ABSTRACT

Dissertation for the degree of Doctor of Philosophy PhD
specialty 6D070900 - "Metallurgy"

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"DEVELOPMENT OF TECHNOLOGY FOR PRODUCING IRON - MANGANESE - CHROME CONTAINING ALLOYS FROM METAL-CONTAINING WASTE ON THE BASIS OF DIRECT METAL REDUCTION"

Assessment of the current state of a scientific or scientific-technological problem being solved. Kazakhstan occupies a leading position in the Eurasian Union in reserves and production of manganese and chromium ores, which are the main source for ferroalloy plants of the republic. Zhairem Mining and Concentrating Complex (Zhairem MCC) works on the basis of manganese ores, and on the chrome ores - the Donskoy Mining and Processing Plant (Donskoy MPP), located in the Aktobe region.

For the preparation of raw materials for ferroalloy plants operating on a charge made up of a large fraction of manganese and/or chrome ores and coke, primary ores are enriched with sediments and sorted with the separation of fine fraction. As a result of such processing, fine fraction waste of less than 5-10 mm is generated, which is removed from the main processing chain and accumulated in dumps.

At present, the volume of accumulated small-scale waste of manganese and chrome ores has increased to the scales that determine the level of ecological safety of the region. From the technological point of view, manganese and chrome waste accumulated in the waste dumps contains rather high concentrations of valuable metals, including manganese and chrome, the presence of which determines the economic feasibility of their extraction. According to the balance of iron, manganese and chromium contained in the accumulated wastes, the possibilities of their technological preparation for metallurgical processing and organization of additional production of high value-added ferromanganese and ferrochrome alloys are reviewed. Involvement in the processing of ballast, substandard waste with the production of high-quality marketable products from them can be used in the future, both for the needs of the country's economy and for export. The solution of this problem requires complex research aimed at creating a highly effective technology for processing these wastes.

Basis and background data for developing the topic. At present, the total volume of accumulated substandard fine waste from the processing of primary manganese (Zhairem MCC) and chrome ores (Donskoy MPP) is about one million tons. Sufficiently high concentration of manganese and chromium in these wastes is quite acceptable and suitable for organization of technology of their processing for the purpose of additional extraction of these metals. For the specifications of traditional technology, they can be processed by pelletizing and returning to the main processing chain. For example, the sintering of fine manganese ore waste can

be done by agglomerative calcinating, but it is quite energy consuming technology. This approach is not acceptable for chrome waste, because of the high softening temperature (sintering) of over 2000°C.

Another possible solution may be a pyrometallurgical process involving direct melting of the fine fraction to extract metals, but this solution requires the development of a completely new technology alternative to the traditional electric ore smelting process.

The core of traditional technologies of ferroalloy plants are electrothermal furnaces, where only lumpy and/or pelletized ore materials are melted. Electricity consumption for ferromanganese smelting reaches 5000 kW/t, and for ferrochrome smelting - up to 9000 kW/t. The initial smelting charge includes pelletized raw materials, metallurgical coke and slag-forming fluxes.

The peculiarity and disadvantages of the existing technology are that the process of reduction melting of ferromanganese and ferrochrome is implemented with 100% power consumption, which greatly increases the cost of the process. Coke is used exclusively as a reducing agent and a nozzle for filtration of melts and released gases. In such a system, the recovery of metal from ore by hard carbon coke is virtually impossible in the solid state due to the limited reaction-contact surface between them. Recovery of metals starts from the moment of melting of the ore part of the charge, when metal oxide melts flow on the surface of coke pieces, i.e. at temperatures above 1250-1350 °C. This indicates that a significant part of electricity is used to heat a large mass of the charge to a given temperature. In this case, the processes of metal recovery are practically inhibited and there is no interaction of metal oxides with coke.

The above shortcomings have been taken into account and eliminated in the developed technology.

Justification of the need to conduct research work. The absence of a rational technology for processing fine fractions from the enrichment of manganese and chrome ores with high manganese and chrome content on the one hand, and their accumulation in geometric progression on the other, causes the need to develop a new technology. The scientific research carried out in the dissertation covers a wide range of theoretical and practical problems aimed at developing technology for metallurgical processing of accumulated manganese and chrome fine waste using it as an additional source of raw materials for the extraction of valuable metals.

On the basis of the detailed analysis of new directions and the theoretical approaches and solutions published in the scientific literature in this direction, technical conditions for the possibility of developing a new technology for processing small-scale wastes containing oxides of valuable alloying metals - manganese and chromium have been established.

It is known that the lower manganese oxides (MnO) and stable chromium oxides (Cr_2O_3) have a high chemical strength and can only be recovered by solid carbon at high temperatures of 1200-1400 °C. However, these oxides, according to the new theoretical positions, acquire a higher interaction activity with solid carbon

in the dispersed state than in the liquid-phase system used in conventional technology. Application of the mechanism of hard phase reduction of iron, manganese and chrome oxides by hard carbon opens up new technological possibilities for effective processing of the above mentioned wastes and organization of production of valuable functional alloys for steel alloying.

Information on the planned scientific and technical level of development, on patent studies and conclusions from them. The scientific and technical level of the developed technology is determined by the use of new achievements of theoretical knowledge and is based on the implementation of the mechanism of direct reduction of irreducible manganese and chrome oxides by carbon in the solid-phase dispersed and ultradisperse system. The essence of the new technology is that disperse and ultradisperse components form complex systems, including the oxides of the corresponding metals and the stoichiometric amount of solid carbon, intended for the reduction of recoverable metals. The implementation of such a mechanism and the established technological modes of the process allowed to obtain samples of high-quality iron-manganese, iron-chrome and combined iron-manganese-chrome alloys from substandard industrial wastes for the first time in the world practice.

Scientific novelty and practical value of the developed technology consists in preparation and processing of mechanically activated complex system, in which all interacting elements are concentrated in strictly proportional ratio.

The analysis of world-class patent researches and innovative patents of Kazakhstan, more than 20 years in depth, shows that the developed technology has no analogues and has a number of theoretical and practical advantages: for the first time the kinetic regularities of solid-phase reduction of metals - iron, manganese and chromium depending on chemical strength of their oxides and temperature of system heating have been established; the results of the study of direct metal reduction from the charge, which is a mechanically activated complex system, show the possibility to regulate the process as a whole. It is established that the reduction process in the prepared charge starts in the solid-phase state starting from the temperature 600 °C, while in the existing technology in electrothermal furnaces the reduction process takes place in the liquid phase after the melting of the material and starts at the temperature 1250 °C.

The use of a mechanically activated complex system as a charge allows to establish kinetic regularities of reduction of each metal depending on temperature on following indicators:

- coefficient of reduction and extraction of iron from the charge - 0.98; manganese - 0.75-0.80; chromium - 0.8-0.85;
- possibility to regulate the composition of smelted alloys by preparation of charge materials from waste in given mass proportions.

Metrological support. During the research work metrological support was determined by the presence of modern physical and chemical methods of analysis, performed with the use of certified methods, measuring instruments, equipment and devices, checked by bodies of State standards of the Republic of Kazakhstan.

Relevance.

Kazakhstan has not only known iron ore deposits, but also large deposits of manganese and chrome ores. Large industrial complexes for ferromanganese and ferrochrome production operate on the basis of manganese and chrome ores mined in Kazakhstan. In world practice, the technology of ferroalloys production is based on smelting lumpy sorted ore together with coke, which is mainly carried out in electrothermal furnaces. According to the ore sorting principle, the charge is prepared for smelting in electric furnaces at Zhairem MCC (manganese raw material) and Donskoy MPP (chromite raw material). Large lumpy ores are sent to ferroalloy plants, while fine screening of manganese and chrome ores is accumulated in dumps. Using these fine wastes to produce ferroalloys using existing technology is very difficult. This is due to the fact that, according to the specifications, oxide pelletized materials must first be obtained from them by agglomeration or pellet production. This requires significant material and energy costs.

The development of a new technology for direct metallurgical processing of fine waste, which ensures high technical and economic performance, is an urgent problem that must be solved.

The novelty of the topic is the development of a technology for producing ferromanganese, ferrochrome and a complex chromium-manganese alloy from substandard small materials (chromium, manganese and iron ore) based on direct reduction of metals.

Scientific novelty of research:

- The decisive role of the technical conditions for providing the kinetics of metal reduction by solid carbon depending on the temperature and the criterion of the reaction-contact surface (RCS) between metal oxides and solid carbon has been established. Such technical specifications are provided by the organization of preparation of ore pellets from dispersed ore-coal charge;
- Kinetic regularities of direct reduction of iron, manganese and chromium from a complex multi-component system have been established for the first time taking into account successive phase transformations of oxides of each metal depending on their strength of chemical bond with oxygen;
- a deterministic method of determination of specific consumption of solid carbon for the reduction of oxides depending on their strength and phase transformation to metal has been introduced for the first time, which provides savings in carbon consumption, as well as direct obtaining of melts of a given composition without carburizing metal;
- for the first time the process of producing manganese and chrome alloys from the charge containing oxide and carbon without coke and electrothermal furnaces was carried out, which provides multiple energy saving.

Connection of work with other research works. Dissertation work was carried out within the framework of state grants of the Science Foundation of the Ministry of Education and Science of the Republic of Kazakhstan on the project: "Scientific research of direct metal reduction and development of technology to

produce a new manganese chromium-containing alloy from accumulated industrial waste". (R&D No. 2210/GF4, contract No. 74 of 12.02.2015 for 2015-2017), financed by the Ministry of Education and Science of the Republic of Kazakhstan within the sub-program "Grant financing of scientific research" on priority "Rational use of natural resources, processing of raw materials and products".

The purpose of the dissertation work is to obtain samples of ferromanganese, ferrochrome and complex manganese chrome-containing ferroalloy from waste and to develop technology that provides high technical and economic performance, as well as the conversion of ballast stocks of real waste into marketable products.

The object of the study is accumulated fine waste from the processing of manganese ores at the Zhairem MCC and chrome ores at the Donskoy MPP.

The subject of the study is a charge based on fine waste of manganese and chrome ores and carbon-containing reducing reagent; kinetics of direct reduction of iron from ore pellets at regime heating of the system within 600-1000 °C; kinetics of direct reduction of manganese and chrome in the temperature range 1200-1500 °C; reduction melting of metallized products; composition and quality characteristics of ferromanganese and ferrochrome melts.

Research tasks:

- Sampling of representative samples of fine waste from the processing of manganese ores at the Zhairem MCC and from the processing of chrome ores at the Donskoy MPP with a comprehensive study of their chemical and mineral composition.
- Determination of technical specifications of reduction of metals by solid carbon depending on temperature and criterion of reaction-contact surface (RCS) between metal oxides and solid carbon.
- Determination of the influence of carbon-containing reducing agent consumption on direct reduction of iron, manganese and chrome from their oxides by carbon.
- Determination of optimal parameters of roasting of mechanically activated complex coal charge with the production of ore-coal pellets.
- selection and substantiation of technological modes of roasting of ore-coal pellets, providing obtaining samples of metallized pellets.
- Establishment of optimal technological parameters of reduction melting of metallized pellets, providing obtaining ferromanganese and ferrochrome with a normalized concentration of carbon.
- Determination of the optimal quantitative ratio of manganese and chromium waste in the charge to obtain a complex manganese-chromium-containing ferroalloy.

Methodological basis.

For preparation of complex iron ore raw materials standard equipment is used: vibration mill 75T-DR.

The processes of firing and direct reduction of metals from their oxides were carried out in standard furnaces SUOL-044/12-M2-U42, RHTC 80-230/15 and

high-temperature furnace Tamman, using the thermocouples of PP and electronic potentiometer KSP-2, which passed the control revision.

The state and quality of solid and liquid products obtained as a result of experimental studies was carried out through a thorough analysis on modern high-precision devices: a tabletop optical emission spectrometer SPECTROLAB JrCCD and an electron microscope JSM 5910. The mass of the initial samples and carbon-containing materials was determined on a Shimadzu ELB 1200 electronic balance in accordance with with GOST 24104-88. To determine the chemical and mineralogical compositions, certified methods and apparatus of the spectrometric method of analysis were used in accordance with GOST 18895-97.

Provisions to be defended:

- methods of preparation of fine manganese and chromium wastes for metallurgical processing by means of composing on their basis complex charge in the form of ore pellets.
- choice and substantiation of mono-charge composition for organization of reduction-smelting processes.
- results of reductive roasting of ore-coal pellets with obtaining metallized pellets.
- results of reduction melting of metallized pellets to produce ferrochrome and ferromanganese samples without carburization of metal corresponding to standard ferroalloys by chemical composition.

Practical relevance of work.

A new technology has been developed for processing accumulated and current substandard industrial waste representing a small-scale fraction from the enrichment of manganese and chrome ores with an additional high recovery of valuable metals in commercial products - ferrochrome, ferromanganese and complex alloy - ferrochrome-manganese.

The technology eliminates the use of expensive coke and electric furnaces, which significantly reduces energy and material costs. Involvement in the processing of industrial waste will improve the environmental situation in the region and free up large areas of land used to store fine fraction of waste from enrichment.

Approbation of the work. The main provisions of the dissertation work were reported at 5 international scientific conferences, among them:

- International Conference "Scientific research of the SCO countries: synergy and integration" (June 14-15, 2018.) - Beijing, China: Minzu University of China, 2018;
- Science and innovation in the XXI century: current issues, discoveries and achievements: V International Scientific Conference. - Pemza: ICNS "Science and Enlightenment" - August 5, 2017;
- Science - education - production: Experience and perspectives of development: materials of XIV International scientific-technical conf. (February 8-9, 2018): Ministry of Education and Science of the Russian Federation; Ural Federal University, Nizhny Tagil. - 2018;

- International Scientific and Practical Conference "Integration of Science, Education and Production - the Basis for Implementation of the Nation Plan". (Saginov Readings #10). 14-15 June 2018, Karaganda;

- International scientific-practical conference "Rational use of mineral and technogenic raw materials in the conditions of Industry 4.0" 14-15 March 2019. Almaty.

Publications. On the topic of dissertation 10 printed works were published, including 1 article in the journal, reviewed by Scopus database, 4 articles from the list of scientific journals recommended by CCSES MES RK, 4 abstracts, 1 patent of RK was received.

The structure and the volume of the thesis. The thesis consists of an introduction, 6 chapters, conclusion and annexes. The work is presented on 118 pages of typewritten text, contains 34 tables and 15 figures. The list of references used includes 74 titles.