

# INVESTIGATION AND COMPARISON OF THE SOFTENING TEMPERATURE OF MANGANESE ORES USED FOR THE PRODUCTION OF COMPLEX LIGATURES BASED ON Fe-Si-Mn-Al

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The article presents the results of studying the beginning, end and temperature range of softening of Kazakhstan manganese ores of the Bogach and Yesimzhal deposits. The experimental study was carried out using a softening unit on the Tamman furnace. The results obtained showed that the ore of the Yesimzhal Deposit has a low softening temperature compared to the ore of the Bogach Deposit, but the ore of the Bogach Deposit has the lowest softening temperature intervals. The dependence of the degree of softening of the investigated manganese ores on the temperature is established. The chemical composition was qualitatively evaluated, and the main phases in the samples of manganese ores were determined by x-ray phase studies.

*Key words:* manganese ore, chemical analysis, XRD (x-ray diffraction), softening temperature, complex ligature (Fe-Si-Mn-Al).

## INTRODUCTION

It is known that a significant improvement in the quality of steel can be achieved by using complex alloys containing aluminum, silicon and manganese, which at the deoxidation stage contribute to a deeper cleaning of steel from oxygen and non-metallic inclusions.

It is known that complex alloys and ligatures are used in the production of steel and special alloys for deoxidation and alloying of steel [1]. Previously, complex ligatures were obtained by fusing several ferroalloys in melting units or in buckets when casting from an ore-thermal furnace. However, this method is not economical. additional costs of electric energy, material costs and carbon monoxide of useful elements are required when several ferroalloys are melted and the environment is polluted [2].

The production of complex ferroalloys requires the use of new types of raw materials, the maximum use of all its components makes it possible to process man-made substandard raw materials and develop low-and waste-free technologies for obtaining ferroalloys [3-5].

Considering the experiments of the above authors, it is obvious that not only manganese and ferromanganese ores are suitable for the production of complex alloys and ligatures, but also poor substandard manganese ores, and low-grade concentrates not used in the production of manganese ferroalloys.

It should be noted that the manganese mineral resource base of the Republic of Kazakhstan has a variety of ferromanganese varieties. In the Republic of Kazakhstan, there are more than 200 radically different ore occurrences of manganese and ferromanganese ores [6-8]. First, it is a wide range of changes in their manganese content from 10 to 30 % and iron from 2 to 35 %, which necessitates an individual technological approach to processing each variety of manganese and ferromanganese ore [9,10]. Second, there are strong differences in the mineral composition of ores (pyrolusite, psilomelan, rhodochrosite, jacobsonite, brownite, hematite, magnetite, hydrohematite, etc.) third, there are differences in the texture and structural structure (grain size, degree of coalescence).

## RESEARCH METHODOLOGY

Consequently, the raw manganese ore deposits of the «Bogach» and «Yesimzhal» presented LLP «Temirtau electrometallurgical plant» was subjected to studies to determine the chemical, x-ray phase analyses, as well as the softening temperature of the ore. Opredelenie technological and production performance.

«Bogach» Deposit is located in the Karaganda region. Ore minerals of primary ores are considered to be brownite (main), hematite, less often ankerite, friedelite, jacobsonite; non-metallic-calcite, quartz, chlorite, gypsum. Ore minerals of oxidized manganese ores-pyrolusite, psilomelan, vernadite, hematite, less often Holland, goethite, braunite, jacobsonite; non-metallic-quartz, kaolinite, mica, calcite and feldspar. Balance reserves of manganese ores by cat.  $A+B+C_1$  – 2193,5 thousand tons, by cat.  $C_2$  - 1007,232 thousand tons [8].

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The field «Yesimzhal» is located in Eastern Kazakhstan. By type, the Deposit is classified as stratiform and is developed in an open-pit manner. The Deposit's ores are oxidized. Balance reserves of manganese ores by cat. A+B+C<sub>1</sub> – 699,84 thousand tons, cat. C<sub>2</sub> – 421,1 thousand tons, and off-balance sheet by cat. C<sub>2</sub> – 305,5 thousand tons [8].

Chemical analysis of the studied ores of the Bogach and Yessymzhal deposits was performed in accordance with known methods [11].

X-ray phase analysis was performed on an XRD 7000c x-ray diffractometer (Shimadza, Japan) with a set of high - and low-temperature cameras and a polycapillary optics system based on the Federal state budgetary institution of science «Institute of metallurgy of the Ural branch of the Russian Academy of Sciences» (Yekaterinburg, Russian Federation). It allows you to measure the intensity of diffracted radiation in a given direction with an accuracy of up to 10 percent and the diffraction angles with an accuracy of up to 10 percent of a minute.

To determine the value of manganese ore materials and achieve optimal technical and economic indicators of Ferroalloy production, information is needed about the metallurgical characteristics of raw materials, on which the technology and production indicators significantly depend.

One of the factors that affect the technological and production indicators is the temperature of the beginning of softening of the ores used, or the temperature of primary slag formation. Participating in the reduction processes, manganese ores are consistently subjected to heating, softening and melting, thus ensuring the convergence of materials into the working space of the furnace. The softening process is accompanied by a reduction of internal pores and closer coupling of particles due to the deformation of the crystal lattice and the formation of new phases, sometimes with a higher melting point exceeding the softening temperature [12, 13].

There is no doubt that the process of softening ore materials is very complex and is determined by a large number of different factors: mineral and chemical composition, material structure, porosity and fraction, which lead to complex changes in the structure of raw materials when heated [14]. Reactions occurring during heating and softening of materials are often superimposed on each other, which makes it difficult to clearly determine the influence of each of them. Therefore, the results of experiments allow us to judge mainly about the relative difference in shrinkage during heating, which allows us to assume a possible difference in the behavior of raw materials in the furnace.

## RESULTS RESEARCH

Preparation of the initial ore sample included ring and cone averaging, reduction, and sampling for complete chemical and x-ray phase analysis.

Ore deposits of the «Bogach» are significantly different in chemical composition and content of impurities from the ore Deposit «Yesimzhal». The chemical composition of ores is shown in Table 1.

Table 1 **Chemical composition of the investigated manganese ores / wt. %**

Deposit	Mn	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	S	P	t/bs	t/es	Δt
Bogach	39,88	10,43	6,78	2,20	5,75	0,70	0,032	0,021	955	1273	318
Yesimzhal	25,53	22,56	13,77	4,86	1,92	0,35	0,054	0,054	886	1234	348

Based on Table 1, the ores of the Bogach and Yesimzhal deposits can be classified as ferromanganese by their ratio of manganese to iron equal to 3,82 and 1,13, respectively.

In the ores of the Bogach Deposit, the accompanying components in the form of silicon, aluminum, calcium and magnesium oxides are insignificant, and the content of each component does not exceed 1 - 7 %, the basicity is 0,72. In the ore sample, the content of phosphorus and sulfur is 0,032 % and 0,021 %, respectively, and this content is optimal for manganese ores.

The ore of the Yesimzhal Deposit can be considered siliceous, since the content of silicon oxide is 13,77 %, while the other accompanying oxides of the elements Al, Ca and Mg are not significant and within 1 - 5 %. The content of phosphorus and sulfur is more than 2 times higher than in the ores of the Bogach Deposit.

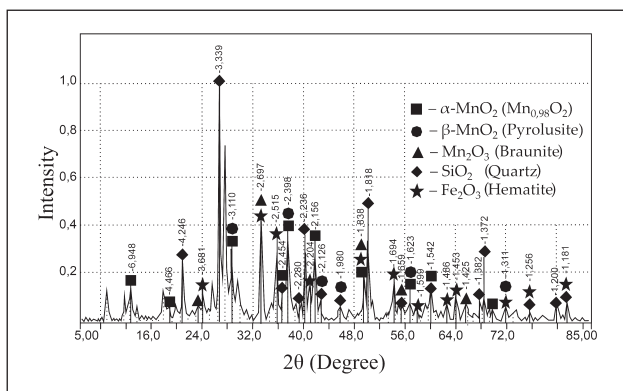
The difficulty of identifying the mineral composition of the manganese ores of the Bogach and Yesimzhal deposits during decoding is that in both ore samples MnO<sub>2</sub> exists as a modification: β-MnO<sub>2</sub> (pyrolusite), α-MnO<sub>2</sub> (mineral ramsdellite).

Figures 1 and 2 show the results obtained by x-ray phase analysis of the samples under study. According to x-ray phase analysis of samples of ore deposits «Bogach» consist of a mixture of the phases: β - MnO<sub>2</sub> (pyrolusite); α-MnO<sub>2</sub> (ramsdellite); SiO<sub>2</sub> (quartz); CaCO<sub>3</sub> (calcite); Mn<sub>2</sub>O<sub>3</sub> (braunite), and ore deposits «Simial» consists of: SiO<sub>2</sub> (quartz); α-MnO<sub>2</sub> (ramsdellite); β - MnO<sub>2</sub> (pyrolusite); Fe<sub>2</sub>O<sub>3</sub> (hematite); Mn<sub>2</sub>O<sub>3</sub> (braunite).

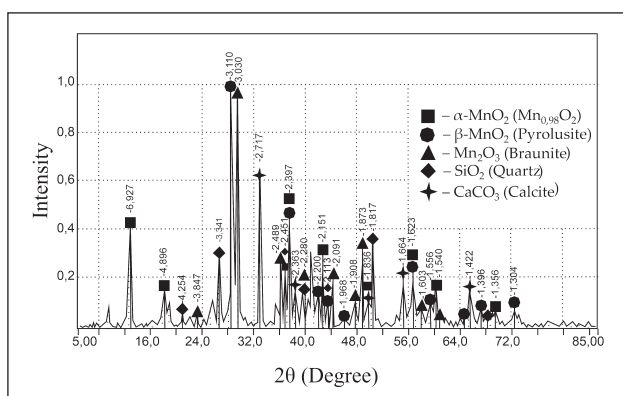
Experiments on softening of ores were carried out in the Tamman furnace in accordance with GOST 26517-85 at uniform heating at a speed of 10 °C/min. Materials were pre-crushed and sieved to obtain a 2 - 5 mm fraction of the material. After that, the ore was placed in a furnace and dried at a temperature of 105±5 °C to remove moisture. Cylindrical alund crucibles were filled with material, compacting the layer until the shrinkage stopped. The height of the compacted sample layer was 50±1 mm.

The installation diagram for determining the softening start temperature and the softening temperature range is shown in Figure 3.

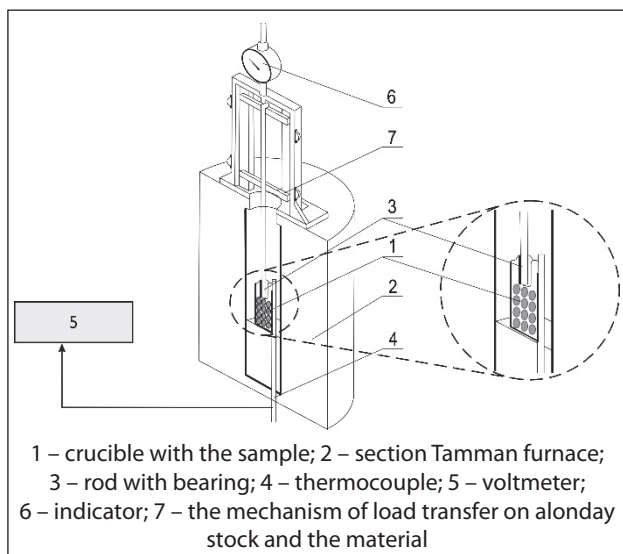
The temperature of the beginning and end of softening was calculated as the arithmetic mean temperatures



**Figure 1** Photograph of manganese ore deposits of the «Bogach»

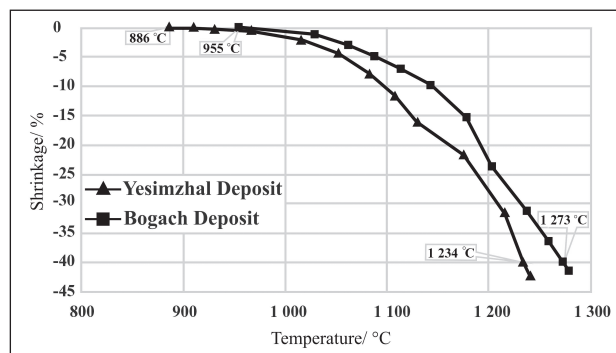


**Figure 2** Photograph of manganese ore deposits of the «Yesimzhal»



**Figure 3** Installation Diagram for determining the softening temperature of ore

and temperature range of softening – the difference between the average temperatures of the beginning and end of softening. The temperature at which the rod was buried in the sample by 1 % of the total layer height was taken as the temperature of the beginning of softening ( $t_{bs}$ ), and the temperature at which the rod was buried by 40% was taken as the temperature at the end of softening ( $t_{es}$ ). The indicator readings were recorded depending on the temperature. Taking into account the natural elongation of the rod during heating, the charge shrink-



**Figure 4** Dependence of the degree of softening of manganese ores on temperature

age coefficient was calculated. The results of experiments on the study of softening of ores from various deposits are shown in Figure 4.

The results of these studies the temperatures of softening, showed that the ore field «Yesimzhal» has a softening temperature lower than the ore deposits of the «Bogach» 886 °C and 955 °C, respectively, but the ore of the Bogach Deposit has the lowest temperature range of softening ( $\Delta t = 318$  °C).

The indicators of the beginning of the softening temperature and the temperature interval ( $\Delta t$ ) are based on the division of ores and concentrates into hard and easy - to-recover ones. The first sample of ore has a low softening start temperature and a long softening interval, and the second sample of ore has a high softening start and a narrow softening interval. The temperature of the end of softening in the Yesimzhal and Bogach ores is 1234 °C and 1273 °C, respectively.

The same work was previously carried out by the authors [15] with Durham oxide and primary oxidized manganese-containing ores and Dzhezdinsky concentrates of grades I and II of the Republic of Kazakhstan.

When analyzing the research results, we considered the influence of possible compounds based on the chemical composition of the ore, which also allows us to judge the quantitative contribution to the softening process of components that are part of both the initial and formed during the heating of minerals and phases.

## CONCLUSIONS

The literature analysis and the presented research results allow us to conclude that significant differences in their physical and chemical characteristics were found in the studied ore softening samples. The temperatures of the beginning, end and temperature intervals of softening of manganese ores of the «Bogach» and «Yesimzhal» deposits were determined experimentally.

Comparison of different chemical and mineralogical composition of manganese-containing raw materials allowed to determine its metallurgical value and give the following results:

- 1 The proven reserves of the studied ore deposits «Bogach» and «Yesimzhal» in total amount to 4

- 627,128 thousand tons, including categories A+B+C<sub>1</sub>d – 2 893,296 thousand tons.
- 2 X-ray phase analysis of the investigated manganese ores showed that they belong to a mixed type of pyrolusite with a periodic predominance of one or another component with brownite inclusions.
  - 3 The preferred raw material from the point of view of the beginning of softening temperatures and the best raw material from the point of view of the softening temperature range is the ore of the Bogach Deposit.
  - 4 It was found that the higher the content of manganese in the ore, the softening process takes place in a zone of high temperatures, and the interval of the softening process decreases.
  - 5 The studied ores can be considered from the point of view of softening temperatures to have favorable metallurgical properties for the smelting of complex ligatures.

## REFERENCES

- [1] V. A. Kudrin. Theory and technology of steel production. LLC «AST Publishing house», Moscow, 2003, pp. 155-169, 528.
  - [2] J. Basson, J. Daavittila, M. Gasik, M. I. Gasik, L. Holappa, H. Jalkanen, I. Mc. Dougall, O. Polyakov, G. Saevarsdotir, M. Tangstad. Handbook of Ferroalloys. Butterworth-Heinemann. London, 2003, pp. 495-505, 536. (<https://doi.org/10.1016/C2011-0-04204-7>).
  - [3] G. V. Medvedev, T. D. Takenov. AMC alloy. Nauka, Almaty, 1979, p. 140.
  - [4] E. K. Mukhambetgaliev, A. B. Esenzhulov, V. E. Roshchin. Alloy Production from High-Silica Manganese Ore and High-Ash Kazakhstan Coal. Steel in Translation, 48 (2018) 9, 547-552. (<https://doi.org/10.3103/S0967091218090097>).
  - [5] S. M. Tleugabulov, A. Kh. Nurumgaliev. Process of producing the complex alloy Stal', 7 (2005), 57-59.
  - [6] E. A. Buketov, T. G. Gabdullin, T. D. Takenov. Metallurgical processing of manganese ores in Central Kazakhstan. Nauka, Almaty, 1979, p.184.
  - [7] K. N. Trubetskoy, V. A. Chanturia, A. E. Vorobyov, etc. Manganese. Mineral resource base of the CIS. Academy of mining Sciences, Moscow, 1999, p. 271.
  - [8] N. M. Zhukov, Z. N. Pavlova, A. A. Antonenko, B. S. Khamzin. Manganese deposits in Kazakhstan. Directory. Almaty, 2019, p.159.
  - [9] Ye. Samuratov, B. Kelamanov, A. Akuov, Ye. Zhumagaliev, M. Akhmetova. Smelting standard grades of manganese ferroalloys from agglomerated thermo-magnetic manganese concentrates Metallurgija 59 (2020) 1, 85-88.
  - [10] M. I. Gasik. Manganese. Metallurgy, Moscow 1992 pp. 198-221 and 608.
  - [11] M. I. Popova. Phase analysis of ferrous metal ores. Directory. Nedra, Moscow 1991, pp. 75-88 and 112.
  - [12] A. K. Zhunusov, L. B. Tolymbekova. Metallurgical processing of manganese ores from the Tur and Zapadny Kamys deposits. Kereku, Pavlodar 2016, p.209.
  - [13] A. V. Petrov, V. V. Cherevik, L. F. Samborsky, N. In. Voskerician. Investigation of phase transformations during heating of manganese concentrates. University news. Ferrous metallurgy (1975) 9, 22-26.
  - [14] Y. Zhang, Y. Zhang, Z. You, Y. Zhao, G. Li, T. Jiang. Study on the metallurgical performances of typical manganese ores. TMS Annual Meeting (2014), pp. 345-352.
  - [15] V. I. Zhuchkov, A. V. Zhdanov, O. V. Zayakin. Research of softening temperatures of manganese raw materials The Melts (2006) 3, 29-32.
- Note:** The responsible for England lan-guage is Albina Yersaiynova, Aktobe, Kazakhstan