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OPPORTUNITIES FOR OBTAINING OF DEOXIDIZING AND ALLOYING ALLOY BY METALLURGICAL UTILIZATION OF VANADIUM WASTE

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ABSTRACT

For the contemporary steel production, deoxidizing and desulfurizing alloys produced via ferroalloys metallurgy are required. Such kind of alloys is silicocalcium. When its production is accompanied by additives containing alloying elements, the alloy obtained has alloying properties at its import in a certain steel grade. Using of a few hundredths of the alloying elements (such as vanadium, niobium, etc.) to the steel quantity increases significantly its strength indexes.

The most common minefields of vanadium contain about 1% vanadium in the form of complex compounds with various elements. This makes uneffective their direct utilization in the ferrous metallurgy. There are corporate organizations that are manufacturing products from vanadium-containing raw materials. One of these products is vanadium catalyst - material that is distributed in factories for production of sulfuric acid. After a certain period of use it is deactivated and deposited and it contains significantly higher amounts of natural vanadium. It contains over 60 % SiO_2. Catalyst utilization in a combination with calcium-containing materials via pyrometallurgical method is an optimal opportunity for both environmental protection and preparation of precious metallurgical alloys as silicocalcium.

Currently in Bulgaria imported and expensive silicocalcium is being used. The paper presents the results of laboratory calculations using three methods for silicocalcium production with increased vanadium content.

Keywords: silicocalcium, vanadium catalyst, metallurgical lime, metallurgical coke, calcium carbide, carbon-soot, carbothermy, silicothermic process.

INTRODUCTION

In the modern metallurgy, the industrial production of silicocalcium alloys is based on three methods following the reactions below [1,2]:

a. $2SiO_2 + CaO + 5C = CaSi_2 + 5CO$ (1)

b. $2SiO_2 + CaC_2 + 2C = CaSi_2 + 4CO$ (2)

c. $2CaO + 5Si = 2CaSi_2 + SiO_2$ (3)

The use of a vanadium catalyst in the processes for silicocalcium obtaining provides the required amount of vanadium in the alloy on one hand and silicon as a main component of the alloy on the other hand. Thus, the addition of expensive and pure alloying elements such as vanadium is avoided. Its obtaining is accomplished directly at the processing of one of the raw materials.

EXPERIMENTAL

Standard mathematical models are used for material and thermal balance calculation at the three methods. The models are described in scientific literature and compiled with the specifity of the alloy obtained. Typical for the processes by reactions (1) and (2) is that they occur in one stage, and by reaction (3) - in two stages. In thermodynamic terms, the extraction of elements from relatively heavy-reducible oxides is not possible without using of carbothermal method. The metallothermal method is the base of the calculations for the second part of the third method. Table 1 presents the chemical composition of the charge materials required for obtaining of silicocalcium by the three methods.

Table 1. Chemical composition of the charge materials.

Charge materials	Chemical composition, %												
	V_2O_5	Fe_2O_3	SiO_2	Al_2O_3	Na_2O	MnO	CaO	P_2O_5	K_2O	C	Fe	S	Volatile
1.V catalyst	4,81	3,98	66,68	0,96	4,59	-	-	-	7,83	-	-	11,15	-
2. Metall. lime	-	-	-	-	-	-	99,0	-	-	-	-	-	1,00
3. Coke	-	1,10	7,27	2,20	-	0,10	0,40	0,04	-	85,45	-	0,12	3,32
4. Calcium carbide	-	0,10	3,20	0,10	-	-	4,24	-	MgO 0,40	2,20	CaC_2 85,40	0,30	Moisture 4,06
5. C-soot	-	-	-	-	-	-	-	-	-	99,00	-	-	1,00
6. Fe-cuttings	-	-	-	-	-	-	-	-	-	-	100	-	-

Table 2. Reduction coefficients (passing) of the raw material components in alloy, slag and gas phase used by the first method for obtaining of silicocalcium.

Raw material components	In the alloy, %	In the slag, %	In the gas phase, %
V_2O_5	98 (as V)	1	1
Fe_2O_3	100 (as Fe)	0	0
MnO	72 (as Mn)	12	16 (as Mn)
Al_2O_3	90 (as Al)	10	0
SiO_2	90 (as Si)	4	6 (as SiO)
CaO (from the coke)	85 (as Ca)	15	0
S (from the catalyst)	0,05 (as S)	0	99,95 (as SiS)
S (from the coke)	0	0	100,00 (as SiS)
P_2O_5	50 (as P)	0	50 (as P)
Na_2O	0	5	95
K_2O	0	5	95
Volatile	0	0	100
Moisture	0	0	100
Obtained CO	0	0	100

Within the first method:

$2SiO_2 + CaO + 5C = CaSi_2 + 5CO$,

the main raw material for obtaining of the alloy is a waste vanadium catalyst and the secondary main raw material - metallurgical lime. Metallurgical coke is used as a reducer [1, 3, 4].

Table 2 shows the reduction coefficients [5 - 8] used for the balance calculations according to the first method.

The main raw material for obtaining of the alloy by the reaction

$2SiO_2 + CaC_2 + 2C = CaSi_2 + 4CO$

is waste vanadium catalyst and the secondary raw material - calcium carbide. Carbon from calcium carbide and carbon soot is used as reducer [1, 3, 4].

Table 3 shows the reduction coefficients used for the balance calculations performed by the second method [5 - 8].

The balance part at the third method ($2CaO + 5Si = 2CaSi_2 + SiO_2$) proceeds in two stages. During the first stage, at high temperature, the main raw material of vanadium catalyst [1, 2] undergoes carbothermal processing with a carbon reducer from metallurgical coke to obtain silicovanadium ferro-alloy. In the second stage, the main raw material is silicovanadium ferro-alloy and the secondary raw material - metallurgical lime. By electric silicothermal method which uses as a reducing agent liquid silicon obtained at the first stage, final silicocalcium alloy is obtained.

At this method the reduction coefficients for calculation from the first stage coincide with those shown in Table 2. The reduction coefficients for the second step of the process are presented in Table 4 [5 - 8].

The calculations at the three methods are performed on the basis of 100 kg of vanadium catalyst, and 12 % calcium in the alloy.

Table 3. Reduction (passing) coefficient of the raw material components in alloy, slag and gas phase used by the second method of obtaining of silicocalcium.

Raw material components	In the alloy, %	In the slag, %	In the gas phase, %
V_2O_5	98 (as V)	1	1
Fe_2O_3	100 (as Fe)	0	0
Al_2O_3	90 (as Al)	10	0
SiO_2	90 (as Si)	4	6 (as SiO)
CaC_2	100 (as Ca)	0	0
CaO and SiO_2 from calcium carbide	0	100 (as Ca_2SiO_4)	0
S	0,05 (as S)	0	99,95 (as SiS)
Na_2O	0	5	95
K_2O	0	5	95
MgO	50 (as Mg)	50	0
Volatile	0	0	100
Moisture	0	0	100
Obtained CO	0	0	100

Table 4. Reduction (passing) coefficient of the raw material components in alloy, slag and gas phase at the second stage of the third method for obtaining of silicocalcium.

Components	In the alloy, %	In the slag, %	In the gas phase, %
Si_{liquid}	92	8 (as SiO_2 in $2CaO.SiO_2$)	0
CaO	60 (as Ca)	40 (as CaO in $2CaO.SiO_2$)	0
Fe	100	0	0

RESULTS AND DISCUSSION

The chemical composition of an alloy, slag and gas phase after computational modeling of the first, second and third method for obtaining of silicocalcium is shown in Tables 5, 6 and 7.

Summarized material balances obtaining of silicocalcium with increased vanadium content in the first, second and third method, are presented in Table 8.

The final results from the heat balances for obtaining of silicocalcium alloy with increased vanadium content in the first, second and third method, are presented in Table 9.

On the basis of conducted calculations, diagrams are established and the results are presented in Figs. 1, 2 and 3. Fig. 1 shows the change of vanadium and silicon in the alloy, according to the method of its obtaining. The diagram of Fig. 2 represents the amount of silicocalcium using 100 kg vanadium catalyst in the initial batch in each of the three methods for its preparation. Fig. 2 shows the variation of the electricity required for obtaining of one ton alloy. Fig. 3 presents the quantity of slag and gas phases.

The quantity of vanadium and silicon in the alloy using a carbon reducer (first and second process for obtaining of silicocalcium) is relatively more than the third process for obtaining of silicocalcium, where liquid silicon is used as a reducing agent (Fig. 1). This is so, because of the use of bigger amount of iron in the process of the third method. Despite the lower content of vanadium and silicon, it is envisaged that such an alloy has low carbon content, a higher absorption rate and it is

Table 5. Chemical composition of alloy.

	First	method	Second	method	Third	method
Elements	kg	%	kg	%	kg	%
V	2,64	9,09	2,64	9,29	2,64	7,29
Fe	2,63	9,06	2,79	9,84	9,44	26,08
Si	19,29	66,45	19,04	67,02	17,73	48,98
Al	0,82	2,83	0,46	1,63	0,82	2,27
Mn	0,01	0,03	-	-	0,01	0,03
Mg			0,01	0,04	-	-
Ca	3,56	12,26	3,40	11,97	4,53	12,51
P	0,005	0,02	-	-	0,005	0,01
S	0,01	0,04	0,01	0,04	0,01	0,03
C	0,06	0,21	0,05	0,18	-	-
Total	29,03	100	28,41	100	36,20	100

Table 6. Chemical composition of slag.

	First	method	Second	method	Third	method
Oxides	kg	%	kg	%	kg	%
V_2O_5	0,05	1,37	0,05	1,28	0,05	0,82
SiO_2	2,77	76,10	2,67	68,11	2,77	45,19
Al_2O_3	0,18	4,95	0,10	2,55	0,18	2,94
CaO	0,02	0,55	-	-	-	-
Ca_2SiO_4	-	-	0,47	11,99	-	-
CaO(coke)+CaO(lime)	-	-	-	-	2,51	40,95
Na_2O	0,23	6,32	0,23	5,87	0,23	3,75
K_2O	0,39	10,71	0,39	9,95	0,39	6,36
MgO	-	-	0,01	0,26	-	-
Total	3,64	100	3,92	100	6,13	100

Table 7. Chemical composition of gas phase.

	First	method	Second	method	Third	method
Oxides and elements	kg	%	kg	%	kg	%
CO	71,84	66,70	64,33	63,96	71,84	66,71
SiS	20,96	19,46	20,93	20,81	20,96	19,46
SiO	1,80	1,67	2,93	2,91	1,79	1,66
Volatile - lime	0,05	0,05			0,09	0,08
Volatile - coke	1,20	1,11			1,15	1,07
Volatile – carbon soot	-	-	0,29	0,29	-	-
Moisture–calc. carbide	-	-	0,25	0,25	-	-
V_2O_5	0,05	0,05	0,05	0,05	0,05	0,05
P	0,005	0,005	-	-	0,005	0,005
Mn	0,003	0,003	-	-	0,003	0,003
Na_2O	4,36	4,05	4,36	4,34	4,36	4,05
K_2O	7,44	6,91	7,44	7,40	7,44	6,91
Total	107,71	100	100,58	100	107,69	100

Table 8. Results from the material balances of the processes for obtaining of silicocalcium.

First method					
Expense			Income		
Raw materials	kg	%	Products	kg	%
V catalyst	100,00	70,92	Alloy	29,03	20,59
Metallurgical coke	36,10	25,60	Slag	3,64	2,58
Lime	4,91	3,48	Gas phase	107,71	76,39
			Miscount	0,63	0,45
Total	141,01	100	Total	141,01	100
Second method					
Expense			Income		
Raw materials	kg	%	Products	kg	%
V catalyst	100,00	74,54	Alloy	28,41	20,92
Calcium carbide	6,37	4,75	Slag	3,92	2,89
Carbon soot	27,78	20,71	Gas phase	100,58	74,05
			Carbon soot-end	2,08	1,53
			Miscount	0,84	0,62
Total	134,15	100	Total	134,99	100
Third method					
Expense			Income		
Raw materials	kg	%	Products	kg	%
V catalyst	100,00	66,39	Alloy	36,20	24,03
Metallurgical coke	34,75	23,07	Slag	6,13	4,07
Lime	6,28	4,17	Gas phase	107,69	71,50
Lime (for the slag)	2,51	1,67	Miscount	0,60	0,40
Fe–cuttings	6,81	4,52			
Total	150,62	100	Total	150,62	100

Table 9. Final results from the heat balance calculations by the three methods for obtaining of silicocalcium.

First method			
Heat income		Heat expense	
Total	341699 kJ	Total	1409992 kJ
		Heat deficit	1068293 kJ
		Electricity	11505 kWh/t
Second method			
Heat	income	Heat	expense
Total	292258 kJ	Total	1271363 kJ
		Heat deficit	979105 kJ
		Electricity	10771 kWh/t
Third method			
Heat	income	Heat	expense
Total	324706 kJ	Total	1463737 kJ
		Heat deficit	1139031 kJ
		Electricity	9807 kWh/t

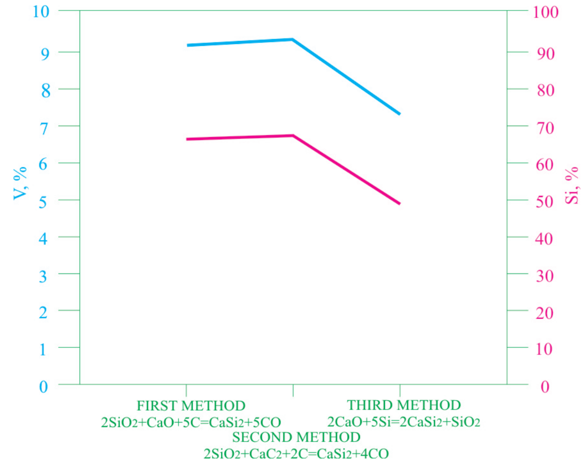

Fig. 1. Vanadium and silicon content in silicocalcium according to the method for obtaining of the alloy.

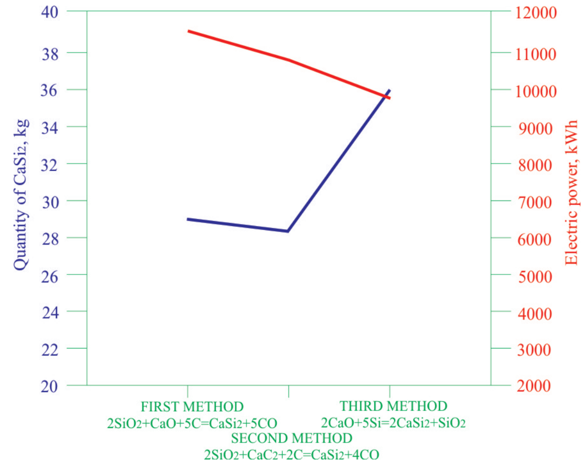

Fig. 2. Variation of the amount of silicocalcium depending on the processing method based upon 100 kg vanadium catalyst used in the charge materials. Electricity required to compensate the heat losses in obtaining of 1 ton silicocalcium by the three methods.

generally more efficient in steelmaking use. In the third method for obtaining of silicocalcium, the quantity of iron creates prerequisites for increased amount of the final alloy (Fig. 2). By this method, relatively smaller amount of energy is required to compensate the heat loss (Fig. 2) due to the two-stage process and using the methods of metallothermy.

CONCLUSIONS

The paper represents the final results of the balance models for obtaining of silicocalcium, using three methods. In all of these balance models, the alloy contains increased amount of scarce alloying element – vanadium on the base of its content in the alloy which is produced by several manufacturing plants. There are opportunities for utilization of waste products, such as deactivated vanadium catalysts, heavily polluting the environment in the regions of their disposal.

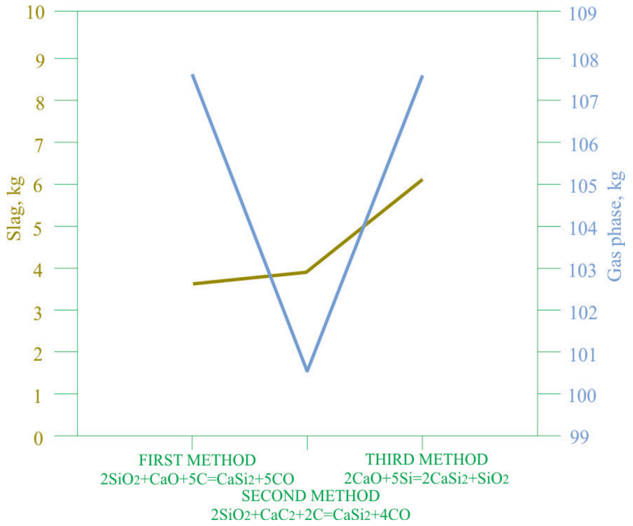

Fig. 3. Variation of the amount of slag and gas phases depending on the method for obtaining of silicocalcium.

REFERENCES

1. H. Erinin, A. Avramov, Metallurgy of ferroalloys, Technics, Sofia, 1979, (in Bulgarian).
2. http://www.oborudunion.ru/i_store/item_1000470055/silikokalciy-sk30.html.
3. M. Rais, Manufacture of ferroalloys, Metallurgy, Moscow, 1975, (in Russian).
4. M. Gasik, N. Liakishev, B. Emlin, Theory and technology of production of ferroalloys, Metallurgy, Moscow, 1988, (in Russian).
5. M. Gasik, I. Taran, V. Gladkih, Physical and chemical processes in electrochemistry of ferroalloys, Science, Moscow, 1981, (in Russian).
6. L. Lozano, D. Juan, Leaching of V from spent sulphuric acid catalysts, J. Minerals Engineering, 35, 3, 2001, 54-59.
7. A. Avramov, Metallurgy of ferroalloys, Technics, Sofia, 1988, (in Bulgarian).
8. D. Dyudkin, V. Kisilenko, Actual Technology of Steel Out-of-Furnace Treatment by Flux Cored Wire, J. Metallurgical and Mining Industry, 2, 2, 2010, 102-106.