

Thermokinetic Study of Manganous Concentrates Dissociation Processes

I.V. Tsvetkov, V.P. Konovalenko /Ph.D. (Eng.)/

National Metallurgical Academy of Ukraine
4 Gagarin Ave., Dnipropetrovsk 49600, Ukraine

Abstract

The results of investigation of microstructure of Nikopol oxide and oxide-carbonate manganous concentrates by X-ray structure microanalysis method as well as the results of thermokinetic research of concentrates dissociation are presented. The interrelation between change of volume and emission rate of gaseous products of concentrates dissociation under their heating up to 1200 °C is established.

Keywords: manganous concentrates, heating furnace, gas-volumetric method, dissociation rate, scanning electronic microscopy

Statement of research problem

Study of manganous concentrates quality applied for ferroalloys production is of great importance in terms of dynamically changing parameters by chemical, mineralogical and fractional composition. In this regard, data on mineral structure of concentrates and changes occurring during their heat treatment are urgent.

Materials, equipment and research technique

The studies were carried out with the use of Nikopol manganous concentrates of oxide grade 1 (o) and oxide-carbonate grade 1 (ox) (Table 1).

The microstructure was investigated using scanning electronic microscope JSM-6360 LA (JEOL, Japan), thermal dissociation of concentrates was studied by means of gas-volumetric method.

The results of scanning electronic microscopical investigation of microstructure of Nikopol manganous concentrates

Oxide manganous concentrates are presented by minerals: pyrolusite MnO_2 , manganite $MnOOH$, psilomelane $MnO \cdot MnO_2 \cdot nH_2O$, cryptomelane $K_{-2}(Mn^{4+}, Mn^{2+})_8O_{16}$, hollandine $Mn^{2+}BaMn_6^{4+}O_{14}$,

etc. [1, 2]. Nikopol oxide manganous concentrate of grade 1(o) is investigated with the use of scanning electronic microscopy. The results of scanning electronic microscopy are summarized in Figure 1.

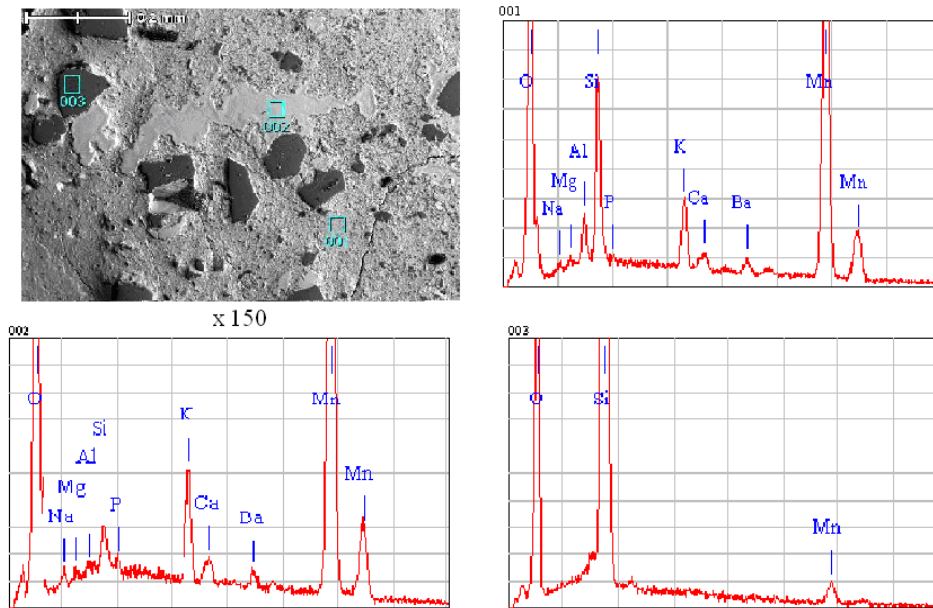
In the light phase (frames 001 and 002), there are several oxide manganese buildups different by composition and structure with insignificant amount of impurity elements. The dark phase (frame 003) is represented by almost pure quartz.

The oxide-carbonate manganous concentrates are presented by a continuous series of solid solutions between calcite and rhodochrosite $CaCO_3$ - $MnCO_3$. Under the real conditions, depending on a kind and quantity of substituent element, manganian carbonates can be presented by calcic rhodochrosite $(Ca, Mn)CO_3$, manganocalcite $(Mn, Ca)CO_3$ [3, 4]. Scanning electronic microscopical investigation of oxide-carbonate manganous concentrates (Figure 2) shows the presence of mineral buildups containing 51.22-66.46 % Mn; 5.39-13.43 % Ca (frames 001 and 002) which are typical for calcic rhodochrosite and manganocalcite, there is also a compound containing 48.14 % Si (frame 003).

Table 1. Chemical composition of representative samples of industrial manganous concentrates

Concentrate	Content, %									
	Mn	P	SiO ₂	CaO	MgO	Al ₂ O ₃	MnO ₂	MnO	Fe	Fe ₂ O ₃
oxide grade 1 (o)	43.6	0.246	12.26	2.97	0.86	1.72	54.72	11.64	1.51	2.16
oxide-carbonate grade 1 (ox)	28.4	0.186	13.76	13.42	1.23	1.50	4.05	33.33	2.43	3.47

ELECTROMETALLURGY



Point No.	O	Na	Mg	Al	Si	P	K	Ca	Mn	Ba	Total, %
001	16.6	0.48	0.34	1.60	5.92	0.32	3.77	0.92	66.64	3.41	100
002	16.2	0.75	0.28	0.08	0.65	0.41	4.11	1.14	73.10	3.28	100
003	35.5	0	0	0	60.5	0	0	0	4.00	0	100

Figure 1. Microstructure of oxide manganese concentrate of grade 1 (o) in secondary electrons, spectrograms of analysis points are marked by frames and chemical compositions of mineral buildups analyzed

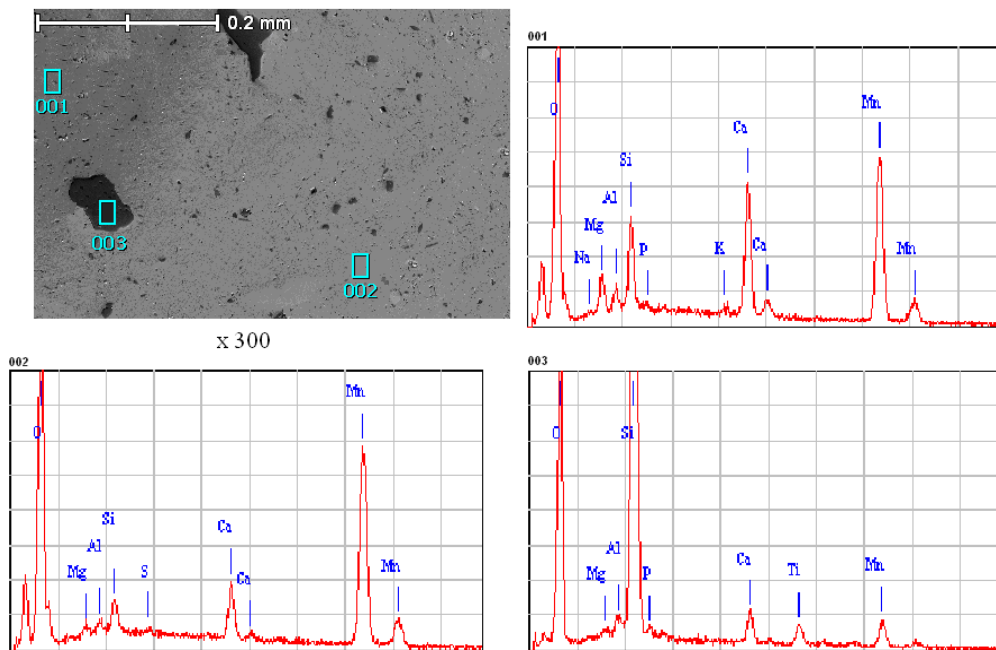
Results of thermokinetic studies of manganese concentrates dissociation

Thermokinetic studies of dissociation were carried out using the plant presented in Figure 3. A crucible with 100 g concentrate sample was placed in a heating furnace and connected to gas counter of GSB-400 type via a gas outlet tube. In a series of tests, the heating rate varied from 3 up to 10 °C/minute. Thermal dissociation of oxide concentrate is caused by decomposition of various manganese minerals subjected to changes during heating. The curves of diagrams describing changes in samples investigated are plotted according to the results of measurements.

Heating rate has an influence upon interaction processes occurring in oxide concentrates. Slow heating at the rate of 3 °C/minute enables to obtain samples with compact texture that proves the completeness of transformations in mineral phases. In case of flash heating, the samples are porous and all the processes influence one another due to their superposition against each other by time.

Heating of oxide concentrates at the rate of 6 °C/minute provides changes in ore components and, as a result of thermal influence, formation of structures providing the best parameters of conducting processes in ferroalloy furnaces. Investigating the curves obtained as a result of experiments carried out, it should be noted that in oxide concentrates there are phases providing an intensive gas emission in the range of temperatures 400-500 °C, 600-700 °C gas evolution is determined by dissociation under the scheme $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$. Peaks related to changes under mechanism $\gamma\text{-MnOON} \cdot \text{N}_2\text{O} \rightarrow \gamma\text{-MnOON} \rightarrow \text{MnO}_2$ are marked in graphs.

During research of oxide-carbonate concentrate dissociation it is observed that heating rate influences gas emission rate in unit of time. As the heating rate increases the plant records intensive emission of gas phase at higher temperatures, which is explained by superposition of decomposition processes of manganese carbonates with various composition on kinetic



Point No.	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Total, %
001	25.71	0.45	2.31	1.35	4.67	0.30	0	0.56	13.43	0	51.22	100
002	25.04	0	0.65	0.57	1.62	0	0.27	0	5.39	0	66.46	100
003	32.86	0	0.24	0.56	48.14	1.02	0	0	4.20	3.66	9.32	100

Figure 2. Microstructure of oxide-carbonate manganous concentrate of grade 1 (ox) in secondary electrons, spectrograms of analysis points are marked by frames and chemical compositions of mineral buildups analyzed

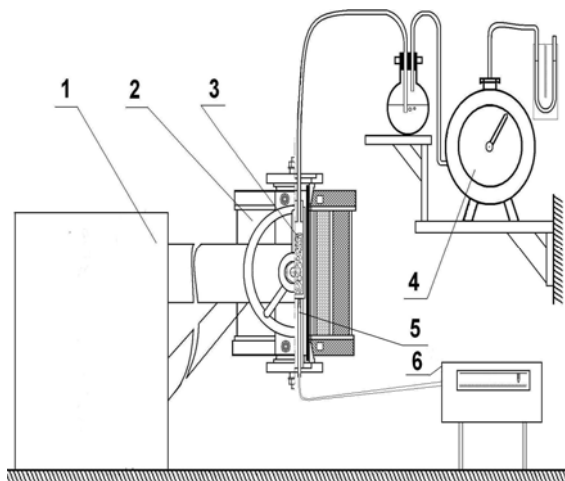


Figure 3. Plant for research of dissociation of oxide and oxide-carbonate manganous concentrates: 1 - transformer, 2 - heating furnace, 3 - crucible with sample, 4 - gas counter GSB-400, 5 - thermocouple PP-1, 6 - galvanometer

factors: heat conductivity of minerals, CO₂ diffusion, velocity of dissociation zone displacement. Researching the lines of diagrams, it is possible to assume the presence of several mineral phases, intensity of which decomposition is found out by the presence of peaks at 450-500 °C, decomposition of calcic rhodochrosite with minimal calcium content, 600-650 °C - decomposition of carbonate compounds with high calcium content, 800-850 °C – dissociation of CaCO₃ containing the low percent of Mn. According to literature data, decomposition of MnCO₃ takes place in the temperature range from 610 up to 635 °C.

Figures 4, 5 present the temperature dependences of evolved gas and the rate of gas emission during dissociation of manganous concentrates of oxide grade 1 (o) and oxide-carbonate grade 1 (ox) at the heating rate of 6 °C/minute which have strongly marked exponent parameters of thermokinetic characteristics.

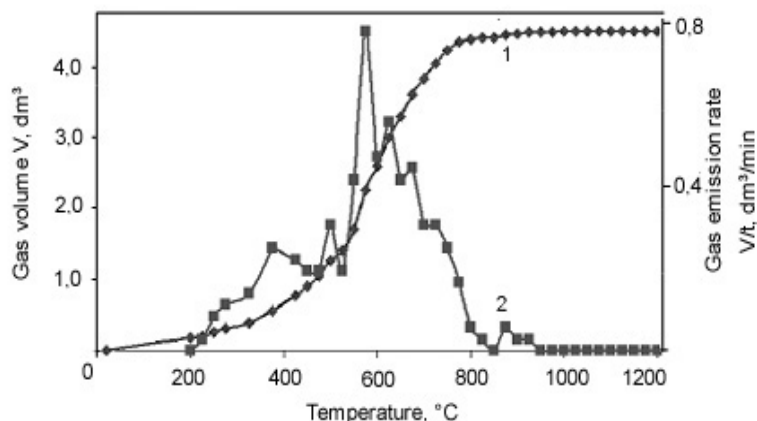


Figure 4. Temperature dependences of evolved gas (1) and gas emission rate (2) during dissociation of oxide manganous concentrate of grade 1 (o) (weight of sample is 100g)

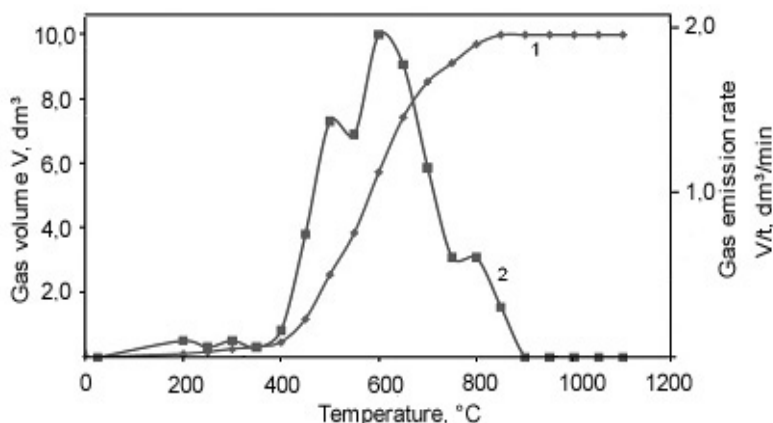


Figure 5. Temperature dependences of evolved gas (1) and gas emission rate (2) during dissociation of oxide-carbonate manganous concentrate of grade 1 (ox) (weight of sample is 100g)

The initial temperature of decomposition processes is 400-450 °C and the final temperature is 950-1000 °C. The experiments carried out with the samples of carbonate concentrate of grade 1 (ox) provide deviation of 1-2 %. In experiments with oxide concentrate of grade 1 (o) the deviation is much higher (7-9 %), which proves much more variety of oxide mineral components while oxide-carbonate concentrate is presented mainly by carbonates with different ratio Mn/Ca. The volume of evolved gas is possible to be compared with calculated stoichiometrical formation of CO₂ from decomposition of carbonates.

Conclusions

1. The microstructure of Nikopol manganous concentrates of oxide grade 1 (o) and oxide-carbonate grades 1 (ox) is studied by X-ray structure microanalysis in secondary electrons, the spectrograms and chemical compositions of mineral compounds which are part of concentrates are investigated. The interrelation between change of volume and rate of emission of concentrates dissociation gaseous products at their heating up to 1200 °C is established. The initial temperature of decomposition processes of both oxide and oxide-carbonate concentrates is 400-450 °C and the final

temperature is 950-1000 °C.

2. Amount of gaseous phase formed due to decomposition of oxide concentrate of grade 1 (o) recorded by the plant is within the limits of 4 – 4.5 dm³, the pattern of gas emission proves high heterogeneity by mineral composition. The volume of evolved gas as a result of decomposition of oxide-carbonate concentrate makes 10.2-10.5 dm³, and at the same time in the area of the most intensive gas emission at temperatures of 450-470 °C, 600-650 °C and 790-820 °C.

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Термокинетические исследования процессов диссоциации марганцевых концентратов

Цветков И.В., Коноваленко В.П. /к.т.н./

Приведены данные исследований микроструктуры никопольских окисных и окисно-карбонатных марганцевых концентратов методом РСМА, а также результаты термокинетических исследований диссоциации концентратов. Установлена взаимосвязь изменения объема и скорости выделения газообразных продуктов диссоциации концентратов при нагревании их до температуры 1200 °C.