REDUCTION OF TITANIUM- MAGNETITE CONCENTRATE CONTAINING VANADIUM

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Abstract

Titanium-magnetite concentrate, obtained from magnetite gabbro from the Samokov region (Bulgaria) contains approximately 65% Fe_{total}, 1,15% TiO_2, 0,3-04% V_2O_3. It is remarkable for its high native alkalinity. Some semi-products suitable for metallurgical work can be obtained from them by correctly chosen technology.

The objects of investigation in this paper are kinetics and degree of titanium-magnetite reduction with solid carbon and hydrogen under the influence of external magnetic field. The relative activation energy of the reduction process is calculated and mathematical equations for its description are worked out. It is found out that the direct reduction of titanium-magnetite concentrate passes in kinetics field – indirect reduction being the limiting stage. The highest intensity of the process can be observed with 2,5 times more reductive agent (carbon) than the stochimetrical amount. Granulometrical composition of the materials influences hydrogen reduction of the concentrate in the magnetic field.

Keywords: concentrate, reduction, degree of reduction, rate of reduction, DTA.

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1. Introduction

Titanium-magnetite concentrates are products of the dressing of titanium-magnetite ores. They are remarkable for high contents of iron, natural alkalinity and low contents of sulphur and phosphorus [1]. The poor titanium concentrates are processed through reduction melted in blast-furnaces, the first stage being electric melting, the second - melting by the scheme tubing oven-electric furnace, through direct reduction by the method of "Krup-Ren process" and also through hydrometallurgical vanadium extraction [2].

The titanium-magnetite concentrates containing vanadium are put to agglomerating scorch when the contents of TiO_2 is not more than 3-4%. Natural alloying pig-iron can be produced from them [3]. In some cases these pig-irons are treated as semiproducts for a getting rich vanadium converter slags. In some cases ferro-vanadium and V_2O_5 can be received by appropriate working [2]. The simultaneous obtaining of iron, titanium and vanadium can be achieved through melting of pellets with high degree of melting in an electric furnace. As a result, it is getting a pig-iron containing vanadium with low contents of phosphorus and titanium slags [4-6] appropriate for ferro alloys production. The last stage of the technological process by pyrometallurgical working of titanium-magnetite concentrates is connected most frequently with obtaining of V_2O_5 or of vanadium alloys [7].

The purpose of this work is to investigate the kinetics of reduction of titanium-magnetite concentrate containing vanadium, which is obtained from magnetite gabbro [8] and to establish the possibilities for its metallurgical utilization.

2. Experimental

2.1. Materials, apparatus and methods of investigation

Titanium-magnetite concentrate is obtained through magnetic separation of uneven mineralized magnetite gabbro from Samokov, in which titanium and vanadium distribution is presented on Fig.1-3.

The chemical composition of titanium-magnetite concentrate is:

Element	Fe total	Fe$_3$O$_4$	V$_2$O$_5$	TiO$_2$	Al$_2$O$_3$	SiO$_2$	CuO	MgO	CaO
Mass. %	65,79	90,92	0,3-0,4	1,16	1,68	2,62	1,20	0,80	1,20

*Fig. 1. Distribution of magnetite and ilmenite in ore materials; white-magnetite; greyilmenite; black-silicate minerals**
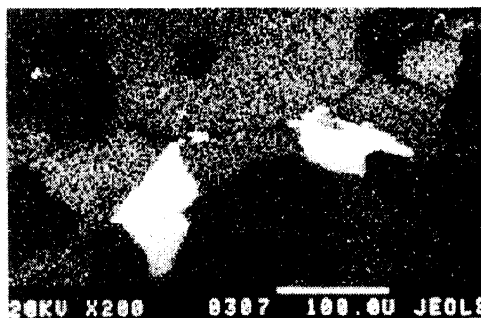

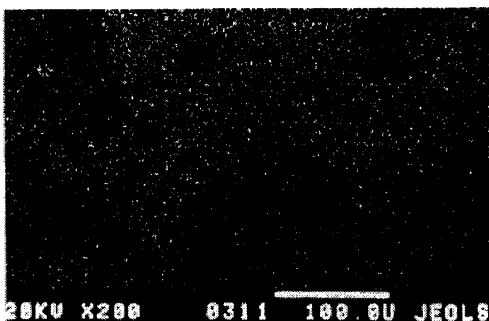*Fig 2. Distribution of titanium in ore and non-ore minerals**

Fig. 3. Distribution of vanadium in ore and non-ore minerals

The phase composition of the concentrate and the products from its reduction are determined by X-ray-analysis and Moesbauer spectroscopy. The spectra are photographed at room temperature. Co^{5+}implanted in chromeis used as emission power. It is found out that the iron finding in materials is predominantly magnetite and a little quantity of hematite. Independent phases of titanium and vanadium are not discovered.

The kinetics of reduction of titanium-magnetite concentrate with solid carbon is investigated in temperature range 293K to 1273K. DTA method and derivatographe "NETSCH"[9] are used. Solid carbon is used as a reductive agent in stoichiometrical, 2 times and 2,5 times more than the stoichiometrical amount. The particle diameter in the mixture is between 0.177 and 0.094 mm. The investigations are carried out in dispensable ceramic crucibles with a cover. Pure argon is blown into the working space of the furnace. The error of DTG is $\pm 1.10^{-4}$ g and for is DTA $\pm 0,5\ ^0C$.

The reduction of titanium-magnetite concentrate with hydrogen for particle size from 0,094 to 0,177 mm is carried out in a magnetically structured bed. This method is elaborated and submited for different heterogenous processes[10, 11, 12] and gives possibility of their intensification without particle size restriction. On this base the ferrous oxides reduction can be realized at lower temperature.

2. 2. Results and discussion

DTA analysis data of the experimental samples are shown in Table 1. The calculated values of the rate (υ) and the degree of their reduction with solid carbon is presented on Table 3. The following formula is used for the calculations:

$$\alpha = \frac{[O]_{em}}{[O]_{theor}}.100,[\%]$$

where $[O]_{em}$ is oxygen emission during the reduction process as CO and CO_2, and $[O]_{theor}$ is the theoretically calculated amount of oxygen contained in the initial sample.

The low-temperature endothermal effects, which are within the range 293K-443K correspond to the evaporation process. The high-temperature endothermal effects (from 828K to 893K) can be explained with the reconstruction of Fe_2O_3 and Fe_3O_4 crystal lattice. An exothermal reaction

takes place in the mixture and it results as an exothermal effect at about 783K. It corresponds to the Fe_2O_3 reduction to Fe_3O_4.

Table 1. Results of DTA of titanium-magnetite concentrate and solid carbon mixtures

No of the mix-tures	Change of the mass, temperature and quantity of reductive agent						Total loss, %
	Temperature, K	Effect	Loss of mass, %	Temperature, K	Effect	Loss of mass, %	
1.	[293 - 398] min 373K	Endothermal	0,6	[668-1063] max 789K min 893K	Exothermal Endothermal	4,9 -	5,5
2.	[2943 - 413] min 363K	Endothermal	1,1	[663-1028] max 783K min 837K	Exothermal Endothermal	4,9 -	6,0
3.	[293 - 443] min 383K	Endothermal	1,7	[633-1028] max 783K min 828K	Exothermal Endothermal	9,5 -	11,2

The phase composition of the products of reduction is determined by Mossbauer spectroscopy. The obtained results are shown in Table 2. It can be observed that α-Fe is present only in the mixture No 2. Higher concentration of Fe^{+2} in the products of reduction can be observed with a reductive agent surplus 2 and 2,5 times more than stoichimetrical quantity.

Table 2. Phase composition of the products of titanium-magnetite concentrate reduction determined by Mossbauer spectroscopy

No of the mixture	Ratio of reductive agent and concentrate quantities	Phase composition, mass %					
		Fe_3O_4	Fe_2O_3	FeO	α-Fe	Fe^{+2}	Fe^{+3}
1.	1:1	17,0	72,0	-	-	-	11,0
2.	2:1	24,0	57,0	-	6,0	13,0	-
3.	2,5:1	20,0	62,0	-	-	12,0	6,0

Table 3. Rate and degree of reduction change of titanium-magnetite concentrate depending on the quantity of solid reductive agent and temperature

No	Mixture 1			Mixture 2			Mixture 3		
	T, K	α, %	$v.10^{-4}$ kg/kg.s	T, K	α, %	$v.10^{-4}$ kg/kg.s	T, K	α, %	$v.10^{-4}$ kg/kg.s
1.	648	0,72	-	663	0,95	-	633	2,26	-
2..	763	1,44	0,067	723	1,89	0,056	723	4,53	0,074
3.	788	2,16	0,095	783	3,79	0,111	783	9,06	0,133
4.	823	3,60	0,222	837	6,63	0,200	828	13,60	0,267
5.	893	7,92	0,286	903	13,30	0,333	898	20,40	0,286
6.	953	12,80	0,333	963	19,90	0,389	963	31,70	0,556
7.	1033	17,20	0,292	1028	24,60	0,238	1028	37,40	0,238
8.	1103	21,60	0,286	1093	29,40	0,278	1093	49,80	0,611
9.	1218	25,90	0,153	1163	34,20	0,333	1163	53,20	0,143

The degree of titanium-magnetite concentrate reduction is the lowest with stoichiometrical content of solid carbon in the mixtures. The cause is the reductive agent quantity and the presence of CO_2 and H_2O in the gas phase. They cluster on the reaction surface of ferrous oxides and hold up their reduction.

The following formula is used for the calculations:

$$\ln m - 2\ln T = A_0 - \frac{E}{RT} \qquad (1)$$

where m is loss of sample weight [kg], T is temperature [°K], R is the gas constant, A_o is a constant, E is the ostensible activation energy [kJ/mol].

The values of the calculated relative activation energy of ferrous oxides reduction in titanium-magnetite concentrate [11] are shown in Table 4. The process passes in a kinetic field, indirect reduction being the limiting stage.

Table 4. Relative activation energy of ferrous oxides reduction containing titanium-magnetite concentrate

No of the mixture	Temperature range, K	Relative activation energy, Ea, kJ/mol
1.	823 – 1018	65,442
2.	833 – 1163	56,250
3.	783 - 1163	44,651

Statistical models of the degree of reduction α[%] of titanium-magnetite concentrate with solid carbon have been derived from the data shown on Table 3. The general type of the models is:

$$\alpha(x) = b_0 + b_1 x + \frac{b_2 \exp(b_3 x)}{b_4 + b_5 \exp(b_6 x)},$$

where x is temperature and $b_0 - b_6$ are model coefficients. The values of the coefficients and some statistics are shown on Table 5.

Table 5. The values of the coefficients and some statistics

Coefficient	Model for		
	Mixture 1	Mixture 2	Mixture 3
b_0	0,0241075409	0,0610225172	0,0605675977
b_1	-0,0004963589	-0,0051181555	-0,0028821860
b_2	0,0059439839	0,0094689609	0,0133138870
b_3	-0,0015693503	-0,0022489719	-0,0024730751
b_4	0,0000281697	0,0000122216	0,0000090800
b_5	1,6522225789	0,2604308550	0,3020140384
b_6	-0,0103624214	-0,0092796987	-0,0096212244
Statistics			
Correlation coefficient	0,99618	0,99766	0,99773
Variance explained	99,237%	99,533%	99,547%

All models have high values of the correlation coefficient and variance explained percentage. They are good enough to be used for prediction of the degree of reduction.

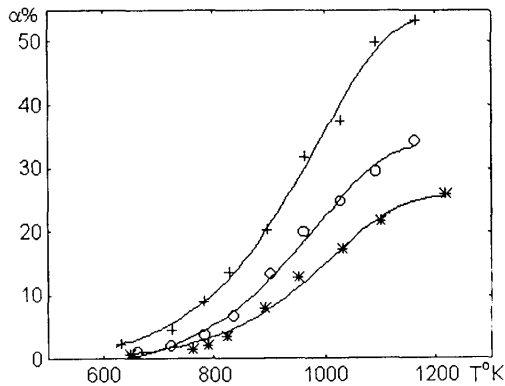The data and the model curves of the investigated mixtures are shown in Figure 4.

Fig. 4. Model curves of the reduction process for the different mixtures
*Legend: *-mixture 1; o-mixture 2; +-mixture 3.*

The results obtained of solid phase reduction of titanium-magnetite concentrate show an unsatisfactory degree of reduction in the investigated temperature range. It is presented only by the oxidic phase of Fe^{+2}. When the amount of solid reductive agent is 2 times more than the stoicometrical one (mixture 2) appearance of α-Fe.(Table 2) is observed.

Consequently, at temperatures of about 1100K and time 30 min the degree of reduction does not exceed 50%. So it does not satisfy the industrial requirements. This result can be explained by the mechanism of the process and the limiting stage of the carbon gasification. The static regime of the investigation should also be considered, because it does not ensure conditions of intensive mass transfer. That is why another investigation of reduction process in a dynamic regime of a flow reactor can hold out new possibilities for realization of the process.

For this purpose we used the elaborated method for reduction [10, 11, 12] in the condition of external magnetic field.

The pure hydrogen (99.995%) has been used as a reductive agent at 873K. The temperature choice for the investigation is done so as to be a little above the triple equilibrium temperature in a diagram of equilibrium composition of the gas phase in the system Fe-O-H. The experimental results are shown in Table 6. The analysis of these results shows that the rate of the process continuously increases to degree of reduction $\alpha=61.5\%$ for particles with diameter 0.177 mm. This almost linear change of α/τ and v/v is different from the traditional investigation result. The big contact surface and the linear velocity of reductive agent used (v=0.5 m/s) are basic reasons for these results according to us. They obscure unfavorable influence of the continuous decreasing of the phase-boundary surface in the reduction process. The high rate of the process determines the necessary time of the concentrate reduction what is lower than 50-60 minutes for the smaller particles. The high degree of fine-dispersed ferrous oxide reduction with hydrogen in external magnetic field enables obtaining of suitable titanium-magnetite concentrate for metallurgical practice.

Table 6. Rate and degree of reduction change of titanium-magnetite concentrate with hydrogen in a magnetic field at 873K depending on granulometrical composition and heating time

No	Time of reduction	Particle size			
		0,094 mm		0,177 mm	
	τ, sek	α, %	$v \cdot 10^6$ gmol/g.s	α, %	$v \cdot 10^6$ gmol/g,s
1.	420	10,0	1,32	3,2	0,66
2.	540	17,5	2,05	7,1	1,03
3.	660	28,2	2,96	11,2	1,26
4.	780	33,6	3,55	17,6	1,72
5.	900	40,0	3,70	23,3	2,15
6.	1020	46,8	3,81	27,9	2,17
7.	1200	54,1	3,70	35,5	2,30
8.	1500	67,5	3,70	47,8	2,58
9.	1800	84,9	3,85	61,5	2,76

3. Conclusions

The kinetics of titanium-magnetite concentrate reduction process has been investigated in temperature range 293-1273K, using solid reductive agent and hydrogen in a magnetic field at 873°K.

1. It has been found out that the solid-phase reduction of the ferrous oxides in the titanium-magnetite concentrate has a higher degree of reduction when the amount of the reductive agent used is 2.5 times more than the stoichometrical one. The calculated values of the relative activation energy show the possibility that the reduction process takes part in the kinetic field with limiting stage of indirect reduction.

2. Experimental results are mathematically processed. Statistical models of the degree of reduction α[%] of titanium-magnetite concentrate have been derived. All models have high values of the statistical criteria used for their evaluation. So they can be successfully used for prediction of the degree of reduction.

3. Additional experiments in hydrogen flow and external magnetic field at 873°K have been carried out in order to increase the degree of reduction of titanium-magnetite concentrate. Higher degree of reduction

has been established comparing to the solid-phase one ($\alpha=84.9\%$ for $d_p=0.094$ mm particle size and $\alpha=61.5\%$ for $d_p=0.177$ mm particle size in the external magnetic field and hydrogen flow reduction comparing to the solid carbon reduction).

The results from both types of the ferrous oxides reduction investigated of titanium-magnetite concentrate give reason to conclude that the process in external magnetic field and hydrogen flow will satisfy better the metallurgical practice.

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