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CARBON-FREE SMELTING OF CHROME-CONTAINING FERROALLOY USING FERROALUMOSILICOCALCIUM AND FERROSILICOCHROME DUST

Abstract. The study examines carbon-free smelting of chromium-containing ferroalloy using ferroaluminosilicocalcium (*FeAlSiCa*) and ferrosilicochrome dust (*FeSiCr*) as complex metallothermic reductants aimed at reducing the carbon footprint of conventional ferrochrome production. Four charge variants with reductant contents ranging from 10% deficiency to 20% excess relative to stoichiometry were investigated. Smelting was conducted at 1650 °C followed by SEM, EDS, and chemical analyses of the obtained products. *Cr-Fe* solid solutions and *Cr-V-N* nitride phases were formed, while silicon excess promoted *Cr-Si* silicides. Chromium recovery reached 86%, and impurity levels remained low ($C \leq 0.10\%$). The alloys satisfied ISO 5448-81 requirements. The optimal composition corresponded to a 10% excess of reductants.

Key words: ferroalloy, ferrochrome, low-carbon ferrochrome, metallothermy, ferroaluminosilicocalcium, ferrosilicochrome, calcium, complex reducing agents, carbon footprint.

Ферроалюмосиликокальций және ферросиликохром шанын қолдана отырып хром феррокорытпасын көміртегісіз балқыту

Аннотация. Зерттеуде дәстүрлі феррохром өндірісінің көміртегісіне тәуелділігін төмендету мақсатында ферроалюмосиликокальций (*FeAlSiCa*) және ферросиликохром шаны (*FeSiCr*) кешенді металлтермиялық тотықсыздандығыштар ретінде қолданылған көміртегісіз балқыту үдерісі қарастырылды. Тотықсыздандығыштардың мөлшері стехиометрияға қатысты 10% кемнен 20% артыққа дейін өзгертілген төрт шихта нұсқасы зерттелді. Балқыту 1650 °C температурада жүргізіліп, алынған өнімдер СЭМ, ЭДС және химиялық талдау әдістерімен зерттелді. Нәтижесінде Cr-Fe қатты ерітінділері мен Cr-V-N нитридтік фазалары түзілді, ал кремнийдің артық мөлшері Cr-Si силицидтерінің пайда болуына әкелді. Хромның алыну дәрежесі 86%-ға жетті, ал қоспалар мөлшері төмен болды ($C \leq 0,10\%$). Қорытпалар ISO 5448-81 талаптарына сәйкес келеді. Оңтайлы құрам тотықсыздандығыштардың 10% артық мөлшеріне сәйкес анықталды.

Түйінді сөздер: феррокорытпа, феррохром, төмен көміртекті феррохром, металлтермия, ферроалюмосиликокальций, ферросиликохром, кальций, күрделі тотықсыздандығыштар, көміртегісіз.

Безуглеродная выплавка хромсодержащего ферросплава с применением ферроалюмосиликокальция и пыли ферросиликохрома

Аннотация. В работе исследована возможность безуглеродной выплавки хромсодержащего ферросплава с использованием ферроалюмосиликокальция (*FeAlSiCa*) и пыли ферросиликохрома (*FeSiCr*) в качестве комплексных металлтермических восстановителей с целью снижения углеродного следа традиционного производства феррохрома. Рассмотрены четыре варианта шихты с содержанием восстановителей от 10% недостатка до 20% избытка относительно стехиометрии. Плавка проводилась при 1650 °C, полученные продукты исследованы методами СЭМ, ЭДС и химического анализа. Установлено формирование твердых растворов *Cr-Fe* и нитридных фаз *Cr-V-N*, при избытке кремния образуются силициды *Cr-Si*. Степень извлечения хрома достигла 86%, содержание примесей было низким ($C \leq 0,10\%$). Полученные сплавы соответствуют требованиям ISO 5448-81. Оптимальной признана шихта с 10% избытком восстановителей.

Ключевые слова: ферросплав, феррохром, низкоуглеродистый феррохром, металлтермия, ферроалюмосиликокальция, ферросиликохрома, кальций, комплексные восстановители, углеродный след.

Introduction

Modern ferrochrome production relies heavily on the carbothermic reduction of chromium oxides, making the process one of the most carbon-intensive in the ferroalloy industry. The use of coke and other carbon-containing reducing agents results in high CO_2 emissions, significant energy costs, and process limitations, particularly in the production of low-carbon ferrochrome for corrosion-resistant steels. Increasing environmental requirements and the transition to low-carbon metallurgy are stimulating the search for alternatives to traditional carbothermic reduction [1–3].

One promising area is the use of metal-thermal reducing agents, which completely eliminate carbon from the process. However, the use of pure *Al*, *Si*, or *Ca* is limited by their cost and the energy intensity of production. Therefore, interest in complex man-made reducing agents with high reactivity and availability is relevant [4–6].

Ferroaluminosilicocalcium (*FeAlSiCa*) is a reducing agent containing active elements with a high affinity for oxygen – *Ca*, *Al*, and *Si*. Its use allows for lower process temperatures, increased Cr_2O_3 reduction, and a reduced carbon footprint, while simultaneously utilizing metallurgical waste. Research into the mechanisms of reduction, phase formation, and product properties using *FeAlSiCa* is an important step

toward developing carbon-free smelting technologies for chromium-containing ferroalloys [6–8].

Materials and methods

During the carbon-free smelting of chromium-containing ferroalloy, chromium concentrate, *FeAlSiCa* and *FeSiCr* dust were used as charge materials.

Chemical analysis of chromium concentrate and metal reducing agents has the following values, %: chromium concentrate: Cr_2O_3 – 52.91; Al_2O_3 – 7.801; SiO_2 – 4.65; MgO – 17.51; CaO – 0.58; Fe_2O_3 – 12.91; S – 0.022; P – 0.003; calcination loses – 15.021; *FeAlSiCa*: *Fe* – 8.13; *Al* – 13.45; *Si* – 66.16; *Ca* – 10.03; C – 0.69; S – 0.017; P – 0.041; Ti – 1.08; V – 0.42; *FeSiCr*: *Fe* – 9.11; *Al* – 4.03; *Si* – 48.08; *Ca* – 1.15; C – 2.00; S – 0.056; P – 0.025; Cr – 1.1; V – 38.73.

FeAlSiCa and *FeSiCr* were introduced in equal proportions in four variants: 10% deficient reducing agents (variant 1); in a stoichiometric amount sufficient for the complete reduction of the main oxides of *Cr* concentrate (variant 2); and also with 10% (variant 3) and 20% (variant 4) excess. A more detailed composition is presented below:

– variant 1, %: 52.3 *Cr* concentrate; 7.8 *FeAlSiCa*; 7.8 *FeSiCr* dust; 31.9 lime;

– variant 2, %: 44.7 *Cr* concentrate; 8.9 *FeAlSiCa*; 8.9 *FeSiCr* dust; 37.4 lime;

– variant 3, %: 39.0 **Cr** concentrate; 9.7 **FeAlSiCa**; 9.7 **FeSiCr** dust; 41.4 lime;

– variant 4, %: 34.6 **Cr** concentrate; 10.3 **FeAlSiCa**; 10.3 **FeSiCr** dust; 44.6 lime.

Melting was carried out in alundum crucibles immersed in a **MgO** backfill (to protect the furnace chamber from potential splashes resulting from violent exothermic reactions) in a chamber furnace in an air atmosphere at a heating rate of 10 °C/min with an isothermal hold at 1650 °C for 30 minutes, followed by cooling in the furnace to room temperature. The charge was a mixture of ground powders with particle sizes $\leq 120 \mu\text{m}$.

The resulting metal and slag samples were examined using a ZepTools ZEM20 scanning electron microscope (SEM) with an Oxford energy-dispersive spectroscopy (EDS) attachment. Individual elements were analyzed using analytical chemistry methods.

Results

Figure 1 shows SEM images of metals obtained by melting using four different methods of introducing **FeAlSiCa** and **FeSiCr**. The images were obtained in backscattered electron detection mode at a magnification of $\times 1000$.

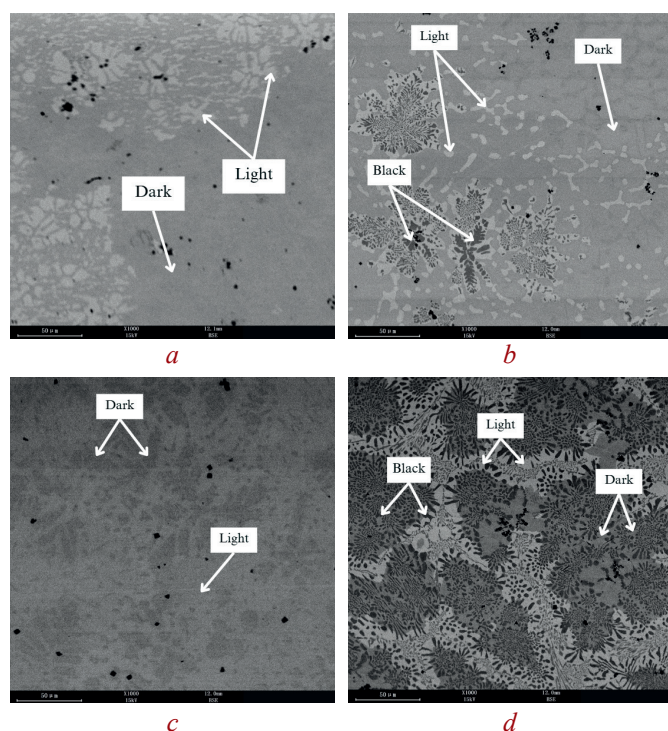


Figure 1. SEM images of metal samples obtained by introducing **FeAlSiCa and **FeSiCr** from batch variants: 1 (a), 2 (b), 3 (c) and 4 (d).**

Сурет 1. **FeAlSiCa және **FeSiCr**-ді партиялық нұсқалардан енгізу арқылы алынған металл үлгілерінің СЭМ кескіндері: 1 (a), 2 (b), 3 (c) және 4 (d).
Рис. 1. Изображения образцов металла, полученные методом СЭМ, с добавлением **FeAlSiCa** и **FeSiCr** из пакетных вариантов: 1 (a), 2 (b), 3 (c) и 4 (d).**

The figure shows that two main phases are formed in variants 1 and 3, and three in variants 2 and 4. According to the averaged EDS results for the light and dark areas (Table 4), the light area

represents the phase with a lower chromium content, while the dark area has a higher chromium content. Another characteristic of the dark phase is the presence of nitrogen or silicon.

Table 1 also presents the results of EDS when analyzing the total spectrum of the entire observed image.

Table 1
Results of EDS analysis of metal samples*, %

Кестме 1
Металл үлгілерінің ЭДС талдау нәтижелері*, %
Таблица 1
Результаты EDS-анализа образцов металлов*, %

Figure	Plot	Cr	Fe	Si	V	N
Fig. 1, a (1st batch variant)	Sum	64.47	30.88	0.66	1.07	2.92
	Light	60.08	38.63	0.89	0.40	-
	Dark	76.66	14.16	-	2.92	6.26
Fig. 1, b (2nd batch variant)	Sum	66.31	28.52	0.14	0.91	4.12
	Light	53.61	46.06	0.33	-	-
	Dark	78.09	11.82	-	2.72	7.37
Fig. 1, c (3rd batch variant)	Sum	63.53	31.87	0.92	2.05	1.63
	Light	58.58	40.12	0.70	0.60	-
	Dark	85.14	4.87	-	5.01	4.98
Fig. 1, d (4th batch variant)	Sum	52.19	36.79	7.59	2.22	1.21
	Light	54.39	37.70	7.28	0.63	-
	Dark	72.46	14.29	12.22	1.03	-
	Black	75.33	9.43	1.78	7.60	5.86

* EDS analysis was carried out on several samples and several areas, and the results were within the error limits of the method used, therefore the results presented in Table 4 can be considered averaged

Comparing the characteristic microstructure of the studied samples and their composition according to the results of EDS, it can be concluded that the metal samples obtained with options 1 and 3 of introducing reducing agents consist of two phases: a light solid solution of **Cr-Fe** and a dark one based on nitrides in the **Cr-V-N** system; in options 2 and 4, silicides are also formed in the **Cr-Si** system (**Cr₃Si** and **Cr₅Si₃**), which is explained by the excess of **Si**, the source of which are reducing agents.

Analyzing the data from the combined spectra, as shown in Table 4, higher chromium contents are observed for charge variants 1 and 2.

Figure 2 shows a map of the element distribution in a metal sample obtained from charge variant 2.

Element distribution maps for variants 1 and 3 are not provided, as they exhibit similar distribution patterns, which is also confirmed by the compositions discussed previously (Table 4).

Nitrogen saturation and the formation of chromium and vanadium nitrides at high temperatures are thermodynamically possible; however, their stability decreases with increasing temperature. High temperatures above 1650 °C can be achieved through exothermic reduction reactions [5], which could result in localized overheating followed by rapid cooling, preventing nitrogen decomposition.

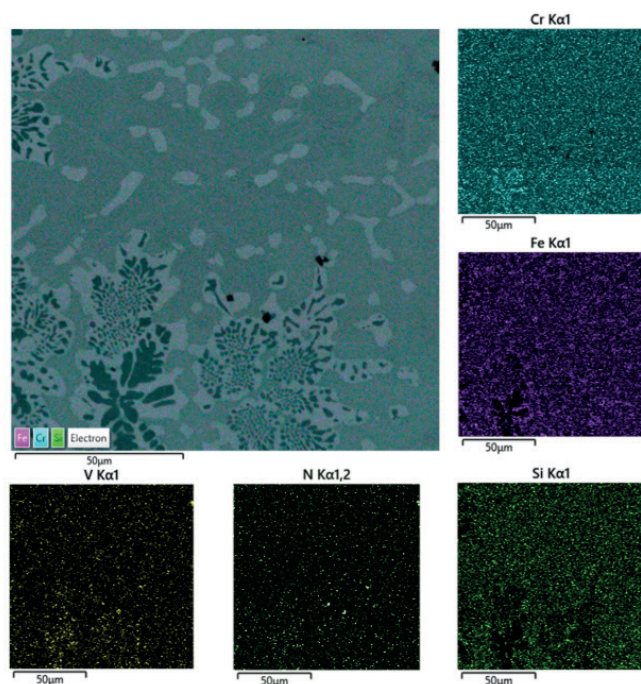


Figure 2. SEM image of a metal sample obtained from the 2nd batch variant in the backscattered electron detection mode, and a distribution map of chromium, iron, silicon, vanadium and nitrogen.

Сурет 2. Кері шашыранқы электронды анықтау режимінде 2-ші партия нұсқасынан алынған металл үлгісінің SEM кескіні және хром, темір, кремний, ванадий және азоттың таралу картасы.

Рис. 2. Изображение образца металла, полученного из 2-й партии в режиме детектирования обратнорассеянных электронов, полученное с помощью сканирующего электронного микроскопа, и карта распределения хрома, железа, кремния, ванадия и азота.

Figure 3 shows a similar element distribution map for a metal sample obtained from batch variant 4.

Figure 3 shows that *Cr* is distributed over the entire surface of the sample, but is more concentrated in dark areas along with *Si* and *N*. *V* is distributed fairly uniformly, primarily rebound with *N*, and is present to a lesser extent in areas enriched in *Si*, which is absent from the black phase.

Using analytical chemistry methods, the content of elements difficult to determine by EDS was determined in all metals, and the average content was: $C \leq 0.10\%$; $S \leq 0.02\%$; $P \leq 0.03\%$. Thus, all the metal samples studied were characterized by low contents of these elements. Nitrogen content was determined using titrimetric analysis, which confirmed an average nitrogen content of 2.6; 3.6; 2.6, and 2.1 for metal samples from variants 1, 2, 3, and 4, respectively.

Ferrochrome samples obtained from batch variants 1, 2, and 3 meet the requirements for the *FeCr60C1N3* grade (low-carbon nitrogen-containing ferrochrome) according to ISO 5448-81. This makes the obtained metal samples suitable for alloying nitrogen-containing stainless steels. The metal obtained from batch variant 4 is close to the requirement for *FeCr60C50Si7LP* (high-carbon ferrochrome) according to

ISO 5448-81, but with a low *C* content and increased *N*; it can also be considered as low-carbon nitrogen-containing ferrochrome with an increased *Si* content. The metal samples also met the listed requirements for low-carbon ferrochrome grades in terms of *C*, *S*, and *P* contents.

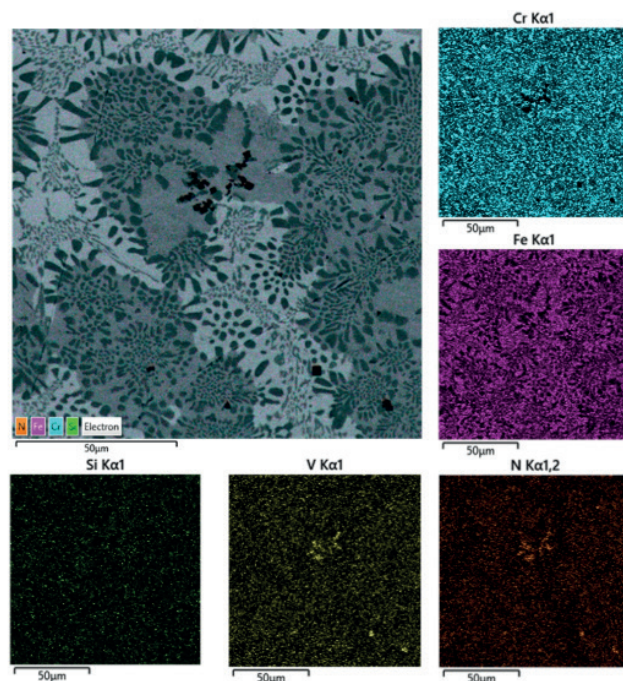


Figure 3. SEM image of a metal sample obtained from the 4th batch variant in EDS mode, distribution map of chromium, iron, silicon, vanadium and nitrogen.

Сурет 3. ЭДС режимінде 4-ші партия нұсқасынан алынған металл үлгісінің SEM кескіні, хром, темір, кремний, ванадий және азоттың таралу картасы.

Рис. 3. Изображение образца металла, полученного из 4-й партии вариантов, полученное с помощью СЭМ в режиме энергодисперсионной спектроскопии (ЭДС), карта распределения хрома, железа, кремния, ванадия и азота.

Discussion

The obtained results can be explained by the thermodynamic and kinetic features of metallothermic reduction in the *Cr-Fe-Si-Ca-V-N* system at high temperatures. The formation of *Cr-Fe* solid solutions in all charge variants confirms effective reduction of chromium oxides by silicon, aluminum, and calcium contained in *FeAlSiCa* and *FeSiCr*. The presence of *Cr-V-N* phases indicates active nitrogen dissolution in the melt, while their stabilization is likely associated with rapid cooling after exothermic reactions, preventing nitrogen degassing.

The formation of *Cr₃Si* and *Cr₅Si₃* silicides in variants with reductant excess is attributed to increased silicon activity. Under moderate reductant content, silicon is primarily consumed in oxide reduction, limiting silicide formation. Thus, the phase composition is strongly governed by the balance between reduction stoichiometry and silicon excess.

The advantages of the proposed approach are related to the use of complex reducing agents that ensure simultaneous par-

ticipation of **Si**, **Al**, and **Ca**, increasing reduction efficiency. The use of ferrosilicochrome dust promotes partial recycling of metallurgical waste. Moreover, eliminating coke reduces carbon contamination and enables the production of low-carbon ferrochrome suitable for nitrogen alloying. The metallothermic mechanism also provides localized temperature intensification without additional external energy input.

Compared with conventional carbothermic ferrochrome production, the developed approach ensures very low carbon content ($\leq 0.10\%$) and high chromium recovery (up to 86%) without direct carbon input. Stable nitrogen alloying was achieved without additional nitrogen injection, which may simplify industrial application.

However, the study has limitations. Laboratory crucible experiments do not fully reproduce industrial heat and mass transfer conditions. Local overheating may lead to phase inhomogeneity, and controlling silicon content remains challenging. Additionally, the absence of detailed thermodynamic modeling limits precise prediction of phase equilibria.

Further work should focus on optimizing reductant ratios, performing thermodynamic simulations, and scaling the process to pilot conditions. Industrial implementation will require control of reaction intensity and economic evaluation of reductant efficiency.

Overall, carbon-free metallothermic reduction using **FeAl-SiCa** and **FeSiCr** dust represents a promising route for producing low-carbon nitrogen-containing ferrochrome, though further optimization and scaling are necessary.

Conclusions

This study investigated the feasibility of carbon-free smelting of chromium-containing ferroalloy using ferroaluminosilicocalcium (**FeAlSiCa**) and ferrosilicochrome dust (**FeSiCr**) as complex metallothermic reducing agents. It was established

that the application of these reductants ensures efficient reduction of chromium oxides with the formation of **Cr-Fe** metallic phases and **Cr-V-N** nitride phases.

The results demonstrated that the phase composition of the produced alloys depends on the ratio of reductants relative to stoichiometry. Under moderate excess of reductants, predominantly **Cr-Fe** solid solutions and nitride phases are formed, whereas a significant excess of silicon leads to the formation of **Cr-Si** silicides. Therefore, the balance between reduction capacity and silicon activity is a key factor in controlling alloy structure and properties.

All investigated variants produced alloys with low impurity contents: carbon $\leq 0.10\%$, sulfur $\leq 0.02\%$, and phosphorus $\leq 0.03\%$. Chromium recovery reached up to 86%, which is comparable to industrial practice. According to chemical composition, the obtained alloys meet the requirements of ISO 5448-81 for low-carbon nitrogen-containing ferrochrome, confirming their suitability for alloying corrosion-resistant and nitrogen-containing steels.

The charge composition with a 10% excess of reductants was identified as optimal, providing high chromium recovery, stable phase composition, and compliance with standard specifications.

The obtained results confirm the potential of using **FeAlSiCa** and **FeSiCr** dust in carbon-free metallothermic ferrochrome production. Further research should focus on thermodynamic modeling of phase equilibria, optimization of charge composition, and scaling the process to pilot and industrial levels.

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