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THEORETICAL BASIS AND ANALYSIS OF EXPERIENCES ON STUDYING THE MECHANISMS OF OXIDES FORMATION DURING OXIDATIVE FIRING OF MOLYBDENUM SULFIDES

Abstract: The article deals with the formation of oxidized particles during oxidative roasting of molybdenum sulfide concentrates and cakes, as well as under-oxidized cinders and dust of molybdenum production. In the course of the work, various factors influencing the oxidative roasting process, parameters and requirements for the supplied and discharged material were investigated. The results of the analyzes are summarized and conclusions drawn on their basis.

Key words: multiple hearth furnace, intensive roasting, calcine, sulfides, molybdenum, cake, soda leaching, oxidative roasting, concentrate, desulfurization, oxidation state.

Language: English

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Introduction

An industrial method for extracting molybdenum includes roasting its concentrate, purifying the obtained calcine by a hydrometallurgical method to MoO₃, and reducing trioxide with hydrogen to metal. Although this method is the main method for the production of molybdenum and has been used for a long time in the industry, research on its application to various concentrates, as well as the kinetics and mechanism of roasting, is ongoing. still in short supply [1]. However, as a result of the well-known disadvantages of pyrometallurgical extraction of molybdenum, hydrometallurgical processes are becoming more and more attractive. Among them, nitric acid leaching, pressure oxygen leaching, electrooxidative extraction, sodium chlorate and

hypochlorite leaching, and bioleaching are more popular [2].

Objects and methods of research.

We have studied the kinetics and mechanics of the solid-state reaction between MoS₂ and MoO₃ for the formation of MoO₂ in an atmosphere with a nitrogen content of 450-700°C using untreated samples of molybdenum production, pressed melange samples and pure MoS₂ and MoO₃ dumplings with the contacting side. The results show that for untreated samples, the reaction reaches a maximum conversion of 67.3% at 650°C in 75 minutes, while for compressed samples, the conversion under similar conditions reached 96.1% in 75 minutes, which reflects the effect of physical conditions of both types of experiments on reaction kinetics [3]. The calculated

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values of the activation energy for the two experimental conditions are coherent with an average value of -44.2 ± 1.9 kJ, which is in the range of reactions in the solid state, controlled by diffusion [4]. For samples with a contacting face above 650°C , the results seem to indicate that molecular diffusion in the solid state and MoO_3 in opposite directions in the newly formed crystal structure of MoO_2 can occur with the established diffusion coefficients of MoS_2 in MoO_2 and MoO_3 in MoO_2 at 650°C to 1.08×10^{-6} and $7.78 \times 10^{-6} \text{ cm}^2/\text{s}$, as well as with constant diffusion coefficients of MoS_2 in MoO_2 and MoO_3 in MoO_2 at 650°C 1.08×10^{-6} and $7.78 \times 10^{-6} \text{ cm}^2/\text{s}$ 973 cde 10^{-5} and $1.13 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively.

formed from aqueous solutions and decomposes at about 120°C to $\text{MoO}_3 \cdot n\text{H}_2\text{O}$ and sulfur. Trisulfide MoS_3 usually contains an excess of sulfur in the form of MoS_3^{+x} , in which $x = 0-0.7$. When heated in an inert atmosphere between 250 and 300°C , it decomposes into MoS_2 and sulfur. Molybdenite (MoS_2) decomposes to Mo_2S_3 and gaseous sulfur in a neutral atmosphere above 1400°C [5]. There are two known molybdenum oxysulfides, MoO_2S and MoS_2 , but they are very unstable and decompose to MoS_2 and oxygen. Several molybdenum oxides have been identified with oxidation states from 2 to 6, most of which are non-stoichiometric, and only two (MoO_2 dioxide and MoO_3 trioxide) are stoichiometric, stable compounds.

Results and discussion.

There are four known molybdenum sulfides: Mo_3S_4 , Mo_2S_3 , MoS_2 and MoS_3 . Sulfide Mo_3S_4 is

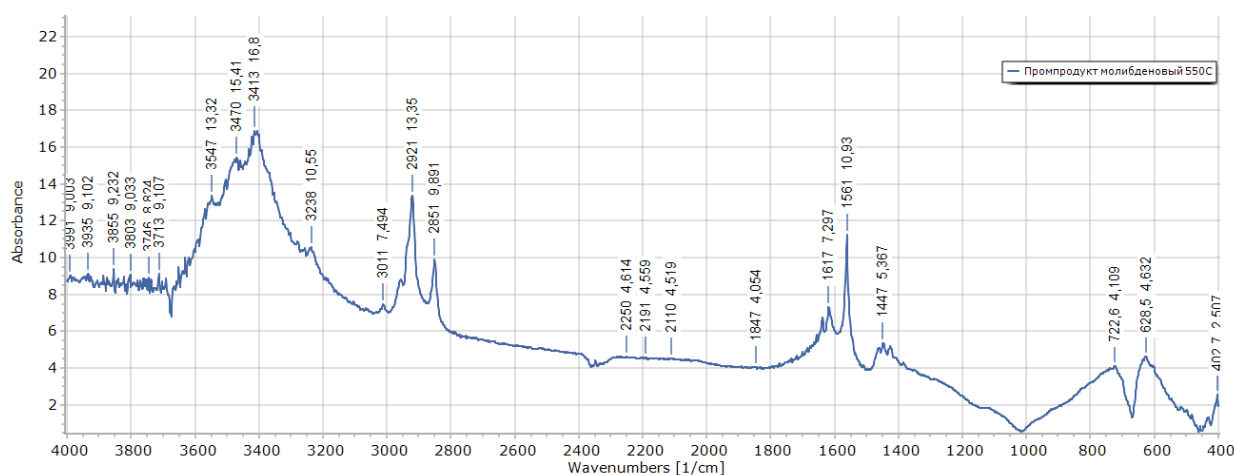


Fig. 1. Results of IR spectroscopy of molybdenum middlings during firing at 550°C .

Some others, such as Mo_5O_{12} , Mo_3O_8 , Mo_2O_5 , Mo_4O_{11} and Mo_9O_{26} , have been found in small amounts in multi-hearth pots and appear to be solid

solutions of MoO_2 and MoO_3 in varying proportions [6-8].

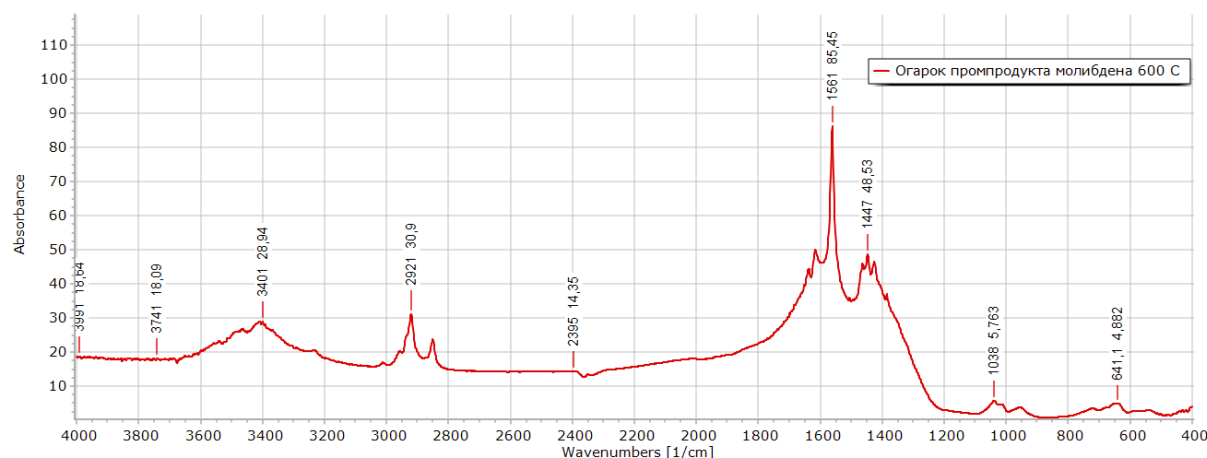


Fig. 2. Results of IR spectroscopy of molybdenum middlings during firing at 600°C .

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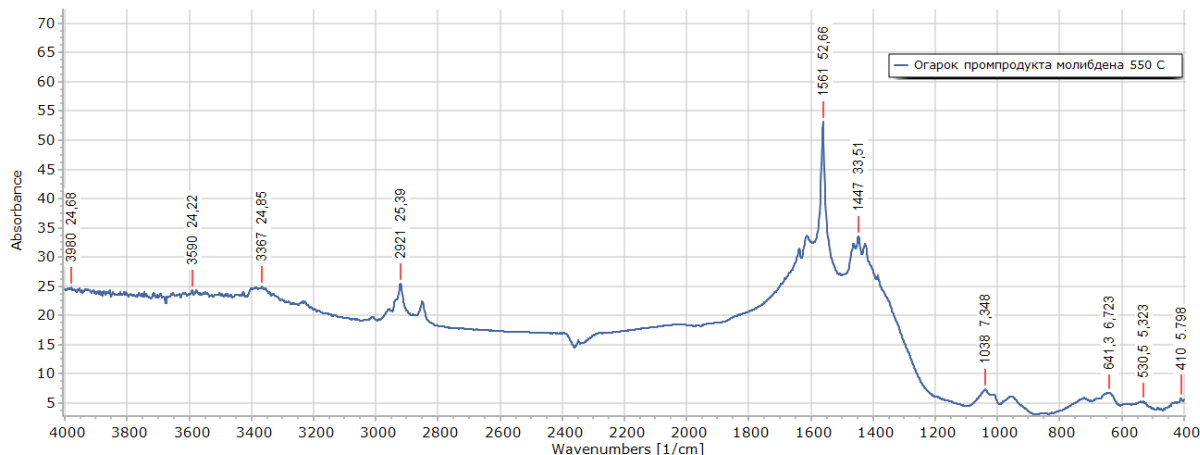


Fig. 3. Results of IR spectroscopy of cinder of molybdenum middlings during roasting at 550°C

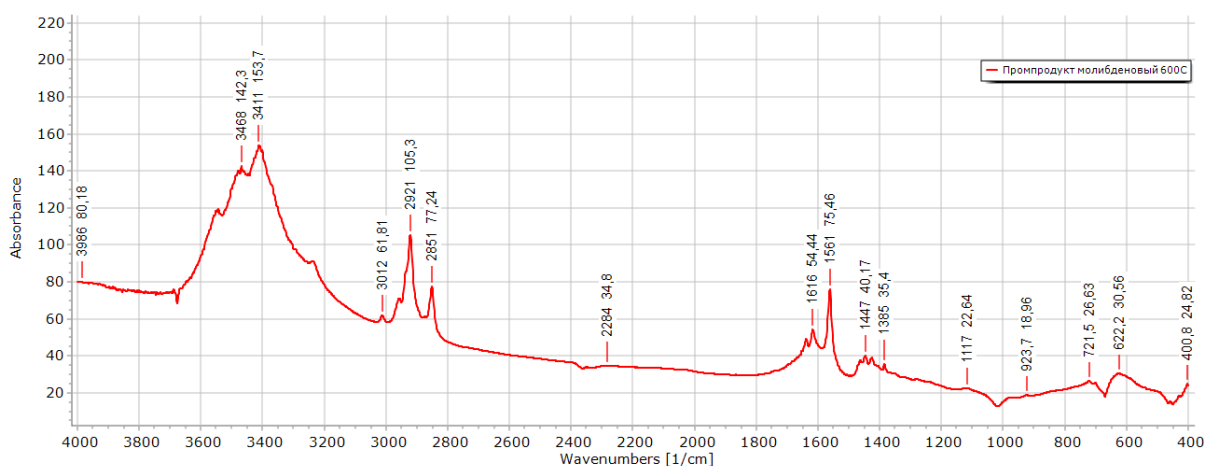


Fig. 4. The results of IR spectroscopy of the cinder of molybdenum middlings during firing at 600°C.

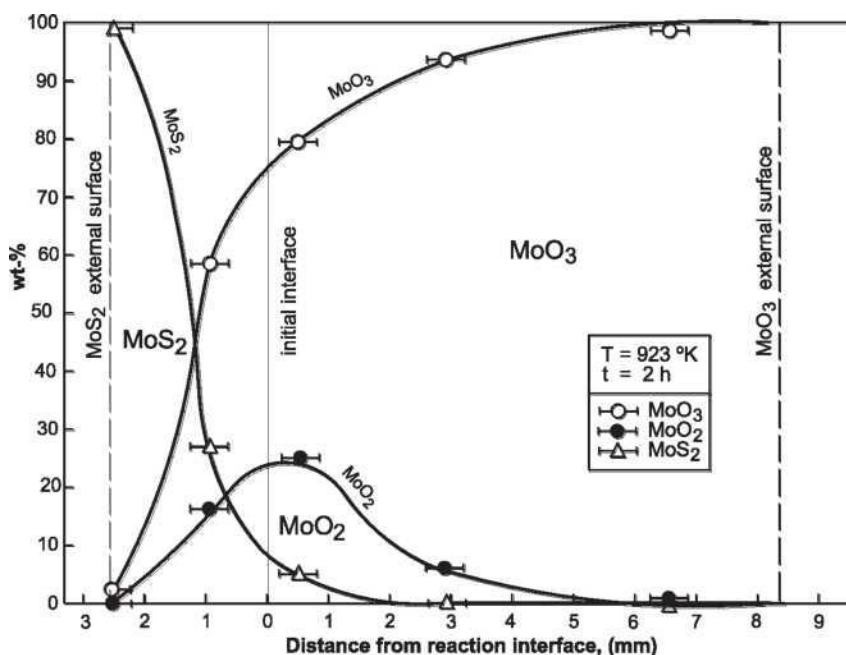


Fig. 5. Concentration profiles of MoO₂, MoS₂ and MoO₃ at 650°C (compressed granules with one contacting surface).

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Conclusion.

The kinetics and mechanism of the solid state reaction between MoS₂ and MoO₃ with the formation of MoO₂ in a nitrogen atmosphere between 450 and 700°C were studied using bulk mixed samples, mixed compressed granules and pure granules of MoS₂ and MoO₃ with a single contacting surface. The results show that for bulk samples the reaction reaches a maximum conversion of 67.3% at 650 °C in 75 min, while for compressed samples the conversion under

similar conditions reaches 96.1%, which indicates the effect of the physical characteristics of both types of experiments on diffusion coefficient of MoS₂ and / or MoO₃ through the newly formed crystalline layer of MoO₂. The calculated activation energies for both experimental conditions agree with an average value of -44.2 ± 1.9 kJ, which is in the range of diffusion-controlled reactions. The literature has not reported any other value for this reaction.

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