ANNOTATION

of the dissertation

RESEARCH AND DEVELOPMENT OF TECHNOLOGY FOR SMELTING CHROMIUM-MANGANESE LIGATURE USING A COMPLEX SILICON-ALUMINUM REDUCING AGENT

submitted for the degree of Doctor of Philosophy (PhD)
in the educational program 8D07202 – "Metallurgy"

KABYLKANOV SULTAN KAIYRBEKOVICH

Relevance of the Dissertation

At present, one of the key scientific and technological challenges in ferrous metallurgy is reducing the energy intensity of steel production, increasing the recovery rate of alloying elements, and ensuring the environmental sustainability of metallurgical processes. This problem is particularly relevant under conditions of depletion of high-grade chromium and manganese ores, high energy consumption in ferroalloy production, and increasing complexity of mineral raw material processing. The conventional use of ferrochrome (FeCr) and ferromanganese (FeMn) involves multi-stage technological operations, leads to additional consumption of energy and resources, and limits the overall efficiency of the metallurgical process.

Under these conditions, the production of chromium and manganese in the form of a single complex ligature is considered a promising scientific and technological approach that can significantly improve the efficiency of the metallurgical system. This approach enhances the recovery of alloying elements in the melt, shortens the technological cycle, reduces energy consumption, and enables more efficient utilization of low-grade domestic raw materials. In addition, the use of complex silicon-aluminum-containing reducing agents improves resource efficiency and aligns with the modern principles of "green metallurgy," aimed at developing next-generation energy-saving technologies.

In this regard, the development of a technology for producing a complex chromium-manganese ligature based on low-grade raw materials is a relevant scientific and technological task for the advancement of the metallurgical industry.

Object of the study

Technology for producing a chromium-manganese ligature from domestic low-grade chromium and manganese ores using a complex silicon-aluminum reducing agent.

Subject of the study

Physicochemical and thermodynamic processes occurring in the slag–metal system during the production of chromium-manganese ligature using complex silicon-aluminum reducing agents, as well as the patterns of their influence on ligature formation.

Objective of the study

Development of a technology for smelting chromium-manganese ligature using domestic low-grade chromium and iron-manganese ores.

Research objectives

To achieve the aim of the study, the following main objectives were set in the dissertation:

- to investigate the physicochemical properties of domestic low-grade chromium and iron-manganese ores, as well as complex silicon-aluminum reducing materials, and to assess their metallurgical suitability;
- to determine the optimal charge composition for producing chromium-manganese ligature based on thermodynamic and mathematical modeling, taking into account the phase state of the metal–slag system, reduction feasibility, and the recovery of elements;
- to conduct laboratory experiments on the smelting of chromium-manganese ligature to verify the results of thermodynamic calculations;
- to perform large-scale laboratory melts in a refining electric arc furnace with a capacity of 100 kVA to evaluate the proposed technology;
- to study the chemical, phase, and microstructural composition of the obtained metal and slag products and to determine the degree of transfer of alloying elements into the metallic phase;
- to develop technological recommendations for the production of chromium-manganese ligature for complex alloying of steel based on the obtained results using low-grade domestic raw materials.

Scientific novelty of the study

For the first time in this dissertation:

1. Using the software packages HSC Chemistry 10 and FactSage 8.4, the thermodynamic regularities of the multicomponent system Fe–Cr–Mn–Si–Al–Ca–Mg–O were comprehensively investigated. Based on non-standard charge materials (low-grade chromium and iron-manganese ores, as well as silicon-aluminum reducing agents), a scientifically substantiated optimal composition for producing chromium-manganese ligature was determined.
2. For the first time, three technological variants for producing chromium-manganese ligature using non-standard reducing agents (AlSiMn, FeSiAl, and FeSiCr dust) have been scientifically substantiated, resulting in ligatures with the following chemical compositions:
   - based on AlSiMn: Cr – 54.18 %, Mn – 20.20 %, Si – 3.08 %;
   - based on FeSiAl: Cr – 24.24 %, Mn – 29.12 %, Si – 2.93 %;
   - based on FeSiCr dust: Cr – 20.45 %, Mn – 40.14 %, Si – 4.39 %.
3. For the first time, a mathematical model describing the processes of aluminothermic and silicothermic reduction of chromium and manganese oxides under three technological variants has been developed based on three-factor experimental-statistical modeling. The proposed model enables a quantitative assessment of the degree of transfer of Cr and Mn into the metallic phase depending on the composition and consumption of silicon-aluminum reducing agents:

for the 1st variant:

- $Y_{Cr} = 1.915 \cdot x^3 – 23.9 \cdot x^2 + 93.475 \cdot x – 12.615$;

for the 2nd variant:

- $Y_{Cr} = 2.2973 \cdot x^3 – 26.993 \cdot x^2 + 99.406 \cdot x – 12.791$;
- $Y_{Mn} = 3.4459 \cdot x^3 – 40.491 \cdot x^2 + 149.12 \cdot x – 69.217$;

for the 3rd variant:

- $Y_{Mn} = 1.8584 \cdot x^3 – 25.987 \cdot x^2 + 116.98 \cdot x – 68.071$.

The obtained regression relationships made it possible to quantitatively assess the effect of reducing agent consumption and oxygen balance on the formation of a complex chromium-manganese alloy, and also served as a basis for determining the optimal process conditions.

For the first time, chromium-manganese ligature was obtained under laboratory conditions using non-standard silicon-aluminum reducing agents according to three technological variants:

- Cr – 53.95 %, Mn – 19.91 %, Si – 3.19 %;
- Cr – 23.93 %, Mn – 28.31 %, Si – 3.21 %;
- Cr – 20.34 %, Mn – 39.51 %, Si – 4.58 %.

The proposed technological variants were implemented taking into account the regularities of aluminothermic and silicothermic reduction of chromium and manganese oxides. The results of the experimental melts were confirmed by tests using analytical control methods and by the developed technological regulations.

Practical significance of the study

The practical significance of the study is determined by the development of a scientifically substantiated aluminothermic–silicothermic technology for producing chromium-manganese ligature. The proposed technology is based on the efficient use of local raw materials (chromium ores from the Kempirsai deposit and iron-manganese ores from the Kerege-Tas deposit), as well as complex silicon-aluminum reducing agents.

As a result of the research, a technological regulation for the smelting of chromium-manganese ligature in an electric arc furnace with a capacity of 100 kVA was developed, and its main technological parameters were determined. The conducted experimental studies demonstrated a high degree of transfer of Cr and Mn into the metallic phase.

Based on the developed regulation, pilot-industrial tests were carried out, during which an experimental batch of chromium-manganese ligature was obtained. The results confirmed the effectiveness of the proposed technology for producing complex ligature and for processing low-grade local raw materials in metallurgical production.

Research methods

In this dissertation, a combination of theoretical and experimental methods was used to investigate the physicochemical regularities and technological parameters of chromium-manganese ligature smelting. The theoretical analysis was carried out through thermodynamic modeling using the HSC Chemistry 10 software and phase diagram analysis using the FactSage 8.4 program.

To determine the phase composition of the raw materials and the obtained products (ligature and slag), X-ray diffraction analysis (XRD) was employed. The microstructure and elemental composition were studied using scanning electron microscopy and energy-dispersive spectroscopy (SEM/EDS), while differential thermal analysis (DTA) was used to evaluate thermal behavior. In addition, chemical and spectrometric analysis methods were applied.

Experimental modeling of the smelting process and optimization of technological parameters were carried out under laboratory conditions using a high-temperature Tamman furnace and an electric arc furnace with a capacity of 100 kVA.

Main results of the study submitted for defense:

- Results of the analysis of physicochemical properties of the initial raw materials (chromium and iron-manganese ores) and complex silicon-aluminum reducing agents (AlSiMn, FeSiAl, FeSiCr dust);
- Results of thermodynamic modeling of the chromium-manganese ligature smelting process;
- Results of multifactor mathematical modeling of dependencies determining the recovery of chromium and manganese;
- Results of laboratory and large-scale laboratory tests of the chromium-manganese ligature smelting process;
- Results of determining the techno-economic indicators of the chromium-manganese ligature smelting process.

Place of research

The dissertation research was carried out at the International School of Engineering of D. Serikbayev East Kazakhstan Technical University, at the experimental facilities of the Zh. Abishev Chemical-Metallurgical Institute, in the laboratory "Ferroalloys and Reduction Processes," as well as in the laboratory of the Department of Metallurgy and Materials Science at Istanbul Technical University (Istanbul, Türkiye).

Description of the main research results

- As a result of the analysis of literature data, it was established that conventional technologies for producing low-carbon FeCr and FeMn are characterized by high energy consumption, a relatively low degree of transfer of alloying elements into the metal, and the separate addition of elements during steel alloying. In addition, these technologies are characterized by multi-stage processing schemes. It was also found that a significant proportion of chromium and iron-manganese ores in the country are low- and medium-grade and are not fully suitable for efficient processing using conventional technologies. In this regard, the necessity of developing a technology for producing chromium-manganese ligature based on the integrated use of low-grade domestic raw materials has been substantiated in order to address these issues.
- The physicochemical properties of the initial charge materials for smelting chromium-manganese ligature were comprehensively investigated. The chemical composition of the chromium ore from the Kempirsai deposit was determined as follows: Cr_2O_3 – 39.86 %, MgO – 27.85 %, Fe_2O_3 – 11.84 %, SiO_2 – 10.93 %. According to X-ray diffraction (XRD) analysis, the main mineral phase is

chromospinel $(Fe,Mg)(Cr,Al)_2O_4$. SEM analysis revealed a heterogeneous structure of the ore with chromite grains of approximately 100 μm in size. According to differential thermal analysis (DTA), moisture removal occurs at approximately 150 °C, phase transformations associated with iron oxidation occur at around 480 °C, and thermal dissociation of magnesium-containing silicates takes place in the temperature range of 600–800 °C. The chemical composition of the Kerege-Tas iron-manganese ore was determined as follows: Mn_2O_3 – 38.29 %, Fe_2O_3 – 39.87 %, SiO_2 – 16.74 %, with an Mn/Fe ratio of 1.75:1. According to XRD analysis, the main phases are hematite (Fe_2O_3) and pyrolusite (MnO_2). SEM/EDS analysis showed a cryptocrystalline structure of the ore with a local manganese content of up to 52.56 %. DTA–TG analysis revealed a total mass loss of 16–17 % and major phase transformations occurring in the temperature ranges of 350–750 °C and 750–1200 °C. The chemical composition of the non-standard silicon-aluminum reducing agents was determined as follows: AlSiMn – Al 8.55 %, Si 48.39 %, Mn 29.04 %; FeSiAl – Al 10.82 %, Si 48.62 %, Fe 40.52 %; FeSiCr dust – Al 1.51 %, Si 32.22 %, Cr 24.10 %. According to XRD analysis, their main phases are silicide compounds such as $Mn_{11}Si_{19}$, FeSi, $FeSi_2$ and Cr_3Si.

- To substantiate the process of producing chromium-manganese ligature, studies were carried out using thermodynamic and mathematical modeling. Using the HSC Chemistry 10.0 software, the influence of temperature regime and reducing agent consumption on the formation of metallic and slag phases in the multicomponent system Fe–Cr–Mn–Si–Al–Ca–Mg–O was evaluated. It was established that at 1400 °C, due to the high thermodynamic stability of Cr_2O_3, complete reduction of chromium is not achieved, whereas at 1800 °C manganese losses increase due to evaporation. In this regard, the optimal process temperature is 1600 °C. It was determined that at a reducing agent consumption of 30 kg for AlSiMn and FeSiAl, and 50 kg for FeSiCr dust, the recovery of Cr and Mn into the metallic phase reaches 99–100%. To control the slag composition, phase modeling was performed in the CaO–MgO–Al_2O_3–SiO_2 system using the FactSage 8.4 software. It was found that an increase in CaO content leads to depolymerization of the slag structure and an increase in its basicity. The formation of merwinite–periclase phases and calcium silicates was demonstrated. In this region, the slag liquidus temperature is 1600–1650 °C, and its viscosity ranges from 0.3 to 1.0 Pa·s, which ensures efficient separation of the metallic and slag phases.

- To quantitatively describe the regularities of the smelting process, a multifactor mathematical model was developed, in which the degrees of transfer of chromium and manganese into the metallic phase were taken as the output parameters. The adequacy of the obtained regression models was confirmed by the values of the coefficient of determination (R^2 = 0.9615–0.9671). The modeling results showed that within a certain optimal range of oxygen balance, at a temperature of 1600 °C and with an optimal reducing agent consumption, the maximum recovery of Cr and Mn into the metallic phase is achieved.

- Based on the results of theoretical, thermodynamic, and mathematical modeling, the technology for producing chromium-manganese ligature was validated under laboratory, large-scale laboratory, and industrial conditions. In laboratory melts carried out in a Tamman furnace at a temperature of 1600 °C with a holding time of 20 minutes, a complex chromium-manganese ligature with the following composition was obtained for three charge variants: Cr – 20.34–53.95 %, Mn – 19.91–39.51 %, Fe – 22.92–44.64 %, Si – 3.20–4.59 %. Crucible melts in an induction furnace demonstrated the exothermic nature of metallothermic reactions, with the main stage occurring at 1200–1300 °C and the melt temperature increasing to 1500–1600 °C. Phase analysis showed that the metallic phase consists of a solid solution α-(Fe,Cr,Mn), as well as silicides FeSi, Fe_3Si, MnSi, Mn_3Si, CrSi, $CrSi_2$, and Cr_5Si_3. The slag phase is dominated by $Ca_2Si_2O_7$, $Ca_2MgSi_2O_7$, MgO, Al_2O_3, and $MgAl_2O_4$, with the content of (Fe,Mn)O being less than 1%, indicating low metal losses. The study of slag rheological properties showed that the optimal basicity is B = 1.5–1.8. It was established that the temperature dependence of viscosity follows the Arrhenius law ($R^2 \approx 0.97–0.99$), and the activation energy according to the Frenkel–Andrade equation ranges from 161.7 to 189.8 kJ/mol.

- Based on the obtained results, large-scale laboratory melts were carried out in a refining electric arc furnace with a capacity of 100 kVA, with a total of 21 experimental heats performed. As a result, the stability of the chemical composition of the metal was confirmed, with average values as follows: for the 1st variant – Fe 22.64 %, Cr 52.76 %, Mn 20.18 %, Si 4.31 %; for the 2nd variant – Fe 41.61 %, Cr 27.72 %, Mn 26.76 %, Si 3.80 %; for the 3rd variant – Fe 34.92 %, Cr 20.58 %, Mn 39.82 %, Si 4.56 %. The slag basicity was maintained within the range of 1.57–1.67, confirming the technological stability of the smelting process. The proposed technology was tested under industrial conditions at Scientific and Production Association "MANGANESE" LLP in an electric arc furnace with a capacity of 250 kVA, where approximately 500 kg of chromium-manganese ligature was produced over a period of 12 days. Techno-economic calculations showed that the use of the proposed complex ligature provides an economic efficiency of 9.86–35.43% compared to conventional low-carbon FeCr and FeMn alloys.

Author's contribution to the dissertation

The main scientific results of the dissertation were obtained with the direct participation of the author under the supervision of the scientific advisor. The author carried out experimental and computational studies using modern laboratory equipment and software packages HSC Chemistry and FactSage. The research results are confirmed by publications in scientific journals indexed in the Scopus and Web of Science databases. Based on the results of large-scale laboratory and industrial tests, a technology for producing chromium-manganese ligature was developed, on the basis of which a technological regulation and a test report were prepared, and a patent of the Republic of Kazakhstan for a utility model was obtained.

Approbation of the study

The proposed technology for smelting chromium-manganese ligature was tested under large-scale laboratory conditions in an electric arc furnace with a capacity of 100 kVA. The results of the tests confirmed the feasibility of its practical implementation, and a technological regulation for the smelting of chromium-manganese ligature was developed.

The main theoretical provisions and scientific results of the dissertation have been implemented in the educational process of the Aktobe Regional University named after K. Zhubanov. The research materials are used in teaching the courses “Theory and Technology of Ferroalloy Production” and “Recycling Technologies in Ferroalloy Production” within the educational program “Metallurgy,” which is confirmed by the corresponding implementation certificate.

The practical significance and industrial value of the work are confirmed by the implementation of the research results at the production facilities of the Scientific and Production Association “Manganese” LLP, as evidenced by the corresponding implementation act.

A total of 15 scientific publications have been published on the topic of the dissertation, including 4 articles in journals indexed in the Web of Science and Scopus databases (3 articles in journals published by the Multidisciplinary Digital Publishing Institute (MDPI), namely Processes, Metals, and Molecules, as well as 1 article in Acta Metallurgica Slovaca).

In addition, 3 articles were published in journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan (1 article in the journal Science and Technology of Kazakhstan, 1 article in the Bulletin of D. Serikbayev East Kazakhstan Technical University, and 1 article in Central Asian Transactions on Materials Structure and Properties), and 3 articles were published in other scientific journals (including the Bulletin of Aktobe Regional University named after K. Zhubanov).

The main scientific results of the dissertation were presented and published in the form of 4 conference papers at international and national scientific and practical conferences:

- 1 conference paper in the proceedings of the XII International Scientific and Practical Conference “Innovative Technologies and Engineering”, dedicated to the 60th anniversary of Karaganda Industrial University (Temirtau, 2023);
- 1 conference paper in the proceedings of the International Scientific and Practical Conference “Integrated Processing of Mineral Raw Materials and Innovations as Key Directions of Economic Modernization” (Almaty, 2023);
- 1 conference paper in the proceedings of the XVII Saginov Readings “Integration of Education, Science, and Production” International Scientific and Practical Conference (Karaganda, 2025);
- 1 conference paper in the proceedings of the V International Scientific and Experimental Conference “Abishev Readings – 2026” “Integration of Science, Digital Technologies, Artificial Intelligence, and Industrial Production in the Mining and Metallurgical Complex of the Republic of Kazakhstan” (Almaty, 2026).

In addition, based on the results of the research, a utility model patent of the Republic of Kazakhstan No. 9126 entitled “Charge for the Production of Chromium-Manganese Ferroalloy” was obtained, issued by the National Institute of Intellectual Property of the Ministry of Justice of the Republic of Kazakhstan (publication date: May 17, 2024).

Structure and scope of the dissertation

The dissertation consists of an introduction, the main part comprising four chapters, a conclusion, and appendices. The total length of the work is 138 pages of typed text. The research materials are aimed at a comprehensive presentation of the dissertation content and are supplemented with illustrative materials: the work includes 66 figures and 21 tables. The list of references comprises 103 sources, including works by domestic and foreign researchers, as well as recent scientific publications.