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TITANIUM AND CHROME OXIDES SYSTEM THERMODYNAMIC DIAGRAM ANALYSIS

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The paper presents the results of a thermodynamic diagram study of oxide smelting products from the processing of chromite and titanium raw materials in order to determine their most technologically advanced compositions, allowing for rational use of raw materials and energy resources. The reliability of the effectiveness of these developments was confirmed by tests carried out on a pilot industrial and industrial scale.

Key words: titanium oxide, chrome oxide, thermodynamic diagram, technology, complex alloy.

INTRODUCTION

State diagrams of various systems contain valuable information about the composition and structure of the proposed smelting products and serve to obtain melts as close as possible to specified compositions and a certain temperature zone of the process, thereby predicting their properties and methods of technological production regimes.

In modern scientific and applied metallurgy, an important place is occupied by the study of the structure of liquid melts obtained by the pyrometallurgical processing of various raw materials. As a rule, raw materials, whether ore or concentrate, contain compounds that are not stable in the liquid state, i.e. disintegrating into stable components after overcoming their liquidus temperature. The generally accepted thermodynamic studies of processes in multicomponent systems are quite complex and require the use of extensive mathematical calculations and are directly related to the need to determine the thermodynamic functions of a large number of independent reactions. In many ways, some data on the properties of substances necessary for determining the Gibbs free energy of reactions are limited or absent, which in such cases excludes the applicability of thermodynamic analysis for studying multi-component systems [1-2].

RESEARCH METHODOLOGY

Thermodynamic diagram analysis (TDA) of complex systems, has recommended itself as the simplest and most accurate method for studying phase patterns in comparison with the classical thermodynamic study of metallurgy processes. The effectiveness of the method as an application to metallurgical technology is the ability to identify the features of the phase structure of the resulting melts in the process of metallurgical processing of various raw materials. Based on the results of such studies, phase diagrams are constructed, which allow tracing the phase metamorphism and predicting the final state of a single system simulating the composition of the melt under study.

Based on the results of the TDA of multicomponent systems, technologies have been developed for processing titanium and chromite raw materials to produce:

- refined grades of ferrochrome using ferrosilicoaluminium as a reducing agent with the achievement of slag stabilization and improvement of technical and economic indicators, etc;
- rich titanium slag by processing of chromium and vanadium-containing ilmenite concentrates that satisfy the requirements of consumers;
- low-grade ferrotitanium from ilmenite concentrates with reduction of loss and consumption of expensive aluminum powder up to 50% with obtaining standard grades (GOST 4761 - 91) due to the use of ferrosilicoaluminium;
- high-grade ferrotitanium (up to 70 % titanium) from rich titanium slag by aluminothermic reduction.

The purpose of the work is to conduct deep physicochemical studies of the thermodynamics of the processes of slag formation of multicomponent oxide systems that simulate the compositions of the resulting slags in the smelting of alloys based on chromium and titanium.

RESULTS RESEARCH

System CaO-MgO-Al_2O_3-SiO_2. The use of domestic high-magnesia ores (MgO about 20 %) in obtaining refined ferrochrome led to a deterioration of technical and economic indicators of smelting. In particular, the

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specific consumption of electric power and charge materials, the loss of under-reduced chromium with waste slags, as well as the slag rate increased. In the modern ferroalloy industry in Kazakhstan, refined grades of ferrochrome are obtained by the silicothermic method (Aktyubinsk Ferroalloy Plant), accompanied by the formation of self-dispersed pulverized slag with a basicity of CaO / SiO_2 more than 2.0. Ferrosilicochrome with a content of 48 - 50 % Si is commonly used as a reducing agent. At the same time, to make sure that all the ferrosilicochrome silicon is oxidized by oxygen from chromium ore to achieve a residual Si content in the commodity metal of up to 2% and to bind the resulting active silica (SiO_2) a large amount of lime is introduced into the charge. The slags obtained with this technology are highly basic, the structure of which contains a significant amount of dicalcium silicate (2CaO • SiO_2). The latter undergoes phase transitions at low temperatures with an increase in the volume of the crystal lattice, which leads to slag scattering. Hence the need to obtain compositions of slags, in which the presence of dicalcium silicate is limited. This can be achieved by increasing the alumina (Al_2O_3) in the slag, which is quite active with respect to silica [3].

To obtain a higher content of Al_2O_3 in the slag during the silicothermic production of refined ferrochrome, a reducing agent is required, which contains aluminum besides silicon in its composition. Such a reducing alloy is a complex alloy developed on the basis of the Chemical-metallurgical institute named after J. Abishev - ferro-silicon-aluminum (FSA) [4 - 7].

The basis of the reduction of chrome ore with silicon and aluminum are reactions:

$(MgO \cdot Cr_2O_3) + 2Al \rightarrow (MgO \cdot Al_2O_3) + 2Cr$

$Cr_2O_3 + 3/2\ Si \rightarrow 2Cr + 3/2SiO_2$

When smelting refined grades of ferrochrome with the use of FSA, slags of a radically new composition are formed. If according to the existing technology, slags are obtained, which are located on the basis of their basicity and the level of aluminum and magnesium oxides in the region of highly basic slags in the phase space of the four-component CaO – MgO – Al_2O_3 – SiO_2 system, i.e. in the 2CaO · SiO_2 – CaO – MgO - Al_2O_3 subsystem (where dicalcium silicate dominates in any part of it), then according to the new technology, slags are formed in another area of the CaO – MgO - Al_2O_3 - SiO_2 system, namely, in its second part, contoured by the phases 2CaO·SiO_2 - 2CaO·MgO·2SiO_2 - MgO· Al_2O_3 - CaO·SiO_2 - 2CaO·Al_2O_3·SiO_2 - CaO·Al_2O_3·2SiO_2, [8].

In it dicalcium silicate no longer dominates. Its existence in the phase space of the last region of the CaO – SiO_2 – MgO – Al_2O_3 system extends only to the planes (triple quasi-systems): 3CaO·2SiO_2 (rankinite) - 2CaO·Al_2O_3·SiO_2 (gelite) - 2CaO·MgO·2SiO_2 (akermanine), MgO ·Al_2O_3 (magnesia spinel) - 2CaO·Al_2O_3·SiO_2 - 2CaO·MgO·2SiO_2 (akermanite) and 2CaO·MgO·2SiO_2 (akermanite) - MgO·Al_2O_3 (magnesia spinel) - 2MgO·SiO_2 (forsterite). Below these planes, dicalcium silicate does not form at all in slags. At the same time, slags produced by the new method are formed just below these areas, since the CaO / SiO_2 ratio in them does not exceed 1,5, the Al_2O_3 content is guaranteed to be more than 12 %, and magnesium oxide is more than 15 %.

Practice shows that such slags are thermodynamically stable and absolutely not subject to scattering. In addition, chromium oxide in such slags is not chemically bound to other oxides, since required for the formation of calcium chromite (CaO · Cr_2O_3) and magneziohromita (MgO · Cr_2O_3) oxides of calcium and magnesium is spent on the forming thermodynamically very stable compounds type forsterite (2MgO · SiO_2), MgO · Al_2O_3 (magnesia spinel), 2CaO · Al_2O_3 · SiO_2 (helenite), 2CaO · MgO · 2SiO_2 (akerma-nit) and wollastonite (CaO SiO_2), while providing low activity of silica and alumina in the slag.

Due to the reduction of the basicity and the increase in the Al_2O_3 content, the slag does not disintegrate and its multiplicity decreases, in contrast to the standard technology, where the basicity of the slag is > 1,8.

Charge consisted of 60 % of chromite ore, 14 % of FSA and 26 % of lime (CaO > 90 %). Two charges (one weight 33kg) of the above composition were consumed per melt. The second charge was fed into the furnace also gradually after the formation of the slag layer in the furnace bath. The release of metal and slag was carried out through one taphole in the cast-iron molds installed in a cascade. After cooling the melt, the metal and slag were weighed and samples were taken for chemical analysis.

The resulting metal contained on average 65-67 % Cr, 0,8-1,5 % Si, 1-3 % C. The ingots of the metal were dense without gas shells and segregations, with a filamentous structure at the fracture characteristic of refined chromium alloys . The weighted average chemical composition of slag produced using the new method was the following,%: Cr_2O_3 – 4,79; SiO_2 – 24,02; Al_2O_3 - 13,18; CaO - 34,42; MgO – 22,36; FeO - 1,2; P - 0,031, and the CaO / SiO_2 basicity was 1,43. After cooling, slags were hard, stone-like, well separated from the metal and did not crumble into fine powder [9].

TiO_2-Al_2O_3-SiO_2-CaO-MgO system. Iron-titanium ores found in the depths of Kazakhstan are represented by a number of derstate deposits, the most famous of which are Satpayevskoye (EKO), Shokashskoye (Aktobe region) and Obukhovskoe (SKO) [10]. At JSC "UK TMK" in the production of titanium sponge the main raw material is a rich titanium slag (RTS). With the aim of partial import substitution of raw materials on the basis of this enterprise, in 1999 a workshop for the production of RTSs in a stationary ore-thermal electric furnace was commissioned. It processes the ilmenite concentrates produced from nearby iron-titanium ores from the Satpayevskoye deposit. Concentrates are characterized by a high content of undesirable impurities, i.e. vanadium oxides (up to 0,6 %) and niobium, which negatively affect the further chlorination of the slag obtained. Currently, in our country there are no industrial enterprises for the production of alloys and master alloys with titanium. The main supplier of titanium-containing alloys is the Russian Federation; semi-finished products were supplied to Arcelor Mittal Temirtau JSC for the deoxidation of low-alloyed steels. In the past, Aktobe ZF produced titanium-iron alloy (branded ferrotitanium 27 % Ti) by traditional out-of-furnace aluminothermic reduction of imported ilmenite concentrate, however, due to certain circumstances, production was soon mothballed.

Real rich titanium slags (RTSs), designed to produce spongy titanium, and slags from the production of ferrotitanium are a multicomponent system of oxide products of the smelting reduction of ilmenite concentrates, but they are based on a relatively small amount of oxides. The phase composition of RTSs and slags of ferrotitanium can be characterized by a five-component system TiO_2-CaO-MgO-Al_2O_3-SiO_2.

Given the above, there is a need to study the physicochemical and metallurgical properties of concentrates and oxide melts. First, it is connected with the determination of the phase composition of the obtained RTSs and slags from the production of alloys based on titanium and the volumes of their location in the five-component system TiO_2-SiO_2-Al_2O_3-MgO-CaO, as well as studying the dynamics of their change under the influence of various factors. The use of instrumental methods in this case requires substantial material costs and time. In recent years, theoretical methods for estimating the phase composition of multicomponent oxide melts have been developed, the formulation of relevant studies has been expedient, which was provided for in the present work.

The priority is to study the phase composition of the resulting slags and determine the volumes of their location in the five-component system TiO_2-SiO_2-Al_2O_3-MgO-CaO, as well as to study the complex metallurgical and physicochemical properties of Shokash concentrates and slag melts to develop effective technological processes of production for RTS and titanium based alloys.

When studying the stable composition of the system TiO_2-Al_2O_3-SiO_2-MgO-CaO using the TDA method, it is necessary to proceed from the breakdown of five boundary subsystems TiO_2-CaO-MgO-Al_2O_3, TiO_2-CaO-MgO-SiO_2, TiO_2-CaO-Al_2O_3-SiO_2, TiO_2-MgO-Al_2O_3-SiO_2 and CaO-MgO-Al_2O_3-SiO_2 to stable elementary polytopes. The reliability of the results of the research with the introduction of refinements is confirmed by the sum of the volumes of stable tetrahedra of each boundary subsystem calculated by the "center of gravity" and "Khiza" methods, they are identically equal to 1 (unit) [11].

The given data on four-component boundary systems are fundamental for the consistent decomposition of the TiO_2-CaO-MgO-Al_2O_3-SiO_2 five-component system modeling compositions formed during the production of RTSs and ferrotitanium, slags, into stable pentatopes (five-vertex volumes). Thus, the investigated phase equilibria congruently (stably) melting compounds of the five system TiO_2-CaO-MgO-Al_2O_3-SiO_2 simulating the composition of titanium slags and slags of aluminum, aluminosilicothermic production of titanium-based alloys, as well as slag melts from smelting titanium-magnetite ores and etc., led to the fact that it consists of 30 stable pentatops (volumes).

Accepted data can be processed analytically to obtain equations for the study of its physico-chemical properties of individual compositions. The simplest and available for software calculation method of deriving transformation equations expressing any secondary subsystem through primary components (TiO_2, CaO, MgO, Al_2O_3 and SiO_2) of the basic system is described in the well-known work of Heath. The criterion for the location of a given composition of melts in one of the subsystems is the positive values of the n-th number of secondary components of a certain volume, which includes the chemical composition of the resulting slags.

The application of TDA results to rich titanium slags and slags from the production of titanium-based alloys consists in finding elemental pentotopes simulating their compositions and the normative distribution of primary phases between secondary compounds of the pentatope under consideration. To determine the manufacturability of the slags produced during the smelting process (melting point, fluidity, etc.), it is necessary to recalculate their weighted average chemical compositions (as in Table 1) into five primary oxides of the TiO_2-CaO-MgO-Al_2O_3 system.

As a result, it became clear that rich titanium slags and ferrotitanium slags obtained from concentrates of the Shokashsky deposit are located in pentatopes under Nos. 29 and 24, respectively, and RTS compositions from the smelting of Satpayevsky and Obukhovsky concentrates are modeled with Pentatopes under Nos. 18 and 29, respectively. Further, taking into account the data on the melting points of the secondary components of a certain pentatope, the modeling composition of the desired slag, it is possible to preliminarily determine its melting point and fusibility.

Table 1 **The weighted average chemical composition of the slags obtained from the smelting of various concentrates / wt. %**

Slag	TiO_2	CaO	MgO	Al_2O_3	SiO_2
Shokashsky	88,86	0,27	0,3	6,254	4,31
Satpayevsky	85,27	0,6	0,5	7,3	6,74
Obukhovsky	87,35	0,7	0,78	6,4	4,1
Ferrotitanium *	22,95	17,4	3,45	45,8	10,4

* - by the technology developed in CMI for the production of low-percentage ferrotitanium from Shokashsky concentrate using ferro-silico-aluminum

Practically applying the method of thermodynamic diagram study of slag melts in order to reduce the content of harmful impurities in rich titanium slags, the effect of the addition of various catalytic additives on the behavior of vanadium and chromium in it was studied. As a result, it was established that additives to the charge mixture of ferromanganese production wastes give a positive result. Used recycled metal with slag inclusions, with the content of the metal phase - 80-90 %. This material was set in the furnace in the amount of 1-5 % by weight of the concentrate [12].

The use of complex reducing agent changes the composition of the final slag. As a result of the oxidation of silicon and aluminum in the process of reduction, mullite is formed ($3Al_2O_3 \cdot 2SiO_2$), the latter increases the activity of TiO_2 in the slag and at the same time enhances the extraction of titanium into the alloy, and also reduces the likelihood of formation of a compound of the thialite type ($Al_2O_3 \cdot TiO_2$). Along with the positive effect of SiO_2 on the TiO_2 activity in the slag, silicon dioxide also lowers the temperature of the process of producing ferro-titanium, creating favorable conditions for the deposition of metal rods.

CONCLUSIONS

From the above theoretical data it follows the confirmation of the fact that the TDA, in which the complex mathematical apparatus is neglected, allows using the phase diagrams of multicomponent systems to predict the optimal composition areas of more technological slags.

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Note: The responsible for England language is Aigul Sarbasova, Aktobe, Kazakhstan.