BORON IN FERROALLOY PRODUCTION

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ABSTRACT

The following study paper presents the results of theoretical, laboratory and experimental research as well as of industrial test trials of the use of boron in the production of pellets, iron, steel, rolled products and ferroalloys. On the example of manufacturing of 500,000 tons of iron ore pellets and metallurgical processing, a positive effect of boron has been shown on the quality of their processing and performance of their production.

Industrial tests confirmed growth in metal production, reduction of materials and energy consumption due to the use of small doses of borate fluxes in the process of smelting of ferrosilicon, silicochrome, ferrochrome. For the first time in the industrial environment the problem of decay (spill) of highly basic slag into a fine powder has been solved by the addition of micro-doses of boron.

We have studied the market of boron ores. Analyses of physical properties of high-quality Turkish boron ores were conducted. Industrial tests were conducted on metallurgical enterprises in Kazakhstan and Russia.

KEYWORDS: *Boron, ferroalloys, iron ore pellets, iron and steel, roll, slag.*

In metallurgy, production of ferroboron (5-20% of boron, the rest is iron) is traditional, as well as boron containing alloys, the usage of which allows to receive high quality steels.

Recently, thanks to the developments of Chemical-Metallurgical Institute (Kazakhstan), another way of usage of boron ore has began to develop [1]. The core of it is provision of boron dopant materials to the batch of production of sinters, pellets, steel, ferroalloys, by doing so it is possible to improve not only the quality of the final product, but also the technical and economic performance of production.

Scientific research and industrial tests were conducted on the usage of borate ores in ferroalloy production. Tests were carried out at Aksu ferroalloy plant in Kazakhstan. Firstly, was decided to use ores to eliminate technological disorders. Experiments were conducted in 63 MVA furnace for ferrosilicon smelting. Positive effect of boron additive was set for the decrease of furnace clogging, and its rapid start of normal operating practices.

Table 1 shows results of 40-days use of borate ore on the same furnace. During the test borate ore of the content (mass %): 15,2 B_2O_3; 3,4 SiO_2; 0,9 FeO; 1,77 Al_2O_3; 18,6 CaO; 9,4 MgO; 19,3 l.o.i. and 31,43 SO_3 of size 0-5 mm was loaded to furnace in the form of separate additives of 700-900 kg per shift, evenly under all electrodes.

The received results were compared to the period of work when borate ore was not used (base period). It covered the work of furnace for the smelting of FeSi65 for 3 previous quartiles, i.e. before the start of the testing period. This comparison is made in table 1. As it is seen, the additive of borate ore helped to significantly improve technical and economic indicators of production of the alloy FeSi65. Thus, growth of the coefficient of silicon extraction to the alloy has been achieved - from 84,77 to 86,23%, as well as productivity of furnace from 7,294 to 7,625 t/hour (4,5%) and the use of furnace capacity from 57,4 to 61,13 MVA, decrease of energy consumption by 1%, quartzite by 19%, fuel by 5%, iron scrap by 8%. During the test period the work of furnace was stable, there was improvement of the work of furnace top: normalization of gassing, reduction of the number of "fistulas" and sintered parts of the charge. Tested method appeared to be effective for elimination of furnaces' disorders and quick way for normalizing its working regime, and that's why this method was recommended for regular use in all departments of the plant on the basis of new technological instructions on furnaces' exploitations.

Table 1: Indicators of industrial smelting of FeSi65 with the introduction of borate ore to the charge

№	Indicators of process	Conventional technology	Experimental technology
1	Furnace capacity, MVA	57,4	61,13
2	Length of time, days	53	41
3	Actual time of furnace work, hour	1130,17	956,82
4	Amount of smelted metal, t		
	a) actual	7636,03	7758,52
	b) basic	7705,01	7864,37
5	average chemical composition of metal, %		
	silicon	65,57	65,89
	aluminium	1,45	1,69
6	The actual consumption of energy and materials for 1 t of ferrosilicon		
	a) electricity, kWt hour/t	7690	7647
	b) quartzite, t	1,880	1,525
	c) coke, t	0,530	0,560
	d) semi/coke, t	0,380	0,305
	e) scrap, t	0,315	0,290
	f) borate ore, t	-	0,008
7	Given consumption of energy and materials for 1 t of base alloyFeSi65		
	a) electricity, kWt hour/t	5278	5223
	b) quartzite, t/t	1,290	1,042
	c) coke, t/t	0,364	0,383
	d) semi/coke, t/t	0,260	0,208
	e) scrap, t/t	0,216	0,198
	f) borate	-	0,005
8	Furnace productivity, t/hour		
	actual	7,294	7,625
	base (65%)	7,358	7,729
9	average extraction of silicon into the alloy, %	84,77	86,23

Proven technology was also tested in the production of silicochrome. In many plants it is melted by two-step process. In the first stage ferrochrome is received, which is then with quartzite and fuel used for silicochrome obtaining. This process can be compared to the production of 45% ferrosilicon, but instead of scrap - ferrochrome is used. The latter is worse solvent than iron, so the power consumption in the smelting of high-silicon silicochrome is higher, than with smelting of 45% ferrosilicon.

The main disadvantage of described technology is clogging of top space by sublimate that are sintered into hard-breakable accretion, the instability of the slag and gas furnace operation regime, uneven donwtake of the charge and its sintering on furnace top. Considering positive effect of the additives of borate ore on the production of ferrosilicon, it was decided to test this technology in industrial furnaces for silicochrome production. Table 2 shows reclaimed operation and technical and economic indicators of silicochrome melting of the grade FeSi48 (48 is content of silicon) and FeSiCr40 in 21 MVA furnace. Table 3 is deciphering its downtime (for 1 month) during base and test periods.

Table 2: Comparative indicators of the work of furnace №47 for melting of FeSiCr by experimental and base technology

Indicators	FeSiCr48		FeSiCr40	
	test	base	test	base
Time of work				
calendar days	9,78	78,0	20,22	12,0
nominal days	9,78	72,81	20,22	12,0
Consumption per 1 t of alloy, kg				
quartzite	1065	1081	943	936
coke	309	465	226	372
semi coke	211	31	235	-
scrap	32	45	41	52
ferrochrome	568	575	696	684
borate ore	10,8	-	9,7	-
Weight of melting, t	5,6	5,1	6,5	6,1
Capacity/day				
in calendar days	69,5	60,1	77,3	73,9
in nominal days	67,5	57,0	74,5	70,9
Use of silicon, %	95,2	96,9	88,6	93,5
Use of chrome, %	89,7	88,4	88,5	90,5
Power, kWt	18053	16179	16472	16471
Consumption of e/energy, kWt hour	6235	6481	5112	5347

Supply of borate ore led to improvement of furnace performance. First of all normalized dejection of charge in funnels, almost disappeared cases of stops and sintering of charge, as well as cases of fistulous gassing.

The previously formed crust was destroyed on the second day already, and the number of fumes dramatically decreased, which led to enlargement of hearth space. The downtime decreased by 57,7% after cleaning the hearth space. Sum of downtimes reduced from 32,77 to 23,45 hour, i.e. by 28% (table 3). With addition of boron ore slag regime was normalized.

Slag became more liquid and flowable, and was produced regularly. It also had positive effect on technical and economic parameters of melting, especially of high-silicon alloy FeSiCr48, despite a slight decline in the use of chromium and silicon (table 2).

Theoretically proven and in industrial conditions tested the way of smelting of refined marks of ferrochrome with borate ore usage [2, 3]. In industry the most widely used method of production of medium and low-carbon ferrochrome is ferrosilicochrome refining from silicon with oxygen of chrome ore.

Simplified form of chemical reaction of this process is

$$Cr_2O_3 + 3/2Si = 2Cr + 3/2SiO_2$$

Table 3: Downtimes of furnace during testing and base periods

№	Name of downtime	Downtime	
		April	**I quarter**
1	Malfunction of arched panels		0,35
2	Stop of the water supply in the cooling syst.		0,83
3	Water leaks in the cooling system	5,10	4,5
4	Cleaning of top space	3,55	8,4
5	Connecting and disconnecting of g/cleaning	13,20	13,75
6	Problems with bypass		0,3
7	Malfunction of furnace transformator	1,20	
8	Disconnecting from overheating		0,03
9	Malfunction of main substation		0,78
10	Absence of tech.ware		0,43
11	Treatment of furnace top		0,70
12	Other	0,40	2,70
	Total	23,45	32,77

According to this method the process consists of the following stages:

- smelting of carbon pig ferrochrome
- obtaining of silicochrome from pig ferrochrome and quartzite
- receipt of refined ferrochrome by oxidation of silicon ferrochrome with chrome ore.

The process of the production of refined ferrochrome can be carried out in an electric furnace as well as out of furnace by mixing in special reactors. Both methods are implemented in industrial enterprises of different countries, both have their advantages and disadvantages and the choice of each of them depends on the quality of used chrome ores, limestone, reducing agent, the availability of appropriate facilities. But it is also known that both methods have similar and so far not fully solved disadvantages, the solution of which will increase the efficiency of the technological process of smelting of refined ferrochrome. Temperature dependence of the Gibbs energy of the reaction is described by:

$$\Delta G^{o}_{T} = -289500 + 47 \cdot T$$

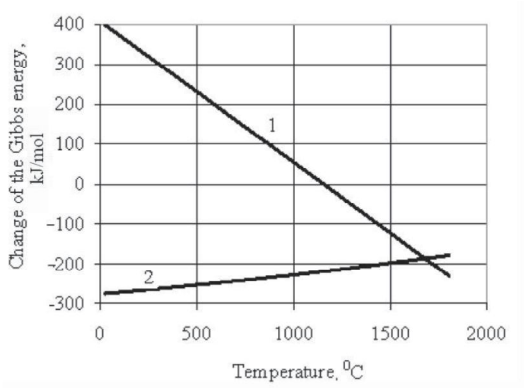
For comparison, considered also the process of carbothermic reduction of chromium:

$$2/3\, Cr_2O_3 + 18/7C = 4/21Cr_7C_3 + 2CO$$

$$\Delta G^{o}_{T} = 503612 - 359{,}45 \cdot T$$

On figure 1 there is graphical interpretation of the process of metal- and carbothermic reduction of chrome. It can be seen that the recovery of chromium by carbon starts when the system reaches a certain temperature.

Another is the nature of the recovery of chromium by silicon. Over the entire investigated range of temperatures change of the Gibbs energy is in the region of negative values, which means thermodynamic probability of this reaction under the given conditions (figure 1). Exothermic character of the reaction causes its energetic flow at low temperatures and decrease its fullness with the rise of temperature in accordance with the principal of dynamic equilibrium.In the temperature range studied for basic charge, exothermic heat effect of oxidation of silicon is not observed (figure 2 a), indicating that this reaction is practically impossible in the given conditions, although thermodynamics (figure 1) shows the opposite. The observed is due to the fact that the participants of the reaction have high melting points and in the experimental conditions are in the solid state when the diffusion process is stalled.



1) recovery of chromium by carbon
2) recovery of chromium by silicon

Figure 1: Dependence of the change of the Gibbs energy reaction of chromium recovery by carbon and silicon on temperature

In practice, these difficulties can be overcome by conducting the process at high temperatures by providing heat input from outside, for example electricity, which, however, increases the cost of the process.

In order to reduce heat level of the process and bring the participants of the reaction to liquid state we have used fusible borate ore.

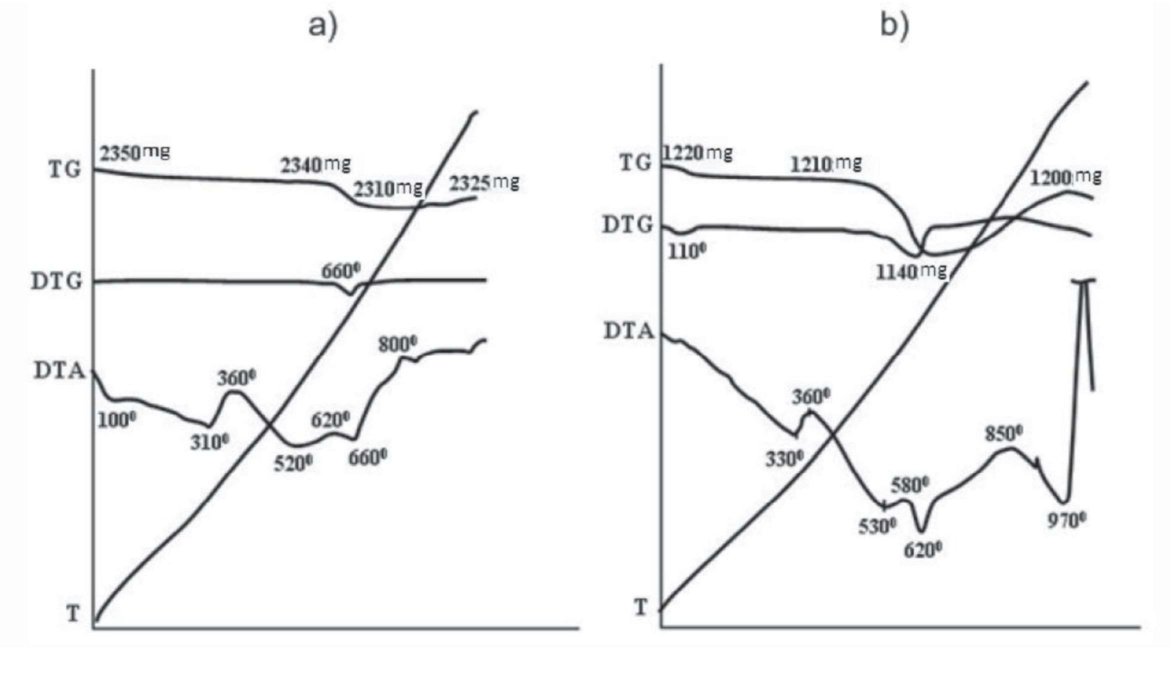
Its addition into the charge – calculating B_2O_3 content being not less than 1 %, ensured the reaction of oxidation of silicon already at 970°C (figure 2, b). One can assume that in industrial conditions described method will help to reduce costs of heat (electricity) for the process and accelerate the production of metal.

The next disadvantage does not have direct negative effect on the technological process. It is consequence of this process. But it questions the existence of the process itself. We are talking about decay of highly basic slag of medium-and low carbon marks of ferrochrome production, that has negative impact on environment not only in the industrial area, but also for tenth and hundredth kilometres away.

The main reason of the decomposition of highly basic slag of refined marks of ferrochrome is polymorphic transformation of dicalcium silicate ($2CaO{\cdot}SiO_2$), which occurs with volume increase (up to 12 %).

Figure 1 exhibits the results of experimental studies by DTA reaction method of silicon oxidation.

Experimentally we have found that the presence of as much as 0,5 % of B_2O_3 in slag prevents decomposition and after cooling slag remains in the form of lump, that is how serious ecological problems can be solved. This method was tested at Aktobe Ferroalloy plant. When the above mentioned conditions are performed, there is growth of metal production (up to 10 %), decrease of electricity consumption (up to 6%) and complete prevention of silicate decomposition. The boron content in the metal was on the level of 0,0035-0,0045%. This circumstance must be emphasized. The fact is that refined marks of ferrochrome are used for smelting of high-quality steel marks, such as stainless steel, and the presence of boron in the latter significantly increases their corrosion resistance and ductility.



a) without boron oxide, b) with boron oxide

Figure 2: Derivatogram (change of sample weight and thermal effects of transformation of mixture) or termogram of mixture of chromium oxide, silicon metal and calcium oxide

The above studies were conducted with borate ores of Inder minefield in Kazakhstan. During long period of time they had been used to produce boric acid and various boron products in Kazakhstan and Russia. Nowadays, the stock of rich ores (15-25% B_2O_3) is exhausted. Availability in big quantities of poor ores (7-8% B_2O_3) is of interest to a number of industries, but they require advance preparation.

Russia has powerful minefield of datolite boron resources in the Primorye Territory (Dalnegorsk city). Established here enterprise produces boric acid, boric anhydride, calcium borate, datolite concentrate. The remoteness of the plant from industrial centres does not allow to count on any noticeable use of products on metallurgical factories of Russia and countries of Central Asia. According to the existing information, about 85% of boron production is exported to foreign countries. For Russian metallurgy there is interest in boron-containing magnetite ores with rich content of iron, from Taiga minefields, located on the Baikal – Amur mainline. Investigation of possibility of effective processing of the ore with the obtaining of high quality naturally alloyed steel by boron were begun over 50 years ago [4-6]. Establishment of full cycle metallurgical plant on the basis of this minefield would promote industrial development of this region.

The current situation in CIS boron market draws attention to other sources of boron. According to stocks (table 4), content B_2O_3 (table 5), proximity to Central Asia and Russia, Turkish boron-containing raw materials are attractive. Boron industry is widely developed in Turkey; it is a world leader of boron production.

Data on special behaviour of boron-containing materials at high temperatures and their physical properties and the impact of these materials on the properties of steel and slag could be used as guidance for metallurgists while using boron-containing ores in their processes.The list and chemical composition of the studied Turkish boron-containing materials are presented in table 5.

According to X-ray analysis borax, colemanite and ulexite are represented by the following boron-containing materials, respectively: $Na_2B_4O_7{\cdot}5H_2O$; $Ca_2B_6O_{11}{\cdot}5H_2O$ and $NaCaB_5O_9{\cdot}8H_2O$.

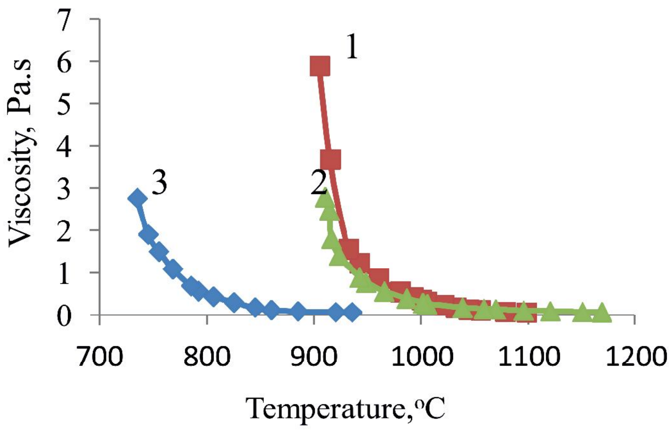
Figure 3 presents the results of investigations of the viscosity of boron-containing raw materials. Temperature dependence of viscosity for these materials is characterized by smooth changes of fluidity while cooling. In a wide interval of temperatures their viscosity does not exceed 0,1-0,2 Pa·s. Low viscosity and crystallization temperature of boron-containing materials (for colemanite - 1004°C, tincal – 863°C, ulexite – 940°C) makes them suitable for use as a flux and slag-forming additives for furnace smelting and out-of-furnace treatment of ferrous and non-ferrous metals.

Table 4: Reserves of boron-containing raw materials in different countries

Countries	Resources	
	B_2O_3, mil.ton	%
Argentina	9	0,7
Bolivia	19	1,5
Chile	41	3,3
China	47	3,8
Iran	1	0
Kazakhstan	102	8,2
Peru	22	1,8
Russia	35	2,8
Turkey	885	71,3
USA	80	6,4
Total	1,241	100,0

Table 5: Chemical content of boron-containing materials

Material	Content, %							$t_{n.cr.}$°C
	B_2O_3	CaO	MgO	SiO_2	Al_2O_3	Na_2O	loi	
Ticalconc.	28,32	3,4	2,85	2,63	-	14,3	39,5	863
Colemanite	38,78	27,9	3,6	5,63	0,69	-	20,9	1004
Ulexite	35,98	18,9	3,1	4,3	0,23	3,8	33,62	940



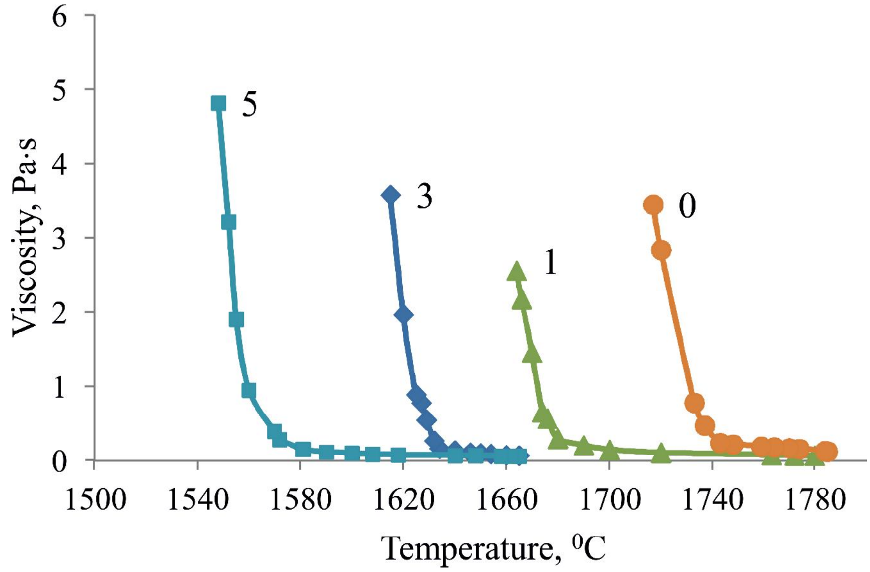
1 – ulexite, 2 – colemanite, 3 – borax

Figure 3: Temperature dependence of viscosity of basic boron-containing materials

We have investigated the effects of colemanite additives on viscosity and temperature of crystallization start of slag of chromium alloys smelting and slag of copper matte smelting. Figure

4, as example, shows the temperature dependence of slag viscosity of the refined ferrochrome production with different amount of colemanite additives. Its content is provided in table 6.

Original slag of Aktobe Ferroalloy Plant (0) has high temperature of crystallization (1743°C), as it is mainly composed by refractory dicalcium(Ca_2SiO_4) silicate. By melting it has low viscosity, as its structure is dominated by single tetrahedrons $SiO_4^{4-}$of dicalcium silicate. Colemanite additives progressively reduce refractoriness of slag (table 6). For example by entering 5% of this additive, temperature of crystallization decreases by 162°C, and the viscosity still remains low. Obtained data allows to select the optimal consumption of colemanite in smelting.



The numbers on the curves – the percentage content of colemanite in the slag

Figure 4: Temperature dependence of slag viscosity of refined ferrochrome

Table 6: Slag of refined ferrochrome

Sample №	Content, %							$t_{n.cr.}$ °C
	CaO	MgO	SiO_2	Al_2O_3	Cr_2O_3	FeO	B_2O_3	
1 (base)	50,29	11,31	26,47	6,12	4,47	1,34	-	1743
2 (1% colemanite)	49,94	11,26	26,32	6,08	4,44	1,33	0,38	1686
3 (3% colemanite)	49,26	11,16	26,04	6,0	4,37	1,31	1,14	1636
4 (5% colemanite)	48,61	11,1	25,76	5,93	4,31	1,29	1,87	1581

The possibility of using colemanite for stabilising slag produced by the collapse of silicate of refined ferrochrome was tested. The amount of added colemanite to the slag ranged from 0,3 to 3,0 %. It was found that reliable stabilization is provided when the colemanite content is 0,65 % and higher. On the X-ray when colemanite content is higher than 0,5 % then only α and β-forms $2CaO{\cdot}SiO_2$ are found to be stabilized, and in decompositioned slag γ-phase. With supplying colemanite into the furnace, it is necessary to determine its consumption with consideration of 10 % loss of boron, 20-30% transition to metal and content of boron oxide in the slag should be more than 0,25 %.

CONCLUSIONS

On the basis of above facts it can be concluded that usage of boron in ferroalloy smelting can improve the quality of ferroalloys, as well as increase technical and economic indicators of production. We plan to expand research work on the use of high quality Turkish boron-containing raw materials in metallurgical processes. In our opinion, implementation of described methods will contribute to overall efficiency of ferroalloys production.

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