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THERMODYNAMIC DIAGRAMMATIC ANALYSIS (TDA) OF THE SYSTEM Al-Si-Mn-Fe

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Preliminary Note – Prethodno priopćenje

The article presents the results of thermodynamic diagrammatic analysis of the Al-Si-Mn-Fe metal system as characterizing the final composition of the manganese-containing complex ferroalloy. By the method of thermodynamic diagrammatic analysis, the phase equilibrium of the Al-Si-Mn-Fe metal system was constructed, and the coexisting phases in the alloy were determined. Experimental samples of the aluminosilicomanganese alloy were studied on an Empyrean Malvern Panalytical X-ray diffractometer (XRD), where the presence of phases in the form of an intermetallic compound was determined - MnSi, $Mn_{15}Si_{26}$, $Al_2Fe_3Si_4$, Al_5Fe_2, FeSi and structurally free silicon.

Key words: Al - Si - Mn - Fe, Gibbs energy, phase, TDA, XRD.

INTRODUCTION

Thermodynamic diagrammatic analysis (TDA) allows obtaining data for the system under study - a phase relationship diagram, where each elementary subsystem is independent. Designed and developed at the CMI named after Zh. Abisheva TDA of complex systems, has established itself as the simplest and at the same time accurate method for studying phase laws in comparison with classical thermodynamic studies of metallurgy processes. The effectiveness of the method, as an application to metallurgical technology, is the ability to reveal the features of the phase structure of the resulting melts in the process of metallurgical redistribution of various raw materials. To elucidate the phase regularities of transformations in metallic systems based on manganese and to establish the regions of compositions in complex metallic melts, in this work, theoretical and practical studies have been composition of the Al - Si - Mn - Fe Fe metal system and a phase diagram has been constructed. The studied four-component metal system characterizes the complex ferroalloy of aluminosilicomanganese - AMS. The first works on smelting the complex alloy AMS were carried out by the authors [1]. Also, the author [2] presents studies of the Al - Si - Mn - Fe metal system, however, the phase region was constructed only considering binary partial systems.

RESEARCH METHODOLOGY

When studying the four-component metal system Al - Si - Mn - Fe by the TDA method, it is necessary to proceed from the division of the boundary subsystems into elementary tetrahedrons. This requires, first of all, to describe the metal compounds that make up the system under consideration. The Al - Si - Mn - Fe metal system consists of elementary triangles Mn - Fe - Al, Mn - Fe - Si, Fe - Al - Si and Mn - Al - Si, which in turn consist of binary private systems.

The Al - Si - Fe subsystem consists of three private binary systems: Fe-Si; Fe-Al and Al - Si. The components of the Al - Si - Fe metal system and their properties have been thoroughly studied by many scientists. The authors of [3] established the existence of the following phases in the Fe-Si binary system: Fe_3Si (α_1), Fe_2Si, Fe_5Si_3, FeSi, Fe_2Si_5, $FeSi_2$. However, the only intermediate phase in the system that exists over the entire temperature range (from melting to room temperature) is FeSi. Five stable phases are formed in the Fe-Al system: Fe_3Al, Fe_3Al (ε), $FeAl_2$, Fe_2Al_5 и $FeAl_3$. The compound Fe_2Al_5 melts congruently [4]. According to the reference data and the results of research works of the authors [5], no congruent compounds were found in the Si-Al binary system. In the Al - Si - Fe ternary system, two stable (FeSi and Fe_2Al_5) binary compounds. The authors of [6] give more than 20 ternary compounds for the Al - Si - Fe system, but most of them were for alloys with a high aluminum content, and the contradiction of many results can also be noted in the work. The author [7] studied the Al - Si - Fe system from the standpoint of crystallization of a ferrosilicoaluminum alloy and gives the following 10 ternary phases: $Al_2Fe_3Si_3$, $Al_5Fe_2Si_2$, $Al_9Fe_5Si_5$, Al_2FeSi, Al_3FeSi_2, Al_8Fe_2Si, $Al_9Fe_2Si_2$, $Al_3Fe_2Si_3$, $Al_2Fe_3Si_4$, $Al_{12}Fe_5Si_3$. In work [8] for the Al - Si - Fe system, the following connections have been established: Al_8Fe_2Si, Al_5FeSi, Al_4FeSi_2, Al_3FeSi, Al_2FeSi and Al_2Fe_2Si. According to Scientific Group Thermodata Europe database (SGTE 2017) 4 ternary com-

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pounds are indicated in the Al - Si - Fe system: Al_2Fe_2Si, Al_2FeSi, $Al_{11}Fe_3Si_6$ and $Al_{14}Fe_3Si_3$, which is confirmed by the work [9]. However, many compounds exist as an intermediate phase in the temperature range, and some of them coincide or are very close in their location on the mass coordinate. For the triangulation of the Al - Si - Fe system, the compound Al_2Fe_2Si was taken. Compound Al_2Fe_2Si most characterizes alumino-silicomanganese at high temperatures and is in optimal proportions along the mass coordinate.

In the metal systems Mn - Fe - Al, Mn - Fe - Si and Mn - Al - Si, the following were established as stable ones characterizing the composition of the complex ferroalloy: Mn_5Si_3, MnSi, MnAl and Al_2MnSi_3. More than 9 compounds are given for the presence of ternary compounds in the Mn - Al - Si metal system ($Al_3Mn_3Si_4$, $Al_3Mn_4Si_2$, $Al_3Mn_3Si_2$, $Al_9Mn_4Si_3$, $Al_8Mn_3Si_9$, Al_9Mn_3Si, $Al_{12}Mn_3Si$, $Al_9Mn_2Si_2$, $Al_9Mn_2Si_2$ and Al_2MnSi_3.), however, many data contradict each other, moreover, many triple conjunctions in the mass coordinate are very close. Basically, the ternary compounds in the Mn - Al - Si metal system are in the aluminum-rich area of more than 30 %.

RESULTS RESEARCH

According to the coordinate of the masses of each phase, triangulation was performed for each system. To carry out the triangulation of this metal system, it becomes necessary to determine the values of the Gibbs energy (ΔG_{298}) of all compounds, formed between the components of the system. Reference data on ΔG_{298} for some connections the systems are taken from [10, 11]. However, ΔG_{298} values are not available for almost many compounds. For the calculation of coexisting phases (triangulation) in the Al - Si - Mn - Fe system, thermodynamic values are taken from the HSC Chemistry 9 database. The HSC Chemistry 9 comprehensive program database is based and updated by SGTE. According to the source [12], the error in calculations using the HSC Chemistry software package is no more than 4 - 6 %, which is quite acceptable. The values of the thermodynamic data of the studied compounds (ΔG_{298}) standard and calculated are given in Table 1.

The triangulation method consists in breaking down ternary systems into elementary triangles of coexisting phases. In this case, the principle of minimizing the Gibbs free energy was used: if the Gibbs change between the products and the reaction participants is negative, then the reaction products in the diagram were connected by a straight line (connections) as coexisting phases. The sequential implementation of this operation leads to obtaining a diagram of the equilibrium coexisting phases in the Al-Si-Mn-Fe metal system. Figure 1 four-piece metal system.

Table 1 **Standard and Calculated Values of ΔG^0_{298}**

№	Compounds	ΔG^0_{298} / kJ / mole
1	FeSi	- 76,5798
2	Fe_2Al_5	- 203,912
3	Al_2MnSi_3	- 309,052
4	Mn_5Si_3	- 278,89
5	MnSi	- 76,7
6	MnAl	-39,476
7	Al_2Fe_2Si	- 158,325

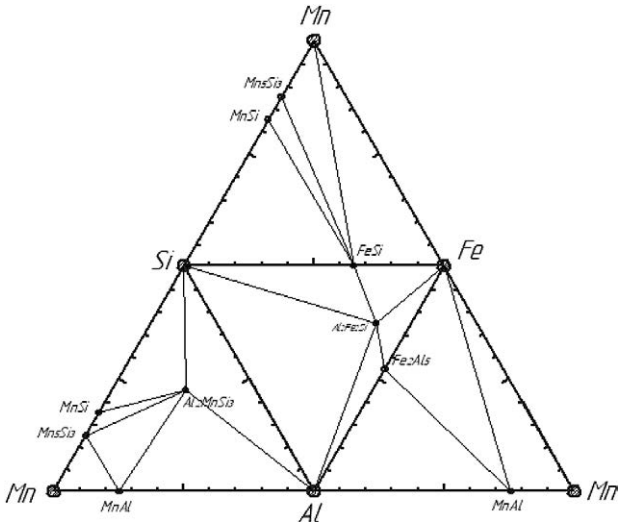

Figure 1 Diagram of a four-component metal system Al - Si - Mn - Fe

The data of thermodynamic diagrammatic analysis of the Al -Si- Mn- Fe system is in good agreement with the results of X-ray diffraction analysis on an Empyrean Malvern Panalytical X-ray diffractometer (XRD). The diffractometer is equipped with a Cu tube (Kα1= 1,541874 Å). The measurements were carried out at room temperature in the range of angles 2θ, in the range from 0° to 90° in step scan mode with a step of 0,013 degrees. Radiographs were processed and decoded using the Match! 3 software and the FullProf - 2021 database. The HighScorePlus, Match! 3 and FullProf-2021 programs are based on the Rietveld method. The Rietveld method consists in the refinement, calculation of the diffraction spectrum according to a given model of the structure according to a given shape of the profiles of diffraction lines [13]. The result of X-ray diffraction

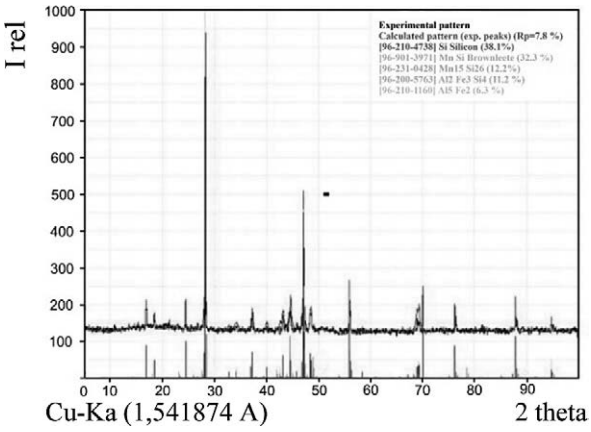

Figure 2 XRD of the aluminosilico-manganese alloy

analysis of aluminosilicomanganese alloys is shown in Figure 2.

The results of X-ray phase analysis show that the phase composition of the complex alloy of aluminosilicomanganese is presented in the form of an intermetallic compound - MnSi, $Mn_{15}Si_{26}$, $Al_2Fe_3Si_4$, Al_5Fe_2, FeSi and structurally free silicon.

CONCLUSION

Thus, a four-component metal system was built. Al - Si - Mn - Fe. In the four-component metal system Al - Si - Mn - Fe, 18 coexisting phase regions were found, which describe the phase composition of the complex ferroalloy under development, aluminosilicomanganese. When smelting metal composition / %: Mn 20 - 25; Si - 35-50; Al - 15 - 25, complex ferroalloy will be in phase regions No. 1, No. 2 and No. 3. The original silicon is consumed for the formation of intermetallic compounds of manganese and iron, that is, the predicted final composition of the alloy is presented in the form of the following phases Mn_5Si_3, MnSi, MnAl and Al_2MnSi_3. The data are supported by X-ray phase studies.

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Note: The responsible translator for English language is Tushiyev Tair, Temirtau, Kazakhstan