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Research into the possibility of producing ferrosilicoaluminum from recycled materials

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Дослідження можливості виробництва феросилікоалюмінію з вторинної сировини

Abstract. *The technology of electrothermal production of ferrosilicoaluminum using recyclable material from abrasive production has been developed, studied and tested in laboratory and semi-industrial conditions. The following were used as burden components: "old charge" from silicon carbide production, sludge from abrasive electrocorundum and silicon carbide, magnetic fraction from electrocorundum production and gas coal. As a result, an alloy containing 61−69% Al+Si was obtained.*
Key words: *ferrosilicoaluminum, recycled materials, recycling, electrothermal production, abrasive production.*

Анотація. *Розроблено, досліджено та випробувано в лабораторних і напівпромислових умовах технологію електротермічного виробництва феросилікоалюмінію з використанням вторинної сировини абразивного виробництва. Як шихтові компоненти використовувалися: "стара шихта" з виробництва карбіду кремнію, шлами абразивного електрокорунду та карбіду кремнію, магнітна фракція з виробництва електрокорунду та газове вугілля. В результаті отримано сплав, що містить 61−69% Al+Si.*
Ключові слова: *феросилікоалюміній, вторинна сировина, переробка, електротермічне виробництво, абразивне виробництво.*

Being one of the most effective deoxidizers, aluminum is widely used in steelmaking for final metal deoxidation. [1] Aluminum is used in the form of ingots of pure or secondary metal. In the first case, the high cost of the deoxidizer significantly affects the cost of production, and in the second case, a considerable amount of non-ferrous metal impurities (Zn, Sn, Cu, Pb, As) gets into the steel, ultimately worsening its quality [2]. In addition, when added into steel, 70-90% of aluminum is oxidized under the influence of air and slag, and the amount that gets into the metal and performs its direct function is difficult to predict. Despite the disadvantages, it is not advisable to reject aluminum for a number of reasons, so research aimed at replacing primary and secondary aluminum with its alloys with other elements is becoming relevant. Performing steel finishing operations using complex deoxidizers allows reducing their consumption, improving the kinetics of deoxidation, reducing heat consumption for their dissolution, and improving the quality of the processed metal [3]. The most universal and promising in this regard may be a complex deoxidizer – ferrosilicoaluminum (FeSiAl).

Ferrosilicoaluminum can be produced in industrial quantities in two ways: by mixing and by joint reduction of aluminum and silicon oxides with carbon in ore-reducing furnaces [1]. Although the mixing method allows for the production of complex alloys of complex composition, it is not economically viable due to the high loss of elements. In addition, the problem of using metallic aluminum remains.

In light of the above, the most promising appears to be the electrothermal technology for the production of complex aluminum and aluminum-silicon ferroalloys, developed and improved by the Department of Electrometallurgy of the Dnipro Metallurgical Institute over many years.

Raw materials

Despite the obvious advantages, this technology is not well developed in Ukraine. The main reason for that is the lack of a reliable raw material base. In Kazakhstan, for instance, the production of FeSiAl is actively expanding [4] due to the use of high-ash coals from the Ekibastuz deposit, which are practically a ready-made mono-charge for production of FeSiAl [5].

Studies of the domestic mineral resource base has shown that aluminosilicate rocks can be used as the ore part of the burden charge for the electrothermal production of ferrosilicon aluminum: bauxites, clays, primary and secondary kaolins, kyanites, sillimanites, etc. The existing deposits of these types of raw materials [6] are either not developed or are used for the production of electrolytic aluminum, electrocorundum, refractories, ceramics, etc.

The most promising natural raw material for smelting FeAl and FeSiAl in Ukraine is bauxite. The largest deposit in Ukraine is Vysokopolske, represented by gibbsite bauxites (33–45% Al_2O_3, 5–9% SiO_2, 26–32%

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Fe_2O_3, 1.9–2.3% TiO_2, 0.1–0.18 CaO), explored reserves are 19 million tons. [7] Vysokopolske bauxite has low content of Al_2O_3, low silicon and calcium modules, so domestic producers do not use it directly for obtaining alumina, especially when there is an opportunity to purchase high-quality ores abroad. At the same time, there are no restrictions on the use of this raw material for the production of complex ferroalloys. At the same time, studies were conducted on the possibility of production ferrosilicoaluminum from pre-agglomerated Vysokopolski bauxite [8], but this technology did not receive further development in our country.

To solve the problem of raw material shortage, the possibility of using man-made secondary materials from abrasive production containing compounds of aluminum, silicon and carbon was considered.

During production of abrasive electrocorundum, electrofilters and a mechanical cleaning system capture dust of following chemical composition, %:

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	C	K_2O	Na_2O	CaO
32−37	15−20	8−10	1−2	40−42	3−4	1−1,5	0,15−0,30

Dust particle size is less than 160 мкм.

During the processing melted abrasive electrocorundum into grinding materials after a whole complex of technological operations (crushing, wet grinding, dehydration, drying) it undergoes primary magnetic enrichment. The magnetic material removed from the technological scheme is represented by a conglomerate consisting of associated low-silicon ferrosilicon and abrasive electrocorundum. The content of each material depends on the technology conditions, the selected crushing scheme and can vary significantly: the content of corundum, for example, can vary from 50 to 70%. The most probable composition of the magnetic material is presented in Table 1.

Table 1. Fractional and chemical composition of magnetic material of electrocorundum production.

Size, mcm/%										
1250	1000	800	630	500	400	315	250	200	160	−160
12,2	8,0	12,5	9,0	12,0	7,0	9,0	7,0	6,1	7,4	9,8

Composition, %мас.								
Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Al	Ti	Si	Fe	C
51,4	0,6	0,5	3,1	0,4	0,6	5,1	34,9	0,7

In the production of silicon carbide grinding materials, wet grinding of the original piece in ball mills produces sludge containing at least 80% SiC, about 5% free carbon, up to 14% SiO_2 and 2–3% Fe. In the same production, the so-called "old charge" that is regularly removed from the process flow chart, containing up to 20% SiC, about 50% SiO_2, more than 25% C and 3–4% Fe_2O_3, 1.5–2.0% Al_2O_3, up to 1% CaO, which are harmful to abrasive production. In winter, the sludge generated during the production of grinding materials from abrasive electrocorundum and silicon carbide is mixed during transportation to filter treatment facilities and has the following composition: 50–58% Al_2O_3, 4–5% Fe_2O_3, 20–25% SiO_2, 5–6% SiC, 5–6% C.

The listed materials are mainly represented by elements which are required for FeSiAl (Si, Al, Fe, C) with a small amount of impurities (Ca, Ti), which do not pose a danger to the finished alloy. This confirms the possibility of their involvement in production.

Silicon carbide in the composition of the burden charge. Technogenic materials of abrasive production contain silicon carbide in significant quantities. Being a complex reducing agent, this compound is capable of having a noticeable positive effect on the production of FeSiAl. The reduction of silicon and aluminum oxides by silicon carbide and carbon occurs according to the reactions:

$$SiO_2 + 2SiC = 3[Si] + 2CO, \quad \Delta G^0_T = 823796 - 320{,}83T; \quad (1)$$
$$SiO_2 + 2C = [Si] + 2CO, \quad \Delta G^0_T = 689818 - 353{,}91T; \quad (2)$$
$$Al_2O_3 + SiC = 2[Al] + SiO_2 + CO, \quad \Delta G^0_T = 723814 - 171{,}57T; \quad (3)$$
$$Al_2O_3 + 3C = 2[Al] + 3CO, \quad \Delta G^0_T = 1346643 - 542{,}02T. \quad (4)$$

The reactions proceed with the absorption of heat, and the specific heat consumption per unit of silicon and aluminum is:

	1	2	3	4
kJ/mole Si(Al)	274,6	689,8	361,9	673,3
MJ/kg Si(Al)	9,81	24,64	13,40	24,94

As can be seen from the calculations, in the case of using SiC as a reducing agent instead of carbon, a reduction in heat consumption is expected for reducing silicon by 2.5 times, and aluminum by 1.8 times. Thus, using silicon carbide as a reducing agent can significantly reduce energy consumption for smelting ferrosilicon aluminum. Metallurgical silicon carbide itself is a very valuable and expensive material, which once again indicates the feasibility of its use in the composition of technogenic raw materials for abrasive production, which in its current form is not used in industry.

Experimental production of FeSiAl. In order to develop a rational technology for producing FeSiAl, experimental production was carried out in a Tamman furnace using various combinations of burden materials. The characteristics of the initial raw materials are given in Table 2. The burden charge under study was heated at the same rate, while the temperature and mass of the burden charge were recorded. Each composition was heated to 1800°C. Based on the lost mass, the degree of reduction of a particular burden charge was calculated. The results of the experimental smelting are given in Table 3.

Table 2. Chemical composition of burden materials for the production of FeSiAl.

Material	Composition, %									
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Si	Fe	SiC	C	ППП
Bauxite	38,4	4,7	32,4	3,5	–	–	–	–	–	21
Quartzite	0,52	97,5	0,63	–	0,9	–	–	–	–	–
Anthracite	1,329	2,528	0,475	–	0,147	–	–	–	95	–
Sludge from the abrasive production	56,82	1,9	4,4	1,57	–	–	–	25,51	8,4	–
SiC “old charge”	2,7	50,57	2,6	–	–	–	0,03	21,4	22	–
Electrocorundum magnetic fraction	54,1	0,6	0,5	3,1	–	5,1	34,9	–	0,7	–

Table 3. Experimental results.

Indicator	Charge		
	1	2	3
Charge composition, %			
Bauxite	44,3	–	47,75
Quartzite	36,25	–	–
Anthracite	19,45	–	2,55
Sludge	–	10	–
SiC “old charge”	–	55	49,7
magnetic fraction	–	35	–
Duration, min	25	28	27
Mass of the metal (calculated), g	13,35	20,53	16,55
Mass of the metal (real), g	9,31	19,57	13,49
Metal reduction degree, %	69,74	95,32	81,51
Metal composition, %:			
Al	14,97	17,12	12,13
Si	28,65	45,97	42,47
Ti	1,07	1,18	0,83
Al+Si	43,62	63,09	54,6

The degree of reduction of burden containing secondary materials turned out to be significantly higher, which is due to the presence of both already reduced metallic phases and a complex reducing agent – silicon carbide. This raw material is of considerable interest and is currently widely used in metallurgical and foundry production. The study of the physicochemical and metallurgical properties of silicon carbide materials as reducing agents, especially in electrometallurgy of ferroalloys, is an urgent task for increasing the efficiency of production.

Experimental studies of FeSiAl production using silicon carbide as a reducing agent

The alloy was produced in a laboratory electric furnace with a capacity of 250 kVA and electrodes with a diameter of 100 mm. The furnace bath had a diameter of 450 mm and a depth of 240 mm. The production was carried out at a voltage level of 49 V and a current of 1–2 kA. 37 experiments were completed and, in total, 399 kg of alloy were produced for the series. The FeSiAl production process was assessed based on 10 experiments (No. 10–19), during which there were minimal violations of the process mode. Based on the results of these experiments, the furnace productivity, specific energy consumption and other process indicators were calculated. The results of the experiments are presented in Table 5.

During the entire series of experiments, no adjustment of the charge was made. 50 kg of briquetted charge was loaded into the furnace, and the process duration, on average, did not exceed two hours.

Table 5. Experiments performance.

№	Duration, hours	Charge, kg	Metal mass, kg	Energy of attempt, kW·h	Energy per ton, kW·h/t	Productivity, kg/h
10	1,58	50	11,0	64	5818	6,96
11	1,33	50	10,5	56	5333	7,89
12	1,48	50	7,2	52	7222	4,86
13	1,70	50	6,3	56	8889	3,71
14	2,08	50	16,5	83,2	5042	7,93
15	2,08	50	10,5	67,2	6400	5,05
16	1,92	50	15,0	65,6	4373	7,81
17	1,92	50	14,0	68,8	4914	7,29
18	2,00	50	12,1	72	5950	6,05
19	2,13	50	15,0	84	5600	7,04
Average	1,82	50	11,81	66,9	5954	6,49

With a constant amount of the charge loaded for the experiment, there was a deviation of the average hourly power consumption from the average value for the company (from 32.3 to 40.5 kW·h, with an average value of 36.82 kW·h). Such furnace operation also affected other indicators: the furnace productivity fluctuated from 3.71 kg/h to 7.93 kg/h, the specific power consumption from 4914 to 8889 kW·h/t. For the same reason, the chemical composition of the products fluctuated: the aluminum content changed from 7.92 to 15.14, and silicon from 58.77 to 51.42% (Table 6). At the same time, the sum of aluminum and silicon in the alloy fluctuated insignificantly. The indicated instability of the average hourly power output is caused mainly by the design feature of the furnace unit: different distances between the electrodes, imperfections of the taphole unit (due to which the taphole opening time was unjustifiably increased), weak contact of the graphite electrode in the electrode holder, led to electrode slippage and forced downtime.

The process was almost slag-free, the aluminum and silicon content were very close to the calculated ones. In some experiments, the aluminum extraction was 79.5%, and silicon 71%.

Table 6. Chemical composition of products.

№	Al	Si	Fe	Ca	C	P	S	Al+Si
10	11,97	53,13	34,31	0,21	0,34	0,044	0,026	65,10
11	13,69	55,24	30,27	0,41	0,35	0,044	0,004	68,93
12	12,03	56,97	30,42	0,21	0,33	0,032	0,003	69,00
13	10,82	58,03	30,71	0,21	0,19	0,027	0,002	68,85
14	7,92	58,77	32,77	0,21	0,25	0,046	0,016	66,69
15	10,03	56,72	32,62	0,11	0,38	0,039	0,102	66,75
16	1067	50,09	38,63	0,11	0,40	0,035	0,037	60,76
17	10,38	51,48	37,67	0,11	0,29	0,034	0,038	61,86
18	9,16	54,27	36,47	0,06	0,04	0,018	0,003	63,43
19	15,14	51,42	32,71	0,11	0,58	0,008	0,031	66,56

The consumption of briquettes was 4234 kg per ton of alloy, including silicon carbide "old charge" – 2530 kg, abrasive electrocorundum and silicon carbide sludge – 616 kg, magnetic material – 873 kg, gas coal – 215 kg. Energy consumption was 10860 kWh/t.

Conclusion

The technology of ferrosilicoaluminum production with use of secondary materials from abrasive production has been developed, studied and tested in laboratory and semi-industrial conditions (more than 67 hours of continuous operation of the electric furnace). As a result, the pilot company carried out 37 smeltings and smelted 399 kg of alloy containing 61-69% Al + Si. The possibility of recycling man-made raw materials that have not yet found application and producing a competitive and high-quality complex deoxidizer has been proven. This scheme, being resource-saving, allows solving issues related to the need for complex use of valuable and scarce mineral raw materials in the national economy and environmental protection. The presence of silicon carbide and metallic iron in the charge made it possible to significantly improve the conditions for the flow of reduction processes, which made it possible, in comparison with the current technological schemes, to reduce the specific energy consumption by 30%.

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