raw" pellets are also being sought to obtain strong pellets with the least formation of defective pellets at the enterprises of TNC Kazchrome JSC [15,16].

The authors of [17] report that since the mid-2000s, the production volume of carbonaceous ferrochrome at the Aksu Ferroalloy Plant of TNK Kazchrome JSC has significantly increased. The involvement in the processing of substandard ore raw materials caused the necessity of working the parameters of a rational smelting technology: determining effective types of carbonaceous reducing agents and improving the quality of the electrode mass to ensure the normal operation of self-baking furnace electrodes.

The authors of [18] present the results of tests on the use of a briquette mono charge in the smelting of carbon ferrochromium. The briquettes charge contained chromium ore, production wastes of high-carbon ferrochromium, intermediate products and various carbonaceous reducing agents. The use of briquettes made it possible to repeatedly increase the contact surface of the reducing agent and ore, which led to the forcing of the technological process.

The authors of [19] present the results of a study on the sintering of chromite fines with the determination of the influence of such factors as the dispersion and dosage of coke fines, the moisture content of the sinter charge and the duration of

ignition on the efficiency of sintering of fine chromite. It is shown that the sintering of chromite fines is characterized by a higher sintering temperature (1450–1500 °C) and a longer cooling time compared to iron ores. The mechanism of consolidation of the chromite agglomerate was determined using a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS). It was found that the consolidation of chromite agglomerate mainly depends on the presence of the liquid phase of olivine along with solid-phase reactions and recrystallization of Cr_2O_3 , which contribute to the strength of the agglomerate.

In [20], a technology for agglomeration of iron ore minerals was proposed and tested, in which cheaper Callovian clays are used as a material for agglomeration.

The idea of using silica-containing wastes as fluxes for producing iron ore pellets is described in [21,22]. Kazakh scientists also proposed to produce ferrofluxing binders for producing strong chromium pellets [23–28].

The presented article is devoted to the so-called slurry tailings of chrome ore beneficiation at the DMPP of “TNC Kazchrome” JSC. This is one of the largest enterprises in the ferroalloy industry in Kazakhstan.

More than 5 million tons of chrome ore are mined here and about 1.8 million tons of ferroalloys are produced per year. The tailings of chrome ore concentration are a waste product and are stored in tailings ponds. Chromium ore tailings contain up to 30% of under-extracted Cr_2O_3 . Tens of millions of tonnes of chrome waste have already accumulated in such tailings ponds. Such wastes being a fine-dispersed product negatively affect the ecological situation in the region and in the case of their processing can be secondary mineral resources (so-called technogenic mineral deposits of chromium raw materials). In our previously published work [29] the results on gravitational enrichment of chrome tailings with obtaining of conditioned fine chrome concentrate are given. However, fine chromite concentrate cannot be used for smelting ferrochrome in AC electric arc furnaces, as it will lead to an increase in dust emission into the gas duct system of furnace units, which will increase the amount of circulating intermediate products.

More details on the charge composition and fluxing components were published in articles [24,25]. An insignificant number of fluxing components during pellet firing favours the formation of fusible iron–calcium silicate compounds, which is confirmed by X-ray phase analysis and electron microscopy. On the basis of the established physicochemical transformations in the composition of the charge of fired pellets the formation of fusible compounds takes place, which harden the pellets to the required strength. Special coke sifts contribute to the temperature increase during pellets firing and partially restore iron and chromium metal oxides during their out-of-furnace treatment, which increases economic indicators of the subsequent smelting of metallurgical raw materials. Figure 1 shows a schematic diagram of the apparatus chain of aggregate-laboratory test apparatus for the production of high-carbon ferrochrome from slurry tailings of DMPP.

The task of the developed technology is to obtain a fine chromium concentrate from chrome ore tailings, then select the charge components, pelletise the obtained fine conditioned chromium concentrate with fluxing components, obtain durable fired pellets and smelt high-carbon ferrochrome from them.

The purpose of this work is to study the physicochemical properties of melting products of durable composite pellets obtained from technogenic waste of chromium production. In the manufacture of composite pellets inexpensive natural raw materials such as ferruginous diatomites, as well as chromium production waste as a flux in the form of mineral part of refined ferrochromium slag, freed from metal corollas, were used.

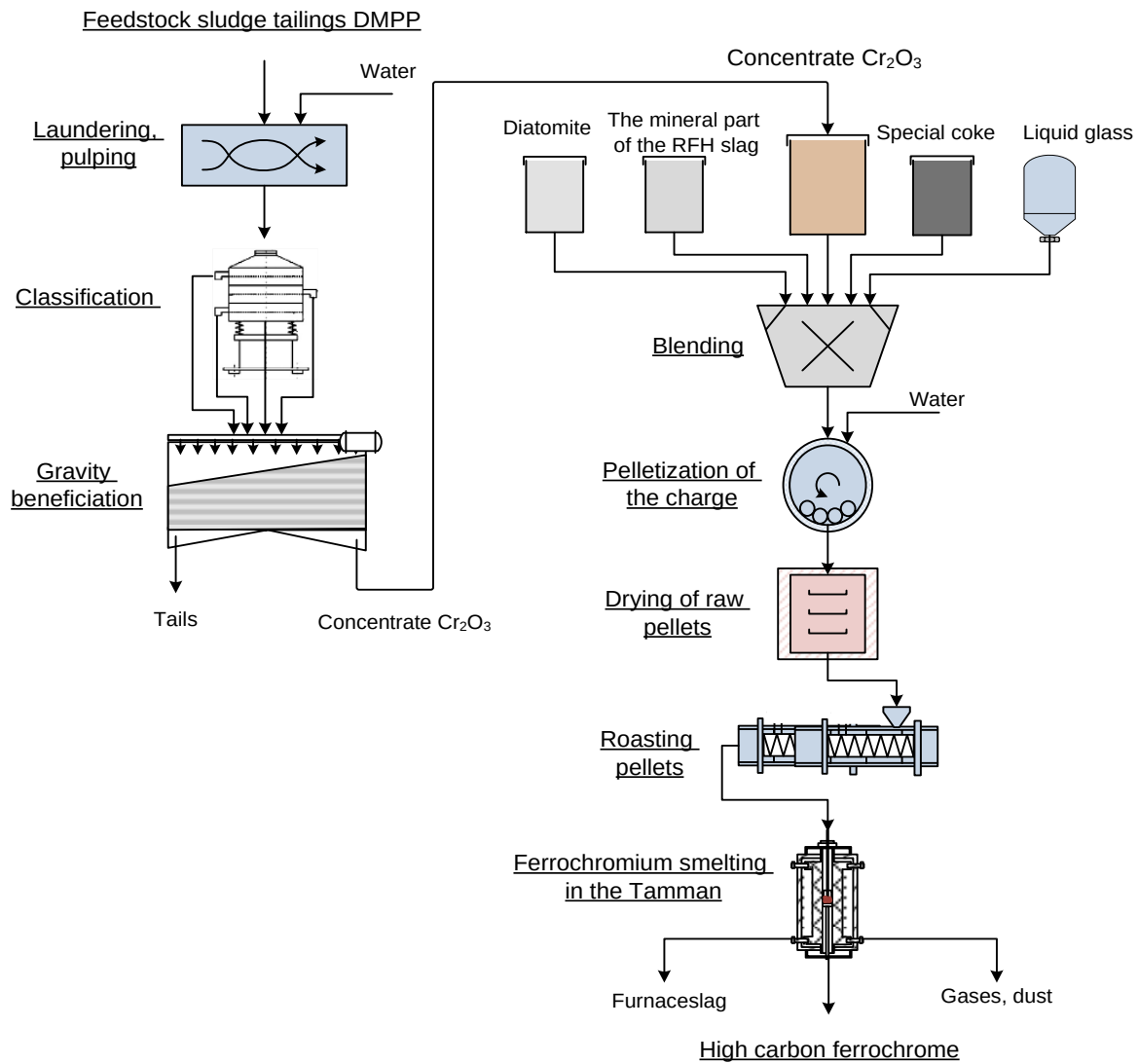


Figure 1. Schematic of enlarged laboratory tests of the technology for production of composite chrome pellets from finely dispersed chrome concentrate with their melting to ferrochrome.

2. Materials and Methods

Materials and equipment: technological sample of sludge tailings of the DMPP of the Dubersay tailing dump of the Republic of Kazakhstan. The chemical composition of the sludge, wt.%: 18.9 Cr, 7.9 Si, 2.4 Al, 0.4 Ca, 15.5 Mg, 9.1 Fe, 0.17 Ti, 0.049 S, 0.002 Zn, 0.002 Cu, 0.14 Ni, 0.05 K₂O. Table 1 shows the chemical composition of the chromium concentrate produced after gravity beneficiation on a concentration table. The solid components of the charge were crushed in a laboratory mixer and sieved on a laboratory sieve with a mesh size of 0.25 mm, the chemical composition of which is presented in Table 2.

Table 1. Chemical composition of chromium concentrate.

Components	Content, %
Cr ₂ O ₃	50.3
SiO ₂	7.00
P	0.05
S (in 2–6 class)	0.05
Cr ₂ O ₃ /FeO = 4.8	
Size (in 2–6 class)—70%	

Table 2. Chemical composition of charge components.

Charge Components	Composition of Charge Components, wt.%										
	Cr ₂ O ₃	Al ₂ O ₃	SiO ₂	FeO	CaO	MgO	TiO ₂	Na ₂ O	P ₂ O ₅	SO ₃	Other
Chrome concentrate	50.3	4.9	10.2	10.4	0.32	19.8	-	-	0.008	0.042	4.03
Ferrous diatomite	0.02	8.03	66.98	10.3	0.64	1.1	1.1	1.3	0.033	0.58	9.917
Mineral part of refined ferrochromium slag	4.1	4.7	23.0	0.15	33.14	6.7	0.12	0.027	0.005	0.0525	28.06

The composition and main chemical and physical properties of special coke from open joint-stock company Sary-Arka are shown in Table 3.

Coal coke (coke nut) LLP “RTF AKTIKA”, Pavlodar, used at the Aksu ferroalloy plant of JSC “TNC “Kazchrome”, the technical characteristics of which are presented in Table 4, was used as a reducing agent in the melting of the charge.

Table 3. Composition and main chemical and physical properties of special coke from open JSC “Sary-Arka”.

Chemical and Physical Properties	Parameters
Size, mm	5.0–40.0
Sulfur content, %	≤1.0
Ash content, %	6.0–10.0
Volatile content, %	4.0–7.0
Structural porosity, %	67.4
Mass fraction of carbon, C	88.0
Humidity, %	15.0–20.0
Specific surface, m ² /g	3.0
Porosity, %	22.0–25.0

Table 4. Qualitative characteristics of coal coke (coke nuts) LLP “RTF ACTICA”.

Indicators	Designation	Standards, %
Ash content on dry basis	A	≤12
Yield of volatile substances	V	≤10
Moisture on working fuel	W	≤12
Sulfur total	S	≤0.5
Mass fraction of carbon	C	89.8
Mass fraction of phosphorus	P	≤0.05
Net calorific value	Q	≥27,214.2 kJ
Fractional composition	-	0–10 mm over 25 mm

The following technological equipment was used when implementing the project: sieve analyser A20 (Vibrotechnik LLC, Saint Petersburg, Russia), laboratory concentration table for gravitational beneficiation SKL-51KTs (“Mekhanobr-Tekhnika” Russia), vibrating grinder IV6 (Vibrotechnik LLC, Russia), laboratory drum-type and cartridge-type autoclave, laboratory press MIP-25R (Research and production enterprise “INTERPRIBOR”, Russia), Tamman oven (JSC “Aramil Plant of Advanced Technologies”, Russia).

Analysis methods: X-ray phase experimental data were obtained on a BRUKER D8 ADVANCE apparatus using copper radiation at an accelerating voltage of 36 kV and a current of 25 mA. X-ray fluorescence analysis was performed on a Venus 200 PANalytical B.V spectrometer with wave dispersion. (Almelo, The Netherlands). The chemical analysis

of the samples was performed on an Optima 2000 DV inductively coupled plasma optical emission spectrometer (Perkin Elmer Inc., Waltham, MA, USA).

A batch of rich chromium concentrate was produced from a technological sample of sludge tailings from the Donskoy Mining and Processing Plant of the Dubersay tailing dump to study the production of complex pellets based on a composition consisting of chromium concentrate, fine fractions of special coke, ferruginous forms of diatomite and silicocalcium compounds.

The following composite components were used as a source for the synthesis of a new type of binder: the mineral part of refined ferrochromium slag (source of CaO and SiO₂), ferruginous forms of diatomite (source of SiO₂ and FeO), fine coke (source of SiO₂, pellet heating temperature controller—pulverized screening of special coke of Sary-Arka Spetskoks LLP Coke Plant), an aqueous solution of liquid glass (binder) [19]. Refined ferrochrome slag (RFS) is a dry pulverized mass with metallic inclusions. Therefore, without additional grinding, it was subjected to sieving on a laboratory vibrating sieve +0.1 mm. A metal concentrate was isolated in an amount of 11.2% of the initial weight of the slag and a metal-free mineral part of the slag was obtained with a residual content of Cr₂O₃—1.78%, including chromium oxide in the form of calcium chromate—1.22%.

Ferrous diatomite and special coke for the reduction of metal oxide were ground and screened on a sieve with a mesh size of 0.25 mm [25,30–32]. The mixture was thoroughly mixed, and a water glass diluted three times was added. It is known from previous studies that liquid glass additives increase the strength of granules before heat treatment [33–35]. Grinding and mixing of raw materials and fusible additives, as well as the introduction of a plasticizer to obtain a charge, were carried out on a vibrating grinder IV-1 and a ball mill BML-6 (Germany). High-level laboratory tests on the smelting of high-carbon ferrochrome have been performed with 2.2 kg of calcinated chromium pellets produced.

The granules were produced on a laboratory granulator. The size of raw granules was from 6 to 10 mm. The raw pellets were kept at room temperature for 24 h, their strength after drying was 124.6 N/pellets (Newton on the pellet). Then pellets were fired in a laboratory muffle furnace at 1200 °C for 60 min, at a heating rate of 15 deg/min. The resulting calcinated pellets were tested for compressive strength on a MIP-25R laboratory press and the average strength was determined. The average strength at a firing temperature of 1200 °C was 5330 N/pellets. The composition of the roasted compositional pellets is similar to the average composition of pellets used at the Aktobe Ferroalloy Plant of “TNC “Kazchrome” JSC. Table 5 shows the composition of the charge.

Table 5. The charge composition for the formation of raw pellets.

Chromic Concentrate, %	Mineral Part of RFS, %	Ferrous Diatomite, %	Special Coke, %	Liquid Glass, %
88.5	3.0	4.0	3.0	1.5

High-level laboratory tests on the melting of calcined compositional pellets with the production of high-carbon ferrochrome were carried out with the addition of a reducing agent in an amount of 17% by weight of the pellets. Coal coke (coke nut) LLP “RTF AC-TICA”, Pavlodar, used at the Aktobe Ferroalloys Plant (AFP) of JSC “TNC “Kazchrome” was used as a reducing agent.

Corundum and graphite crucibles for melting metals, which have a sufficiently long operating period and have a good resistance to oxidation and the thermal and mechanical effects of the melt, were used for melting.

The chemical composition of the calcined pellets was of the following composition, wt. %: 39.4 Cr₂O₃, 11.3 Fe₂O₃, 6.4 Al₂O₃; 10.7 MgO; 17.3 SiO₂; 0.008 P₂O₃; 0.016 SO₃; 1.9 CaO; 1.1 Na₂O, 0.051 K₂O; 0.23 TiO₂; 0.2 NiO; 0.028 ZnO.

Table 6 shows the distribution of the elements chromium, iron, oxygen and carbon in the initial products, alloy, slag; the gas phase was not analysed.

Table 6. Distribution of elements of chromium, iron, oxygen and carbon in smelting products.

Melting Temperature, °C	Pellet Cake, g	Coke Nut “RTF Aktika”, g	Composition, wt. %			
			Cr	Fe	O	C
Entry						
1750	170	30	35.1	10.28	50	25.5
1750	170	30	35.1	10.28	50	25.5
1800	170	30	35.1	10.28	50	25.5
1850	170	30	35.1	10.28	50	25.5
Output						
	Ferrochrome alloy, g		Cr	Fe	O	C
1750	39.0		60.5	20.4	-	8.98
1750	40.0		54.9	22.4	-	9.2
1800	62.4		62.5	22.4	-	9.0
1850	62.2		64.82	22.9	-	8.94
	Slag, g					
1750	140		8.42	2.21	43.0	1.62
1750	135		8.96	3.42	42.4	1.2
1800	115		3.4	1.4	41.7	0.8
1850	110		2.64	0.75	42.7	0.8

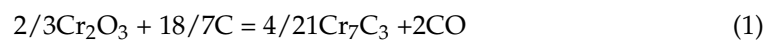
3. Results

Enlarged laboratory studies were carried out on laboratory equipment in a Tamman resistance furnace with a transformer power of 80 kW, in the experimental workshop of AFP of “TNC “Kazchrome” JSC. The Tamman Resistance Furnace is a research facility designed to simulate metallurgical processes at high temperatures up to 1850 °C. This high-temperature unit is equipped with a heater, the working space of which is a graphite tube. Temperature is controlled smoothly in the furnace, using a voltage regulator, which is included in the primary winding of the power transformer that makes it possible to obtain a current of several thousand amperes at the output busbars at low voltage (from 0.5 to 15 V).

The used Tamman furnace is vertical and is intended for modelling of metallurgical processes of ferroalloy smelting at the operating ferrochrome production. During the experiments, the space of the furnace was closed with a refractory lid without creating vacuum or any pressure. The charge was dosed with coke, which provided a reducing atmosphere in the working zone of the furnace.

The temperature was measured with a VR-5 20 tungsten–rhenium thermocouple, the hot junction point of which was brought to the bottom of the crucible in a reinforced corundum protection tube. Figure 2 shows a schematic diagram of the furnace.

The chemistry of high-carbon ferrochrome production is described by the following equations:



The iron formed by reaction (2) dissolves in chromium carbide, resulting in carbonaceous ferrochromium $(\text{Cr, Fe})_7\text{C}_3$. The theoretical carbon content in this carbide is 8.7%.

The possibility of obtaining durable annealed pellets from finely dispersed chromite concentrate and obtaining standard grades of high-carbon ferrochrome was investigated; therefore, the task of research did not include the study of slag phase viscosity and experimental temperatures. Experimental melting in the charge with annealed pellets was carried out at the operating temperatures of industrial furnaces of the existing production. The calculated composition of the slag phase is close to the production values, their melting temperatures should be the same and are in the range of 1750–1850 °C. The added fluxes in the form of diatomite and mineral part of refined ferrochrome (RFCh) slag lower the melting temperature and improve the slag phase composition. In melting tests of high-carbon

ferrochrome in Tamman furnace, good separation into slag and ferrochrome occurred, indicating satisfactory slag viscosity.

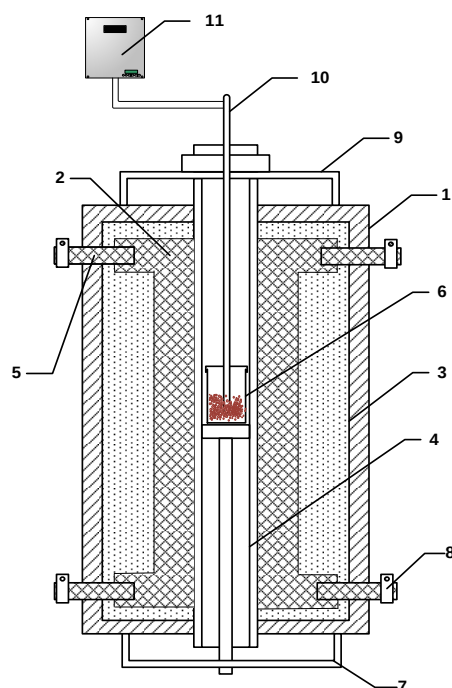


Figure 2. Schematic diagram of the Tamman laboratory-production furnace. 1—furnace body, 2—graphite heater, 3—refractory backfill (alumina Al_2O_3), 4—alund pipe, 5—graphite current lead, 6—crucible with charge and reducing agent, 7, 9—refractory cover, 8—current lead terminals, 10—thermocouple, 11—thermocontroller.

Four melts were performed. The first melt was performed at a temperature of $1750\text{ }^{\circ}\text{C}$ in the Tamman furnace. Due to the small volume of the furnace, where the charge must correspond to the size of the reducing agent, the charge mixture with a particle size of 0.25 mm and in an amount of 200 g was poured into a graphite crucible and heated to the required temperature of $1750\text{ }^{\circ}\text{C}$. On the recommendation of the shop staff, the burnt pellets were pre-crushed, as the pellets were too large for the graphite crucible. In this case, the charge with the reducing agent was compactly located in the graphite crucible and uniform melting of the charge ensured complete separation into slag and metal.

On an industrial scale, large lumps of chrome ore and coke (or special coke) pellets were loaded into AC electric arc furnaces. Since the pellets were much smaller in size than chrome ore and coke nuts, they were not pre-crushed when loaded into the furnace before reduction.

When the desired temperature was reached, the crucible with the weighed sample was kept for 30 min . After cooling to room temperature, slag in the amount of 140 g and an alloy in the amount of 39 g was formed in the crucible. The yield of the alloy was 19.5% , and alloy and slag were sent for sample preparation for physicochemical studies.

The second melt was performed at a temperature of $1750\text{ }^{\circ}\text{C}$ in a Tamman furnace in a graphite crucible under similar conditions. Melting products were as follows: the weight of the alloy was 40 g , the yield was 20% and the slag weight was 135 g .

The third melt was performed at a temperature of $1800\text{ }^{\circ}\text{C}$ in a Tamman furnace, the charge was poured into a corundum crucible, heated to the required temperature and kept for 30 min . Slag in the amount of 115 g and the alloy in the amount of 62.4 were formed in the crucible (Figure 3); the yield of the alloy was 31.2% and the slag and alloy were sent for sample preparation.



Figure 3. Alloy produced by melting at a temperature of 1800 °C.

The fourth melt was performed at a temperature of 1850 °C in a Tamman furnace, the charge was poured into a corundum crucible, heated to the required temperature and kept for 30 min. Slag was formed in the amount of 110 g and an alloy was formed in the amount of 62.2 g in the crucible, the yield of the alloy was 31.1% (Figure 4). The slag and alloy were sent for sample preparation.



Figure 4. Alloy (a) and slag (b), produced by melting at a temperature of 1850 °C.

It was noticed that the separation of the alloy from the slag runs better in corundum crucibles, since the walls of the graphite crucible are also a reducing agent. The optimal melting parameters were determined as follows: temperature 1850 °C and exposure 30 min [35–38].

The alloys samples produced during melting in the Tamman furnace were studied by chemical, X-ray fluorescence, speciation and phase analyses. Table 7 shows the parameters of the experimental melts.

Table 7. Conditions of laboratory experiments on the melting of pellets with a holding time of 30 min.

Exp. No.	Temperature Exp. °C	Charge Sample, g	Coke, g	Alloy, g	Yield, %	Slag, g	Yield, %	Residual Error, g	Chromium in Alloy, %	Extraction of Chromium into the Alloy, %
1	1750	170	30	39.0	19.5	140	70	21	60.54	46.8
2	1750	170	30	40.0	20.0	135	67.5	25	54.98	46.63
3	1800	170	30	62.4	31.2	115	57.5	22.6	62.5	77.4
4	1850	170	30	62.2	31.1	110	55.0	27.8	64.82	80.0

According to the results showed in the Table 6, the yield of alloys was 31.2 and 31.1% at ferrochrome melting temperatures of 1800 and 1850 °C, respectively. The maximum chromium content of 64.82% was at 1850 °C, the extraction of chromium into the alloy was 80%. As the temperature rises, the yield of slag decreases, and the yield of the alloy

increases. Also, with increasing temperature, the extraction of chromium into the alloy increases. The results of melting according to the composition of the obtained alloys and slags are shown in Tables 8 and 9.

Table 8. The composition of the produced alloys at different temperatures.

Material	Elements Content, %										
	Cr	Si	Al	Fe	S	P	Mg	Co	Ni	C	Others
Alloy at 1750 °C	60.5	2.0	2.3	20.4	0.02	0.011	3.5	0.2	0.44	8.98	1.65
Alloy at 1750 °C	54.9	2.8	2.4	22.4	0.02	0.011	4.8	0.2	0.66	9.2	2.61
Alloy at 1800 °C	62.5	1.6	0.1	22.4	0.04	0.008	2.3	0.189	0.62	9.0	1.24
Alloy at 1850 °C	64.82	0.87	0.043	22.9	0.033	0.029	0.044	0.182	0.44	8.94	1.72

Table 9. The composition of the produced slags at different temperatures.

Material	Element Content, %							
	Cr ₂ O ₃	SiO ₂	Al ₂ O ₃	FeO	SO ₃	P ₂ O ₅	MgO	CaO
Slag at 1750 °C	12.3	16.4	15.3	2.84	0.24	0.005	37.2	1.62
Slag at 1750 °C	13.1	15.6	10.82	4.4	0.2	0.005	23.4	2.5
Slag at 1800 °C	4.94	25.6	17.7	1.8	0.3	0.006	41.4	2.1
Slag at 1850 °C	3.86	30.7	18.5	0.96	0.3	0.006	47.93	1.3

The carbon content in the alloys varies from 8.94 to 9.2%, which corresponds to the content of high-carbon ferrochrome (Table 9). There was a maximum chromium content of 64.82% in the alloy at the melting temperature of 1850 °C; this alloy can be attributed to FeCr60C90LP ferrochrome grade according to the international Chinese standard, which has a low phosphorus content of no more than 0.03% and sulphur content of no more than 0.1%. Under this standard, 58% of high-carbon ferrochrome of “TNC “Kazchrome” JSC is exported to China.

According to the results showed in the Table 8, the minimum content of chromium oxide is in the slag at a melting temperature of 1850 °C. During melts with 1750 °C temperature, the loss of chromium in slags is higher than at 1850 °C temperature. This is due to the fact that at a sufficient temperature, the viscosity of the slag decreases, the reduced metal pellets become less entangled in the slag and coagulate into the melt.

The melting point of high-carbon ferrochrome, containing 65–70% Cr and 6–8% C, is –1550 °C, so the slag should have a melting point of ~1650 °C [4]. The required number of fluxes is determined by the melting diagram of the SiO₂-MgO-Al₂O₃ ternary system (Figure 5). Optimal areas of phase compositions of slag are marked by dots on the diagram, hence, the composition of slag in the smelting of high-carbon ferrochrome conversion is as follows, %: SiO₂ 27–33 (34–36); MgO 30–34 (33–38); Al₂O₃ 26–30 (20–26); Cr₂O₃ < 8 (3–6).

The polished sections (anschliffs) of samples of two alloys and one slag were made. All samples were viewed under microscopes LEICA DM 2500P and selectively electron-probe microanalyzer Superprobe 733 made by JEOL, Japan. The method of X-ray spectral microanalysis was used in the study of samples. Analyses of the elemental composition of samples and photography in different types of radiation were performed using energy dispersive spectrometer INCA ENERGY firm OXFORD INSTRUMENTS, England, installed on electron-probe microanalyzer brand Superprobe 733, at an accelerating voltage of 25 kV and probe current of 25 nA. The error of analysis was plus or minus 5% RH. Element concentrations were determined in the range from 100% to 0, n%.

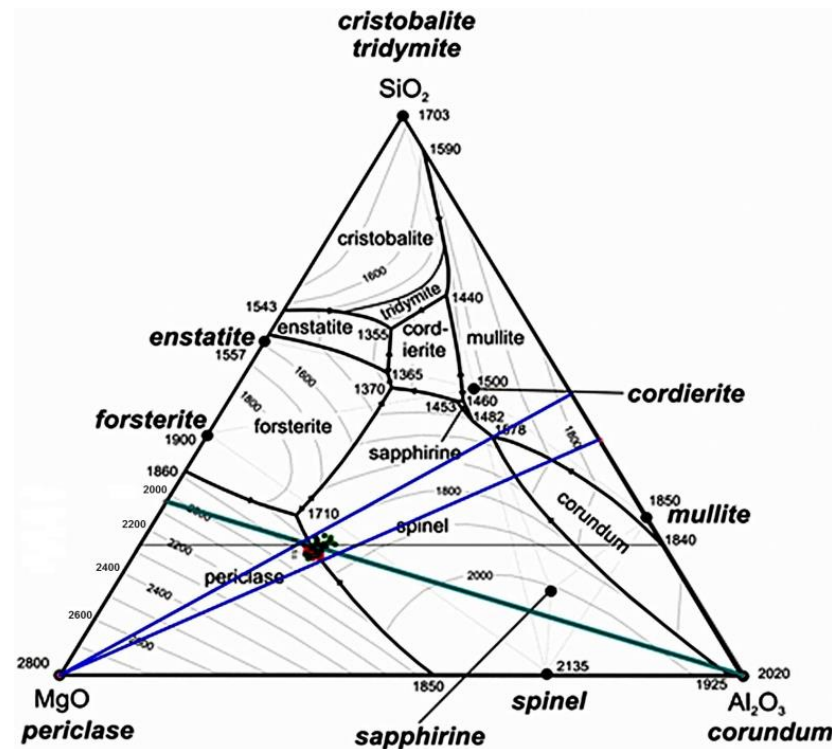


Figure 5. State diagram of MgO-SiO₂-Al₂O₃ system.

Under an optical microscope, alloy samples appear similar and close in composition. They are not homogeneous and consist of dark cracks and light spots of the alloy. The dark cracks in the alloy are usually produced by chromium carbide, the alloy structure was difficult to determine. Figure 6 shows sample 1 of the ferrochromium alloy at 1850 °C.

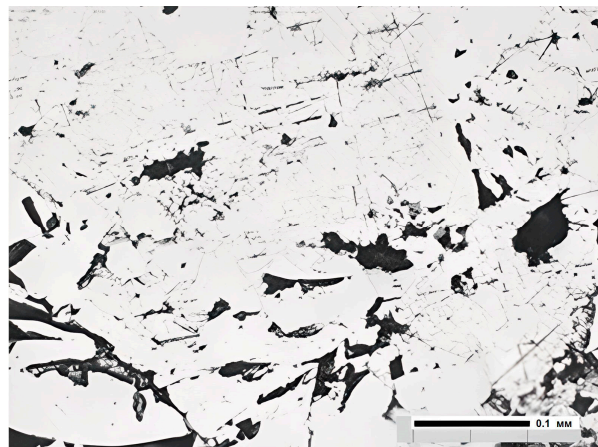


Figure 6. Fe-Cr alloy (Sample 1), temperature 1850 °C. Anschliff, magnification 200×.

A photo-electron probe microscope was used for determination of the composition of the point selected by the operator on the electron microanalyzer in secondary electrons—SEI (Figure 7, Table 10). Analysis of the composition of the point showed a high content of chromium and iron, impurities of vanadium and nickel are present in the iron-chromium alloy, as they were present in the chromium concentrate and transferred to the metal during smelting. The alloy structure is formed by primary carbides (Cr, Fe)₇C₃ and a eutectic of primary carbide and carbides Cr₃Fe and Cr₇C₃. The primary carbides are needle shaped and octahedral in cross section.

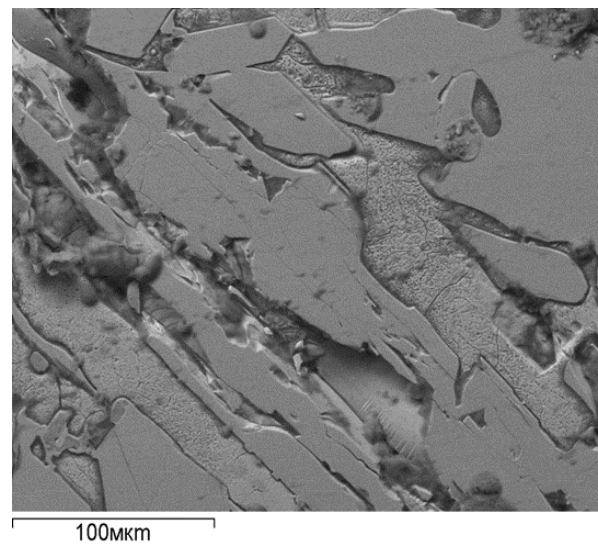


Figure 7. Fe–Cr alloy (Sample 1), temperature 1850 °C. Secondary electron image—SEI.

Table 10. Composition of sample point 1 selected by the electron microanalyzer operator.

Spectrum	Composition, wt.%				
	V	Cr	Fe	Ni	Total
Spectrum 1	0.32	76.06	23.27	0.35	100.00

Figure 8 show the diffraction pattern and X-ray phase analysis of Sample 1, alloy at a melting temperature of 1850 °C. The analysis was performed using a D8 Advance diffractometer (BRUKER), Cu–K α radiation.

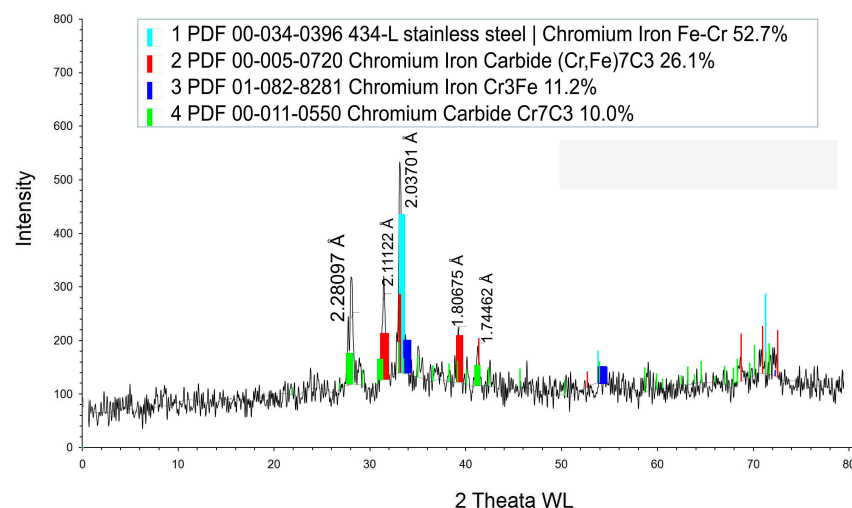


Figure 8. X-ray diffraction pattern of the alloy at a melting temperature of 1850 °C.

Crystal optical, electron probe and X-ray phase analyses show that the sample 1 alloy consists of an iron–chromium alloy, iron–chromium carbide, chromium iron and chromium carbide, which indicates a ferrochromium alloy [39–42].

Photographs and compositional determination data of an analysed section of sample 2 on the ansliff plane of the alloy optical crystallography are presented (Figure 9).

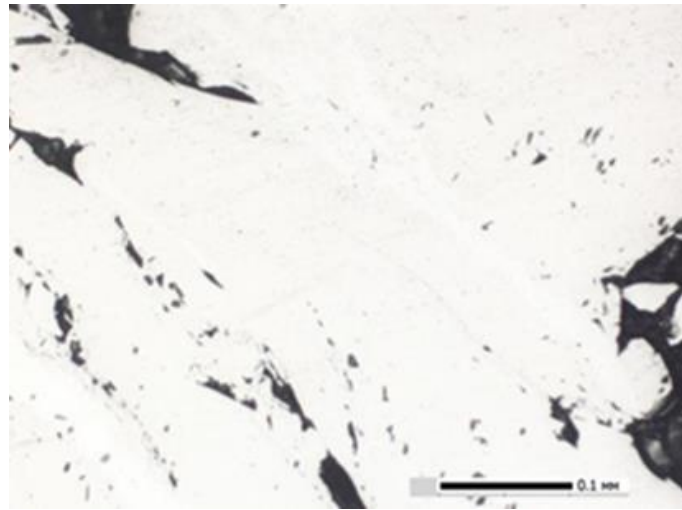


Figure 9. Iron-chromium alloy (Sample 2), temperature 1800 °C. Anschliff, magnification 200×.

In Figure 10, photo of BEI Compo electron microanalyzer in backscattered electrons, judging by the contrast in the structure, areas with increased iron content are observed. The shells in the photo were apparently obtained during sample preparation, where brittle and hard carbides were located.

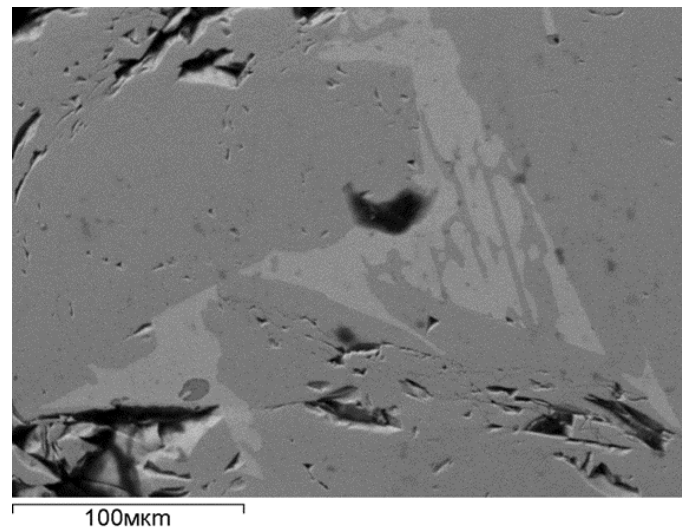


Figure 10. Fe–Cr alloy (Sample 2), temperature 1800 °C. Backscattered electron image BEI Compo.

The composition of the point selected by the operator on the electron microanalyzer was determined (Table 11). In the second sample, a point slightly different in colour intensity from the first analysed point was also analysed. It also consisted of iron and chromium with other contents of these elements and contained silicon, phosphorus and nickel as impurities.

Table 11. Composition of sample point 2 selected by the electron microanalyzer operator.

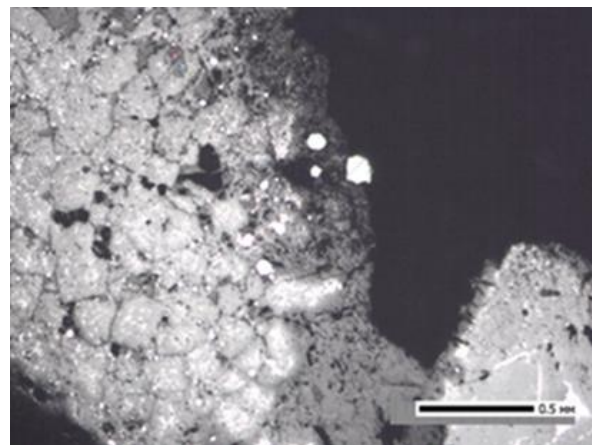
Spectrum	Composition, wt.%						Total
	Si	P	Cr	Fe	Co	Ni	
Spectrum 1	1.43	0.38	16.59	77.11	0.33	4.16	100.00

Table 12 shows the phase analysis of a ferrochromium alloy at a temperature of 1800 °C.

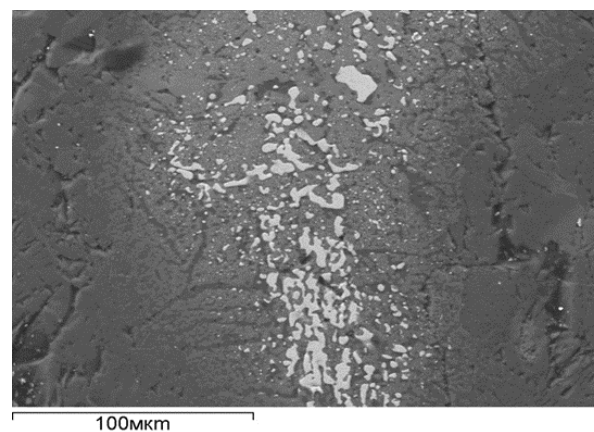
Table 12. Phase analysis of a ferrochromium alloy at a temperature of 1800 °C.

Card Number	Compound Name	Formula	%
PDF 00-034-0396	434-L stainless steel Chromium Iron	Fe-Cr	48.2
PDF 00-005-0720	Chromium Iron Carbide	(Cr, Fe) ₇ C ₃	25.2
PDF 01-082-8281	Chromium Iron	Cr ₃ Fe	10.4
PDF 00-011-0550	Chromium Carbide	Cr ₇ C ₃	16.2

Sample 5 of slag obtained at a melting temperature of 1850 °C, shown in Figure 11, was analysed. The slag is a porous material mainly consisting of magnesium, silicon, calcium and aluminium oxides.

**Figure 11.** Slag (sample 5) at 1850 °C. Anschliff, magnification 40×.

The photo of the electron microanalyzer of the anschliff of sample 5 is presented (Figure 12) and the composition of the point selected by the operator is given (Table 13). Inclusions of ferrochrome on the local area shows that in the slag there are micro-particles of ferrochrome entangled in the slag during the separation of metal and slag.

**Figure 12.** Slag (Sample 5), temperature 1850 °C. BEI Compo backscattered electron image.**Table 13.** Composition of sample point 5 selected by the operator of the electron microanalyzer.

Spectrum	Composition, wt.%				
	Mg	Cr	Fe	Ni	Total
Spectrum 1	0.60	39.26	59.45	0.69	100.00

Table 14 shows the phase analysis of the ferrochrome alloy at the melting temperature of 1750 °C.

Table 14. Phase analysis of a ferrochromium alloy at 1750 °C.

Card Number	Compound Name	Formula	%
PDF 00-034-0396	434-L stainless steel Chromium Iron	Fe-Cr	45.2
PDF 00-005-0720	Chromium Iron Carbide	(Cr, Fe) ₇ C ₃	24.1
PDF 01-082-8281	Chromium Iron	Cr ₃ Fe	7.0
PDF 00-011-0550	Chromium Carbide	Cr ₇ C ₃	23.7

Phase analysis of alloys at different temperatures showed that the phases of the ferrochromium alloy change with increasing temperature from 1750 to 1850 °C, the phase of the iron–chromium alloy increases from 45.2 to 52.7%, the chromium–iron carbide phase increases from 24.1 to 26.1%, the phase of chromium carbide decreases from 23.7 to 10.0% and the chromium–iron phase increases from 7 to 11.2%.

4. Discussion

As a result of gravity concentration, a conditioned fine concentrate was obtained from the slurry tailings of the Dubersay tailing dump of the DMPP of “TNC “Kazchrome” JSC. The chrome content was raised from 27.6% Cr₂O₃ of fine tailings to 50.3% Cr₂O₃ in a chrome concentrate where the ratio Cr₂O₃/FeO = 4.8. The production of complex pellets based on a composition consisting of chromium concentrate, fine fractions of spetskoke, ferrous form of diatomite and silica–calcium compounds was studied in advance.

Mineral part of refined ferrochrome slag (source CaO and SiO₂), which is a waste product, ferrous forms of diatomite (source SiO₂ and FeO) and water solution of liquid glass were used as a source for synthesis of a new type of binder and fluxes. Fine coke (source SiO₂, regulator of pellet heating temperature—dusty screenings of special coke) is the waste of coke production, in this case used in roasting pellets.

The obtained complex pellets made it possible to enlarge the finely divided raw chrome concentrate and to combine in the pellets the fluxes having a positive effect on the liquid flowability of the slag and sufficient separation of ferrochrome from slag.

Ferrochrome with the phase composition of iron–chromium Fe–Cr, iron–chromium carbide (Cr, Fe)₇C₃, iron–chromium Cr₃Fe, chromium carbide Cr₇C₃ corresponding to the grade of high-carbon ferrochrome FeCr60C90LP according to the international Chinese standard was obtained from the given melting of composite pellets at temperatures 1750–1850 °C. The carbon content of ferrochromium alloys varies from 8.94 to 9.2%, which corresponds to high-carbon ferrochromium. The maximum chromium content is 64.82% in an alloy with a melting temperature of 1850 °C, in which the low phosphorus content is not more than 0.03% and sulphur not more than 0.1%.

5. Conclusions

The research on the use of finely dispersed conditioned chrome concentrate obtained by gravity beneficiation of waste sludge tailings from the Dubersay tailings dump of the DMPP of JSC “TNC “Kazchrome” has been completed. For palletization of finely dispersed conditioned chromium concentrate with the content of the charge consisting of various wastes of ferroalloy production such as refined ferrochrome slag, fine special coke sifting and natural ferruginous diatomite were investigated.

As a result of experimental works, the conditions for the synthesis of composite pellets using fine chromite concentrate with the content of 50.3% Cr₂O₃ obtained on the basis of gravitational beneficiation of sludge tailings from the Dubersay tailings dump were determined. The investigated composition of charge for synthesis of composite pellets allows the smelting of standard grades of high-carbon ferrochrome with chromium content more than 60%, and also with a low content of phosphorus not more than 0.03% and sulphur not more than 0.1%.

Physico-chemical analysis of the melting products confirmed the achieved quality of the obtained high-carbon ferrochrome and high extraction of chromium in the metal phase, which amounted to 80% at the melting temperature of 1850 °C and corresponds to the achieved indicators of the operating ferroalloy production.

Further work should be directed to the development of technological regulations for the creation of a pilot plant for chemical-gravity beneficiation of slurry tailings with the production of conditioned chromite concentrate and the production of composite annealed pellets using tube furnaces.

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