

STUDYING THE Fe-Al-Si SYSTEM IN RELATION TO FERROSILICON-ALUMINUM ALLOY CRYSTALLIZATION

Received – Priljeno: 2019-04-23

Accepted – Prihvaćeno: 2019-07-10

Preliminary Note – Prethodno priopćenje

In the work there have been calculated the values of enthalpies for a number of ternary compounds and carried out triangulation of the Fe–Al–Si system. The main areas of the compounds crystallization have been determined in relation to industrial compositions of ferrosilicon-aluminum. There has been carried out the analysis of possible causes of some alloy compositions self-grinding and recommended compositions with guaranteed stable physical characteristics.

Keywords: Fe–Al–Si system, crystallization, ferrosilicon-aluminum alloys, leboite phase, enthalpy.

INTRODUCTION

Studying the metal Fe-Al-Si system is one of the important tasks for the production of silicon-aluminum alloys with specified properties and characteristics. The analysis of the literature data shows that the main amount of research deals with aluminum alloys with non-significant additives of other components. In the Republic of Kazakhstan the technology of smelting a complex alloy of ferrosilicon aluminum (FSA) from high-ash coals was developed and industrially utilized. The alloy is a substitute for ferrosilicon and metallic aluminum or secondary aluminum of the AB85-87 grade when processing ordinary and low-alloyed steels.

According to the technical specifications (ST DGP 38911750-001-2019), the alloy can contain 40 - 65 % of silicon, 7,5 – 22,5 % of aluminum, iron the rest (Table 1).

Additionally, the alloy may contain 0, 5 – 1,2 % of Ti, 0,3-0,7 % of Ca, and not more than 1 % in total of Cr and Mn entering the alloy from steel chips.

The carbon content, depending on the aluminum content in the alloy, can vary in the range of 0,1 – 0,35 %.

Similar to the ferrosilicon alloy, some compounds of the FSA alloy are prone to cracking and dispersal to a powder.

For example, the FSA alloys of different grade composition were smelted in the conditions of the plants of AiK LLP (Ekibastuz) and KSP Steel LLP (Pavlodar) in electric furnaces of ore-thermal type with the capacity of 5 - 21 MVA. In practice, it was noted that in some cases when storing the alloy within more than 10 days, cracking of the alloy pieces and even complete dispersion into a fine-crystalline powder state was observed. This was especially characteristic of the alloy grades

Table 1 **Grades and chemical composition of ferrosilicon aluminum / wt. %**

FSA grade	Silicon, not less than	aluminum	sulfur	phosphorus
			not more than	
FS65A10	60	7,5 – 12,5	0,02	0,07
FS 65A15	60	12,5 -17,5	0,02	0,07
FS65A20	60	17,5-22,5	0,02	0,07
FS55A10	50	7,5-12,5	0,02	0,07
FS55A15	50	12,5-17,5	0,02	0,07
FS55A20	50	17,5-22,5	0,02	0,07
FS55A25	50	22,5-27,5	0,02	0,07
FS45A10	40	7,5-12,5	0,02	0,07
FS45A15	40	12,5-17,5	0,02	0,07
FS45A20	40	17,5-22,5	0,02	0,07

FS45A15 and FS45A20 with the content of 43 - 48 % Si and 12, 5 – 17,5 % Al. It is noted that for high grades of FSA with the content of more than 50 % Si and more than 15 % Al, destruction of the alloy pieces during long-term storage was not observed.

In this regard, it is of certain interest to study the metal Fe-Al-Si system in the field of compositions of industrial FSA alloy.

It is known from the literature sources that the main factors for destruction of siliceous alloys, in particular ferrosilicon, are the presence of the metastable ζ -phase of leboite having the composition $\text{FeSi}_{2,3}$ or Fe_3Si_7 , as well as the presence of an increased impurities content: phosphorus, calcium and aluminum.

According to [1], the impurities of phosphorus, calcium, and aluminum during crystallization of the ingot crystallize along the grain boundaries of the Si and Fe_xSi_y crystals in the form of calcium phosphide, calcium carbides and aluminum, i.e. the excess discharge phases. So, when interacting with water vapor, calcium phosphide (Ca_3P_2) decomposes to form phosphorus hydride (PH_3) and calcium hydroxide. Calcium and aluminum carbides, reacting with moisture in the air, form

A. Z. Issagulov, A. F. Chekimbayev, T. S. Makayev, A. A. Babenko (e-mail: sanya_kazah@mail.ru, KSTU, Karaganda State Technical University, Karaganda, Kazakhstan.

acetylene and bulk calcium and aluminum hydroxides. All this contributes to the cracking and further disintegration of ferrosilicon pieces.

The observed cracking of ferrosilicon pieces at relatively low contents of calcium, aluminum and phosphorus are explained by polymorphic transformations of the ζ -phase.

When the ferrosilicon ingot is cooled, crystallization of leboit begins at the temperature of 1 220 °C. Then, at 937 – 940 °C, $\text{FeSi}_{2,3}$ (B) eutectoidally decomposes into Si and a low-temperature modification $\text{FeSi}_{2,3}$ (H). At this, by increasing the volume of new phases by 17 % and internal stresses, cracking of ferrosilicon ingots occurs [2].

To reduce the effect of leboite, ferrosilicon FS45, FS65, FS75 grades are usually smelted with the exception for the silicon content in the alloy of 52 - 62 % with the phosphorus content not more than 0.05 % according to GOST 1415-93.

In contrast to ferrosilicon, the content of phosphorus in FSA does not usually exceed 0,02 %. The role of calcium is not unambiguous, and its effect on the destruction of alloy pieces can practically be excluded, since calcium will preferably be in the alloy in the form of stable aluminides or calcium silicides.

The carbon content in the FSA alloy does not exceed 0,15 – 0,20 % for the FS55A15-20 grades, and 0,20 – 0,35 % for the FS45A15-20 grades. Of the possible carbides of this system: Fe_3C , SiC , Al_4C_3 and CaC_2 , at the temperatures of the smelting process only aluminum carbide can be stable. The analysis of the alloy with different aluminum contents shows that with increasing the aluminum content in the alloy there is increasing the amount of carbon. This is explained by the fact that aluminum carbide, unlike other carbides, tends to dissolve in molten aluminum, which was noted in study [3]. The effect of aluminum carbide is insignificant due to its low content and instability in the presence of high silicon content.

The microstructural analysis of high grade ferrosilicon aluminum [4] shows the presence of three main phase components of the alloy. This is a siliceous phase with a low content of iron, an aluminum phase also alloyed with iron and an eutectic phase containing silicon, aluminum and iron. Localization of calcium and phosphorus is presumably observed in the eutectic phase.

Since the content of phosphorus, carbon and calcium does not exceed the regulated values, it can be assumed that destruction of the alloy pieces occurs for another reason. This may be due to possible recrystallization of the leboite phase that can also be contained in some formulations of FSA.

EXPERIMENTAL STUDIES

Equipment and tools

To determine the formation of possible compounds during crystallization of FSA, the triangulation of the Fe–Al–Si ternary system was carried out using the known thermodynamic data.

The analysis of the literature data indicates that experimental and theoretical studies of the Fe-Al-Si metal system are insufficient in the field of compositions of the industrial alloy of ferrosilicon aluminum. Basically, for this system, studies were carried out for compounds with the aluminum content of 50 - 90 %, characteristic of aluminum alloys.

There are no chemical compounds in the Si-Al binary system. For binary Fe-Si and Fe-Al systems there are known stable compounds, the values of the enthalpies of which are presented in Table 2.

The enthalpy of the Fe_2Al_7 compound was calculated by the method of additivity of the thermodynamic constant values in the following way: $\Delta H(2\cdot\text{Fe}_2\text{Al}_3) - \Delta H(\text{FeAl}_2) - \Delta H(\text{FeAl}) = \Delta H(\text{Fe}_2\text{Al}_7)$.

During crystallization of the FSA melt, the phenomenon of extrusion of a low-melting eutectic mixture to the ingot surface was observed, which contained all three components of the Fe-Al-Si system. Studying the microstructure of the FSA alloy also shows the absence of a pure aluminum phase, which indirectly indicates the presence of ternary compounds during alloy crystallization. Therefore, studying the Fe-Al-Si system without involving the data of ternary compounds will not be correct.

Table 2 Values of the compounds enthalpy for the binary Fe-Si and Fe-Al systems

Compound	$-\Delta H_{298}^{\circ} / \text{kJ/mol}$	Source	Compound	$-\Delta H_{298}^{\circ} / \text{kJ/mol}$	Source
Fe_3Si	93.80	[5]	Fe_3Al	61.92	[5]
Fe_5Si_3	234.30	[5]	FeAl	51.05	[5]
FeSi	76.576	[5]	FeAl_2	81.59	[5]
FeSi_2	76.149	[5]	Fe_2Al_3	193.3	[5]
$\text{FeSi}_{2,33}$	69.454	[5]	FeAl_3	112.13	[5]
Fe_3Si_7	208.36	[5]	Fe_2Al_7	253.96	[2]
FeSi_3	154.454	[6]			

It can be seen from the data of Table 2 that in the literature there are the data of the composition of ternary compounds of the Fe–Al–Si system, identified by various methods, but there are no experimental and adequate calculated values of the enthalpy or Gibbs energy. So in studies [7-9] more than 20 compositions of ternary compounds for the system Fe-Al-Si are given. Most of these compounds were identified when studying the alloys with a high content of aluminum. From the indicated variety of ternary compositions, we selected 8 compounds that crystallized in the area of the FSA alloy composition of interest (Table 3). The enthalpy calculation for ternary compounds was carried out using the above method of additivity of the thermodynamic values of similar compounds. The use of these values of enthalpies does not pretend to high accuracy, but they are sufficient for calculating the thermal effect of reactions and performing triangulation with defining possible compounds during alloy crystallization.

Triangulation of a set of compounds of the Fe–Si–Al system, marked in the field of an equilateral triangle,

Production of an alloy with the content of less than 40 % Si and 15 - 25 % Al, which is at least 55 % of the Si and Al sum is of certain interest. The melting point of the FeSi_2 compound is 1 210 °C, for FeSi it is 1 410 °C, the $\text{Fe}_2\text{Al}_3\text{Si}_3$ eutectic is 1 100 °C. The use of the FSA alloy of such a composition can completely cover the required amount of aluminum without the additional use of aluminum metal.

It should be noted that even when a stable alloy is obtained, spattering processes are possible upon receipt of ingots with the thickness of more than 100 mm and slow crystallization. This is due to changing the composition of the alloy over the thickness of the ingot, when the iron-containing components, due to their increased density, sink to the lower layers, while the upper ones are enriched with light components. To prevent segregation, it is imperative to observe a fixed ingot thickness of less than 100 mm and the possibility of the sharp overcooling of the melt after casting.

CONCLUSION

Thus, on the basis of calculations performed and triangulation of the Fe-Si-Al system, the main areas of crystallization of the FSA compound alloys of various compositions have been revealed. The crystallization region of the metastable leboite phase has been determined. The expediency of smelting a FSA alloy with the content of 44 - 48 % Si has been established. It is recommended to produce a low-grade alloy with the content of 40 - 41 - 42 % Si and the content of not more than 19 - 17 - 14 % Al, respectively. For alloys with the content of more than 50 % Si, it is recommended to keep the Al content at least 15 %.

These studies have been carried out within the framework of the Industrial Contract between Karaganda State Technical University and Plant of Integrated Alloys LLP

No. 0118 RCD0211 “Metallographic and petrographic studies of high-ash coal samples from the Kushokoy coal mine, various grades of ferrosilicon aluminum and steel treated with ferrosilicon aluminum alloy”.

REFERENCES

- [1] Povolotskiy V. D., Komissarov T. A., Minayev V. M. Study of the causes of crushability of ferrosilicon, Publishing house. Ferrous metallurgy (1987)8, 31-35.
- [2] Zubov V. L., Gasik M. I. Electrometallurgy ferrosilicon, Dnepropetrovsk, System technology 2002, 704.
- [3] Gasik M. I., Emlin B. I., Klimkovich N. S., Khitrik S.I. Aluminum Melting // Metallurgy, 1971, 304.
- [4] Chekimbayev A. F., Akhmetov A. B., Baysanov S. O., Tolymbekov M. Zh., Nurimanov M. A. Influence of the phase composition of the ferrosilicoaluminium alloy on the nature of the non-metallic inclusions formed. Int. scientific and practical conf. “Abishev readings-2011”-Karaganda, 2011, 415-416.
- [5] Glushko V. P. Thermal constants of substances // Reference in 10 vol. (1972)2.
- [6] A. G. Ryabukhin. O. N. Enthalpy of formation of silicides of 3d elements of the periodic system DI Mendeleev <http://dspace.susu.ru/bitstream/handle/0001.74/240/12.pdf>.
- [7] Gautam Choosh. Al-Fe-Si ternary alloys ver lagsgesellschaft, VCH-Weinheim, (1992) 5, 394-438.
- [8] Issagulov, A. Z.; Kulikov, V. Yu.; Chsherbakova, Y. P. Kovaleva, T. V.; Kvon, Sv. S. The corrosion resistant coating with halloysite nanoparticles, *Metalurgija* 55 (2016)3, 426-428.
- [9] Issagulov, A. Z.; Kvon, S. S.; Kulikov, V. Yu. Cr-Ni system alloys composition impact on durability value, *Metalurgija*, 55(2014)4, 621-623.
- [10] Protsyuk A. P., Karapetiants M.Kh. On thermodynamic study of processes in multicomponent systems // *Journal of Applied Chemistry* 50 (1977)1, 169-175.

Note: The responsible for England language is Nataliya Drag, Karaganda Kazakhstan