Technology of Obtaining New Generation of Complex Ferroalloy with the Use of Kazakh Barite Ore

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ABSTRACT

The application of modern out-of-furnace processes of refining steel is limited by their high cost. Therefore, shift to the refining and modification of metal by the new complex ferroalloys containing alkaline-earth metals (AEM), which are chemically active to oxygen, sulfur and other detrimental impurities, such as barium-containing silicomanganese, can be considered as alternative treatment technique.

The theoretical aspects of this technology are based on a thermodynamic diagrammatic analysis of phase equilibriums in the systems BaO-SiO_2-MnO-FeO (B-S-M-F) and Ba-Si-Mn-Fe in homogeneous liquid-phase condition. The full calculation of the thermodynamic constants of reactions was performed with the use of Gibbs software package developed by the scientists of Chemical and Metallurgical Institute named after Zh. Abishev for plotting the diagrams of B-S-M-F and Ba-Si-Mn-Fe systems material correlations in homogeneous liquid-phase condition.

The main source of barium in the ferroalloy is sulphate barite ores. The largest region in terms of reserves of barite and its production is the Central Kazakhstan. Currently, barite ore of the Zhumanai deposit is a promising raw material for production of new generation of complex barium-containing ferroalloy by its geographical location, physical condition (solid material), chemical composition, mass %: 74.35 $BaSO_4$; 8.54 SiO_2; 0.4 Al_2O_3; 2.91 CaO; 0.046 MgO; 0.1 W; 0.52 ignition loss and reserves.

In the Chemical and Metallurgical Institute named after Zh.Abishev, the technique of obtaining new generation of complex ferroalloy using Zhumanay deposit barite ore was developed - nonstandard silicomanganese with modifying agent in the form of barium by one-step slagless carbonthermal reduction. Average ferroalloy composition, mass %: 46.66 Mn; 37.13 Si; 5.64 Ba; 4.45 Fe; 0.59 C; 0.023 S; 0.038 P. Barium content in ferroalloy was defined by gravimetric method. The following extraction degree of the leading components was achieved, %: 84.9 Mn; 77.9 Si; 78.3 Ba. The developed technique allows bringing the processes of obtaining silicomanganese, silicobarium and ferrosilicon together. The ferroalloy is to be applied to manufacture metal with high operational properties.

Keywords: *thermodynamic diagram analysis, Gibbs energy, material correlations diagram, sulfate barite ore, complex ferroalloy, slagless carbonthermal reduction, barium.*

1 INTRODUCTION

Liquid steel treatment by chemically reactive elements and its deep refining, modification and microalloying is an integral part of modern manufacturing techniques of high-quality and competitive products [1].These elements include alkaline earth metals (AEM)- Ca, Sr, Ba which have significant sensitivity to oxygen, sulphur, phosphorus as well as high chemical reactivity [2, 3]. The steel modification effect is connected with the influence on crystallization mechanism when macro- and microstructure is disintegrated, and there occur changes in the nature, form and topography of non-metallic inclusions and others second phases at a very small (0.05-0.2 %) amounts of additives and almost constant contents of basic components. Modification of the cast iron changes the degree of dispersion and morphology of phase components [4]. The paper [5] states the results of research testifying that barium has high refining performance when modifying non-metallic inclusions.

Silicobarium, silicocalcium, silicocalcium with barium are the most widely spread complex ferroalloys and their production has been developed by many ferroalloy plants of the Russian Federation. For example, the production of silicocalcium by silicothermal method as well as silicocalcium with aluminum was developed by Chelyabinsk Electrometallurgical Works OJSC as a larger producer of ferroalloys in Russia. The production of silicocalcium with zirconium, alluminium and vanadium is developed by Klyuchev Ferroalloys Plant. The production activity of Spezferrosplav LLC and Research Institute of Metallurgy OJSC is related to obtaining different modifiers and addition alloys for iron and steel casting including ferrosilicium with barium and silicocalcium with barium. The production of the bariumstrontium modifier BSK-2 according to specification TU 1717-001-75073896-2005 was developed by SPC Metalltekhnoprom LLC.

Flux cored wire with charging materials on the basis of silicocalcium, ferrocalcium, ferrosilicobarium is also widely used in metallurgical practice. Ferrosplav CJSC is the leading producer in this area in Russia. The results of approbation of the flux cored wire with silicocalcium-barium charging material at out-of-furnace treatment of rail steel

and cast iron treatment are given in papers [6] and [7], respectively. ORPE Technologiya produces a series of grades of fine-crystalline 'chips' – modifiers with thickness up to 3-5 mm [8] for out-of-furnace treatment of iron and steel using special casting machine [9], as well as flux cored wire with different charging materials.
At present neither barium- not calcium-containing ferroalloys are produced in Kazakhstan. Production of barium-containing complex ferroalloys in Kazakhstan was stopped in 1994 due to perestroika and break of economic relationships in the Union of Independent States, although, the authors of works [10-12] reported fundamental and industrially important results of researches.

2 MAIN PART

2.1 Methodological basis

The development of theoretical basis of chemical engineering and metallurgical processes at the various stages of research is characterized by figures of isobar-isothermal potential - ΔG (Gibbs energy) for certain reactions as well as by balance of equilibrium constant determining the correlation between the reaction products and initial substances in the K_p balance point. Physicochemical basis for the process of obtaining complex barium-containing ferroalloy production based consists in thermodynamic diagram analysis (TDA) of multicomponent BaO-SiO_2-MnO-FeO (B-S-M-F) and Ba-Si-Mn-Fe systems with the application of PC Gibbs. The Gibbs software package developed by the scientists of Chemical and Metallurgical Institute named after Zh. Abishev allows determining the changes of enthalpy, entropy, heat capacity, Gibbs energy of the reaction in homogeneous liquid-phase condition at various temperatures accounting for all the phase transitions for all the systems components as well as calculating the equilibrium constant of the reaction.

The B-S-M-F system is composed of binary compounds of B-S-M, B-F-S, F-S-M, B-F-M subsystems. The B-F-M system is a totality of solid solutions of manganese oxides, ferric oxides and barium oxides. Calculations of thermodynamic constants, including Gibbs energy of reactions with the application of PC Gibbs for the B-S-M-F system were carried out at 298.15–2500 K temperatures range. The calculation results are demonstrated in Table 1. The diagram of substance correlation (DSC) of B-S-M-F system at a temperature of 2500 K was plotted on the basis ofe obtained thermodynamic data; this diagram is presented in Figure 1.

Table 1: Thermodynamics of reactions in B-S-M-F system (T=2500K)

Chemical equation	ΔG^0_{2500}, (kJ/mol)
B-S-M system	
B + M_2S = BS + 2 M	- 66.0
2 BS + M_2S=B_2S_3 + 2M	176.5
B_2S_3+2 MS=2 BS_2+M_2S	- 156.8
B-S-F system	
B + F_2S=BS + 2 F	- 147.2
B_2S_3 + 2 F=2 BS + F_2S	- 123.5
$2BS_2$ + F_2S=B_2S_3 + 2FS	- 127.7
M-S-F system	
F_2S + 2 MS=2 FS +M_2S	- 432.6
F_2S + 2 M = 2 F + M_2S	- 74.2

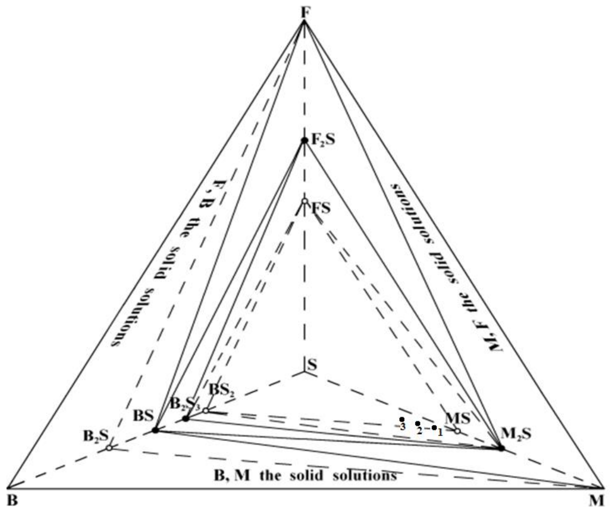

Figure 1: Diagram of substance correlation in B-S-M-F system at T=2500K:● - congruent compound; ○ - incongruent compound
1 – composition of the charge for alloy No. 1;
2 – for alloy No. 5; 3 – for alloy No. 8 (Table 4)

On the basis of conducted B-S-M-F system tetrahedration it is obvious that it consists of 5 congruent tetrahedrons: B-F-BS-M, M-F-M_2S-BS, F-BS-M_2S-F_2S, F_2S-BS-B_2S_3-M_2S, F_2S-B_2S_3-M_2S-S. Predicted slag composition required for the alloy with 1.5 % barium content and more is located in F_2S-BS-M_2S-S quasi-system. Ba-Si-Mn-Fe system is a totality of binary compounds of Ba-Si-Mn, Ba-Fe-Si, Fe-Si-Mn, Ba-Fe-Mn subsystems. The Ba-Fe-Mn system is manganese, ferrum and barium solid solutions. The calculated values of ΔG^0_{2500} Gibbs energy of the reactions with the application of PC Gibbs for the Ba-Si-Mn-Fe system are demonstrated in Table 2. The DSC of Ba-Si-Mn-Fe system at temperature of 2500 K was plotted based on the obtained thermodynamic data; this diagram is presented in Figure 2.

On the basis of tetrahedration of the Ba-Si-Mn-Fe system it is obvious that it consists of 6 congruent tetrahedrons: Ba-Fe-$BaSi_2$-Mn, Mn-Fe-Mn_5Si_3-$BaSi_2$, Fe-$BaSi_2$-Mn_5Si_3-Fe_2Si, Fe_2Si-$BaSi_2$-Mn_5Si_3-FeSi, FeSi-Mn_5Si_3-MnSi-$BaSi_2$, FeSi-$BaSi_2$-MnSi-Si.

Table 2: Thermodynamics of reactions in Ba-Si-Mn-Fe system (T=2500K)

Chemical equation	ΔG^0_{2500}, (kJ/mol)
Ba-Si-Mn system	
$3Ba+2Mn_5Si_3=3BaSi_2+10Mn$	- 247.3
Ba-Si-Fe system	
$Ba+2Fe_2Si=4Fe+BaSi_2$	- 99.2
Mn-Si-Fe system	
$8FeSi_2+11MnSi=8FeSi+Mn_{11}Si_{19}$	579.1
$4FeSi+Mn_5Si_3=5MnSi+2Fe_2Si$	29.0
$6FeSi+5Mn=Mn_5Si_3+3Fe_2Si$	- 92.9
$3Fe_2Si+5Mn=Mn_5Si_3+6Fe$	- 25.2

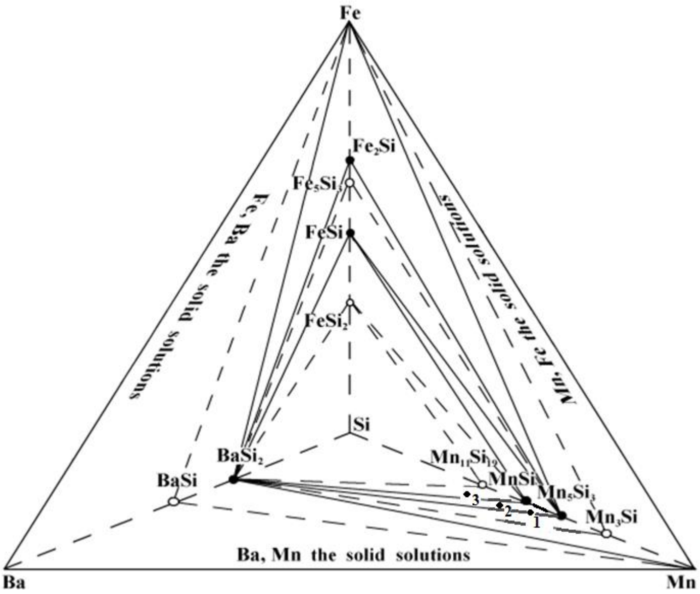

Figure 2: Diagram of substance correlation in Ba-Si-Mn-Fe system at T=2500K: 1 – alloy No. 1; 2 – alloy No. 5; 3 – alloy No. 8 (Table 4)

It was found that in order to produce an alloy containing 1.5% Ba, the ratio Si/(Mn+Fe) must be 0.6; for the alloy containing 5% Ba the ratio Si/(Mn+Fe) - 0.7; for the alloy containing 10% Ba the ratio Si/(Mn+Fe) - 1.

2.2 Experimental part

Practical significance of the work consisted in carrying out less-detail preproduction testing in the ore-smelting 0.2 MV·A electric furnace on the pilot at the experimental technological site of CMI named after Zh. Abishev. The manganese ore from Mynaral deposit, barite ore from Zhumanai deposit, quartzite from Tekturmas deposit, carbonaceous reducing agent were used as charge materials for melting of the alloy (Table 3) [13].

Table 3: The characteristics of charge materials

Ore materials	Components content, mass. %										
	Mn_2O_3	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**BaO**	**P_2O_5**	**SO_3**	**W**	**Ignition loss**
Mynaral manganese ore	71.67	0.70	8.35	1.25	2.21	1.35	-	0.11	0.82	0.4	7.75
Zhumanay barite ore	-	0.44	8.54	0.4	2.91	0.046	48.85	n/d	25.50	0.1	0.52
Tekturmas quartzite	-	0.66	97.05	0.76	0,77	n/d	-	0.03	n/d	0.12	-
Carbonaceous reducing agent	**Technical analysis, %**				**Chemical composition dry ash residue, mass. %**						
	C_{solid}	A^{work}	$V_{general}$	W^{analit}	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	P_2O_5	SO_3
Coke	82.70	11.83	2.90	2.57	9.61	49.57	23.02	7.01	2.07	0.37	2.80
Note: n/a – not available.											

The granulometric composition of the charge materials, mm is: fr. +8-90 manganese ore from Mynaral deposit, fr. +8-70 barite ore from Zhumanai deposit, fr. +8-45 quartzite from Tekturmas deposit, fr. +8-65 coke.

The campaign of less-detail laboratory tests of smelting barium-containing silicomanganese was carried out on the basis of the charge calculation result. Optimal technological parameters of the process of smelting the alloy in ore-smelting 0.2 MV·A transformer furnace are: voltage U=24 V and current strength I=180-190 A. The furnace is equipped with graphitized electrode with a diameter of 150 mm and conductive bottom. There was a jet of hot metal. The gas escaped evenly along the whole surface of the mouth. The descent of the charge in operating bath of the furnace was active, there were no flaws and arbitrary slides of the charge. The alloy was flushed every two hours into the iron pans. After the process of metal flashing through the notch the gas torch was coming out of it. The process of smelting the alloy was characterized by definite problems, notably, formation of oxide carbide goop, that led to the disturbed operation of the furnace and inopportune opening of the notch. Smelted ingots were then subject to chemical analysis following their cooling and sampling. The slag quantity was negligibly small. Charging composition was the following: 50 kg of manganese ore from Mynaral deposit; 7.4 kg of barite ore from Zhumanai deposit; 40 kg of quartzite from Tekturmas deposit; 36.3 kg of coke.

2.3 Results and discussions

The ingots of smelted alloys were subject to chemical analysis after cooling and sampling, the results are given in Table 4 [14]. Barium content in the alloy was defined by the gravimetric method.

Table 4: The chemical composition of ferroalloy

№	The content of elements, mass %								
	Mn	Si	Ba	Ca	Mg	C	Fe	S	P
1	56.17	35.28	1.56	0.79	0.12	0.71	1.60	0.019	0.044
2	57.02	35.28	1.83	0.68	0.19	0.42	1.70	0.019	0.045
3	45.10	39.45	4.06	0.69	0.19	0.56	4.96	0.024	0.042
4	50.21	35.85	5.02	0.62	0.19	0.56	1.63	0.021	0.034
5	48.51	36.57	5.32	0.62	0.17	0.67	2.12	0.019	0.043
6	41.70	35.28	6.70	0.82	0.14	0.46	11.62	0.023	0.034
7	42.55	37.30	8.12	0.94	0.19	0.52	5.89	0.023	0.027
8	37.44	43.17	10.84	0.84	0.11	0.71	3.15	0.035	0.042

One can see from the results of the chemical analysis given in Table 4 that when manganese content in the alloy exceeds 55 %, the barium content in the alloy decreases. This fact may be ascribed to appearance of free (not bonded with silicon) manganese according the data obtained by thermodynamic diagram analysis of the Mn-Si-Ba-Fe system (Figure 2). This causes a decrease in barium solubility.

The manganese content in the alloy less than 40% is not enough for the formation of slush manganese silicates in the steel during reacting of manganese and silicon with oxygen dissolved in steel and the level of its recovery in the liquid steel is reduced that causes a deterioration of the metal quality due to an increase in non-metallic silicate inclusions while increasing the alloy consumption at the same time.

The barium content in the alloy less than 1.5 % where the manganese to silicon ration of 1.6 doesn't practically influences the properties of treated steel, but if the barium content is more than 10%, then the alloy spilling occurs that makes it impossible to apply it for steel treatment due to the alloy fine fractions loss with the gases escaping from the steel; the barium recovery rate declines and the alloy production cost increases.

It was found during scientific and experimental research that the barium transfer into the alloy is conditioned by the accompanied process of silicon reduction. Thus, beginning from the silicon content in the alloy of 35%, there is an increase in the barium content in the alloy from 1.5% to 10% and more as the silicon content in the alloy increases up to 40% and more.

On the basis of the campaign results of smelting barium-containing silicomanganese the efficient composition of charge materials [15] was determined in which the recovery of the leading components was 84.9 Mn; 77.9 Si; 78.3 Ba. As a result of less-detail laboratory tests 45 kg of the alloy was produced. The power consumption was 344 kW/h.

3 CONCLUSIONS

On the basis of the results of thermodynamic diagrammatic analysis of the B-S-M-F and Ba-Si-Mn-Fe multicomponent systems it was established that the optimal charge composition required for smelting of the alloy with 1.5% barium content and more is located in the F_2S-BS-M_2S-S tetrahedron area. The large-scale laboratory tests of smelting technique for the production of the complex ferroalloy – barium-containing silicomanganese were carried out in ore-smelting electric furnace with a 200 kV·A transformer with the natural raw material of Kazakhstan. The leading components reduction rate is the following, %: 84.9 Mn; 77.9 Si; 78.3 Ba. The alloy is designed for metal production high operational performance.

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