

DEVELOPMENT OF TECHNOLOGY FOR PRODUCING COMPLEX BORON-CONTAINING ALUMINUM-SILICON FERROALLOY

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The purpose of the work is the creation of a boron-containing ferroalloy to improve the quality of ferrous metals. Thus, a single-stage, slag-free and waste-free technology is created with the maximum use of all useful components of the charge. Within the framework of this work, a complete thermodynamic modeling of the method for producing an alloy was performed based on studying the chemistry of the process and the dynamics of changes in the phase and elemental composition of melting products in the temperature range of 500–3000 K, which showed that the boron-containing metal is formed due to the formation of the AlB_{12} phase, and the process must be carried out at temperature of at least 1800 °C to form the final composition of the ferroalloy. Exceeding it is not desirable due to the transition of the charge components into the gas phase. As a source of boron, it was found expedient to use the Inder borate ores of the Atyrau region and Turkish colemanite. Large-scale laboratory tests were carried out in ore-thermal furnaces with a capacity of 200 kVA to obtain complex boron-containing aluminum-silicon alloys. The possibility of practical production of a boron-containing aluminum-silicon ferroalloy using coals from the Kuu-Chek and Borly deposits has been proved. So, according to the chemical analysis of the experimental metal, the FeSi45Al10B1 alloy contained (wt.%): 43.76 Fe, 45.08 Si, 10.01 Al and 1.02 B, and the FeSi50Al20B1 alloy — 28.5 Fe, 49.89 Si, 20.5 Al и 1.03B. According to the proposed process, 98% extraction of boron from ore into metal is achieved.

Keywords: thermodynamic modeling, complex boron-containing alloy, borate ore, high-ash coal; carbothermic process, one-stage technology, slag-free process.

Theoretical Analysis

The ultimate goal of the project is to create a boron-containing aluminum-silicon ferroalloy for the steelmaking industry. The task at hand was to determine its optimal phase and chemical compositions. The common practice is to produce a complex alloy of ferrosilicoaluminum (FSA) from high-ash coal, due to its containing all the necessary components for alloy production: silicon oxide (SiO_2), aluminum oxide (Al_2O_3), and carbon (C) acting as a reducing agent. Kazakhstan has large reserves of such coals.

In this study, the production of boron-containing ferrosilicoaluminum is planned. The market offers Kazakh borate ore from the Inder deposit, boron anhydride (B_2O_3), and high-quality Turkish borate ore (colemanite). It was decided to produce the new alloy from coals from the Kuu-Chek deposit and the Borly deposit with ash content of 47% and 55%, respectively.

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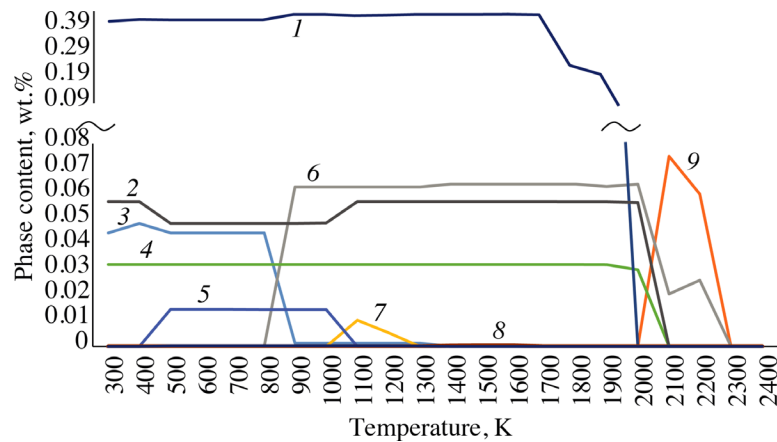


Fig. 1. Slag-phase composition dynamics versus temperature: 1 — SiO_2 ; 2 — Al_2O_3 ; 3 — CaB_2O_4 ; 4 — MgB_4O_7 ; 5 — FeAl_2O_4 ; 6 — $\text{Ca}_2\text{B}_2\text{O}_5$; 7 — FeSiO_3 ; 8 — B_2O_3 , 9 — CaAl_2O_4 .

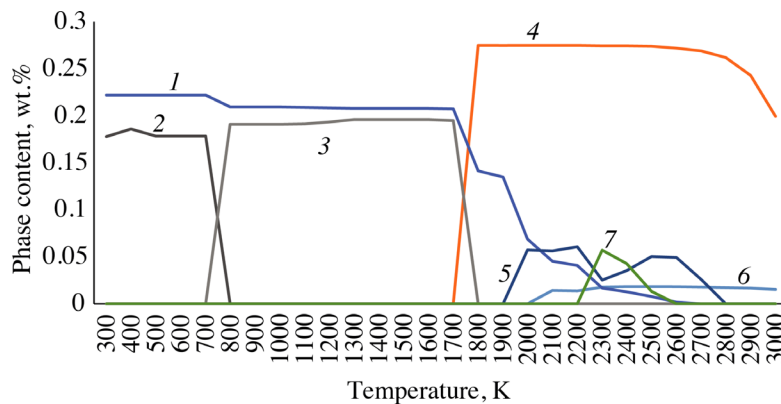


Fig. 2. Metal phase composition dynamics versus temperature: 1 — C; 2 — Fe; 3 — Fe_3C ; 4 — FeSi; 5 — Si; 6 — AlB_{12} ; 7 — CaSi_2 .

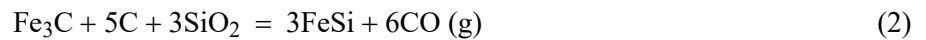
The success of experimental research depends on establishing the correct temperature level of the process. At low temperatures, some elements may not be reduced, while at excessively high temperatures, they may transition into the gaseous phase. To find the optimal temperature level, a complete thermodynamic modeling of the studied process was performed in the temperature range of 300–3000 K using the “Terra” software complex. The calculation results for the production of the FS45A10B1 alloy are shown in Figs. 1 and 2. It can be seen that metal formation does not occur until 800 K. In the temperature range of 300–800 K, the interaction of free oxides in the charge leads to the appearance (Fig. 1) of dicalcium borate $\text{Ca}_2\text{B}_2\text{O}_5$ (curve 6), calcium monoborate CaB_2O_4 (curve 3), magnesium borate MgB_4O_7 (4), and hercynite FeAl_2O_4 (curve 5). Beyond 800 K, the interaction of free iron (from the chips) and carbon from the coal leads to the appearance of iron carbide Fe_3C (curve 3 in Fig. 2) according to reaction



In the temperature range of 1700–1800 K, there is a sharp decrease in the amount of Fe_3C , SiO_2 , and carbon (C), and the appearance of FeSi. The possible cause of this is the reaction

	T	Cp	H	S	G	Reference
1	Fe ₃ C+5C+3SiO ₂ =3FeSi+6CO(g)					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	K	kJ	J/K	kJ		
4	273,000	1806,802	1059,282	1517,618	3,993E-291	-290,399
5	373,000	1808,296	1064,350	1411,293	2,224E-198	-197,653
6	473,000	1805,108	1057,060	1305,119	7,249E-145	-144,140
7	573,000	1800,960	1049,159	1199,792	4,149E-110	-109,382
8	673,000	1795,244	1039,994	1095,328	9,538E-086	-85,021
9	773,000	1788,263	1030,342	991,809	9,419E-068	-67,026
10	873,000	1778,722	1018,780	889,327	6,081E-054	-53,216
11	973,000	1773,171	1012,758	787,758	5,086E-043	-42,294
12	1073,000	1767,816	1007,518	686,750	3,678E-034	-33,434
13	1173,000	1756,487	997,209	586,762	7,393E-027	-26,131
14	1273,000	1751,477	993,108	487,251	1,012E-020	-19,995
15	1373,000	1746,860	989,614	388,120	1,710E-015	-14,767
16	1473,000	1742,656	986,657	289,311	5,493E-011	-10,260
17	1573,000	1738,884	984,178	190,773	4,618E-007	-6,336
18	1673,000	1735,557	982,125	92,461	1,297E-003	-2,887
19	1773,000	1946,082	1107,223	-17,025	3,174E+000	0,502
20	1873,000	1945,290	1106,790	-127,727	3,651E-003	3,562

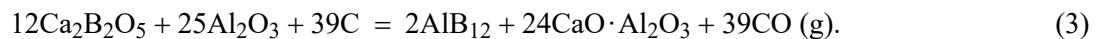
Fig. 3. Thermodynamic characteristics of FeSi formation.



the negative change in Gibbs energy of which starts at 1773 K and amounts to $\Delta G_{1773\text{K}} = -17.025$ kJ/mol (Fig. 3).

The two-calcium borate $\text{Ca}_2\text{B}_2\text{O}_5$ (see curve 6, Fig. 1) and alumina (see curve 2, Fig. 1) are preserved in the charge until high temperatures. At a temperature slightly above 2000 K, there is a sharp and simultaneous decrease in their quantity in the charge, accompanied by the appearance of aluminum boride AlB_{12} in the metal (see curve 6, Fig. 2), and calcium monoaluminate CaAl_2O_4 in the slag (see curve 9, Fig. 1).

It can be assumed that this is a consequence of the reaction occurring:



The negative value of the change in Gibbs energy is observed at 2073 K and amounts to $\Delta G_{1773\text{K}} = -215.328$ kJ/mol (Fig. 4).

The obtained data allow us to conclude that in order to obtain metal of the desired composition, the temperature in the melting furnace should be maintained at a level of at least 2073 K (1800°C). Exceeding this temperature is undesirable due to the transition of the components of the charge into the gas phase (Fig. 5).

However, in industrial furnaces, local overheating of the metal and slag (under electric arcs) cannot be avoided [1], and therefore it is necessary to work with a closed and high chimney to capture the fumes, and to use aspirated dust as an additive in the production of pellets and agglomerates, as it contains valuable components [2–4].

In the exhaust gases, CO dominates as a product of carbon reduction of oxides, but there are also losses of silicon, iron, aluminum, and boron in the form of silicon monoxide and gaseous elements.

Results						
File	Edit	Format	Help			
	T	Cp	H	S	G	Reference
1	$12\text{Ca}_2\text{B}_2\text{O}_5 + 2.5\text{Al}_2\text{O}_3 + 39\text{C} = 2\text{AlB}_{12} + 24\text{CaO} + \text{Al}_2\text{O}_3 + 39\text{CO}(\text{g})$					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	K	kJ	J/K	kJ		
4	273,000	14022,834	7421,634	11996,728	0,000E-001	
5	473,000	14037,219	7475,242	10501,430	0,000E-001	
6	673,000	13957,366	7337,805	9019,023	0,000E-001	
7	873,000	13784,154	7116,797	7571,190	0,000E-001	
8	1073,000	13651,848	6980,141	6162,156	9,897E-301	-300,004
9	1273,000	13532,239	6877,752	4776,860	9,466E-197	-196,024
10	1473,000	13427,801	6801,411	3409,323	1,232E-121	-120,909
11	1673,000	12076,882	5949,377	2123,574	4,920E-067	-66,308
12	1873,000	11889,586	5843,505	944,700	4,485E-027	-26,348
13	2073,000	11725,502	5760,169	-215,328	2,668E-005	5,426
14	2273,000	11585,267	5695,502	-1360,609	1,862E+031	31,270
15						
16	Ca ₂ B ₂ O ₅		Extrapolated from		2000,000 K	
17	CaO*Al ₂ O ₃		Extrapolated from		1800,000 K	
18						
19						
20						

Fig. 4. Thermodynamic characteristics of AlB_{12} formation.

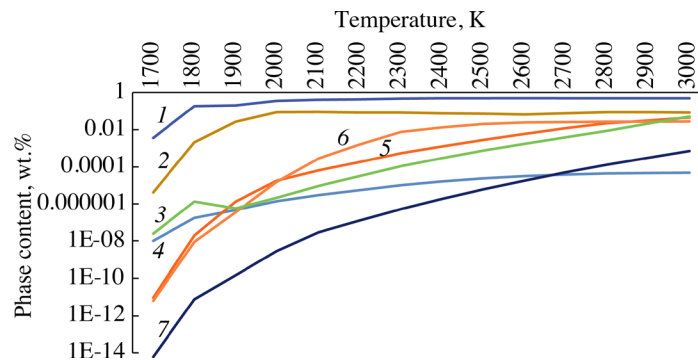


Fig. 5. Gas phase composition dynamics versus temperature: 1 — CO; 2 — SiO; 3 — Fe; 4 — P; 5 — Si; 6 — Al; 7 — B.

Materials and Procedure

Based on the obtained thermodynamic models, large-scale laboratory tests were conducted on the smelting of boron-containing aluminum-silicon ferroalloy. The practice of smelting aluminum-silicon alloys is limited [5–8]. It has been established that the deficiency of the reducer in the charge should be 2–3%. Borly coal contains 17–19% volatiles, which hinder the access of oxygen in the air to the hearth during electric smelting, thereby mainly impeding the combustion of carbon [9–11].

For the production of the complex alloy FSAB, a ore-thermal electric furnace with a current-conducting bottom of 250 kVA power was used. The electric furnace is powered by the transformer TSE 250–380/50. The arc discharge temperature of 2500–4500°C is provided by a graphite electrode with a diameter of 200 mm. The furnace is lined with firebrick. The furnace bath is elliptical with axes of 75–90 cm, elongated towards

the tapping side. The distance from the electrode to the tapping block is 25–29 cm, and to the back wall of the furnace is 41–45 cm. The depth of the bath is 85–90 cm. The furnace bottom is made of ramming mass that has been coked for 8 hours under current on a cushion of blast furnace coke with periodic furnace shutdown. The furnace transformer has 10 voltage levels, V: 20; 24.5; 28.1; 33; 40; 49; 56.2; 66 and 80.

The furnace's electrical parameters were selected to conduct the technological process with high technical and economic indicators — 40 V and a load of 400 A on the high side [12–14]. In order to carry out the tests, the preparation of the charge materials was performed in accordance with the technological requirements. The experimental batch of charge materials underwent technical operations for sampling for chemical analysis through the use of triple-quenching and mixing.

Chemical and technical compositions of the selected charge materials:

- High-ash coal from the Borly deposit, fractions 10–60 mm, with a technical composition: *C* — 55.04%; *V* — 19.03%; *W* — 0.6%; *S* — 25.66% and mineral components of ash: SiO₂ — 57.8%; Fe — 4.35%; Al₂O₃ — 29.07%; CaO — 1.4%; MgO — 3.56%;
- High-ash coal from the Kuu-Chek deposit, fractions 10–60 mm, with a technical composition: *C* — 35.12%; *V* — 20.8%; *W* — 0.7%; *S* — 44.08% and mineral components of ash: SiO₂ — 64.4%; Fe — 2.65%; Al₂O₃ — 29.0%; CaO — 1.5%; MgO — 1.9%;
- Colemanite, with the following chemical composition: B₂O₃ — 40.2%; Fe₂O₃ — 0.09%; Al₂O₃ — 0.4%; P₂O₅ — 0.02%; CaO — 27.6%; SiO₂ — 5.5%; hydrated moisture — 23.19%;
- Quartzite, with the following chemical composition: SiO₂ — 97.76%; Fe₂O₃ — 0.66%; Al₂O₃ — 0.77%; P₂O₅ — 0.03%; CaO — 0.78%;
- Shavings, with the following chemical composition: Fe — 98.98%; Si — 0.31; P — 0.03%; C — 0.24%; Mn — 0.41.

The electric furnace was preheated for 3 hours on a coke cushion, which served as an electrical conductor and maintained the temperature. After the preheating period, the electric furnace was thoroughly cleaned of any remaining coke cushion residue. The electrical parameters during the preheating period were as follows: secondary voltage of 40 V, current strength of 200–210 A on the high side. The smelting process was carried out continuously, with the charge being loaded in small portions as the hearth settled, and periodic release of metal into the cast iron molds. Each metal release was weighed, and samples were taken for chemical analysis.

The main objective of the smelting process was to achieve complete reduction of all major elements from the oxides of high-ash coal, using a continuous, stable, and easily adjustable slag-free process.

Results and Discussion

The charge was calculated taking into account the complete reduction of ore oxides and coal ash. Thus, high-ash coals from the Borly and Kuu-Chek deposits contain almost half of the oxides that make up the ash [17, 18]. The charge was adjusted by changing the weight of the ore, as changing the weight of the coal would simultaneously change the amount of oxides in the charge.

The working charge was used during smelting with a reductant deficiency, with the calculated stoichiometry, as well as with an excess of the reductant.

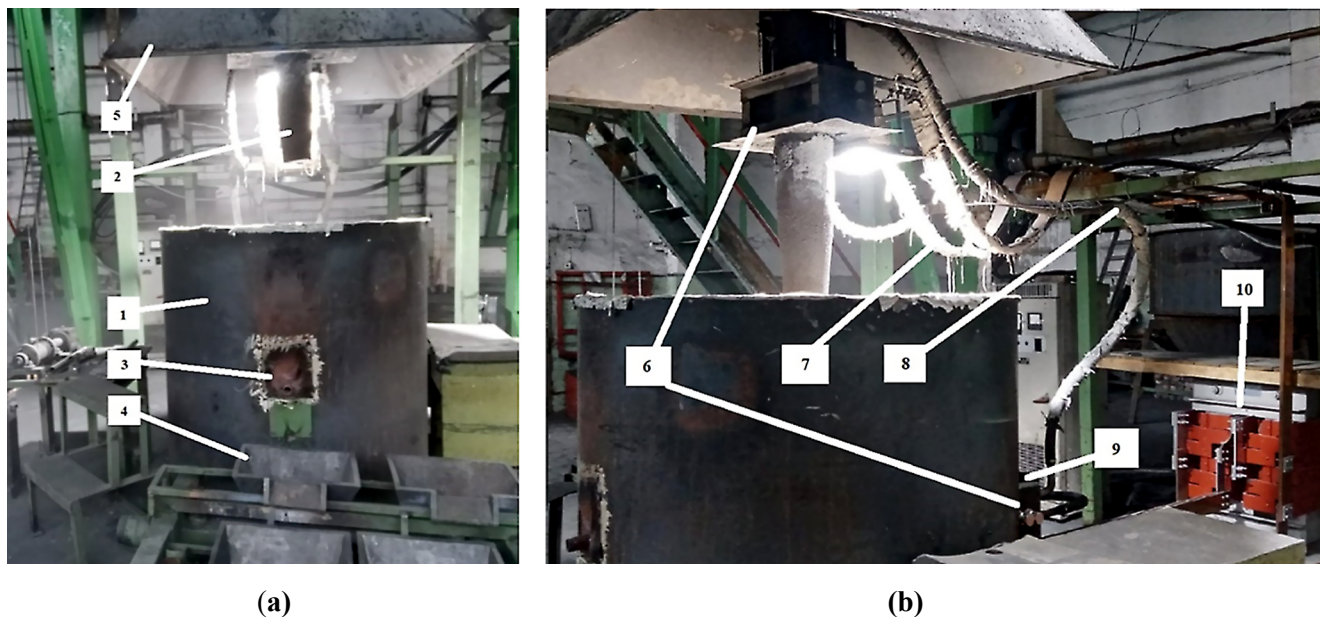


Fig. 6. General view of a single-phase ore-thermal furnace — (a) front view, (b) side view: 1 — ore-thermal furnace casing; 2 — upper electrode; 3 — tap-hole block; 4 — cascade molds; 5 — exhaust hood; 6 — water-cooled copper plates; 7 — elements of high-current system; 8 — water cooling elements; 9 — lower electrode; 10 — transformer.

When operating with a reductant deficiency of up to 10%, active electrode consumption began, and after the metal was tapped, the slag would solidify on the hearth, which was removed with metal rods. The gas permeability of the furnace lining deteriorated. Normal furnace operation was achieved by adding reductant under the electrode.

When operating with an excess of reductant of up to 10%, carbide deposition occurred under the electrode, which led to electrode expulsion, loss of temperature in the reaction zone, and hindered the tapping of the alloy from the furnace. To stabilize the smelting process when carbides formed in the furnace, quartz was added under the electrode.

Through experimentation, the optimal composition of the charge was found to be 2% reductant deficiency. With this stoichiometry, no slag accumulated in the furnace and no carbides formed. The load on the transformer on the high side remained within 400 A. To actively extract the metal before tapping, the load was increased to 450 A. Periodically, when there was no active self-flow of the charge, the furnace lining around the electrode was repaired.

The duration of the smelting process was 30 hours, not including the time for preheating the furnace lining. The conducted tests showed the absence of active self-flow of the charge, which results in the formation of crucibles around the electrodes covered with the charge from above. The diameter of the crucible was 330–390 mm. The size of the crucibles was judged by the width of the charge collapse zone during metal pouring. Such operation of the furnace bath has its positive and negative aspects.

The positive aspect is that in the absence of intense self-flow, there is overheating of the reaction zone, ensuring more complete progress of the reduction reactions. On the other hand, overheating of the crucibles increases heat losses and unevenness of the current load. The chemical composition of the obtained boron-containing ferrosilicoaluminum is presented in Table 1.

The general view of the single-phase ore-thermal furnace is shown in Fig. 6.

During the experimental trials, the following amounts were consumed: high-ash coal — 935 kg; colemanite — 39.68 kg; quartzite — 156.08 kg; chips — 68.75 kg. 356.93 kg of complex boron-containing

Table 1
Chemical Composition of Ferro-Silicon Aluminum Obtained by a Single-Stage Slag-Free Method

Alloy	Tapping number	Component content, wt. %					Metal weight, kg
		Al	Si	Fe	B	P	
FeSi45Al10B1	1	8.12	40.24	50.734	0.87	0.036	18.29
	2	8.79	40.94	49.285	0.95	0.035	20.15
	3	9.79	41.23	47.933	1.01	0.037	24.8
	4	9.89	42.12	46.96	1.0	0.03	23.77
	5	10.05	44.32	44.572	1.03	0.028	26.44
	6	10.02	44.99	43.995	1.01	0.025	25.5
	7	10.1	45.08	43.767	1.02	0.033	25.85
FeSi50Al20B1	8	15.76	46.18	36.99	1.04	0.030	20.18
	9	16.44	47.98	34.471	1.08	0.029	22.2
	10	18.72	48.65	31.59	1.01	0.03	24.42
	11	19.78	50.26	28.906	1.03	0.024	26.06
	12	20.18	50.5	28.314	0.98	0.026	25.24
	13	20.5	49.89	28.552	1.03	0.028	23.88
	14	20.34	50.12	28.513	1.0	0.027	24.67
	15	20.17	50.1	28.681	1.02	0.029	25.48

ferrosilicoaluminum was obtained, and the electricity consumption per ton of alloy was 2700 kWh. The electricity consumption was significantly low due to the activity of the silicon-aluminum complex in the alloy composition, as well as the reduction in process temperature thanks to boron.

Fifteen batches were produced, seven batches of FS45A10B1 alloy and eight batches of FS50A20B1 alloy. The insufficient recovery of aluminum and silicon in the first two batches can be attributed to the furnace not reaching the necessary temperature regime. After the seventh batch, a flushing batch was conducted with a change in the charge for the FS50A20B1 alloy.

The aforementioned results of technological tests indicate the possibility of obtaining complex boron-containing ferrosilicoaluminum through a one-stage slag-free method.

CONCLUSIONS

Full thermodynamic modeling has been performed, which has shown that boron-containing metal is formed as a result of the formation of the AlB_{12} phase, and the process must be carried out at a temperature of at least 1800°C to achieve the final composition of the ferroalloy.

Experimental-industrial tests of the technology have been conducted under production conditions using a 250 KVA transformer in an ore-thermal furnace. The possibility of practical production of boron-containing aluminum-silicon ferroalloy has been proven, utilizing high-ash coals from the Kuu-Chek, Borly deposits.

Under experimental-industrial conditions, an alloy with the following mass % composition has been obtained: 28.5% Fe, 49.89% Si, 20.5% Al, 1.03% B, suitable for steel alloying.

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REFERENCES

1. B. N. Parsunkin, S. M. Andreev, M. V. Usachev, A. K. Nalivkin, and E. S. Mikhaltchenko, "Optimization of temperature and power mode control during technological periods of electric arc melting," *Vestnik Magnitorsk. Gos. Univ. im. G. I. Nosova*, No. 4 (20), 30–34 (2007).
2. B. Kelamanov, Ye. Samuratov, A. Akuov, O. Sariyev, L. Tastanova, and A. Abdirashit, "Thermodynamic-diagram analysis of Fe–Ni–C–O system," *Metalurgija*, **61**, No. 1, 261–264 (2022).
3. B. Kelamanov, M. Tolymbekov, K. Kaskin, and A. Baisanov, "Thermal analysis of agglomerated nickel ore," *Proc. of the 12th Int. Ferroalloys Congress: Sustainable Future*, 657–659 (2010).
4. A. I. Karlina, "Development of technology for conditioning waste from silicon production for use in ferrous metallurgy," *Proc. of the 8th All-Russian Sci. and Techn. Conf. with Int. Part.*, 148–156 (2018).
5. A. S. Orlov, A. Z. Isagulov, O. R. Sariyev, and M. Z. Tolymbekov, "Production of aluminum-chromium-silicon alloy from unconditioned materials," *Steel in Translation*, **48**, No. 9, 558–563 (2018).
6. S. Baisanov, M. Tolymbekov, T. Takenov, and A. Chekimbaev, "Development and development of technology for obtaining ferrosilicon aluminum," *Physical-Chemical and Technological Issues of Metallurgical Production in Kazakhstan*, Iskander, Almaty 1, 41–53 (2002).
7. S. O. Baisanov, A. S. Baisanov, Ye. Zh. Shabanov, and Ye. K. Mukhambetkaliyev, "Development of smelting technology of complex ferroalloy with the use of high-ash coals," *KnE Materials Science, Theoretical and Practical Conference with International Participation and School for Young Scientists*, **5**, No. 1, 46–53 (2019).
8. A. A. Zagorodnii, A. V. Kolba, V. A. Kalinushkin, O. V. Sykchin, A. I. Sokolov, and S. I. Ivanitsa, "Creating conditions for the use of aluminum ferrosilicon in metallurgical production to reduce economic losses," *Tekhnologiya Metallov*, No. 2, 3–8 (2012).
9. S. V. Kim, O. A. Bogoyavlenskaya, S. K. Kudarinov, A. S. Orlov, and V. V. Orlova, "Prospects for production of smokeless fuel briquettes from coal from open pit mines in Kazakhstan," *Mining Informational and Analytical Bulletin*, No. 9, 147–158 (2020).
10. S. V. Kim, A. S. Orlov, V. V. Orlova, O. A. Bogoyavlenskaya, and S. Kh. Kudarinov, "Smokeless fuel briquettes from carbonized energy coal fines," *Ugol*, No. 6, 41–45 (2020).
11. V. A. Tarasov, "Possibilities of increasing energy efficiency of ore recovery processes by using energy potential of charge materials," *Vest. Chuvash Univ.*, No. 2, 278–284 (2006).
12. Ye. Mukhambetgaliyev, S. Baysanov, A. Baysanov, D. Zhiembaeva, and V. Tolokonnikova, "Evaluation of physical and chemical properties of charge materials from the point of possibility of receiving the alloy of aluminosilicomanganese," *Proc. of INFACON XIII — 13th Intern. Ferroalloys Congress: Efficient Technologies in Ferroalloy Industry*, 317–323 (2020).
13. A. A. Akberdin, A. S. Kim, A. S. Orlov, and R. B. Sultangaziev, "Diagram of the phase composition of the Fe–Si–Al system and its isothermal sections," *CIS Iron and Steel Review*, **23**, 76–80 (2022).
14. B. S. Dmitrievskii and A. V. Bashkatova, "Mathematical modeling of AC EAF electrical parameters," *Izv. Vuzov. Chernaya Metallurgiya*, **62**, No. 7, 571–577 (2019).
15. B. T. Ermagambet, B. K. Kasenov, M. K. Kazankapova, E. E. Kuanyshebekov, and A. T. Nauryzbaeva, "Electrophysical properties and heat capacity of a porous carbon material from coal of the Maikube basin," *Solid Fuel Chemistry*, **54**, No. 3, 180–185 (2020).
16. E. K. Mukhambetgaliyev, A. B. Esenzhulov, and V. E. Roshchin, "Alloy production from high-silica manganese ore and high-ash Kazakhstan coal," *Steel in Translation*, **48**, No. 9, 547–552 (2018).
17. T. A. Safonova and I. V. Drozdova, "Coal industry of Russia and Kazakhstan: parameters, comparative assessment, development potential," *Proc. Int. Sci. and Pract. Conf., Ural State Mining University, Yekaterinburg*, 430–431 (2020).
18. G. A. Ulyeva, "Interaction between the pore structure and reactivity of solid carbon-containing reducing agents," *Koks i Khimiya*, No. 4, 18–21 (2021).