THEORETICAL AND PRACTICAL ASPECTS OF SMELTING NEW COMPLEX ALLOY - ALUMOSILICOMANGANESE WITH CALCIUM

A. Baisanov, A. Kopabaev, S. Baisanov, M. Tolymbekov, M. Dzhundibaev

Abishev Chemical-Metallurgical Institute
e-mail: alibekbaisanov@mail.ru

ABSTRACT

Thermodynamic calculations of Al-Si-Ca-Mn-O-C system using "ASTRA - 4" software for three real charge compositions were carried out to identify basic condensed and gaseous phases, whose formation is possible in the smelting of alumosilicomanganese with calcium (alloy CAMS). Calculations proved the thermodynamic possibility of obtaining AlSiMnCa alloy and allowed to describe the mechanism of simultaneous carbothermic reduction of Al, Si, Ca, and Mn by solid carbon. Dynamics of changing of basic coexisting phases composition of Al-Si-Ca-Mn-O-C system in the temperature range of 1000-2700K was studied and described. Semi-industrial pilot smelting in 200 kVA SAF allowed to obtain a new type of complex calcium-containing alloy - CAMS from high-ash coal of Saryadyr deposits and dump slag of LC ferromanganese. The metal was produced by one-stage carbothermal slag-free method.

KEYWORDS: *Complete thermodynamic analysis, alumosilicomanganese with calcium, dump of manganese slag, high-ash coal.*

INTRODUCTION

The four main elements, a deoxidizers of steel - calcium, manganese, silicon and aluminum - are mainly produced separately in the form of ferroalloys: ferrosilicon, ferromanganese, silicomanganese. Production involves high-grade materials: manganese ores, concentrates, quartzite, limestone, coke, alumina, cryolite, etc. Production of manganese concentrates, bauxite and coke is a separate labor-intensive industry with high consumption of energy, raw and auxiliary materials. Deoxidation of steel with Al requires secondary or electrolytic aluminium. In general, technology of mentioned four basic deoxidizers is a multi-stage, complicated and costly.

Currently, the Abishev Chemical-Metallurgical Institute is studuing the possibility of using domestic high-ash coal from deposits of Borly, Saryadyr and Bogatir (Ekibastuz coal) as the carbon reductant. The ash of such coal is an attractive source of silicon and aluminum. Using excessive fixed carbon in coal as a catalyst when smelting FeMn dump slags we can obtain integrated alloy containing manganese, silicon, aluminum and calcium by carbothermal slag-free method.

Until recently, the alloys of such composition were not produced by conventional carbothermal way in submerged arc furnaces. The reason for this was very low production capacity of existing SAF techniques and this, in turn, was caused by the uncertainty of the nature of the processes occurring in the system Fe-Si-Al-Ca-O-C at high-temperature conditions.

Existing method of complex ferroalloy production of displacement by mixing of pure metals (silicon, aluminum, calcium, manganese, etc.) is very ineffective and costly, its application justified only by the absence of alternative technologies and high demand for such product.

THERMODYNAMIC CALCULATIONS

Modern metallurgical practice offers little examples of a joint recovery (metallurgical smelting) of a complex multi-component charge by one-stage slag-free process. Common slag-free production of ferrosilicon, calcium carbide and silumin is based on recovery of one or maximum two oxides contained in the charge.

Therefore, as part of ongoing research we carried out a thermodynamic analysis of the system Fe-Si-Al-Ca-O-C on program complex "ASTRA-4".

The program complex "ASTRA-4" was developed in the MSTU after name Bauman and adapted to calculate equilibria composition in multicomponent metallurgical systems by Institute of Metallurgy, Ural Branch of Russian Academy of Sciences [1-3]. Basic calculation principle is that equilibrium is defined as phase composition corresponding to the maximum entropy of isolated system.

Complete thermodynamic analysis of Al-Si-Ca-Mn-O-C-containing system has been carried out for the three real charge compositions (insufficient carbon, normal mode and excessive carbon) for CAMS smelting to determine optimum parameters of carbothermal process (table 1).

Table 1: Composition of charge and chemical composition of charge components

No.	Amount of reductant	Composition of charge, kg		Chemical composition of the mixture charge materials,%						
		Slag	Coal	MnO	FeO	SiO_2	Al_2O_3	CaO	C	Ar
1	Excessive	10	20	9,8	1,29	29,53	16,1	14,38	28,89	0,01
2	Normal	17	20	12,76	1,3	29,07	15,12	18,94	22,8	0,01
3	Insufficient	25	20	14,89	1,29	28,74	14,42	22,2	18,45	0,01

As a result, the thermodynamic studies using the program complex "ASTRA-4" allowed to describe the dynamics of possible change of basic condensed and gaseous phases composition up to 2700K, figure 1, 2 and 3.

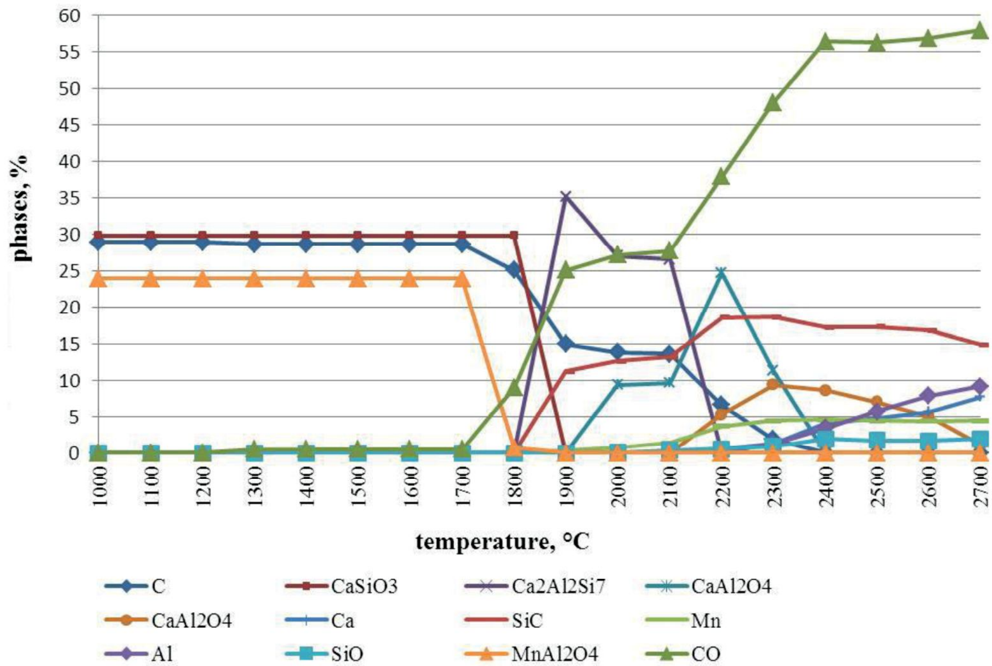

Figure 1: The temperature dependence of the main phase transition of the charge mix No.1

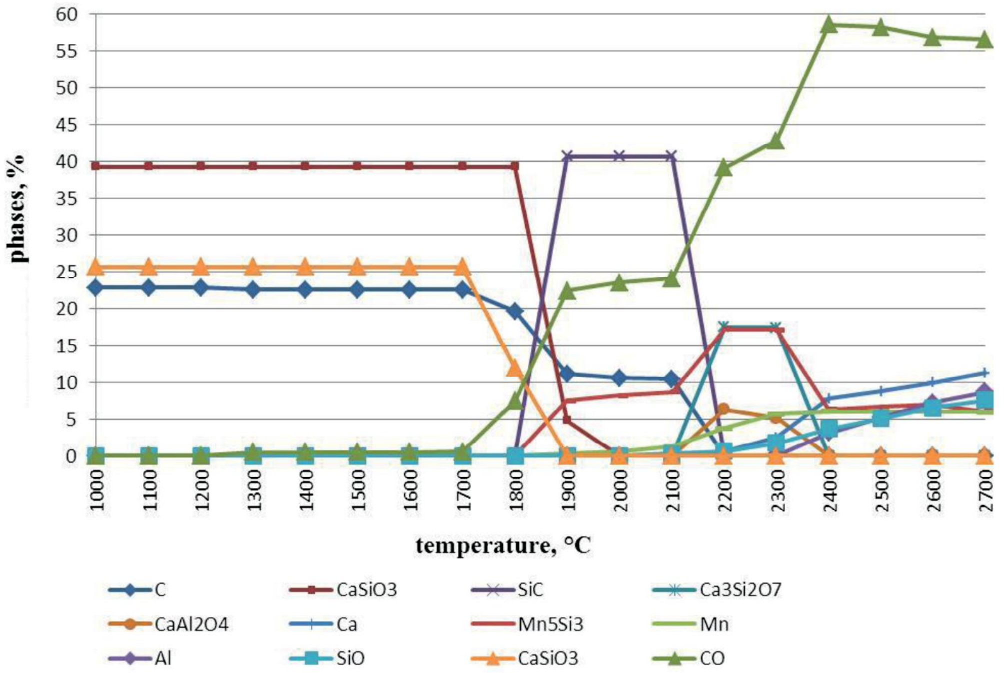

Figure 2: The temperature dependence of the main phase transition of the charge mix No.2

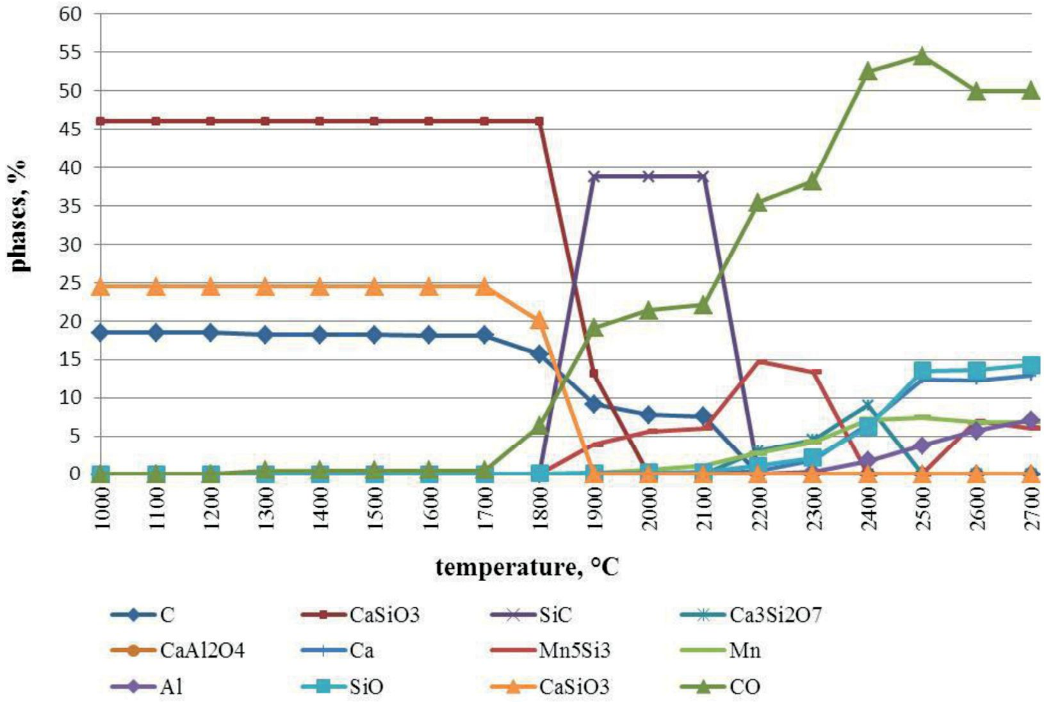

Figure 3: The temperature dependence of the main phase transition of the charge mix No.3

Thermodynamic calculations showed that the optimal charge composition corresponds to normal ration of carbon (charge No.2 in the table 2). The explanation is as follows:

At slag/coal ratio 10/20 kg the condensed phase at 2300K and 2500K will contain 18,61% and 17,28% of silicon carbide, respectively and 9,39% and 7,03% of calcium carbide, respectively, and residual solid carbon in the amount of 1,24%. It is clear that subsequent formation of carbides in the real process of smelting in such conditions will lead to skulling of furnace bath and may cause an emergency shutdown of furnace.

In charge No.3 with insufficient carbon, on the contrary, the formation of excessive amounts of slag will be observed. Estimated slag composition is as follows: 27,9% $Ca_3Al_2O_6$ and 4,52% $CaAl_2O_4$. Parallel to this the formation of increased amounts of gaseous SiO - 13,51%, as well as silicon carbide 13,37% will take place. However, a positive effect is higher amount of calcium – 12,44% due to increased share of slag which is a main source of calcium oxide. Highest concentration of $CaSi_2$ - 7,55% is observed in case of charge No. 3, which is a positive factor. Oxides $Ca_3Al_2O_6$ and $CaAl_2O_4$ existing at 2300 K, will disappear when heated to 2500K. In the second charge mixture, a slight carbide formation can occur, but in real conditions, due to loss of carbon on furnace top, the process will eventually come to normal mode.

Table 2: The content of the main gaseous and condensed phases (%) at 2300-2500K coexisting with different charge

Phase	Consumption of slag per 20 kg of high-ash coal					
	10 kg		17 kg		25 kg	
	Temperature, K					
	2300	2500	2300	2500	2300	2500
CO	48,08	56,30	42,80	58,26	38,20	54,48
Mn	4,46	4,45	5,72	6,07	4,23	7,45
SiO	0,87	1,73	1,70	5,05	2,14	13,51
Al	1,21	5,71	0,04	5,18	0,24	3,76
Al_2O	2,18	2,17	0,03	2,39	0,19	3,13
Ca	1,24	4,73	2,52	8,74	1,83	12,44
κ-C	1,86	0,00	0	0	0	0
κ-$Ca_3Al_2O_6$	0	0	6,32	0,00	27,90	0,00
κ-$CaSi_2$	0	0	0	7,55	0,00	4,35
κ-SiC	18,61	17,28	17,08	6,67	13,37	0
κ-$CaAl_2O_4$	11,30	0,00	17,38	0	4,52	0
κ-CaC_2	9,39	7,03	5,16	0	0	0
κ-MnSi	0	0	0	0	6,41	0,00
Total	100,0	99,4	98,8	99,9	92,6	99,1
κ -condensed phase						

It is important to note that major part of silicon, calcium and aluminum will exist in gaseous form, as seen in the table 2. This requires the technical measures for their catching and condensation which is normal technique for most ferroalloy production schemes.

Thus, the conducted thermodynamic calculations allowed deeper insight into the basic chemical processes occurring in the smelting of CAMS by carbothermal method.

LAB-SCALE SMELTING OF CaAlMnSi ALLOY

Results of thermodynamic calculations were considered and assessed by lab-scale pilot smelting in 0,2 MVA submerged arc furnace.

Complex alumosilicon alloys with alkaline earth elements have a great prospect in metallurgy of iron and steel, as modifiers, deoxidizers and desulfurization. They have a relatively low melting point and high density, which contributes to the overall absorption of the metal during deoxidation of steel. Calcium complex alloys are also active dephosphorizer. In contrast to deoxidation of metal with standard ferroalloys, complex alloys with alkaline earth elements globalize and evenly distribute the non-metallics in the metals, which ensures strengthening of cast iron and ductility of steel.

Pilot smelting of complex alloy alumosilicomanganese with calcium by slag-free carbothermal method was carried out in 0,2 MVA lab SAF with transformer capacity. A single-phase furnace has a conductive bottom and is powered by two 100 kVA transformers. a large-arc-phase laboratory graphite conductive hearth furnaces with transformer capacity of 0,2 MVA. The furnace has 150 mm graphite electrode and fireclay bricks lining. Furnace bath has elliptic with axes 50-60cm elongated towards the taphole. The distance from the electrode to the taphole block is 17-18 cm and from electrode to the rear wall of bath is 27-28 cm. Bath depth of 30-35 cm. The bottom is made of electrode paste subject to carbonization for 8 hours under current load with periodic shutdowns. Furnace transformer has four voltage steps: 18,2; 24,2 V; 36,6 and 48,8 V. During the experiments we worked at voltage levels 24,4 and 36,6 V.

After 12 hours run-up period the furnace bath was cleaned from the remnants of coke bed. Electric regime of run-up period: the secondary voltage 24,6 V and current on the high voltage side of 150-200 A.

The main objective of pilot smelting was to achieve the full recovery of all oxides of the charge which consisted of dump LC FeMn slag and high-ash coal. The smelting was done by continuous slag-free process. Technology of this method is based on the joint recovery of calcium, manganese, silicon and aluminum. Raw materials used in the pilot campaign included dump slag of refined ferromanganese (grain size 10-40 mm) and high-ash coal of Saryadyr deposits of the same grain size. These materials are classified as industrial waste of no practical use.

The melting was carried in a continuous way, with a charge fed manually in small portions matching the donwtake of charge. Charge materials were loaded around the electrode forming a cone. Metal was tapped into cast iron moulds every two hours. Each tapping was weighted and samples were taken for chemical analysis.

The charge composition was calculated for full recovery of oxides contained in slag and coal. There charge compositions were tested within the pilot campaign.

RESULTS

In the first period (excessive carbon) the charge consisted of 20 kg of high-ash coal and 6 kg of manganese slag. The smelting continued for 6 hours with smooth flow of process and stable amperage at 150-160 A. light signs of skulling were noted by the end of first period.

In the second period (insufficient carbon) smelting was carried out at 24 V and a current of 180-200A, the process was under steady electric mode, with some skulling of the crucible, which was characterized by a deeply immersed electrode.

Best performance was achieved in the third period with normal coal/slag ratio. In general, the melting process on this stock characterized by active runout of metal, “hot” process throughout the period and steady growth of calcium content in the alloy. Chemical composition of each tapping is given in table 3.

CONCLUSION

Lab-scale smelting campaign confirmed the feasibility of new technology of smelting CaAlMnSi alloy from high-ash coal of Saryadyr deposits and dump slag of refined ferromanganese.

This enables to develop complex and resource-saving technology of melting new type of ferroalloy which can be used in the steel industry as a deoxidizer, and also as reductant in the production of medium and low carbon grades of ferromanganese.

Obtained alloy is characterized by the following chemical composition: 11-17% Mn; 31-43% Si; 25-31% Al; 5-10% Ca; 12-23% Fe; 019-024% P.

At the moment, the obtained data are insufficient for economic assessment of new technology. However, the results of pilot smelting allow approximate estimation of production cost and economic efficiency of industrial production.

Table 3: Chemical composition and weight of the obtained metal

No. tapping	Content of the components mass. %						Metal weight, kg
	Mn	Si	Al	Ca	Fe	P	
1	12,62	34,59	26,72	3,69	22,19	0,19	4,3
2	10,48	43,07	37,81	5,88	2,48	0,28	8,9
3	13,88	31,5	29,94	4,62	19,84	0,22	5,5
4	11,74	36,19	32,06	5,04	14,73	0,24	6,6
5	15,12	37,95	36,53	6,04	4,21	0,15	3,6
6	16,34	34,11	34,34	5,71	9,29	0,21	3,6
7	16,96	31,54	35,9	6,21	9,16	0,23	6,0
8	17,56	33,06	40,06	5,2	3,97	0,15	5,3
9	11,74	24,82	25,92	6,21	31,15	0,16	13,1
10	17,66	38,18	22,21	6,72	14,28	0,24	5,7
11	15,02	41,9	24,54	8,06	9,65	0,19	8,1
12	15,94	37,08	29,28	8,73	8,74	0,17	6,6
13	15,82	37,35	30,29	9,07	6,87	0,28	6,8
14	16,4	48,49	18,3	10,41	5,43	0,24	9,0

According to the results of lab-scale test the specific consumption of materials and energy per 1 ton of CaAlMnSi is as follows:

- dump FeMn slag 740 kg;
- high-ash coal 2110 kg;
- electric energy 14,21 MWt·h.

Given the cost of slag and coal (logistics included) about $50-60 the production cost of new alloy will amount to $1900-2000 per ton. Major share of production cost (up to 85%) is due to relatively high energy consumption.

Utilization of dump slag and high-ash coal, previously considered as industrial wastes, would help to improve the environmental situation, while low cost of wastes ensures comfortable cost production. It is necessary to consider that in real smelting conditions the consumption of high-ash coal would be substantially higher that estimated stoichiometry.

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