THE COMPREHENSIVE ANALYSIS OF PHYSICAL AND CHEMICAL PROPERTIES AND METALLURGICAL VALUE OF FOREIGN MANGANESE RAW MATERIALS USED DURING FERROALLOY PRODUCTION

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The results of benchmark analytical studies of domestic and foreign manganese-ore raw materials have been presented. The requirements for quality indicators of manganese ores and concentrates according to the normative documents of various countries have been compared. The metallurgical properties and reduction kinetics of samples of manganese raw materials from different deposits have been investigated. The optimal portion of imported raw materials in the burden mixture for manganese ferroalloy production in conjunction with the required phosphorus content in them has been estimated.

The selection of rational recycling technology as well as technical and economic parameters of manganese ferroalloy production is largely determined by the quality of manganese-ore raw materials: chemical, mineralogical and particle compositions, as well as physical properties. The manganese ore deposits are very unevenly distributed all over the world; their material composition is also irregular, which is attributed to the ore genesis [1].

Most of the world developed reserves of manganese ores (over 80%) are concentrated in Republic of South Africa (RSA), which is the largest producer and exporter of them. In Ukraine, the balance reserves are about 2 billion tons; however, over 70% of domestic manganese ore are rebellious and refer to carbonate and oxide-carbonate species. The distinctive feature of manganese ores of domestic deposits is relatively low manganese content and elevated phosphorus and silica concentration [2], which makes it impossible, as opposed to the most foreign ores, to use raw materials without preliminary beneficiation and lumping.

For adequacy of raw materials estimation, it is required to benchmark quality indicators of manganese concentrates produced in Ukraine and abroad (Table 1).

Table 1. Technical requirements specified for quality of manganese ores and concentrates for ferroalloy melting

Component	Mass fraction, %							
	For ferromanganese				For silicon manganese			
	Ukraine, I grade	Western Europe		USA, grade A	Ukraine, II grade	Western Europe		USA, grade B
		I grade	II grade			I grade	II grade	
Mn, min	43.0	48.0	46.0	46.0	34.0	44.0	40.0	40.0
Fe, max	-	-	7.5	8.0	-	9.0	12.0	16.0
SiO_2, max	-	7.0	9.0	12.0	-	10.0	12.0	15.0
P, max	-	0.12	0,15	0.18	-	0.15	0.15	0.30

Note: the requirements are specified for Nikopol oxide concentrates, concentrates and ores of foreign producers.

The difficulties with production of competitive manganese alloys using domestic raw materials have been particularly exacerbated in recent years, when, on the one hand, domestic enterprises have begun to increase production of low-phosphorus grades of silicon manganese and ferromanganese, and, on the other hand, the increased cost of power resources made uncompetitive earlier existing pyrometallurgical technology of raw materials dephosphorization. This required the use of imported manganese ores at Ukrainian ferroalloy plants.

As such, the samples of manganese ores of various chemical and fractional composition (Tables 2-5), which are widely used in the production of manganese ferroalloys at domestic enterprises nowadays, have been investigated. These include samples of manganese ore deposits in Georgia, Brazil, Australia and Ghana.

Table 2. Chemical composition of investigated samples of manganese ores

Item No.	Country-producer	Mass fraction of components, %									
		Mn	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	P_2O_5	Na_2O	K_2O	LOI
1	Georgia	47.20	12.09	1.88	1.92	0.75	1.86	0.47	0.21	0.59	3.29
2	Brazil	47.60	9.30	1.20	1.03	1.34	9.30	0.14	0.23	1.15	2.29
3	Australia	47.00	13.05	1.63	2.67	0.98	8.94	0.07	0.12	0.03	3.88
4	Ghana-I	30.00	14.05	2.65	4.65	5.08	1.72	0.16	0.28	0.24	31.6
5	Ghana-II	39.79	19.30	4.20	0.40	0.12	7.10	0.32	0.19	0.63	5.02
6	Ghana-III	30.50	13.52	2.20	4.81	4.85	1.05	0.25	0.24	0.21	32.6

Table 3. Investigation results of common physical properties of manganese ores

Item No.	Country-producer	Mass fraction of moisture, %	Density, kg/m^3			Total porosity, %	Impact (DSTU 3200-95)
			bulk	apparent	true		strength of fraction over 5 mm, %
1	Georgia	4.0	1740	2400	3880	38.14	31.0
2	Brazil	8.4	2940	4210	4270	10.92	58.0
3	Australia	2.8	2110	3850	4020	4.23	75.6
4	Ghana-I*	1.6	2300	3240	3270	1.4	71.0
5	Ghana-II	7.2	2090	-	3670	-	-
6	Ghana-III	1.6	2120	3190	3370	5.3	72.0

** Manganese ore from Ghana I and III – carbonate, Ghana II – oxide.*

Analyzing the investigation results of manganese ore physical properties shown in Table 3, it should be noted that the ores are slightly porous, except ore from Georgia, and have higher true density as compared to the domestic manganese concentrate. The mechanical strength (for fraction of over 5 mm) of lump manganese ore is low, and behind in strength of manganese sinter produced from domestic concentrates.

Table 4. Mineralogical composition of investigated samples of manganese ores

Item No.	Country-producer	Manganese distribution by mineral phases, %											
		Ore phase		Pyrolusite		Mineral groups of psilomelane		Braunite		Manganite		Manganese carbonates (rhodochrosite, calcium rhodochrosite)	
		Mn	M	Mn	M	Mn	M	Mn	M	Mn	M	Mn	M
1	Georgia	47.20	76.4	43.7	69.1	-	-	-	-	3.2	6.1	0.3	1.2
2	Brazil	47.60	78.6	16.3	25.8	14.6	25.3	16.7	27.5	-	-	-	-
3	Australia	47.00	77.2	2.5	3.9	3.2	5.4	40.5	66.0	-	-	0.8	1.9
4	Ghana-I	30.00	78.5	1.1	1.7	-	-	1.2	1.9	-	-	27.7	74.9
5	Ghana-II	39.7	66.2	18.3	29.0	17.0	29.4	3.8	6.0	-	-	0.6	1.8
6	Ghana-III	30.5	77.8	-	-	-	-	-	-	-	-	30.5	77.8

Table 5. Mass fraction of impurity elements in samples of manganese ores

Item No.	Country-producer	Mass fraction of components, %			
		B (boron)	As (arsenic)	Pb (lead)	Hg (mercury)
1	Georgia	0.0090	0.0050	0.0010	less than 0.0030
2	Brazil	0.0110	less than 0.0050	0.0150	less than 0.0030
3	Australia	0.0160	less than 0.0050	0.0150	less than 0.0030
4	Ghana-I	0.0110	0.0075	0.0010	less than 0.0030
5	Ghana-II	0.0090	0.0150	0.0020	less than 0.0030
6	Ghana-III	0.0200	0.0100	0.0010	less than 0.0030

As shown in Table 5, the imported ores under analysis have slightly higher content of non-ferrous metals (boron, arsenic, lead, mercury) impurities, which are mainly connected with the ore manganese minerals.

The presence of arsenic and boron compounds in the mineral and raw components of metallurgical burden provides for necessity to take a series of additional measures to reduce their harmful impact on the steel quality. The recycling of As-containing manganese and iron ores is complicated by the reason that oxide compounds of arsenic, especially arsine (AsH_4), belong to the group of industrial toxic substances. The problem of boron and arsenic, until recently, has not attracted the attention of ferroalloy producers.

It shall be noted that any content regulatory of these elements in the manganese-ore raw materials is absent in the brochures. Moreover, it is known that Vale de Rio Doce (Brazil, 1994), for the ore consisting mainly of manganese dioxide (MnO_2 – 81.34-80.00%), imposed restrictions for arsenic up to 0.0044% in the first grade and up to 0.0048% in the second grade, and for lead up to 0.021% and up to 0.024% by grades respectively.

Similarly with manganese phosphides, it is believed that boron and arsenic, which are present in the burden, shall be completely transformed into the alloy during manganese ferroalloy melting, and this assumption is evidenced by the chemical analyses of ferroalloy furnace aspiration dust, which is almost free from the above mentioned elements. As concerns lead and mercury, their presence does not affect significantly the quality of manganese ferroalloys, since majority (over 90%) of these impurities is removed (carburized) in the gas phase during manganese ferroalloy melting.

It shall be noted that some elements and compounds, which are present in Mn-containing raw materials, such as alkali metal oxides (Na_2O and K_2O), silicon oxide, lead, mercury, zinc, et al. and enter the furnace high temperature zone, are transformed into gaseous phase, ascend to the upper levels of ferroalloy furnace stack and descend on the burden materials. In such a case, phase transformations result in the heat transfer from the lower levels of the stack to the upper ones and may increase the burden temperature at the upper levels and the furnace top respectively. When the certain concentrations have been reached, the circulating substances with burden can form scull and free-running mixtures, which adversely affect the gas-dynamic and electric conditions of electric melting. Also, the accumulation of heavy metals insoluble in the ferroalloys on the furnace hearth has been observed.

The chemical and mineralogical investigations make it possible to calculate the burden, excluding the possibility of free-running phase formation in the ferroalloy furnace stack volume. It has been established that certain manganese and silicate compounds (glass and tephroite) are formed during manganese ore reduction at relatively low temperature of 750-800°C.

The investigations on determination of manganese ore reducibility and initial fusion temperature have been carried out in accordance with standard procedures (DSTU-3202-95; DSTU-3203-95) under generator gas atmosphere.

A lot of papers [3-5] have been dedicated to the investigation of manganese minerals, ores and concentrates reducibility; however, the paper [5] has been devoted to the investigation of Brazilian, African and Australian ores; but the available literature data are often ambiguous. It is known that MnO_2 and $MnCO_3$ dissociate at relatively low temperatures of 510 and 176°C respectively. Manganese oxide and carbonate reduction in the ores in question occurs at lower temperatures rather than their dissociation (Fig.1).

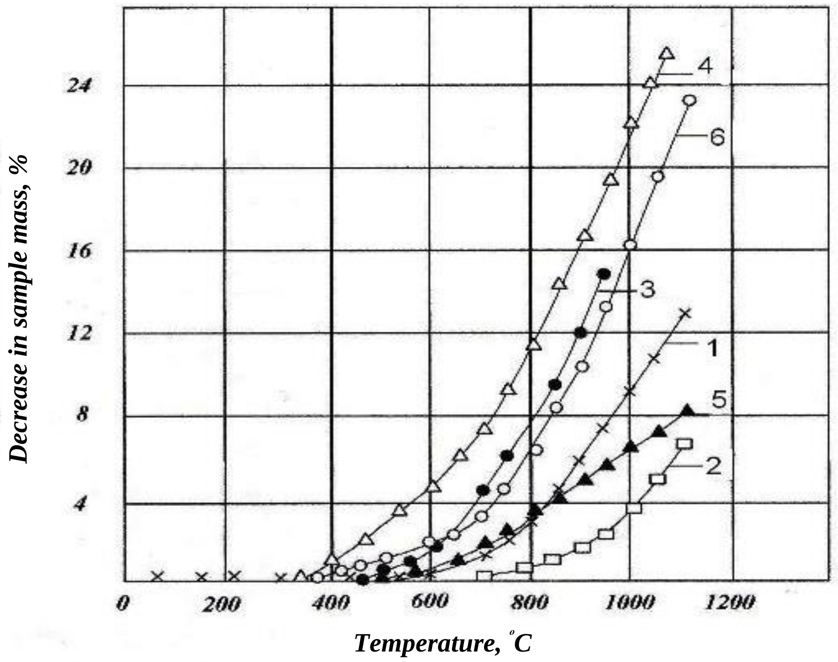

Fig. 1. Kinetics of sample mass decrease in the reaction zone during heating in the reduction medium (figures near the curves represent sample number)

The curves of sample mass decrease (Fig. 1) depending on the temperature graphically demonstrate these conclusions. The manganese ore samples in question at the same temperature and at all other things constant lose mass due to dehydration, decarbonization and dissociation of manganese minerals at different rates.

Fig. 2 illustrates the results of investigations devoted to the determination of manganese ore initial fusion temperature during heating in the reduction medium. The initial reduction temperature is considered to be the temperature, at which the reduction of linear dimensions of the test samples is more than 10%, when they are subjected to the permanent mechanical load.

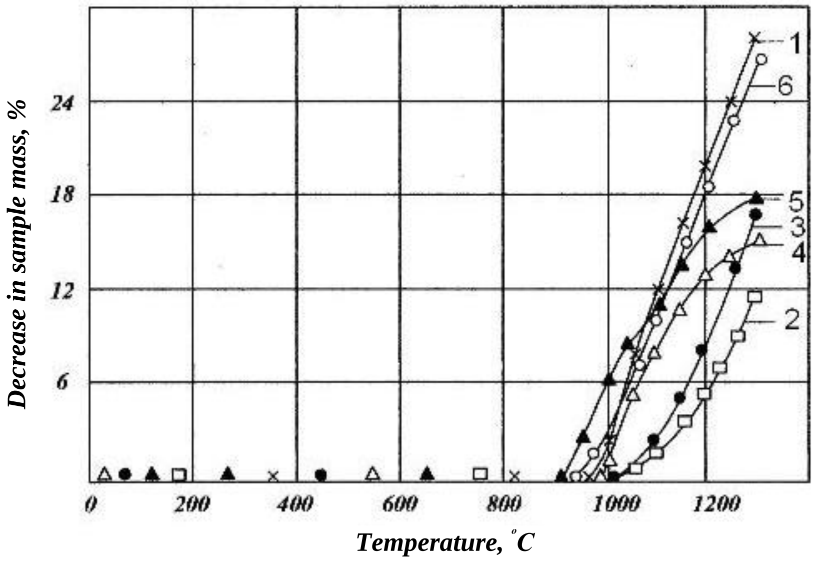

Fig. 2. Sample mass decrease in the reaction zone during heating in the reduction medium (figures near the curves represent sample number)

The specific feature of manganese ore reduction is an appearance of liquid phase at relatively low temperature of 750-800°C.

Originally, the liquid phase is observed in the individual microvolumetric particles on the periphery of minerals, particularly, on the feldspar $(K, Na)\cdot[AlSiO_3O_8]$ and quartzite (SiO_2) grains bordering the manganosite (MnO).

In case of temperature growth over 800°C, the volume of liquid melt increases and the silicate melt can impregnate significant portion of ore mass. Low temperature of liquid phase origination is attributable to the fact that Mn-containing source material includes potassium, sodium, calcium and silicon oxides, which, together with highly reactive manganosite, form a complex low-melting system in terms of chemical composition. The local X-ray spectral analysis of fusion area reveals high K, Na, Ca and Si content.

The influence of base ore nature and its material composition on reducibility and fusion temperature and, in its turn, on structure and properties of slag melts is obvious. The slag viscosity shall contribute to the rapid drippage into alloy, interdiffusion between the oxides and reducing agent, and, consequently, rapid process reaction, and, finally, to the optimal distribution of temperature gradients in the melt. Unfortunately, manganese and slag losses only in the form of metal beads during production of manganese alloys are significant. In particular, when melting silicon manganese, they reach 7.0% due to the high final slag viscosity.

Therefore, in general, physical and chemical properties of source mineral raw materials under ferroalloy production conditions are the factors that determine the mechanism, kinetics and statics of reduction process.

For technological processes of manganese ferroalloy production, the manganese ores and concentrates are favorable, as they are characterized by high fusion temperature contributing to the deeper manganese reduction at the initial stage of the reduction process, when the burden is in the solid state. However, some of these ores require great power consumption and refer to irreducible ones in view of almost complete bonding of manganese oxide in the tephroite ($MnSiO_4$), rhodonite ($MnSiO_3$), jacobsite ($MnFe_3O_4$) and other thermodynamically stable compounds. Moreover, some of them, especially jacobsite, have low electrical resistance.

The low-melting Mn-containing materials are distinguished by high fluidity, which is especially unfavorable for the technology, when their portion is significant in the burden. At the same time, heavy accumulation of the above mentioned melts having simultaneous high electrical conductivity and hindering the completion of dissociation, decarbonization and reduction of manganese oxides and carbonates occurs in the furnace. Therefore, in any case, the use of the investigated manganese ores in the burden for melting of silicon manganese in the ratios required to produce an alloy of the specified quality is more preferable rather than from sinter and ore of domestic production.

The results of differential thermal analysis (DTA) of samples of oxide, oxide-carbonate and carbonate ores and concentrates are shown in Fig. 3 and Table. 6.

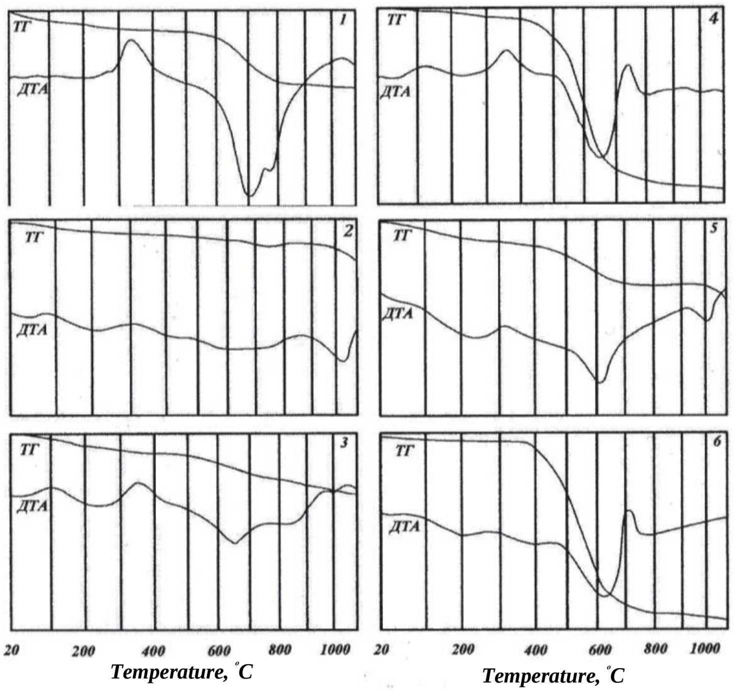

Fig. 3. Nature of differential heating curves (DTA) and changes in manganese ore mass samples (TGA):

1, 2, and 3 is a sample number of manganese ore delivered from Georgia, Australia and Brazil, respectively: 4, 5 and 6 is a sample number of manganese ore delivered from Ghana-I, Ghana-II and Ghana-III, respectively.

Table 6. Results of thermal analysis of manganese ore samples

Effect No.	Sample number											
	1		2		3		4		5		6	
	Country-producer											
	Georgia		**Brazil**		**Australia**		**Ghana-I**		**Ghana-II**		**Ghana-III**	
	Effect sign and tempera-ture (°C)	**Mass loss, %**	**Effect sign and tempera-ture (°C)**	**Mass loss, %**	**Effect sign and tempera-ture (°C)**	**Mass loss, %**	**Effect sign and temperature (°C)**	**Mass loss, %**	**Effect sign and tempera-ture (°C)**	**Mass loss, %**	**Effect sign and temperature (°C)**	**Mass loss, %**
1	(-) 100	} 1.66	(-) 57	0.61	-	} 2.11	-	}0.96	(-) 60	1.32	**(-) 60**	0.605
2	-		(-) 180	0.44	(+) 115		**(+)** 125		-	1.82	-	0.605
3	-		(-) 240	0.64	(-) 260	0.90	-		(-) 270	1.58	(0210	0.34
4	(+) 340	1.82	-		(+) 350	0.77	**(+)** 340		(+) 340	}1.75	-	
5	-	}0.80	(-) 390	}1.00	-		-		(-) 400		-	
6	-		(-) 610		-		(-) 640	}24.38	-		(-) 420	
7	(-) 700	} 8.26	-	}1.21	(-) 650	2.95	-		(-) 625	5.54	-	
8	-		-		-		**(+)** 725		-	}0.67	(-) 627	25.71
9	(-) 760		-		-		-		-		(+) 705	
10	-		(-) 740		-		**(-)** 772	2.30	-		-	}2.79
11	-		**(-)** 780		(-) 840	1.77 '	-		-		(-) 770	
12	-		-		-		**(-)** 990	0.87	-		(-) 980	1.14
13	-		-		(-) 1010	1.36	-		C-) 1010	1.51	-	
14	(+) 1030		(-) 1050	2.15	-		-		-		-	
I	-	113.31		16.05		£9.86		*1* 29.34		I 14.18		131.19

Note: Effect sign (+) - exothermic, (-) - endothermic.

It shall be noted that the sample 1 is manganese ore mainly represented by pyrolusite (MnO_2); the sample 2 is predominantly represented by braunite (Mn_2O_3); the sample 3 contains pyrolusite, psilomelane and calcite. Furthermore, the exothermic reactions caused by the secondary oxidation of the resulting manganese oxide (MnO), which is thermodynamically unstable under these conditions and reacts with oxygen, including oxygen that results from the dissociation of higher manganese oxides, occur in all the above described three samples, especially in the sample 1 (Fig. 3) within the temperature range of 300-400°C. This interpretation is consistent and evidenced in the paper [6].

The sample 4 is mostly represented by rhodochrosite. Moreover, manganese ore contains some calcite and psilomelane. Moreover, small amount of natrolite-type zeolite has been revealed. The main component of the sample 5 (see Fig. 3) is pyrolusite (58.4%) and psilomelane. In addition, the aforesaid sample contains some braunite and zeolite. The sample 6 is represented by manganese carbonate ore, mainly consisting of rhodochrosite (about 67%). The ore contains manganese calcite that causes mass loss, which is equal to 2.79% (Table 6) within the temperature range of 660-680°C; there are some psilomelane and zeolite as well. The thermograms of manganese ores in terms of behavior are varied and mutually dissimilar. The difference of the endothermic effect value is caused by difference in quantity of Mn-containing minerals and chemical composition of the gangue. Thermal decomposition of higher oxides and dissociation of carbonates occur in a wide temperature range due to the different thermal and physical properties of minerals.

The quality of foreign ores was compared with Ukrainian concentrates (I and II grades), based on the relative module parameters (Table 7), which represent the ratio of mass fraction of element or component in the ore to the mass fraction of manganese in it or the relationship between the total of oxide components and the total of the other components in Mn-containing raw materials, expressed in the unit fractions.

Table 7. Chemical composition and module parameters of manganese ore and concentrate samples

Item No.	Country-producer	Mass fraction, %			Content ratio, unit fractions	
		Mn	**Fe**	**P**	**P/Mn**	**$(CaO+MgO)/SiO_2$**
1	Georgia	47.20	1.300	0.207	0.00438	0.2069
2	Brazil	47.60	6.500	0.0060	0.0013	0.2548
3	Australia	47.00	6.250	0.032	0.0007	0.2703
4	Ghana-I	30.00	1.201	0.070	0.0023	0.6925
5	Ghana-II	39.70	4.962	0.140	0.0035	0.0269
6	Ghana-III	30.50	0.734	0,110	0.0036	0.7145
7	Ukraine. Concentrate: I grade II grade	 43.0 36.0	 1.509 1.494	 0.176 0.202	 0.0041 0.0056	 0.2890 0.2440

The analysis of values of phosphorus module (P/Mn), as an indicator of specific phosphorus content with regard to the manganese content, shows that Ukrainian manganese concentrates are characterized by the worst indicators of this parameter rather than foreign ores. The module of iron is drastically higher than the module of ore from Brazil, Australia and oxide-carbonate Ghana, which does not provide for production of manganese ferroalloys and, foremost, of silicon manganese with higher manganese content as compared to the basic one (65%). Nowadays, the above described factor is the most important one providing for high competitiveness of silicon manganese at the world market.

At the same time, the availability of high-grade ores allows the foreign producers to melt quality manganese ferroalloys directly from lump ores, while it is impossible to recycle Ukrainian manganese ores without additional and expensive items of the conversion stage, including beneficiation of low-grade ore with production of concentrates from it and their agglomeration, at which manganese recovery and power consumption are 97% and 150 kWh/t, respectively.

As concerns the samples in question it is necessary to focus on the ore under the number 4 and 6, which refers to the carbonate manganese ores.

The difficulty with inclusion of carbonate manganese ore in the metallurgical conversion stage is preliminary determined by high heat consumption of carbonate raw materials of about 240 kWh/t of material for decomposition of carbonates, as well as the destruction of ore lumps to produce 20-30% of fines (fraction of less than 5 mm) at high-speed heating, which reduces the gas permeability of the burden [3].

However, the carbonate raw materials have natural basicity of 0.6-0.7, which partially eliminates the addition of limestone to the burden and the melting temperature of carbonate ores and concentrates is by 100-200°C more than the oxide ones, which improves the thermodynamic and kinetic conditions of reduction processes.

The investigations demonstrated that during melting of high-carbon ferromanganese with phosphorus of 0.35% according to the scheme adopted at PJSC Nikopol Ferroalloy Plant using low-phosphorous charge slag (LFCS) of fluxfree ferromanganese melting, the power consumption was 4054 kWh/t, and manganese recovery was 82.2% (considering production waste). The use of imported ore in the burden in order to produce similar quality alloy made it impossible to achieve significant advantages in terms of manganese recovery, and the power consumption was slightly increased. However, if we consider additional power consumption during agglomeration (≈ 150 kWh/t) and LFCS melting (850-900 kWh/t), the total through power consumption exceeds 5000 kWh/t.

The comparison of the values of the silicon manganese melting with phosphorus of 0.15-0.25% looks even more clearly. As for the melting of such quality alloy the raw materials with phosphorus module of max 0.002 can be used, the alloy was melted using over 80% of low-phosphorous slag and high-grade Australian ore. Thus, when the phosphorous is reduced in the alloy from 0.25 to 0.15% (which is equivalent to LFCS part growth in the burden from 82 to 93%), the manganese recovery is decreased from 72 to 60% and the specific power consumption is increased by 6-7%. The use of Australian ore will make it possible to enhance considerably the manganese recovery (≈ 82%) and reduce power consumption by 200-250 kWh/t.

These results show that using domestic raw materials for the production of silicon manganese with phosphorus of max 0.35%, the quantity of low-phosphorous slag in the burden in order to achieve relatively acceptable indicators shall not exceed 90-95 kg/t of alloy. The increase of LFCS portion during melting of metal with phosphorus of 0.15-0.25% leads to the dramatic reduction of all process parameters. In such a case, the absolute priority is given to the high-grade imported ores with phosphorus module of equal to or less than 0.002.

Summary

The comparative analysis of chemical, mineralogical compositions and physical characteristics of imported and domestic manganese ores and concentrates, as well as the investigations of phase composition transformation regularities during reduction and heat treatment have been carried out.

It has been evidenced that the main distinguishing feature of manganese raw materials in question manufactured by foreign producers is a low value of phosphorus module (P/Mn < 0.0035) and silica (SiO_2/Mn from 0.5 and lower), which makes it possible to achieve high technical and economic parameters in the ferroalloy production.

The analysis of metallurgical value of domestic and imported raw materials during alloy melting has established that it is possible to blend all types of raw materials with various phosphorus content during silicon manganese production, however, in view of low melting temperature of low-phosphorous charge slag (LFCS), its portion in the burden shall not exceed 40-45% (when melting the alloy with P content up to 0.35 %). In order to produce alloy with phosphorus content within the range of 0.15-0.20%, it is more appropriate to use imported ores with LFCS additional charging.

References

[1] Ferroalloys of Ukraine – 2000 / M.I. Gasik, O.G. Gantserovsky, A.N. Ovcharuk, I.P. Rogachev // Dnepropetrovsk: State Research and Development Enterprise "System Technologies" – 2001 – P. 143.

[2] M.I. Gasik, N.P. Lyakishev, Physicochemistry and technology of electric ferroalloys: Collage textbook // Dnepropetrovsk: State Research and Development Enterprise "System Technologies" – 2005 – P. 448.

[3] A.G. Kucher, The investigation of physical and chemical transformations in the carbonate manganese concentrations during their heat treatment // Book: Current challenges and perspectives of electrometallurgical production – Dnepropetrovsk: State Research and Development Enterprise "System Technologies" – 1999 – P. 48-54.

[4] V.V. Krivenko, A.N. Ovcharuk ,The investigation of mechanical and thermal exposure on the manganese concentrate and sinter in the oxide and reduction media // Metallurgical and mining industry – 2002 – No. 2 – P. 21-23.

[5] B. Sorensen, S. Gaal, M. Tangstad a.o. Properties of manganese ores and their change in the process of calcinations. Proceeding of The Twelfth International Ferroalloys Congress. Volume 2. 2010. Helsinki, Finland. V.P. 439-448.

[6] S.G. Grishchenko, T.F. Raichenko, N.M. Moskalyova, On interaction between chemical and mineralogical composition and reducibility of manganese-ore materials from various deposits. Report I. Special aspects of genesis and condition of source manganese-ore materials // Bulletin of the Academy of Sciences USSR – Metals – 1991 – No. 3 – P. 13.